FLUOROSULFATES OF THE NOBLE METALS, AND THEIR USE IN NOVEL SUPERACID SYSTEMS

by

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B.Sc., Honours, The University of British Columbia, 1976

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

in

THE FACULTY OF GRADUATE STUDIES
Department of Chemistry

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
September 1980

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Abstract

This study was initiated by the search for novel superacid systems based on HSO$_3$F, the strongest simple protonic acid. Therefore, the synthesis of binary metal fluorosulfates, M(SO$_3$F)$_n$, was investigated, with special emphasis on compounds where M is in a medium or high oxidation state and formally coordinatively unsaturated, i.e., $n = 3, 4$ or $5$. Preferably, the resulting fluorosulfate would also display a sufficiently high thermal stability with respect to dissociations giving rise to SO$_3$ or S$_2$O$_5$F$_2$, and reasonable solubility in HSO$_3$F.

In order to obtain suitable binary fluorosulfates, a new, generally applicable synthetic method was developed, involving the oxidation of a metal with S$_2$O$_6$F$_2$ in the presence of HSO$_3$F:

\[ M + \frac{n}{2} S_2O_6F_2 \rightarrow M(SO_3F)_n, \]

where M is primarily a 4d or 5d transition metal, in particular, palladium, platinum, gold and iridium. This fluorosulfonation mixture combines the strong oxidizing ability of S$_2$O$_6$F$_2$ with the good solvating property of HSO$_3$F towards ionic solutes. The ability of these binary fluorosulfates to act as fluorosulfate ion acceptors was established by the synthesis of anionic complexes of the type $[M(SO_3F)_{n+m}]^{m-}$, where $m = 1, 2$.

Both Au(SO$_3$F)$_3$ and Pt(SO$_3$F)$_4$ were found to act as ansolvodiacids in HSO$_3$F by the removal of fluorosulfate ions from the solvent ionization equilibrium:
2\text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^-, \\
to form [\text{Au(SO}_3\text{F})_4]^- or [\text{Pt(SO}_3\text{F})_6]^{2-}. Results from conductivity measurements indicate the resulting superacids have acid strengths comparable to that of the HSO\text{F}_3\text{F-SbF}_5\text{SO}_3 system and definitely superior to the HSO\text{F}_3\text{F-SbF}_5 system. In both cases, the variety of ternary fluorosulfates synthesized included unusual cations such as Br_3^+ and Br_5^+. In the case of platinum, evidence for poly-nuclear oligomeric anions of the type of [\text{Pt(SO}_3\text{F})_5]_n^- were obtained; similar observations were also made in the tin system.

The oxidation of palladium yielded \text{Pd(SO}_3\text{F})_2 and a mixed valency compound, \text{Pd(II)[Pd(IV)(SO}_3\text{F})_6], both containing Pd(II) in a rather uncommon octahedral coordination sphere and a \text{3A}_2\text{g} electronic ground state. These magnetically dilute compounds allowed meaningful magnetic results and ligand field parameters to be interpreted.

Both \text{Ir(SO}_3\text{F})_3 and \text{Ir(SO}_3\text{F})_4 could be synthesized, along with some ternary fluorosulfate complexes. Some preliminary results were also obtained on the fluorosulfates of germanium, molybdenum, niobium and tantalum.
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ACKNOWLEDGEMENT

I would like to express my sincere appreciation to Professor F. Aubke, my research supervisor, for his inspirations and guidance during my years of graduate study.

Thanks are also extended to other members of the faculty and staff of this department for their assistance in various aspects of this research, in particular, Professor R.C. Thompson and Dr. P.C. Leung for stimulating discussions, Dr. S.O. Chan for taking some of the n.m.r. spectra, and the glass-blowing and mechanical shops for the construction of most of the apparatus used. Professors J. Trotter and N.L. Paddock are thanked for reading parts of the manuscripts. Mrs. B. Krizsan is thanked for some of the illustrations. I would also like to thank my typists for doing such a fine job: Mr. Derek Lee and Miss Roselyn Lee, who did most of the typing, and Ms. Dorathea Baker and Mrs. Bev Gray.

The receipts of a National Science and Engineering Research Council Post Graduate Scholarship and a Dr. F.J. Nicholson Fellowship are gratefully acknowledged.
TO

MY PARENTS
CHAPTER 1  INTRODUCTION

1.A GENERAL INTRODUCTION

Fluorosulfuric acid, HSO₃F, was first prepared by Thorpe and Kirman by the reaction between sulfur trioxide and anhydrous hydrogen fluoride ¹:

HF + SO₃ → HSO₃F.  \hspace{1cm} (1.1)

Although completely ionic salts of the acid, such as KSO₃F, can be recrystallized from their neutral aqueous solutions ², HSO₃F itself is nevertheless unstable in water, in which it is hydrolyzed almost spontaneously according to:

HSO₃F + H₂O → HF + H₂SO₄. \hspace{1cm} (1.2)

The instability of the S-F bond towards hydrolysis is also illustrated by the fact that most fluorosulfates are extremely sensitive to moisture. While there have been questionable reports on the existence of pure aqueous solutions ³,⁴ and hydrates ⁵ of the acid, HSO₃F is incompatible with the aqueous system for all practical purposes ⁶⁻⁹. On the other hand, the acid has been studied extensively as an ionizing and protonic non-aqueous solvent. This can be reflected in a number of reviews on HSO₃F and its derivatives, in particular those by Lange ¹⁰, Gillespie et al ¹¹,¹², Thompson ¹³, Jache et al ¹⁴,¹⁵ and Olah et al ¹⁶. The subject has also been described in related articles by Cady ¹⁷, Williamson ¹⁸, and, De Marco and Shreeve ¹⁹. In addition, the versatility of HSO₃F can be illustrated by its
use as a fluorinating agent in reactions with oxides and oxyacid salts, summarized in an article by Englbrecht 20.

HSO₃F is the strongest simple protonic acid, more so than HSO₃CF₃, H₂S₂O₇, H₂SO₄, HSO₃Cl and HClO₄. Its high dielectric constant makes it a very suitable medium for the formation and generation of ionic solutes 21.

Since the neat solvent displays such a high acidity, it is not surprising that HSO₃F is widely used as a basis for superacid systems (sometimes called 'magic acids' by some workers in the field of carbonium ion chemistry 22, 23). The definition of a superacid is by no means universal; some refer to it as any protonic acid with an acidity greater than that of 100% H₂SO₄ 12. According to this classification, HSO₃F itself would be a superacid. Another definition, preferred and subsequently used in this thesis, views a superacid as a multicomponent system with an acidity unattainable by simple protonic acids.

In terms of solvo-system terminology, an acid in HSO₃F increases the acidium ion concentration, [H₂SO₃F⁺]. It can accomplish this either by the protonation of the solvent according to:

$$\text{HA} + \text{HSO₃F} \rightleftharpoons \text{H₂SO₃F⁺} + \text{A}^- \ , \ \ (1.3)$$

or by the removal of the fluorosulfate ion, SO₃F⁻, from the self ionization equilibrium by:

$$\text{A} + 2\text{HSO₃F} \rightleftharpoons \text{H₂SO₃F⁺} + \text{A} \cdot \text{SO₃F⁻} \ . \ \ (1.4)$$

Due to the extremely high acidity of HSO₃F, the direct protonation of HSO₃F by a simple protonic acid is not possible.
While most solutes are bases in HSO₃F, only a few strong Lewis acids have been found to act as ansolvo-acids according to equation (1.4).

The most thoroughly studied superacid system in HSO₃F contains the fluoride or fluoride-fluorosulfates of antimony (V) as the ansolvo-acids. The fluoride-fluorosulfates are usually formed in situ in these mixtures by the addition of SO₃ in a reaction such as ²⁴:

\[
\text{SbF}_5 + \text{SO}_3 \rightarrow \text{SbF}_4(\text{SO}_3\text{F}).
\]

These compounds have been found to be stronger acids than the pentafluorides in HSO₃F; SbF₂(\text{SO}_3\text{F})₃, identified only in HSO₃F solutions, gives rise to the strongest acid of the group. It is apparent that the successive substitution of fluorine atoms by fluorosulfate groups increases the acidity of the superacid system ¹¹. This leads to the expectation that the pentakis-(fluorosulfate) should yield a solution of even greater acidity than the fluoride-fluorosulfates. Unfortunately, a higher degree of substitution is not possible in this system, and only SbF₄(\text{SO}_3\text{F}) ²⁵ and SbF₃(\text{SO}_3\text{F})₂ ²⁶ have hitherto been isolated; attempts to prepare Sb(\text{SO}_3\text{F})₅ have failed ²⁷.

Although there is no implied correlation between the acidity and basicity of a solvent, the existence of the highly electrophilic acidium ion, H₂\text{SO}_3\text{F}⁺, in a superacid system indicates that other unusual cations may be stabilized in the medium. The complexation of the strongest base in the fluorosulfuric acid system—\text{SO}_3\text{F}⁻, to give larger, less
nucleophilic anions such as \([\text{SbF}_2(\text{SO}_3\text{F})_4]^-\), is expected to decrease the basicity of the resulting solution. Therefore, in order for an ansolvo-acid to give rise to a strongly acidic and weakly basic solution in HSO\(_3\)F, it must possess strong Lewis acidity towards SO\(_3\)F\(^-\) with the resulting complex anion, \(A\cdot\text{SO}_3\text{F}^-\), showing minimal reverse dissociation according to:

\[
A\cdot\text{SO}_3\text{F}^- \rightleftharpoons A + \text{SO}_3\text{F}^- .
\]  

(1.6)

In the antimony (V) fluoride-fluorosulfate superacid system, additional modes of dissociation of the compounds in solution by 22,24:

\[
[\text{SbF}_2(\text{SO}_3\text{F})_4]^- \rightleftharpoons [\text{SbF}_3(\text{SO}_3\text{F})_3]^- + \text{SO}_3 ,
\]  

(1.7)

and the decomposition of the ansolvo-acids themselves by 26:

\[
\text{SbF}_3(\text{SO}_3\text{F})_2 \rightleftharpoons \text{SbF}_4(\text{SO}_3\text{F}) + \text{SO}_3 ,
\]  

(1.8)

can lead to the formation of \(\text{SO}_3\), a reasonably powerful oxidizing agent. The presence of \(\text{SO}_3\) may give rise to oxidative side reactions in these media, in particular with species such as carbonium ions 22 and polyhalogen cations 28-30.

Hence, it becomes necessary to look for other fluorosulfates that may be better ansolvo-acids in the HSO\(_3\)F solvent system than those presently known. A good fluorosulfate acceptor should have the following properties:

a) a reasonable thermal stability, especially towards \(\text{SO}_3\) elimination and ligand redistribution reactions,

b) an incompletely filled coordination sphere in order to facilitate the addition of \(\text{SO}_3\text{F}^-\) group(s),

c) a high solubility in HSO\(_3\)F to give reasonable
concentrations, and

d) a low oxidative power, to reduce side reactions and to allow the study of a wide range of species.

A review of the previously reported fluorosulfates reveals that only a few form anionic complexes, and of these, none are really suitable as ansolvo-acids. For example, although salts containing the anion - $[\text{Sn}(\text{SO}_3\text{F})_6]^{2-}$ can be prepared $^{31,32}$, $\text{Sn}(\text{SO}_3\text{F})_4$ is virtually insoluble in $\text{HSO}_3\text{F}$ $^{33}$. Both $\text{Br}(\text{SO}_3\text{F})_3$ and $\text{I}(\text{SO}_3\text{F})_3$ form anionic complexes of the type of $[\text{Hal}(\text{SO}_3\text{F})_n]^-$ $^{31,34,35}$, but they can also exist in cationic species of the type - $[\text{Hal}(\text{SO}_3\text{F})_2]^+$ $^{28,31}$. This indicates that the $\text{Hal}(\text{SO}_3\text{F})_3$ can act as both an acceptor and a donor towards a $\text{SO}_3\text{F}$ group. Not surprisingly, $\text{I}(\text{SO}_3\text{F})_3$ has been found to be amphoteric in $\text{HSO}_3\text{F}$, capable of both acidic and basic reactions in the solvent $^{36}$. Furthermore, both these compounds are oxidizing $^{37,38}$, and thus are unsuitable as ansolvo-acids in the $\text{HSO}_3\text{F}$ acid system.

It appeared that other fluorosulfates would have to be synthesized, and possibly by new methods. Fluorosulfates of the 4d and 5d elements have not been studied extensively, but are likely suitable for the following reasons:

a) The halides of these metals are capable of the formation of halocomplexes, indicating Lewis acidity in the halides system which most likely should extend to the fluorosulfate system.

b) The Lewis acidity of this type of fluorosulfates is
expected to increase with the metal's oxidation number, and high oxidation states of these metals are relatively easily attainable.

In order to establish that the metal fluorosulfate will accept fluorosulfate ions, the successful synthesis of anionic fluorosulfato-complexes will provide the first test. The characterization of these ternary fluorosulfates by various spectroscopic means, including Raman, i.r., n.m.r. and u.v.-visible, should facilitate their subsequent detection in superacid systems. Their acidic behavior in HSO$_3$F can then be assessed by the use of electrical conductivity measurements.

In HSO$_3$F, as in H$_2$SO$_4$ and H$_2$O, the ions produced by autoprotolysis display much higher mobilities than any other ions in the solvent. This has been explained by the concept that they conduct by the proton-transfer mechanism in these strongly hydrogen bonded solvents. Consequently, strong acids and strong bases give rise to highly conductive solutions in HSO$_3$F, and titrations with KSO$_3$F (a strong base in HSO$_3$F) can then be used to distinguish between acidic and basic conductivities.

In the following sections in this chapter, a few important topics will be reviewed in more detail.

1.B PROPERTIES OF HSO$_3$F

The properties of HSO$_3$F are compared with those of the more familiar protonic solvents, H$_2$SO$_4$ and H$_2$O, in Table 1.1.

As can be seen, HSO$_3$F has a long liquid range; and a low
TABLE 1.1 Properties of HSO₃F, H₂SO₄ and H₂O (at 25°C)

<table>
<thead>
<tr>
<th></th>
<th>HSO₃F ¹³</th>
<th>H₂SO₄ ³⁹</th>
<th>H₂O ⁴⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freezing point, °C</td>
<td>-88.98</td>
<td>10.371</td>
<td>0.00</td>
</tr>
<tr>
<td>Boiling point, °C</td>
<td>162.7</td>
<td>290</td>
<td>100.00</td>
</tr>
<tr>
<td>Density (g·cc⁻¹)</td>
<td>1.7264</td>
<td>1.8269</td>
<td>0.9971</td>
</tr>
<tr>
<td>Viscosity (cp)</td>
<td>1.56</td>
<td>24.54</td>
<td>0.8904</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>-120</td>
<td>100</td>
<td>78.33</td>
</tr>
<tr>
<td>k (Ω⁻¹cm⁻¹)</td>
<td>1.085×10⁻⁴</td>
<td>1.044×10⁻²</td>
<td>4.3×10⁻⁸</td>
</tr>
<tr>
<td>Λ⁺</td>
<td>185</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Λ⁻</td>
<td>135</td>
<td>166</td>
<td>200</td>
</tr>
<tr>
<td>Kₐp (mol²kg⁻²)</td>
<td>3.8×10⁻⁸</td>
<td>2.7×10⁻⁴</td>
<td>1.0×10⁻¹⁴</td>
</tr>
<tr>
<td>-H₀</td>
<td>15.07</td>
<td>11.93</td>
<td>-7.00</td>
</tr>
</tbody>
</table>

viscosity. These two factors have made HSO₃F a very useful medium for n.m.r. studies at low temperatures ²²,²⁴,⁴¹⁻⁴⁵. In such conditions, individual components of an exchange reaction can be identified.

In contrast to H₂SO₄, in which a series of dissociative reactions, represented by equations (1.9) to (1.12), have been observed ³⁹,

\[
\begin{align*}
2\text{H}_2\text{SO}_4 & \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{HSO}_4^- & K = 2.7 \times 10^{-4} & (1.9) \\
2\text{H}_2\text{SO}_4 & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HS}_2\text{O}_7^- & K = 5.1 \times 10^{-5} & (1.10) \\
\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{H}_3\text{SO}_4^+ + \text{HS}_2\text{O}_7^- & K = 1.4 \times 10^{-2} & (1.11) \\
\text{H}_2\text{O} + \text{H}_2\text{SO}_4 & \rightleftharpoons \text{H}_3\text{O}^+ + \text{HSO}_4^- & K = 1 & (1.12)
\end{align*}
\]

HSO₃F undergoes only two minor autodissociative reactions in the pure state ⁴⁶:

\[
\begin{align*}
2\text{HSO}_3 & \rightleftharpoons \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^- & K = 3.8 \times 10^{-8} & (1.13) \\
\text{HSO}_3\text{F} & \rightleftharpoons \text{HF} + \text{SO}_3 & K < 3 \times 10^{-7} & (1.14)
\end{align*}
\]

For all practical purposes, these dissociations do not interfere with the interpretation of conductivity and cryoscopic data in
HSO₃F

A decrease in intermolecular association in HSO₃F, due to the presence of one less hydrogen per molecule than in H₂SO₄, can be reflected in its lower viscosity and the lower molar conductivities for H₂SO₃F⁺ and SO₃F⁻. Nevertheless, the ion mobilities of the autoprotolysis ions are still much higher than those of the other ions in HSO₃F. For example, K⁺ has a λ⁺ value of only 17 in HSO₃F (the data for H₂SO₃F⁺ and SO₃F⁻ are listed in Table 1.1). The high acidity of HSO₃F as compared to other strong acids in terms of H₀ of the pure acids is illustrated below 12,47-49:

HF(-11)<H₂SO₄(-11.93)<HSO₃Cl(-13.80)<HSO₃CF₃(-14.00)<HSO₃F(-15.07).

1. C SUPERACID SYSTEMS BASED ON HSO₃F

As mentioned previously, the SbF₅-3SO₃ superacid has been found to be the strongest acid in HSO₃F. Solutions of SbF₅ in HSO₃F, although slightly less acidic, have been used extensively in organic chemistry for the stabilization of carbonium ions, because they contain less SO₃. The SbF₅-HSO₃F system is very complex, and can be represented by the following equilibria 22,24:

\[ \text{HSO}_3^+ + \text{SbF}_5 \rightleftharpoons \text{HSbF}_6 \ (1.15) \]
\[ \text{HSbF}_6 + \text{HSO}_3^+ \rightleftharpoons \text{H}_2\text{SO}_3^+ + \text{SbF}_5 \text{(SO}_3\text{F})^- \ (1.16) \]
\[ 2\text{HSbF}_6 \rightleftharpoons \text{H}_2\text{SO}_3^+ + \text{Sb}_2\text{F}_{10}\text{(SO}_3\text{F})^- \ (1.17) \]
\[ \text{HSO}_3^+ \rightleftharpoons \text{HF} + \text{SO}_3 \ (1.18) \]
\[ 2\text{HF} + 3\text{SbF}_5 \rightleftharpoons \text{HSbF}_6 + \text{HSb}_2\text{F}_{11} \ (1.19) \]
\[ 3\text{SO}_3 + 2\text{HSO}_3 \rightleftharpoons \text{HS}_2\text{O}_6\text{F} + \text{HS}_3\text{O}_9\text{F} \ (1.20) \]
This interactive series of reactions gives rise to different dominant species in solutions, depending on the concentration of SbF$_5$. This can lead to side reactions and may present difficulties when attempts are made to isolate a particular product from the mixture. Also, because the mixture is so complex, the use of spectroscopic techniques such as F-19 n.m.r. and Raman are difficult.

Since SbF$_5$ is an ansolvo-acid of the HSO$_3$F system, other pentafluorides of Group V elements, such as AsF$_5$ and TaF$_5$, should also be expected to behave as acids in the solvent. While they do give rise to conducting solutions in HSO$_3$F, these solutions are only very weakly acidic (when either PF$_5$ or NbF$_5$ is dissolved in HSO$_3$F, the resulting solutions are hardly conducting). Titrations of these solutions with KSO$_3$F also indicate only weakly acidic behaviors. Broad and ill-defined conductivity minima at the base/acid ratios of 0.06, 0.01, and 0.31 are found for solutions of BiF$_5$, AsF$_5$ and AsF$_5$·SO$_3$, respectively. In the HSO$_3$F-AsF$_5$ system, SO$_3$ presumably behaves as it does in the HSO$_3$F-SbF$_5$ system.

While the conductometric titration with KSO$_3$F can provide a semi-quantitative assessment of a solute's acidity in HSO$_3$F, a ranking of its acidity can be made by two other methods discussed below:

a) The Bronsted acidity of a solution governs the degree of protonation of bases in it. By using a series of weakly basic nitro-aromatic compounds, the Hammett Acidity Function, $-H_0$, has been determined for a number of strong acids and superacids.
The results parallel those obtained from conductometry, namely, that the effectiveness of a solute in increasing the acidity of HSO₃F increases in the order of SO₃<AsF₅<SbF₅<SbF₅-3SO₃. The behavior of SO₃ as an extremely weak acid in HSO₃F, forming polyfluorosulfuric acids of the type H(SO₃)ₙF, has also been demonstrated by the spectroscopic methods of Raman and F-19 n.m.r. A 7% molar solution of SbF₅·3SO₃ in HSO₃F gave an H₀ value of -19.35, the highest one measured thus far. The lack of suitable bases prevented the extension of the work to more concentrated, and presumably more acidic solutions. By an extrapolation of the results obtained at lower concentrations in the HSO₃F-SbF₅ system, the 1:1 molar mixture - sometimes called 'magic acid' - has an H₀ value of -19.5, making that solution an extremely acidic medium. Figure 1.1 shows the H₀ function plot for a number of solutes in HSO₃F.

While the original H₀ measurements, as defined by Hammett, were obtained by the spectrophotometric monitoring of the concentrations of the base and its protonated species, an alternative method has been proposed recently by Sommer. This method is based on determining the increase in the barrier of rotation around the phenyl-carbonyl bond, in compounds such as p-methoxy-benzaldehyde, upon protonation as measured by n.m.r. shifts. A value equivalent to H₀ of -21.4 was obtained for a 25 mol% of SbF₅ in HSO₃, suggesting an extremely high proton donating ability in the medium. However, the increase in the rotation barrier for the C-C bond in the indicator could conceivably be dependent
-H_0 functions of some acids and bases in HSO_3F

![Graph showing -H_0 functions of some acids and bases in HSO_3F](image-url)
on the increased viscosity of these strongly hydrogen bonded solutions containing high concentrations of SbF$_5$. Thus, this may not be a true measure of the protonating ability of such highly concentrated superacids. This could explain the conclusion reached in the study that HF-SbF$_5$ (which has a higher viscosity than HSO$_3$F-SbF$_5$) is the much more acidic medium of the two.$^{52}$

In any event, it should again be pointed out that the usefulness of a superacid system is reflected in the protonating ability, but also on the lack of basicity in the system. The greater charge delocalization in the HSO$_3$F based superacid is illustrated in the following basicity measurements.

b) The nucleophilicity, or basicity of a solution, determines the stability of a cationic species in it. An alkyl cation, for example, can rearrange with or without deprotonation during its lifetime in the acid, depending on the nucleophilicity of the acidic species. Using tritium-labelled alkanes, Krammer studied the extent of the isomerization and exchange reactions of alkanes in a series of acids containing different Lewis acids.$^{53,54}$ A selectivity parameter, I/E, defined as the ratio of:

$$\frac{k(\text{isomerization})}{k(\text{exchange})},$$

was derived for each of the mixtures studied. The results, represented in Figure 1.2, show that I/E parallels $H_0$ within a given acid, but the correlation is solvent dependent. Alternatively, a strong acid is usually also a weak base in a given solvent system.
FIG 1.2 RELATIONSHIP BETWEEN I/E AND $-H_o^{53}$
1.D APPLICATIONS OF SUPERACIDS

The low bascity of superacid systems has also been used to advantage in the study of highly electrophilic, non metallic polyatomic cations, in particular, polyhalogen cations. The 'hardness' and electrophilicity of a particular cation are expected to increase with a decrease in its size. Thus, while $I_7^+$, $I_5^+$ and $I_3^+$ are stable in 100% $H_2SO_4$, the smaller $I_2^+$ can only be obtained either in oleum or in $HSO_3F$. In the bromine system, the oxidation of $Br_2$ in the superacid medium of $HSO_3F-SbF_5-SO_3$ according to:

$$3Br_2 + S_2O_6F_2 \rightarrow 2Br_3^+ + 2SO_3F^-,$$

(1.21)
gives rise to $Br_3^+$, but, in the more basic $HSO_3F$, the cation disproportionates:

$$Br_3^+ + SO_3F^- \rightarrow Br_2 + BrSO_3F^-.$$

(1.22)

Similarly, the smaller $Br_2^+$ ion is found to be unstable even in the extremely weakly basic medium of $HSO_3F-SbF_5-SO_3$:

$$2Br_2^+ + 2HSO_3F \rightarrow Br_3^+ + BrSO_3F + H_2SO_3F^+.$$

(1.23)

Contrary to earlier reports, there is no evidence for the existence of either $Cl_2^+$ or $Cl_3^+$ in superacid solutions. However, $Cl_3^+$-containing salts have been identified in the reaction of a mixture of $Cl_2$ and CIF with either $AsF_5$ or $HF-SbF_5$ at $-78^\circC$.

The fact that strong protonic acids can catalyze rearrangement and nucleophilic substitution reactions involving large organic molecules has been known for a long time. Very recently,
Olah found that superacid systems, at high temperatures and pressures, can protonate small alkanes such as methane to form species like CH$_5^+$. The subsequent condensation of such cations to form larger, longer chained alkanes is a process of obvious industrial importance.

1.E PREPARATION OF METAL FLUOROSULFATES

Fluorosulfate chemistry displays a similarity to halogen chemistry in that the S$_3$O$^-$ group can be viewed as a pseudohalogen. Consequently, many of the synthetic methods used commonly in the synthesis of halides can be adapted to the fluorosulfate system with only minor changes.

1.E.1 SOLVOLYSIS OF ACID SALTS IN HSO$_3$F

As is common for the preparation of salts of a strong acid, fluorosulfates can be made by simple displacement reactions such as $^2, ^{21, 61-63}$:

$$\text{HSO}_3\text{F} + \text{KCl} \underset{\rightarrow}{\text{HCl + KSO}_3\text{F}}.$$  

(1.24)

The oxidation state of the metal involved remains unchanged and since this is an ionic reaction, it is especially applicable to the synthesis of alkali or alkali earth fluorosulfates. If the acid salt is polymeric, an incomplete reaction often occurs. For transition metal fluorosulfates that show limited solubilities in HSO$_3$F, such as Cu(SO$_3$F)$_2$, a complete reaction does not take place without the addition of KSO$_3$F to increase the basicity of
the medium \(^{62}\). As expected, the formation of a volatile acid such as HCl or HBr, as the by-products from the reaction greatly simplifies the preparation. Conversely, for carboxylates or other salts that give rise to non-volatile acids, the products, which need to be insoluble in HSO\(_3\)F in these cases, have to be separated by filtration. Furthermore, the solvolysis of compounds such as carbonates or nitrates will give H\(_2\)O as one of the products, and therefore cannot be used.

1.E.2 OXIDATION OF METALS BY HSO\(_3\)F

Hydrohalic acids are frequently used to react with metals to give metal halides directly. Just as some metals can reduce H\(_2\)SO\(_4\) to SO\(_2\), HSO\(_3\)F has been found to be reduced to SO\(_2\) and even elemental sulfur. Besides, most metals are inert even in the boiling acid, either because HSO\(_3\)F cannot oxidize the metal or because an insoluble surface layer is formed \(^{64}\).

1.E.3 INSERTION OF SO\(_3\) INTO M-F BONDS

The formation of fluoride-fluorosulfates of As(V) and Sb(V) in HSO\(_3\)F by the insertion of SO\(_3\) into the metal-fluorine bonds has been discussed \(^{24,50}\):

\[
[SbF_5(SO_3F)]^- + nSO_3 \rightarrow [SbF_{(5-n)}(SO_3F)_{n+1}]^- \quad (1.25)
\]

Species with \(n\) of up to 3 have been identified in solution. When no acid is present, the substitution is incomplete, forming only one product when an excess of SO\(_3\) is used \(^{65}\).
\[ \text{SbF}_5 + \text{SO}_3 \rightarrow \text{SbF}_4(\text{SO}_3\text{F}) \, . \] (1.26)

When this method is applied to other metal fluorides, complete reaction is found only for alkali and alkaline earth metal fluorides\(^2,66,67\). For example, the difluorides of nickel and copper, when subjected to \(\text{SO}_3\), yielded only about 20% conversions\(^68\).

\[ \text{NiF}_2 + 2\text{SO}_3 \rightarrow \text{Ni(}\text{SO}_3\text{F})_2 \, . \] (1.27)

The reaction of \(\text{CrF}_5\) with \(\text{SO}_3\) did not give a fluorosulfate of \(\text{Cr(V)}\), but did provide a novel synthesis of \(\text{S}_2\text{O}_6\text{F}_2\)\(^69\).

\[ \text{CrF}_5 + 5\text{SO}_3 \rightarrow \text{S}_2\text{O}_6\text{F}_2 + \text{Cr(}\text{SO}_3\text{F})_3 \, . \] (1.28)

A final obstacle in these reactions is the tendency for \(\text{SO}_3\) to polymerize, giving rise to asbestos-like materials of rather low volatility, making product separation difficult and awkward.

To summarize, the above three synthetic routes are of limited use in the synthesis of metal fluorosulfates. Furthermore, they do not provide a means to obtain metals in high oxidation states.

1.E.4 **OXIDATIVE FLUOROSULFONATION WITH \(X\text{SO}_3\text{F}; X=\text{Ha}1 \text{ OR } \text{SO}_3\text{F}\)**

This general scheme combines fluorosulfate addition together with oxidation, analogous to the direct reaction of a metal or its salts with a halogen.

1.E.4.1 **BIS(FLUOROSULFURYL) PEROXIDE**

\(\text{S}_2\text{O}_6\text{F}_2\), discovered by Cady and Dudley, is most efficiently prepared by the flow reaction of \(\text{SO}_3\) with \(\text{F}_2\) in the presence of
AgF₂ as a catalyst \(^{70,71}\).

\[
2\text{SO}_3 + \text{F}_2 \rightarrow \text{S}_2\text{O}_6\text{F}_2 .
\]  

(1.29)

It has a low dissociation energy of 22 kcal/mol, yielding \(\text{SO}_3\text{F}\) radicals, and can be regarded as a pseudohalogen in this respect \(^{72,73}\):

\[
\text{F}_0^\text{2SO-OSO}_2\text{F} \leftrightarrow 2\cdot\text{OSO}_2\text{F} .
\]  

(1.30)

Oxidative reactions with \(\text{S}_2\text{O}_6\text{F}_2\) can give a variety of fluoro-sulfate-containing compounds, depending on the choice of starting materials. A few illustrative examples are given below:

a) **Oxidative addition of \(\text{SO}_3\text{F}\)**

\[
\text{MF}_3 + \text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{MF}_3(\text{SO}_3\text{F})_2 \quad \text{M} = \text{As} \quad ^{74}, \text{Sb} \quad ^{26}
\]  

(1.31)

\[
\text{CeF}_3 + \frac{1}{2}\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{CeF}_3(\text{SO}_3\text{F}) \quad ^{75}
\]  

(1.32)

b) **Halogen displacement**

\[
\text{MCl}_x + \frac{5}{2}\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{M}(\text{SO}_3\text{F})_x + \frac{5}{2}\text{Cl}_2
\]  

(1.33)

\(\text{M} = \text{Ga(III)} \quad ^{76}, \text{Sn(IV)} \quad ^{33}\).

c) **Metal oxidation**

\[
\text{Mo} + 3\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{MoO}_2(\text{SO}_3\text{F})_2 + 2\text{S}_2\text{O}_5\text{F}_2 \quad ^{75}.
\]  

(1.34)

\(\text{S}_2\text{O}_6\text{F}_2\), being a nonionizing liquid, has very poor solvating properties towards ionic solids. Many metals are unreactive towards this strong oxidizing agent because of the rapid passivation of the metal surfaces. On the other hand, \(\text{S}_2\text{O}_6\text{F}_2\) is easily transferred and handled in glass vacuum lines and it can be obtained readily and in good yields by reaction (1.29). The solubility problem mentioned previously may be solved by the availability of a suitable solvent to increase the reactivity.
of $S_2O_6F_2$.

1.E.4.2 HALOGEN (I) MONOFLUOROSULFATES

Halogen (I) mono-fluorosulfates, formed by the direct reaction between the halogen and $S_2O_6F_2$,

$$\text{Hal}_2 + S_2O_6F_2 \rightarrow 2\text{HalSO}_3F \quad \text{Hal=F, Cl, Br, I} , \quad (1.35)$$

are themselves also very strong oxidizing agents and should therefore be very useful in the preparation of metal fluorosulfates. Their relative effectiveness as the active reagents in such reactions is outlined below:

a) Fluorine (I) monofluorosulfate

$FSO_3F$ is sometimes formed as a by-product during the synthesis of $S_2O_6F_2$ by reaction (1.29) when fluorine is present in excess. It is an extremely powerful oxidizing agent, and reactions with it usually lead to the simultaneous addition of fluorine and fluorosulfate, as in $^{26}$:

$$\text{SbF}_3 + FSO_3F \rightarrow \text{SbF}_4(\text{SO}_3F) . \quad (1.36)$$

The major obstacle to the investigation of $FSO_3F$ chemistry is its unpredictable tendency to detonate.

b) Chlorine (I) monofluorosulfate

Like $FSO_3F$, $ClSO_3F$ is the only binary fluorosulfate of the halogen. It can be made only by a high temperature ($125^\circ C$) reaction which takes a week to complete. It must also be stored and handled in metal apparatus since it reacts with trace amounts of moisture in glass to give a red viscous liquid $^{77}$. It has not
been used extensively in synthetic fluorosulfate chemistry also because of the ready availability of \( \text{BrSO}_3\text{F} \) which can substitute for \( \text{ClSO}_3\text{F} \) in most cases but does not have any of its disadvantages.

c) **Bromine (I) monofluorosulfate**

\( \text{BrSO}_3\text{F} \), although extremely hygroscopic like the other halogen fluorosulfates, has been found to be an extremely versatile oxidative fluorosulfonating reagent. This easily synthesized red liquid appears to be associated and supports the solvation of ionic species \(^{38,78}\). It can be safely stored and handled in glass and can be distilled in vacuo at room temperature. \( \text{BrSO}_3\text{F} \) reacts with chlorides or bromides to give the corresponding fluorosulfates \(^{79}\) according to:

\[
\text{MCl}_n + n\text{BrSO}_3\text{F} \rightarrow \text{M(SO}_3\text{F)}_n + \frac{n}{2}\text{Br}_2 + \frac{n}{2}\text{Cl}_2 .
\]

When alkali metal chlorides are used, complexation takes place and salts of the type \( \text{M(I)Br(SO}_3\text{F)}_2 \) are formed \(^{80,81}\). In the few reported reactions involving noble metals, \( \text{BrSO}_3\text{F} \) was found to oxidize and dissolve the metals directly:

\[
\text{M} + n\text{BrSO}_3\text{F} \rightarrow \text{M(SO}_3\text{F)}_n + \frac{n}{2}\text{Br}_2
\]

\( \text{M=Au, Pt}^{82}, \text{Ag}^{83,84} \). \( n=3, 4, 1.33 \).

d) **Iodine (I) monofluorosulfate**

\( \text{ISO}_3\text{F} \) is expected to be only a mildly oxidizing and fluorosulfonating agent. Since it is a solid which is difficult to prepare, it has mainly been used for the study of poly- and inter-halogen cations \(^{37,85,86}\).
In conclusion, for the purpose of this study, all the previously described synthetic reagents have their advantages and disadvantages (either in terms of their physical or their chemical properties). It would be desirable to devise a general synthetic method which can be applied to specific compounds with only minor modifications needed.

1.F TRANSITION METAL FLUOROSULFATES

The chemistry of the 3d metals is, in general, better explored and understood than that of the heavier transition elements. It is therefore not surprising that most of the fluorosulfates of the 3d elements are known, with the metals in the normal oxidation numbers of +2 and +3. These are easily prepared by the solvolysis of the corresponding chloride or other salts in HSO$_3$F followed by filtration. These fluorosulfates are insoluble in the acid, indicating high degrees of polymerization in the solid state. This is supported by results from vibrational spectroscopy. In addition, the oxyfluorosulfates VO(SO$_3$F)$_3$ and CrO$_2$(SO$_3$F)$_2$ have also been reported. These fluorosulfates are unsuitable as ansolvo-acids in HSO$_3$F.

For the heavier elements, the binary fluorosulfates of Cd and Hg, prepared by:

\[
\begin{align*}
\text{Cd}(\text{C}_6\text{H}_5\text{COO})_2 + 2\text{HSO}_3\text{F} & \rightarrow \text{Cd}(\text{SO}_3\text{F})_2 + 2\text{C}_6\text{H}_5\text{COOH} \quad (1.39) \\
\text{Hg} + \text{S}_2\text{O}_6\text{F}_2 & \rightarrow \text{Hg}(\text{SO}_3\text{F})_2 \quad (1.40)
\end{align*}
\]

are also polymeric, with tridentate SO$_3$F groups. Gold and platinum dissolve in BrSO$_3$F and adducts have been isolated from
the reaction mixtures. Oxyfluorosulfates with the metals usually in the highest attainable oxidation states are known; examples are: NbO(SO$_3$F)$_3$, TaO(SO$_3$F)$_3$, ReO$_3$(SO$_3$F), ReO$_2$(SO$_3$F)$_3$, MoO$_2$(SO$_3$F)$_2$ and WO(SO$_3$F)$_4$. With the high positive charge on the metals in these compounds, they should be expected to possess Lewis acid properties. Since these compounds have not been fully characterized, a more detailed investigation of them and of related systems is also the intention of this study.

1.G VIBRATIONAL MODES OF THE SO$_3$F GROUP

The analysis of the vibrational spectrum of the SO$_3$F group can provide information regarding the type of coordination and the extent of interactions with the cations. This is a distinct advantage a SO$_3$F group has over monatomic ligands such as F$^-$ or Cl$^-$. A free SO$_3$F$^-$ ion has C$_{3v}$ symmetry, but this can be reduced to C$_S$ or even C$_1$ with a corresponding increase in the number of vibrational modes from 6, (3A$_1$ + 3E), to 9, (6A$'$ + 3A$''$), when one or two oxygen atoms are coordinated. Coordination of all three oxygen atoms or even including the fluorine atom in a tridentate or tetradeutate manner will restore C$_{3v}$ symmetry to the ligand and reduce the number of bands back to six, (3A$_1$ + 3E). All of the vibrational modes of SO$_3$F are both i.r. and Raman active. Hence, the vibrational spectra of SO$_3$F groups can be divided into two main groups:
a) 6-band spectra produced from ionic, tridentate and tetra-dentate SO$_3$F groups with C$_{3v}$ symmetry.

b) 9-band spectra produced from mono- and bi-dentate SO$_3$F groups which have C$_s$ or C$_1$ symmetry.

Since there are three degenerate E modes when the fluoro-sulfate group has C$_{3v}$ symmetry, these are susceptible to splittings by site symmetry or by aspherical cations producing polarization effects. The splittings can be seen in the SO$_3$ stretching region at -1200 to 1300 cm$^{-1}$.

Within the two groups of 6- and 9-band spectra, a further distinction can be made based on the band positions. Firstly, coordination of oxygen or fluorine will weaken and thus lower the stretching frequencies of the S-O and S-F bonds. Secondly, electron withdrawal via the coordination of oxygen will strengthen the remaining S-O and S-F bonds. This, according to Cruickshank and Webster 92, is due to the increased back donation from the filled p$^\pi$ orbitals of oxygen or fluorine to the empty d$^\pi$ orbitals on sulfur now that the sulfur atom has become more positive. Hence the S-F stretching frequency can be used as a diagnosis to determine if coordination of the oxygen atom is present. Invariably, the S-F stretch shifts to a higher frequency for covalently bound SO$_3$F groups. Examples of the band patterns for the various types of coordination of the SO$_3$F group are shown in Fig 1.3 and discussed subsequently:

a) ionic ——— KSO$_3$F, being an ionic crystalline salt 93,
Fig 1.3 VIBRATIONAL BAND PATTERN FOR THE SO$_3$F GROUP

Ionic, $C_{3v}$

Ionic (Perturbed), $C_{2v}$

Monodentate, $C_{s}$

Bidentate, $C_{s}$

Tridentate, $C_{3v}$

Tetradentate, $C_{3v}$

$\nu_{SO}$

$\nu_{SF}$

$\delta SO_3F$

KSO$_3$F $^{93}$

NOSO$_3$F $^{94}$

KBr(SO$_3$F)$_4$ $^{35}$

(CH$_3$)$_2$Sn(SO$_3$F)$_2$ $^{97}$

Ni(SO$_3$F)$_2$ $^{87}$

Ti$_3$Cl$_{10}$(SO$_3$F)$_2$ $^{100}$

1500

1000

500

200 cm$^{-1}$
gives a vibrational spectrum representative of ionic fluorosulfate with bands at 1285, 1079, 745, (594, 586), 570 and 407 cm$^{-1}$.

b) ionic perturbed —— With strongly polarizing and sometimes asymmetrical cations such as NO$^+$ and NO$_2^+$, splittings of the E modes are observed. For example, $\nu_4$, (SO$_3$ stretch), becomes split by about 35 cm$^{-1}$ in NO(SO$_3$F) $^{94}$.

c) covalent monodentate —— In Hal-SO$_3$F, the symmetry of the molecule is reduced to Cs, and the vibrational spectra show nine distinct bands. For example, in ClSO$_3$F, $\nu$(S-F) is increased to 830 cm$^{-1}$ and $\nu$(S-O) are found at 1478, 1225 and 856 cm$^{-1}$ $^{95}$.

d) covalent bidentate —— As a bidentate ligand, the SO$_3$F group is usually found in the bridging mode between two metal ions, as in (CH$_3$)$_2$Sn(SO$_3$F)$_2$ $^{96,97}$. For this type of coordination, $\nu$(S-O) are found at ~1400, ~1150 and ~1070 cm$^{-1}$. While the example given here can be classified as containing bridging SO$_3$F groups spanning two identical metal ions, another type, which may be termed 'aniso-bidentate bridging' seem to occur in cases when the two metal ions have different charges. The spectra for such species, as in M(II)[M(IV)(SO$_3$F)$_6$] $^{84,98}$ contain bands typical for both monodentate and bidentate SO$_3$F groups.

e) covalent tridentate —— The 3d transition metal bis(fluorosulfates) are polymeric, each SO$_3$F ligand being coordinated to three different metal centres $^{87,99}$. The symmetry of the anion is restored to C$_3v$. This type of coordination can be distinguished from the ionic C$_3v$ situation by the high $\nu$(S-F)
of about 850 cm$^{-1}$ for these compounds.

f) covalent tetradentate In the unique case involving Ti$_3$Cl$_{10}$(SO$_3$F)$_2$, the vibrational spectra for the compound indicate a C$_{3v}$ symmetry for the SO$_3$F group. ν(S-F), however, is significantly lowered to 660 cm$^{-1}$, presenting evidence for the coordination of the fluorine atom as well.

Ionic fluorosulfates are not the only type that can show cation-anion interactions; in fact, most spectra of fluorosulfates have additional complexities caused by solid state splittings. Generally, vibrational spectra do provide useful information concerning the environment of the fluorosulfate group and the type of coordination. A number of diagnostic band positions together with their intensities normally allow a clear distinction between monodentate and bidentate coordinations, the two most commonly encountered types.
2.A INTRODUCTION

This chapter will deal only with general experimental techniques and the sources of starting chemicals used in this study; specific syntheses will be described in the appropriate chapters. Since most of the compounds involved are extremely moisture sensitive, an environment excluding air, (or more specifically, water), had to be employed.

Standard vacuum line techniques were used for the handling of volatile materials; all stop-cocks were of the greaseless teflon stem valve type from Kontes. Reactions were performed in one-part Pyrex reaction vials of about 30mL capacities, fitted with the teflon stop-cocks. Some typical glass apparatus used in this study is shown in Fig 2.1. When high gas pressures were anticipated in a reaction, 3mm thick-wall reactors were used in place of the standard 1mm-wall reactors.

In order to reduce the sources of contaminations, teflon coated stirring bars were used only when necessary. For the preparation of solutions for conductometric studies that required stirring, a glass-encapsulated stirring bar was used in a flat end reactor. In the course of the study, some specific situations required special modifications to the standard apparatus; a few are described in the appropriate chapters or shown in Fig 2.1.
FIG 2.1 EXAMPLES OF GLASS APPARATUS

standard reactor  vacuum filter
All reactions were monitored by weight differences in the reaction vials. The removal of volatile materials after a reaction had completed usually proceeded by evacuating first at room temperature or below, followed by a further evacuation at ~40°C. The latter step was necessary especially in cases involving HSO₃F or BrSO₃F, as both have extremely low vapor pressures at room temperature.

Occasionally, the calculated yields from some reactions appeared to be low, with attack of the reaction vessel and the subsequent weight loss as SiF₄ the primary reason. In particular, high temperature reactions involving any fluorosulfate-containing reactants and extended reaction times were vulnerable to such an attack. Nevertheless, the reduction in the weights of the reactors were usually below 10mg and did not justify the use of less convenient vessels such as those made of fluoro-plastics (Kel-F) or metal. For reactions involving BrF₅ or fluorine at high pressure, Monel reactors were used.

2.B GENERAL EQUIPMENT

2.B.1 DRYBOX

The handling of hygroscopic materials that had limited volatilities at room temperature necessitated the use of a dry box — a Vacuum Atmosphere Corporation Dry-Lab, Model HE-43-2 fitted with a Dri-Train Model HE-93-B recirculating unit. The inert atmosphere of dry nitrogen gas was constantly drawn through
a molecular sieve chamber to maintain its purity.

2.B.2 ELECTRICAL CONDUCTIVITY

The conductivity cell, shown in Fig 2.2, is similar to the design of Barr et al\textsuperscript{21}. This cell allowed the measurement on solutions with between ~7 to ~100mL of volumes. The platinum-black coating of the electrodes was renewed from time to time by electroplating from a solution of H\textsubscript{2}PtCl\textsubscript{6}\textsuperscript{101}. The cell constants were determined using aqueous KCl solutions of ~0.01M\textsuperscript{102} and had values from (5.367 ± 0.007) to (5.353 ± 0.017) cm\textsuperscript{-1}.

The quantitative measurements of conductivity were carried out using a Wayne-Kerr Universal Bridge, Model B221A. The cell temperature of (25.00 ± 0.01)°C was maintained by immersion into an oil bath of ~35L capacity, regulated by a Sargent Thermonitor, Model ST. It was noted that after about 5 minutes, most of the solutions studied did not show any further variations in their conductivities. The equilibration period for all solutions was about 10 minutes in the oil bath after each addition of new materials to the cell.

In the beginning of this study, the addition of solutes or solvent to the cell was by the use of weight droppers, shown in Fig 2.3. It had previously been noted that the introduction of small amounts of moisture into the cell during the insertion and removal of the dropper led to a small but consistent rise in the conductivity of pure HSO\textsubscript{3}F of the order of 10\textsuperscript{-5} Ω\textsuperscript{-1}cm\textsuperscript{-1}\textsuperscript{103}. 
FIG 2.2  CONDUCTIVITY CELL

FIG 2.3  WEIGHT DROPPER
Because of the small quantities of solutes used in this study (~1 mmol), and the low molecular weight of water (18 g·mol⁻¹), it was decided that this interference was not acceptable. Furthermore, the formation of HF and H₂SO₄ from the hydrolysis of HSO₃F would introduce two basic solutes in HSO₃F. Obviously, conductometric studies of acids in HSO₃F, the main objective of this study, would be adversely affected by this side reaction.

The volumetric addition of solutions, although limited in accuracy by the buret (±0.02 mL), provided an alternative that excluded the exposure to moisture. Such a buret is illustrated in Fig 2.4. Designed to be filled in the Dry box, which limited its maximum capacity to ~20mL, the buret's accuracy was maximized by using large volumes of dilute solutions. The actual measurement of the density of the solution to be added did not have to be performed as the buret was used as a fractionating device only. As long as the initial and final volumes and weights were known the intermediate quantities were calculated as a fraction of the total quantity. This also minimized errors due to the increase in the internal bore of the buret from etching, which would make any density measurements derived from other sources meaningless. This volumetric addition produced results that were better reproducible and less error prone than the method which monitors successive additions by weight.
FIG 2.4
VOLUMETRIC DROPPER

graduated buret
2.B.3 I.R. SPECTROMETRY

Routine i.r. spectra at room temperature were recorded on either a Perkin Elmer, Model 457, or a Pye Unicam Model SP1100, Grating Spectrophotometer, providing low frequency limits of 250 and 400 cm\(^{-1}\), respectively. Spectra were taken on thin solid films pressed between AgBr, AgCl or BaF\(_2\) windows with a transmission range down to ~250 cm\(^{-1}\), ~400 cm\(^{-1}\) or ~800 cm\(^{-1}\), respectively. The high reactivity of the fluorosulfates studied precluded the use of mulling agents or other window materials. For solution spectra in HSO\(_3\)F, thin teflon films were used to protect the windows, (only the O-H region was of interest).

For low temperature spectra at ~80K, a Perkin-Elmer Model 225 Grating Spectrophotometer with a low frequency limit of 200 cm\(^{-1}\) was used. The cell was of the Hörnig-Wagner design\(^{114}\), consisting of an evacuable Pyrex Dewar with a pair of CsI windows. The Dewar cooled a brass sample window holder directly. Volatile samples could be condensed onto a cooled CsI window and solid samples could be directly deposited.

All spectra were calibrated with a polystyrene reference.

2.B.4 RAMAN SPECTROMETRY

Raman spectra were usually obtained with a Spex Ramalog 5 spectrophotometer equipped with a Spectra Physics Model 164 argon ion laser and using the 514.5 nm exciting line. The samples were contained in melting point capillaries. For compounds that were
brown or red, the green laser was found to cause local decomposition. Therefore, for these compounds, Raman spectra of reduced resolution were sometimes obtained using a Cary 81 spectrophotometer equipped with a Spectra Physics Model 125 He-Ne laser with a 632.8 nm exciting line. The samples were contained in 5 mm flat end Pyrex tubes.

A low temperature cell for the Ramalog 5, shown in Fig 2.5, was developed to enable the recording of spectra of compounds that were unstable to the laser at room temperature. The sample capillary was held in the brass sample holder (cooled to -80K) with grease. Generally, compared to spectra obtained at room temperature, better resolution was obtained. Shifts of bands to lower wavenumber, of the order of 3 to 5 cm\(^{-1}\), were also noted.

2.B.5 ELECTRONIC SPECTROMETRY

Diffuse reflectance spectra of powdered solids from 350 to 740 nm were obtained on a Bausch and Lomb Spectronic 600 Spectrophotometer. For absorption spectra on mulls (in C\(_6\)F\(_{17}\)SO\(_2\)F or fluorolube oil), or solutions in HS\(_3\)F, a Cary 14 Spectrophotometer with a range from the near i.r. to 210 nm, was used. Standard silica solution cells used were of 1 or 10 mm path lengths. Solid mulls were pressed between quartz plates of 2.5 cm diameters and held inside a teflon sample holder.
FIG 2.5  LOW TEMPERATURE RAMAN CELL

- inner part of Dewar
- outer jacket
- brass sample holder
- quartz windows
2.B.6 MAGNETOCHEMISTRY

Magnetic susceptibilities were measured using a Gouy apparatus described by Clark and O'Brien. The calibration was performed using Hg[Co(SCN)$_4$]. The temperature of the sample was controlled by the rate of evaporation of liquid nitrogen around the chamber.

Diamagnetic corrections were taken from Landolt-Börnstein and listed in Table 2.1.

2.B.7 NUCLEAR MAGNETIC RESONANCE

$^1$H — Using a Varian T-60 or a Varian EM-360, both operated at 60 MHz, spectra were recorded of solutions contained in 5 mm n.m.r. tubes and referenced to external TMS.

$^{19}$F — C.W. spectra were recorded on a Varian EM-360 operated at 56.45 MHz using 5 mm n.m.r. tubes. The lock signal was provided by either external CFC$_3$ or internal HSO$_3$F. F.T. spectra were recorded on a Varian XL-100 operated at 94.1 MHz locked on external D$_6$-acetone. All $^{19}$F-spectra are referenced to CFC$_3$ with shifts to lower field considered negative.

$^{119}$Sn, $^{195}$Pt — F.T. spectra were obtained on a Brüker Spectrospin 80 operated at 29.88 MHz for $^{119}$Sn and 21.72 MHz for $^{195}$Pt. 10 mm n.m.r. tubes were used, and the spectrometer was locked to external D$_6$-acetone. No specific references for the chemical shifts were used.
### Table 2.1 DIAMAGNETIC SUSCEPTIBILITIES \(^{107}\) (in cgs units)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Susceptibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Au}^{3+})</td>
<td>(-27 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Cs}^{+})</td>
<td>(-31 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Ir}^{3+})</td>
<td>(-34 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Ir}^{4+})</td>
<td>(-28 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Pd}^{2+})</td>
<td>(-25 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Pd}^{3+})</td>
<td>(-22 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Pd}^{4+})</td>
<td>(-18 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Pt}^{4+})</td>
<td>(-28 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{Sn}^{4+})</td>
<td>(-16 \times 10^{-6})</td>
</tr>
<tr>
<td>(\text{SO}_3\text{F}^-)</td>
<td>(-40 \times 10^{-6}) (by analogy with (\text{SO}_4^{2-}))</td>
</tr>
</tbody>
</table>

Pascal constants: \(\text{Br} \sim -30.6 \times 10^{-6}\), \(\text{Cl} \sim -20.1 \times 10^{-6}\), \(\text{O} \sim -4 \times 10^{-6}\)

### Table 2.2 CHEMICALS USED WITHOUT PURIFICATION

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Source</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Au}), -20 mesh</td>
<td>Alfa</td>
<td>99.995</td>
</tr>
<tr>
<td>(\text{Au}_2\text{O}_3)</td>
<td>Alfa</td>
<td>reagent grade</td>
</tr>
<tr>
<td>(\text{Ge}), -325 mesh</td>
<td>Alfa</td>
<td>99.999</td>
</tr>
<tr>
<td>(\text{GeO}_2)</td>
<td>MCB</td>
<td>99.999</td>
</tr>
<tr>
<td>(\text{Ir}), -60 mesh</td>
<td>Alfa</td>
<td>99.9</td>
</tr>
<tr>
<td>(\text{Mo}), -200 mesh</td>
<td>Alfa</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>(\text{Pd}), -60 mesh</td>
<td>Alfa</td>
<td>99.9</td>
</tr>
<tr>
<td>(\text{Pt}), -60 mesh</td>
<td>Alfa</td>
<td>99.9</td>
</tr>
<tr>
<td>(\text{PtCl}_2)</td>
<td>Strem</td>
<td>99.9</td>
</tr>
<tr>
<td>(\text{Sn}), 20 mesh</td>
<td>BDH</td>
<td>99.97</td>
</tr>
<tr>
<td>(\text{W}), -100 mesh</td>
<td>Alfa</td>
<td>99.98</td>
</tr>
</tbody>
</table>
2.C CHEMICALS

2.C.1 USED WITHOUT PURIFICATION

These are mostly metal powder of high purity for which no purification was necessary or practical. They are listed in Table 2.2 along with their purities and their sources.

2.C.2 PURIFICATION REQUIRED

a) The alkali metal chlorides were dried in a 120°C oven
   - KCl - 99.9% from MCB
   - CsCl - 99.5% from BDH

b) BaCl₂ was obtained by the dehydration of BaCl₂·2H₂O (99.0%, Analar, BDH) in a 120°C oven.

c) Br₂ from Milinkroft (AR grade) was purified by storage in a Pyrex vessel containing P₂O₅ to remove moisture and KBr to remove Cl₂.

d) Cl₂ from Matheson was passed through KMnO₄ to remove HCl and bubbled through concentrated H₂SO₄ to remove moisture.

e) SO₂ from Matheson, was liquidfied in a Pyrex vessel containing P₂O₅ as the desiccant.

f) NOCl from Matheson, was liquidfied and stored in a Pyrex vessel with CaSO₄ as the desiccant.

g) HSO₃F, from Allied Chemical, was purified by double distillations in a Pyrex apparatus at 1 atm. of dry nitrogen 2¹. The constant boiling fraction at 163°C was either collected into a conductivity cell or into a large Pyrex storage vessel for
synthetic uses. The freshly distilled acid had a specific conductance of 1.1-1.3×10^{-4} \text{ Ω}^{-1}\text{cm}^{-1}.

h) \text{HSO}_3\text{CF}_3 \text{ from Minnesota Mining and Manufacturing Company was distilled from concentrated } \text{H}_2\text{SO}_4 \text{ at about 15 torr of dry nitrogen. The fraction with a boiling point of } 120°C \text{ was collected.}

2.C.3 SYNTHESIS REQUIRED

a) \text{S}_2\text{O}_6\text{F}_2 \text{ was prepared by the reaction between } \text{SO}_3 \text{ and } \text{F}_2 \text{ in a } \text{N}_2 \text{ flow system catalyzed by } \text{AgF}_2 \text{. The crude product was condensed as a liquid in Pyrex traps cooled by dry ice. Most of the FSO}_3\text{F was allowed to escape by warming the product to room temperature. Any excess } \text{SO}_3 \text{ was removed by washing the crude product with concentrated } \text{H}_2\text{SO}_4 \text{ followed by the subsequent separation of the two immiscible layers using a separation funnel. The product was then exacuated at dry ice temperature to remove the last traces of FSO}_3\text{F and then vacuum distilled into a large one-part Pyrex storage vessels stoppered with Kontes teflon stopcocks.}

b) \text{BrSO}_3\text{F} \text{ was prepared by reacting } \text{Br}_2 \text{ with a slight excess of } \text{S}_2\text{O}_6\text{F}_2 \text{ in a long stem Pyrex reactor. The excess of } \text{S}_2\text{O}_6\text{F}_2 \text{ was required to prevent the presence of unreacted } \text{Br}_2 \text{. The crude product was pumped briefly to remove any oxygen formed and then stored.}

c) \text{ClSO}_3\text{F} \text{ was prepared by the reaction of a mixture of } \text{Cl}_2 \text{ with } \text{S}_2\text{O}_6\text{F}_2 \text{ in a Monel reactor at } 125°C \text{ for 5 days. Excess
reactants were removed by evacuation at dry ice temperature. The product was stored in the monel reactor.

d) ClO$_2$ was prepared from the reaction of NaClO$_3$ and H$_2$SO$_4$ in the presence of oxalic acid according to Brauer$^{118}$. The product was used immediately for the preparation of ClO$_2$SO$_3$F.

e) ClO$_2$SO$_3$F was synthesized by distilling a large excess of S$_2$O$_6$F$_2$ into a thick wall reactor containing ClO$_2$ at -198°C$^{109}$. The reactor was allowed to warm up slowly to room temperature. The resulting 2-layer liquid was pumped in vacuo to remove the excess S$_2$O$_6$F$_2$.

2.C.4 ELEMENTAL ANALYSES

These were performed by Analytische Laboratorien (formerly A. Bernhardt) Gummersbach, West Germany.
CHAPTER 3  PALLADIUM-FLUOROSULFATE

3.A  INTRODUCTION

In the periodic group of Ni-Pd-Pt, the chemistry of palladium has received the least amount of attention in the past. As is commonly found in transition metal chemistry, a gradual increase in the stability of higher oxidation states of the metal is noted as one goes down the group. Therefore, nickel is usually found in the +2 oxidation state, Ni(IV) being the highest one observed; platinum, on the other hand, exhibits both the +2 and +4 oxidation states, Pt(VI) being the highest one known. Both the +2 and +4 oxidation states of palladium are also quite common, but it is unlike platinum in that the divalent state is found to be more prevalent, examples for Pd(IV) being somewhat rare. The highest obtainable oxidation state of palladium is +5, and as is usually the case, it is found in a fluoride, the recently reported $O_2^+\text{[PdF}_6\text{]}^-$, and possibly $O_2^+\text{[Pd}_2\text{F}_{11}\text{]}^-$ 111. While many organometallic compounds of palladium, like those of nickel and platinum, display oxidation states of 0 and +1, it is interesting to note that Pd(III), and also Pt(III), are exceedingly rare, and only a few examples such as the dicarbollyl of Et$_4$N[Pd-(π-2,3B$_9$C$_2$H$_{11}$)$_2$] 112 have been reported. Generally, these compounds with palladium in the formal oxidation state of +3 are hard to make (electrochemical methods are often used), and require chelating or π bonding ligands to delocalize the metal's charge.
In the coordination chemistry of Ni(II), the d^8 ion usually exists in either one of three configurations: octahedral, e.g. [Ni(H_2O)_6]^{2+}; square planar, e.g. [Ni(CN)_4]^{2-}; or, tetrahedral, e.g. [NiCl_4]^{2-}. Magnetochemistry can provide an excellent means of differentiating between the three geometries: square planar complexes are diamagnetic while both octahedral and tetrahedral ones are paramagnetic, with magnetic moments that should correspond to two unpaired electrons. Because the tetrahedral configuration has a ^3T_1 ground state, a large orbital contribution to its magnetic moment is expected, resulting in \( \mu_{\text{eff}} \) values being much higher than the spin only value of 2.83 \( \mu_B \). This can also lead to a complex temperature dependence of the magnetic susceptibility, rather than the Curie-Weiss law behavior observed for octahedral compounds. For Pd(II) and Pt(II), diamagnetic square planar complexes are almost exclusively found. The increase in ligand field splitting for these two heavier elements of the group causes the d_{x^2-y^2} orbital to be extremely high in energy, i.e., antibonding. Thus, a square planar configuration, in which the strongly antibonding d_{x^2-y^2} can remain vacant, is favored. Also due to the large \( \Delta_0 \), Pd(IV) and Pt(IV) are invariably octahedral, with a ^1A_2g electronic ground state.

The palladium-fluorine system represents some rather interesting anomalies and will be briefly reviewed because similarities between the corresponding fluoro- and fluorosulfato- compounds are to be expected.
PdF₂, formed by the reduction of the trifluoride by either SF₄ or SeF₄, is the only paramagnetic binary Pd(II) compound. A magnetic moment of 1.84 μₜ for PdF₂, suggesting the presence of a paramagnetically concentrated system, is reported. The rutile structure of PdF₂, with an octahedral coordination for Pd(II), and almost linear Pd-F-Pd bonds, allows antiferromagnetic coupling via the superexchange mechanism. Therefore, it is not surprising to find that in mixed crystals of PdF₂-ZnF₂, the effective magnetic moment of Pd(II) increases with the amount of ZnF₂ diluent present, and at infinite dilution, an extrapolated yeff of -3.2μₜ for PdF₂ is obtained. Paramagnetism is also found for some derivatives of PdF₂, such as CsPdF₃, ZnPdF₄, and Pd(II)M(IV)F₆, with M=Ge, Sn, Pd, Pt; but BaPdF₄ is reported to be diamagnetic. Although PdO is diamagnetic, a compound which may be formulated as K₈Pd(II)Pd(IV)₃O₁₁ is paramagnetic, with a magnetic moment of 2.76μₜ for Pd(II). In contrast to the difluoride, the other palladium dihalides and their complexes are diamagnetic. For example, β-PdCl₂, isomorphic with the corresponding platinum chloride, consists of Pd₆Cl₁₂ clusters with square planar [PdCl₄] units linked by chlorine-bridges.

While the other halogens form only the dihalides, fluorine, because of its high oxidizing power, is capable of supporting two additional binary fluorides: Pd₂F₆ and PdF₄. PdF₆, expected to be an even stronger oxidizing agent than PtF₆, has not been
successfully synthesized.\footnote{122}

Palladium dibromide dissolves in BrF$_3$ to form a compound of the composition of PdF$_3$·BrF$_3$ which, upon heating, decomposes to form the trifluoride.\footnote{123} The trifluoride is paramagnetic, and its formulation as PdF$_3$ gives a magnetic moment of 2.04µ$_B$, suggesting a low spin $d^7$ electronic configuration for Pd(III).\footnote{124} The absence of Jahn-Teller distortion in the solid state led Bartlett to invoke a mixed valency composition - Pd(II)Pd(IV)F$_6$, for the compound.\footnote{108} The recalculated magnetic moment of 2.88µ$_B$ for Pd$_2$F$_6$ is consistent with the presence of high spin $d^8$ Pd(II) and low spin $d^6$ Pd(IV), both in octahedral ligand fields. A recent neutron diffraction study shows Pd$_2$F$_6$ to be isomorphous with Pd(II)M(IV)F$_6$, with M=Ge, Sn, Pt\footnote{125}, and M(II)Pd(IV)F$_6$, with M=Mg, Ca, Zn, Cd.\footnote{126} Although the two types of palladium species in the solid state cannot be distinguished in terms of their ionic radii, they can be found in two regular octahedral sites of different dimensions.

The tetrafluoride can be obtained by the direct fluorination of the trifluoride at 300°C and 7 atm.\footnote{127} PdF$_4$ is diamagnetic\footnote{108}, and a neutron diffraction study indicates octahedral coordination for Pd(IV).\footnote{128} In view of the high oxidation state for palladium in PdF$_4$, the low spin $d^6$ electronic configuration found is not unexpected. Diamagnetic complexes of the type of M$_2$[PdF$_6$], with M=K, Rb, Cs, can be readily obtained by the fluorination of the complex chloride with either fluorine\footnote{129} or BrF$_3$.\footnote{130}
Both these Pd(IV)-containing fluorides are strong oxidizing agents, for example, they are capable of converting XeF$_2$ to XeF$_4$. This is consistent with the generally observed trend that Pd(IV) is usually more strongly oxidizing and more difficult to obtain than the corresponding Pt(IV) compounds. To summarize, the fluorides of palladium show some marked differences when compared to the other halides: a) higher oxidation states can be obtained in the fluoride system; and b) the difluoride and some of its derivatives deviate from the square planar geometry in favor of octahedral structures. Furthermore, the existence of [PdHal$_4$]$^{2-}$ and [PdHal$_6$]$^{2-}$, with Hal=F, Cl, indicates halide ion acceptor properties of the palladium halides. The formation of [PdCl$_6$]$^{2-}$ complexes is interesting in that the parent compound - PdCl$_4$, has not been prepared.

The investigation into the hitherto unknown palladium fluoro-sulfate system is expected to contribute further insights into both the halide and fluorosulfate systems.$^{98,132}$

3.B  EXPERIMENTAL

3.B.1  SYNTHESIS OF PALLADIUM BIS(FLUOROSULFATE)

3.B.1.1  OXIDATION OF PALLADIUM METAL WITH BrSO$_3$F

\[
Pd + 2\text{BrSO}_3\text{F} \rightarrow \text{Pd(SO}_3\text{F)}_2 + \text{Br}_2 \tag{3.1}
\]

In a typical reaction, palladium metal (508 mg, 4.77 mmol), was allowed to react with an excess of BrSO$_3$F (~5 mL) at ~110°C for 2 weeks. This slow reaction led to the formation of a purple powder in the mixture. The removal of all volatile materials
yielded Pd(SO$_3$F)$_2$, (1.437 g, 4.72 mmol).

Pd(SO$_3$F)$_2$ is a light purple, hygroscopic, polycrystalline solid. It appears to lack any solubility in either BrSO$_3$F or HSO$_3$F. When heated to above -250°C, it decomposes, with condensations of SO$_3$-like crystals forming on the cooler part of the melting point capillary, suggesting a decomposition scheme of:

$$
\text{Pd(SO}_3\text{F)}_2 \rightarrow \text{PdF}_2 + 2\text{SO}_3
$$

Analysis

<table>
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<th></th>
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3.B.1.2 THERMOLYSIS OF Pd$_2$(SO$_3$F)$_6$

$$
Pd_2(\text{SO}_3\text{F})_6 \rightarrow 2\text{Pd(SO}_3\text{F)}_2 + \text{S}_2\text{O}_6\text{F}_2
$$

The decomposition of Pd$_2$(SO$_3$F)$_6$, (323 mg, 0.343 mmol), at -160°C in vacuo yielded Pd(SO$_3$F)$_2$, (277 mg, calc'd 244 mg), detected as the sole solid product by its Raman spectrum. S$_2$O$_6$F$_2$ was identified as the only volatile product (plus traces of SiF$_4$) by both i.r. and Raman spectroscopy. The reaction cannot be taken to completion because of the presence of small amounts of undecomposed Pd$_2$(SO$_3$F)$_6$ on the cooler part of the reaction vial inaccessible by heating.

3.B.1.3 REDUCTION OF Pd$_2$(SO$_3$F)$_6$ WITH Br$_2$

$$
Pd_2(\text{SO}_3\text{F})_6 + \text{Br}_2 \rightarrow 2\text{Pd(SO}_3\text{F)}_2 + 2\text{BrSO}_3\text{F}
$$

Br$_2$, (-3 mL) was added to a sample of Pd$_2$(SO$_3$F)$_6$, (443 mg, 0.549 mmol), and the mixture was heated at 100°C for $\frac{1}{2}$ hour.
The removal of all volatile material yielded Pd(SO$_3$F)$_2$, (339 mg, 1.113 mmol), identified by the i.r. spectrum of the purple solid obtained.

3.B.2 SYNTHESIS OF PALLADIUM TRIS(FLUOROSULFATE)

$$2\text{Pd(SO}_3\text{F)}_2 + \text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{Pd}_2\text{(SO}_3\text{F)}_6$$  \hspace{1cm} (3.5)

An excess of S$_2$O$_6$F$_2$ (~5 mL) was added to Pd(SO$_3$F)$_2$, (398 mg, 1.31 mmol). An immediate reaction was evident from the gradual darkening of the solid. The mixture was then heated at ~80°C for 12 hours to insure a complete conversion. After the removal of all volatile materials, Pd$_2$(SO$_3$F)$_6$ was obtained, (5.18 mg, 0.642 mmol).

Pd$_2$(SO$_3$F)$_6$ is a dark brown, hygroscopic powder. It displays no observable solubility in either S$_2$O$_6$F$_2$ or HSO$_3$F. It is thermally stable up to ~180°C at atmospheric pressure, although decomposition occurs at the lower temperature of ~120°C in vacuo according to equation (3.3).

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<td>23.68</td>
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3.B.2.2 OXIDATION OF PALLADIUM METAL WITH S$_2$O$_6$F$_2$/HSO$_3$F

$$2\text{Pd} + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{Pd}_2\text{(SO}_3\text{F)}_6$$  \hspace{1cm} (3.6)

A mixture of S$_2$O$_6$F$_2$/HSO$_3$F, (~5 mL), was distilled into a reactor containing palladium metal (215 mg, 2.02 mmol). After heating the mixture at ~100°C for 3 days, a reddish-brown solution
containing dark brown solids was formed, and all metal had reacted. The removal of all volatile materials yielded \( \text{Pd}_2(\text{SO}_3\text{F})_6 \), (794 mg, 0.984 mmol).

### 3.B.3 SYNTHESIS OF HEXAKIS(FLUOROSULFATO)PALLADATE (IV) COMPLEXES

#### 3.B.3.1 PREPARATION OF \( \text{Cs}_2[\text{Pd}(\text{SO}_3\text{F})_6] \)

\[
\text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{HCl} \quad (3.7)
\]

\[
2\text{CsSO}_3\text{F} + \text{Pd} + \text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{Cs}_2[\text{Pd}(\text{SO}_3\text{F})_6] \quad (3.8)
\]

\( \text{HSO}_3\text{F} \) (~3 mL) was added to a mixture of palladium metal, (100 mg, 0.940 mmol), and \( \text{CsCl} \), (316 mg, 1.877 mmol). After the removal in vacuo of all of the \( \text{HCl} \) formed from the initial solvolysis of \( \text{CsCl} \), a mixture of \( \text{S}_2\text{O}_6\text{F}_2/\text{HSO}_3\text{F} \), (~5 mL), was distilled into the reactor. An immediate reaction occurred at room temperature, with the color of the solution taking on a deep red color. Further heating of the reactants at ~100°C for 3 days led to the dissolving of all the metal powder. The removal of all volatile materials yielded a solid which analyzed as \( \text{Cs}_2[\text{Pd}(\text{SO}_3\text{F})_6] \), (902 mg, 0.933 mmol).

The compound can also be made by the reaction of a 2:1 ratio of \( \text{CsCl} \) and palladium metal with ~5 mL of \( \text{BrS}_3\text{F} \). A typical reaction requires about 14 days at ~100°C.

\( \text{Cs}_2[\text{Pd}(\text{SO}_3\text{F})_6] \) is a dark red, hygroscopic, crystalline solid which is soluble in both \( \text{BrS}_3\text{F} \) and \( \text{HSO}_3\text{F} \). It decomposes at ~200°C.
Analysis
Calculated % 27.50 11.01 11.79
Found % 27.25 10.85 11.67

3.B.3.2 PREPARATION OF Ba[Pd(SO₃F)₆]

\[
\text{BaCl}_2 + 2\text{HSO}_3\text{F} \rightarrow \text{Ba}(\text{SO}_3\text{F})_2
\]

(3.9)

\[
\text{Ba}(\text{SO}_3\text{F})_2 + \text{Pd} + 2\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_6]
\]

(3.10)

In a manner analogous to the preparation of Cs₂[Pd(SO₃F)₆], a mixture of Ba(SO₃F)₂, formed from the solvolysis of BaCl₂, (310 mg, 1.490 mmol), in HS0₃F, and palladium metal, (158 mg, 1.490 mmol), was reacted with S₂O₆F₂/HSO₃F, (~5 mL). An immediate reaction also occurred at room temperature, with the formation of a bright red precipitate. The reaction mixture was heated at ~90°C for 7 days as the reaction was quite slow due to the insolubility of the product. The removal of all volatile materials yielded Ba[Pd(SO₃F)₆], (1.233 g, 1.471 mmol).

An attempt to react a stoichiometric mixture of BaCl₂ and palladium metal with BrSO₃F was unsuccessful as Ba(SO₃F)₂ was found to be insoluble in BrSO₃F.

Ba[Pd(SO₃F)₆] is an orange-red, hygroscopic powder. It is slightly soluble in HS0₃F and is thermally stable up to ~200°C.

Analysis
Calculated % 16.39 12.70 22.95 13.60
Found % 16.24 12.64 22.89 13.82
3.B.3.3 PREPARATION OF \((\text{ClO}_2)_2[\text{Pd(SO}_3\text{F)}_6]\)

\[
2\text{ClO}_2\text{SO}_3\text{F} + \text{Pd} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow (\text{ClO}_2)_2[\text{Pd(SO}_3\text{F)}_6] \quad (3.11)
\]

Palladium metal, \((129 \text{ mg, } 1.212 \text{ mmol})\), was reacted with a mixture of \(\text{ClO}_2\text{SO}_3\text{F} \approx 0.5 \text{ mL}\) and \(\text{S}_2\text{O}_6\text{F}_2 \approx 5 \text{ mL}\). After maintaining a reaction temperature of \(-70^\circ\text{C}\) for 3 days, dark red crystals were formed together with the disappearance of all the metallic reactant. The removal of all volatile materials at \(-60^\circ\text{C}\) yielded \((\text{ClO}_2)_2[\text{Pd(SO}_3\text{F)}_6]\), \((1.013 \text{ g, } 1.212 \text{ mmol})\).

\((\text{ClO}_2)_2[\text{Pd(SO}_3\text{F)}_6]\), \((749 \text{ mg, } 0.896 \text{ mmol})\), was also prepared by the reaction of \(\text{Pd}_2(\text{SO}_3\text{F})_6\), \((322 \text{ mg, } 0.446 \text{ mmol})\), with a mixture of \(\text{ClO}_2\text{SO}_3\text{F} \approx 0.5 \text{ mL}\), and \(\text{S}_2\text{O}_6\text{F}_2 \approx 2 \text{ mL}\), according to:

\[
2\text{ClO}_2\text{SO}_3\text{F} + \frac{3}{2}\text{Pd}_2(\text{SO}_3\text{F})_6 + \frac{1}{2}\text{S}_2\text{O}_6\text{F}_2 \rightarrow (\text{ClO}_2)_2[\text{Pd(SO}_3\text{F)}_6] \quad (3.12)
\]

The product is a very dark red, hygroscopic, crystalline solid. It is soluble in both \(\text{HSO}_3\text{F}\) and \(\text{ClO}_2\text{SO}_3\text{F}\), and melts with decomposition at \(-200^\circ\text{C}\).

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<td>13.68</td>
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</table>

3.B.3.4 PREPARATION OF \((\text{NO})_2[\text{Pd(SO}_3\text{F)}_6]\)

\[
4\text{NOCl} + \text{Pd} \rightarrow (\text{NO})_2[\text{PdCl}_4] + 2\text{NO} \quad (3.13)
\]

\[
(\text{NO})_2[\text{PdCl}_4] + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} (\text{NO})_2[\text{Pd(SO}_3\text{F)}_6] + 2\text{Cl}_2 \quad (3.14)
\]

By the reaction of palladium metal, \((110 \text{ mg, } 1.034 \text{ mmol})\), with a large excess of \(\text{NOCl} \approx 3 \text{ mL}\), at room temperature for
12 hours, \((\text{NO})_2[\text{PdCl}_4]\), (316 mg, 1.025 mmol), was obtained. This intermediate, insoluble in \(\text{NOCl}\), was identified by its i.r. spectrum which has two bands at 2150, \((\nu\text{N}-\text{O})\), and 332 cm\(^{-1}\), \((\nu\text{PdCl}_4)\). This solid was then reacted with a mixture of \(\text{S}_2\text{O}_6\text{F}_2/\text{HSO}_3\text{F}\), (~6 mL), at 80°C for 1 hour. The removal of all volatile materials at ~70°C yielded \((\text{NO})_2[\text{Pd(SO}_3\text{F)}_6]\), (780 mg, 1.025 mmol).

It can also be obtained by the oxidation of \((\text{NO})_2[\text{PdCl}_4]\) by \(\text{BrSO}_3\text{F}\), according to:

\[
(\text{NO})_2[\text{PdCl}_4] + 6\text{BrSO}_3\text{F} \rightarrow (\text{NO})_2[\text{Pd(SO}_3\text{F)}_6] + 2\text{Cl}_2 + 3\text{Br}_2,
\]

although a large excess of \(\text{BrSO}_3\text{F}\) has to be used for the formation of a pure product.

\((\text{NO})_2[\text{Pd(SO}_3\text{F)}_6]\) is a bright red, hygroscopic, crystalline solid. It is soluble in \(\text{HSO}_3\text{F}\) and less so in \(\text{BrSO}_3\text{F}\). It melts with decomposition at ~200°C.

Analysis

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3.4.1 SYNTHESIS OF PALLADIUM(II) HEXAKIS(FLUOROSULFATO) METALLATES(IV)

3.4.1.1 PREPARATION OF \(\text{PdPt(SO}_3\text{F)}_6\)

\[
\text{Pd(SO}_3\text{F)}_2 + \text{Pt(SO}_3\text{F)}_4 \xrightarrow{\text{HSO}_3\text{F}} \text{Pd[Pt(SO}_3\text{F)}_6]\] (3.16)

Platinum metal, (224 mg, 1.148 mmol), was converted into \(\text{Pt(SO}_3\text{F)}_4\) by oxidation with a mixture of \(\text{S}_2\text{O}_6\text{F}_2/\text{HSO}_3\text{F}\). \(\text{Pd(SO}_3\text{F)}_2\),
formed by the reaction of palladium metal, (121 mg, 1.128 mmol), with a mixture of \( \text{S}_2\text{O}_6\text{F}_2 / \text{HSO}_3\text{F} \) followed by the subsequent reduction of \( \text{Pd}_2(\text{SO}_3\text{F})_6 \) with \( \text{Br}_2 \), was added to a solution of the \( \text{Pt}(\text{SO}_3\text{F})_4 \) in \( \text{HSO}_3\text{F} \). No reaction was apparent at room temperature. After heating the mixture at ~50°C for 3 days, a green homogeneous precipitate formed. The solid obtained after a filtration of the suspension was washed with \( \text{HSO}_3\text{F} \) and dried at ~80°C in vacuo.

\( \text{Pd}[\text{Pt}(\text{SO}_3\text{F})_6] \) is a light green, hygroscopic powder. It appears to be insoluble in \( \text{HSO}_3\text{F} \) and is thermally stable up to ~200°C.

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3.B.4.2 PREPARATION OF \( \text{Pd Sn}(\text{SO}_3\text{F})_6 \)

\[
\text{Pd}(\text{SO}_3\text{F})_2 + \text{Sn}(\text{SO}_3\text{F})_4 \stackrel{\text{HSO}_3\text{F}}{\longrightarrow} \text{Pd}[\text{Sn}(\text{SO}_3\text{F})_6]
\]  \hspace{1cm} (3.17)

\( \text{Pd}[\text{Sn}(\text{SO}_3\text{F})_6] \) was prepared in a reaction similar to that for \( \text{Pd}[\text{Pt}(\text{SO}_3\text{F})_6] \). \( \text{Pd}(\text{SO}_3\text{F})_2 \) (539 mg, 1.770 mmol) was mixed with a stoichiometric amount of \( \text{Sn}(\text{SO}_3\text{F})_4 \) formed from the reaction of tin metal (210 mg, 1.770 mmol) with \( \text{S}_2\text{O}_6\text{F}_2 / \text{HSO}_3\text{F} \). No reaction occurred when \( \text{HSO}_3\text{F} \) was added to the mixture; when the reactor was heated at ~70°C, a slow reaction, evident from the gradual clearing of the initially cloudy solution, took place. After 7 days in this condition, all the purple \( \text{Pd}(\text{SO}_3\text{F})_2 \) solids had changed into a blue powder, and the supernatant became clear.
The solids were filtered, washed with HSO₃F and dried at ~70°C in vacuo.

Pd[{Sn(SO₃)₆}] is a light blue, hygroscopic powder. It is apparently insoluble in HSO₃F and decomposes at ~250°C to a light purple solid.

Analysis

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3.B.5 SYNTHESIS OF TETRAKIS(FLUOROSULFATO)PALLADATE(II) COMPLEXES

3.B.5.1 REDUCTION OF Cs₂[Pd(SO₃)₆] BY Br₂/SO₂

Cs₂[Pd(SO₃)₆] + 2SO₂ $\xrightarrow{Br₂}$ Cs₂[Pd(SO₃)₄] + 2S₃O₈F₂ (3.18)

Cs₂[Pd(SO₃)₆], was prepared by the reaction of palladium metal, (100 mg, 0.940 mmol), and CsCl, (316 mg, 1.877 mmol), with S₂O₆F₂/HSO₃F. After all volatile materials were removed in vacuo, SO₂ (~4 mL) and Br₂ (~1 mL) were added to the solid. The reaction mixture was stirred at room temperature for 1 day. The removal of all volatile materials gave a light brown material which analyzed as Cs₂[Pd(SO₃)₄], (721 mg, 938 mmol).

Cs₂[Pd(SO₃)₄] is a light brown hygroscopic powder which melts with decomposition at ~195°C. It is slightly soluble in HSO₃F, but deposits Pd(SO₃)₂ immediately; the filtered solid shows only the i.r. spectrum of Pd(SO₃)₂.

Analysis

<table>
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<tr>
<th></th>
<th>Cs</th>
<th>Pd</th>
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<th>F</th>
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<td>13.66</td>
<td>16.54</td>
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</table>
3.B.5.2 

REDUCTION OF \( \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_6] \) BY \( \text{Br}_2/\text{SO}_2 \)

\[
\text{Ba}[\text{Pd}(\text{SO}_3\text{F})_6] + 2\text{SO}_2 \xrightarrow{\text{Br}_2} \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_4] + 2\text{S}_3\text{O}_8\text{F}_2
\] (3.19)

In a manner analogous to the preparation of \( \text{Cs}_2[\text{Pd}(\text{SO}_3\text{F})_4] \), \( \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_6] \) (196 mg, 0.941 mmol), prepared from the reaction of \( \text{BaCl}_2 \) and palladium metal (100 mg, 0.940 mmol) with \( \text{S}_2\text{O}_6\text{F}_2/\text{HSO}_3\text{F} \), was reduced with a mixture of \( \text{Br}_2/\text{SO}_2 \) to give a compound suggesting the formulation of \( \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_4] \), (602 mg, 0.941 mmol).

\( \text{Ba}[\text{Pd}(\text{SO}_3\text{F})_4] \) is a very light brown hygroscopic powder. It decomposes at ~200°C to a purple solid. It is insoluble in \( \text{HSO}_3\text{F} \).

\( (\text{NO})_2[\text{Pd}(\text{SO}_3\text{F})_4] \) can also be prepared likewise.

**Analysis:**

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<th>Pd</th>
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<th>F</th>
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<td>Found %</td>
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<td>20.03</td>
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</table>
3.C DISCUSSION

3.C.1 SYNTHESIS AND GENERAL DISCUSSION

3.C.1.1 BINARY FLUOROSULFATES

Pd(SO$_3$F)$_2$ can be prepared by one of three methods:

a) the oxidation of palladium metal with BrSO$_3$F,

b) the reduction of Pd$_2$(SO$_3$F)$_6$ with Br$_2$, and

c) the controlled pyrolysis of Pd$_2$(SO$_3$F)$_6$.

Reaction a) has two precedents: the interaction of gold and platinum with BrSO$_3$F is reported to yield the corresponding Au(III) and Pt(IV) fluorosulfates $^{82}$. However, palladium metal is found to be much less reactive towards BrSO$_3$F, and long reaction times at high reaction temperatures of ~160°C are required. Further differences can be found in the solubilities of the three products in the reaction media: while both Au(SO$_3$F)$_3$ and Pt(SO$_3$F)$_4$ dissolve readily to form rather stable intermediates, Pd(SO$_3$F)$_2$ precipitates from the reaction mixture and no evidence of complex formation is evident. The high thermal stability, and its seeming insolubility in both BrSO$_3$F and HSO$_3$F even at temperatures up to ~160°C, are consistent with Pd(SO$_3$F)$_2$ having a polymeric structure.

Although reaction a) provided the only direct synthesis of Pd(SO$_3$F)$_2$, the reduction of Pd$_2$(SO$_3$F)$_6$ by Br$_2$ was subsequently found to be the preferred method because of the ready availability of the trisfluorosulfate. Also, the product from reaction a) was found to contain traces of a brown substance, most likely
Pd$_2$(SO$_3$F)$_6$, which had to be decomposed by evacuation at -120°C. The observation seems to imply that BrSO$_3$F is capable of the oxidation of palladium metal to the tetravalent state, and this is indeed found in the preparation of soluble [Pd(SO$_3$F)$_6$]$^{2-}$ complexes. The successful reduction of Pd$_2$(SO$_3$F)$_6$ to Pd(SO$_3$F)$_2$ by Br$_2$, commonly used as an oxidizing agent, indicates the strong oxidizing ability of Pd(IV), in keeping with general observations regarding the chemistry of palladium $^{119,131}$.

The purple color of Pd(SO$_3$F)$_2$ provides an interesting comparison with other binary Pd(II) compounds: PdF$_2$ is also purple in color, but the other dihalides are brown. This may suggest an octahedral coordination for Pd(II) in the bis(fluorosulfate), as in the difluoride.

The facile preparation of Pd$_2$(SO$_3$F)$_6$ by the oxidation of the metal with a solution of S$_2$O$_6$F$_2$ in HSO$_3$F illustrates the importance of the presence of a suitable solvating medium in these reactions, even though the product may only be slightly soluble in HSO$_3$F. Without the addition of HSO$_3$F, the oxidation of the metal hardly proceed at all, even at -160°C at a high pressure of S$_2$O$_6$F$_2$ in a Monel reactor.

An alternate formulation of the tris(fluorosulfate) as Pd(SO$_3$F)$_3$ would imply the presence of Pd(III), a very uncommon oxidation state and in contrast to the trifluoride, which is the mixed valency compound of Pd(II) Pd(IV)F$_6$ $^{108}$. It is very likely that such an analogy exists in the fluorosulfate system, and
58

experimental evidence consistent with the formulation will be discussed subsequently.

3.C.1.2 FLUOROSULFATO COMPLEXES OF PALLADIUM

Both the binary fluorosulfates of palladium are insoluble in HSO₃F, thus precluding their uses as superacids in HSO₃F. However, the formulation of the tris(fluorosulfate) as a mixed valency compound suggests the existence of a [Pd(IV)(SO₃F)₆]²⁻ species and a Pd(II)[M(IV)(SO₃F)₆] species, much like [PdF₆]²⁻ and Pd[M(IV)F₆] in the fluoride system. Therefore, complexation reactions were attempted.

A general preparative route to complexes containing [Pd(SO₃F)₆]²⁻ is the oxidation of the metal by S₂O₆F₂/HSO₃F in the presence of a basic fluorosulfate. This method has also been used successfully in the preparation of complexes containing other metals in high oxidation state. The reaction involving ClO₂SO₃F did not require HSO₃F as a solvent because the former is a supercooled liquid at room temperature and can act as an ionizing solvent.

The synthesis of (NO)₂[Pd(SO₃F)₆] by the reaction of (NO)₂[PdCl₄] with S₂O₆F₂ illustrates the oxidation of Pd(II) to Pd(IV) with the replacement of Cl⁻ by SO₃F⁻. The moderate reaction temperature of ~80°C minimized the formation of ClO₂SO₃F (by the oxidation of Cl₂ with S₂O₆F₂ in the presence of glass) although a small amount of a ClO₂SO₃F-like, red liquid was
detected as a by-product. The complete removal of this contami­
nant in vacuo at -70°C is indicated by the agreement in the ana­
lytical result for the NO²⁺-complex. Since both the ClO₂⁺- and 
the NO²⁺-complexes of [Pd(SO₃F)₆]²⁻ have nearly identical thermal 
stabilities, the preferential formation of the latter may be due 
to:

a) the greater volatility of ClO₂SO₃F, and/or 
b) the higher lattice energy expected for (NO)₂[Pd(SO₃F)₆] 
due to the smaller size of the cation.

Although only four examples of complexes containing 
[Pd(SO₃F)₆]²⁻ are reported here, other complexes containing M(I) 
and M(II) cations are expected to be obtainable using the general 
methods described here.

The synthesis of Pd(II)[M(IV)(SO₃F)₆] involved the addition 
of a slight excess of M(SO₃F)₄, where M=Pt, Sn, to Pd(SO₃F)₂ 
followed by digestion in HSO₃F and subsequent filtration of the 
insoluble products. The excess is needed to ensure a stoichio-
metric ratio in the end products because of difficulties encoun-
tered in weighing the fluorosulfates accurately in the dry box. 
The rather low solubility of Sn(SO₃F)₄ in HSO₃F ³³ dictated a 
rather long reaction time. However, in the reaction involving 
the very soluble Pt(SO₃F)₄, only a very slight increase in the 
reaction rate was noted; this provided more evidence for the 
extremely high degree of polymerization and insolubility for 
Pd(SO₃F)₂. The colors of these compounds (light blue for
Pd[Sn(SO₃F)₆] and light green for Pd[Pt(SO₃F)₆], also departed from the dark colors usually associated with square planar Pd(II) compounds. Thus the Pd(II) ion in these two fluorosulfato-complexes may be octahedrally coordinated.

In the preceding reaction, Pd(SO₃F)₂ acts formally as a SO₃F⁻ donor, i.e., a base. Attempts were also made to involve the bis(fluorosulfate) in anionic complex formation; initially, these attempts were unsuccessful:

a) CsSO₃F was found not to undergo any direct complexation reaction with Pd(SO₃F)₂, even after heating the mixture in HSO₃F at ~160°C. The solid obtained after filtration gave only an i.r. spectrum of unreacted Pd(SO₃F)₂.

b) The attempted solvolysis of (NO)₂[PdCl₄] in HSO₃F at ~160°C produced an inhomogeneous mixture of white and brown solids (the starting material is brown). The i.r. spectrum taken of this mixture showed only bands due to NOSO₃F. The weight of the final product suggests that the solvolysis reaction must have occurred according to:

\[(NO)₂[PdCl₄] + 2HSO₃F \rightarrow 2NOSO₃F + PdCl₂ + 2HCl \quad (3.20)\]

Subsequently, a sample of PdCl₂ was indeed found not to react with HSO₃F at ~160°C, most likely a result of its high degree of polymerization.

c) The solvolysis of (NO)₂[PdCl₄] in BrSO₃F also led to the oxidation of Pd(II) to Pd(IV). This implies that the formation of Pd(SO₃F)₂ from the reaction of BrSO₃F with the metal may be
due to the insolubility of Pd(SO$_3$F)$_2$ in the reaction medium rather than as a consequence of the limited oxidizing ability of BrSO$_3$F.

d) Because of the ability of Br$_2$ to reduce Pd$_2$(SO$_3$F)$_6$ to Pd(SO$_3$F)$_2$ at elevated temperature, the reduction of Cs$_2$[Pd(SO$_3$F)$_6$], Ba[Pd(SO$_3$F)$_6$] and (NO)$_2$[Pd(SO$_3$F)$_6$] with Br$_2$ were attempted. But even at a reaction temperature of ~120°C, only (NO)$_2$[Pd(SO$_3$F)$_6$] showed any signs of a reaction taking place, and the product is a mixture of unreacted (NO)$_2$[Pd(SO$_3$F)$_6$], and some white/purple solids which could be NOSO$_3$F and Pd(SO$_3$F)$_2$.

e) As the lack of a suitable solvent could have led to the demise of the above reduction attempt, a mixture of Br$_2$/HSO$_3$F was heated with Ba[Pd(SO$_3$F)$_6$] at ~70°C for 1 day. The removal of volatile materials yielded a light brown product with a weight corresponding to the composition of BaPd(SO$_3$F)$_4$. An i.r. spectrum of the product, however, showed the presence of some bands due to Pd(SO$_3$F)$_2$, and therefore, although a reduction had taken place, some decomposition of the product had also occurred.

Since the reduction of a fluorosulfate with Br$_2$ usually leads to the formation of BrSO$_3$F, if it can be removed from an equilibrium, the reaction may be encouraged to proceed more effectively. SO$_2$ was used as such a BrSO$_3$F scrubber. The successful reduction of [Pd(SO$_3$F)$_6$]$^{2-}$ complexes with a Br$_2$/SO$_2$ mixture at room temperature probably proceeds via the following scheme:

\[
[Pd(SO_3F)_6]^{2-} + Br_2 \xrightleftharpoons[K<<1]{<1} [Pd(SO_3F)_4]^{2-} + 2BrSO_3F \tag{3.21}
\]
SO$_2$ alone, like Br$_2$ by itself, did not react with Cs$_2$[Pd(SO$_3$F)$_6$] at temperatures up to ~100°C. Equation (3.21) appears to be shifted to the left, since the soluble [Pd(SO$_3$F)$_6$]$^{2-}$ complexes can be synthesized in a Br$_2$/BrSO$_3$F mixture. By the careful removal of all the SO$_2$ and most of the Br$_2$, the slightly less volatile S$_3$O$_8$F$_2$ was identified by its gas i.r. spectrum.

This procedure employing Br$_2$/SO$_2$ as the reduction couple could be applied to the preparation of Pd(SO$_3$F)$_2$ from Pd$_2$(SO$_3$F)$_6$ and conceivably other systems in which the presence of BrSO$_3$F may be unacceptable. The faster reaction time at a lower reaction temperature and the presence of relatively inert and volatile by-products are the major advantages of this method.

The difference in reactivity of the ionic [Pd(SO$_3$F)$_6$]$^{2-}$ complexes as compared to Pd$_2$(SO$_3$F)$_6$ may be attributed to their different thermal stabilities. While Pd$_2$(SO$_3$F)$_6$ decomposes at ~120°C in vacuo to give S$_2$O$_6$F$_2$, the ionic complexes are stable up to ~200°C, and their decomposition products contain SO$_2$F$_2$, identified by its i.r. spectrum. SO$_2$F$_2$ is also found in the gaseous thermolysis products of Au(SO$_3$F)$_3$ and Pt(SO$_3$F)$_4$, and is a result of complete breakdown of the compound rather than via step-wise reduction.

3.C.1.3 ATTEMPTED SYNTHESIS OF Pd(SO$_3$F)$_4$

The synthesis of [Pd(SO$_3$F)$_6$]$^{2-}$ strongly suggests that the
binary compound, Pd(SO$_3$F)$_4$, may be obtainable as well. Although solid Pd(SO$_3$F)$_4$ could not be isolated, some evidence for its existence in strongly oxidizing solution has been obtained:

a) Pd$_2$(SO$_3$F)$_6$ is virtually insoluble in HSO$_3$F, but the clear solution containing the solid immediately took on a dark red color when S$_2$O$_6$F$_2$ was added. The u.v. spectrum of the solution is identical to that produced by (NO)$_2$Pd(SO$_3$F)$_6$ in HSO$_3$F, with a $\lambda_{max}$ at 320 nm. As expected, the solubility of Pd(SO$_3$F)$_4$ in such a mixture increased with increasing proportion of HSO$_3$F (visually monitored), but even at a S$_2$O$_6$F$_2$/HSO$_3$F ratio of less than 1/20, the solubility of Pd$_2$(SO$_3$F)$_6$ is less than a few mg per 20 mL.

b) Using a Soxhlet type extraction device made of sintered-glass, the only product obtained after 21 days of extraction at 70°C was Pd$_2$(SO$_3$F)$_6$, formed slowly in the filtered liquid.

c) The oxidation of palladium metal by S$_2$O$_6$F$_2$/HSO$_3$F from 25°C to 100°C did not lead to the formation of Pd(SO$_3$F)$_4$. In order to minimize the decomposition of Pd(SO$_3$F)$_4$ at elevated temperature in vacuo, the removal of S$_2$O$_6$F$_2$/HSO$_3$F was performed at room temperature (a very long process). Nevertheless the solid isolated afterwards was invariably Pd$_2$(SO$_3$F)$_6$.

d) The attempted high pressure oxidation of Pd$_2$(SO$_3$F)$_6$ at 200°C for 7 days with an excess of S$_2$O$_6$F$_2$ in a Monel reactor did not lead to a further oxidation of palladium.

To rationalize all the above observations, some speculations concerning the palladium-fluorosulfate system can be made:
a) There are many precedents where high oxidation states may be obtained in anionic complexes when the parent compounds are not known. Some pertinent examples are the $[\text{PdCl}_6]^{2-}$ complexes and $O_2^{+}[\text{PF}_6]^{-}$, with neither PdCl$_4$ nor PdF$_5$ obtainable so far.

b) The decrease in decomposition temperatures from Pd(SO$_3$F)$_2$ (250°C) to Pd$_2$(SO$_3$F)$_6$ (120°C) indicates a marked drop in the thermal stability in the series. Pd(SO$_3$F)$_4$, if obtainable, may not be very stable at room temperature.

c) The equilibrium:

$$\text{Pd}_2(\text{SO}_3\text{F})_6 + S_2\text{O}_6\text{F}_2 \underset{\text{HSO}_3\text{F}}{\overset{\text{HSO}_3\text{F}}{\leftrightarrow}} 2\text{Pd}(\text{SO}_3\text{F})_4,$$

is expected to be strongly dependent on the relative concentrations of HS$_3$F and S$_2$O$_6$F$_2$. In order to obtain a high concentration of the presumably soluble Pd(SO$_3$F)$_4$ in HS$_3$F, a low S$_2$O$_6$F$_2$/HSO$_3$F ratio is required because S$_2$O$_6$F$_2$, being a covalent liquid, decreases the ionizing ability of the solvent. This in turn would almost certainly drive the equilibrium back to the left as the oxidizing strength of the solvent mixture is decreased. As an added disadvantage, the subsequent removal of both S$_2$O$_6$F$_2$ and HS$_3$F at the end of the reaction favors the formation of the insoluble and more thermally stable Pd$_2$(SO$_3$F)$_6$.

d) The observed formation of S$_2$O$_6$F$_2$, presumably via SO$_3$F radicals, in the pyrolysis of Pd$_2$(SO$_3$F)$_6$ is very unusual in terms of the thermal decomposition paths of metal fluorosulfates. Only a few other examples can be found: Xe(SO$_3$F)$_2$, XeF(SO$_3$F)$_{135,136}$ and Ag(SO$_3$F)$_2$; and all of these are extremely strong oxidizing
agents. Furthermore, although the \([\text{Pd}(\text{SO}_3\text{F})_6]^{2-}\) complexes are very stable entities, they are extremely corrosive materials capable of oxidizing \(\text{Br}_2\) to \(\text{BrSO}_3\text{F}\) and producing the most serious attacks on \(\text{AgCl}\) i.r. windows of all the solid compounds examined in this study. All these observations point to an extremely strong oxidizing ability of \(\text{Pd(IV)}\), and the energy required for its formation must be recovered from sources such as increased lattice energy for the ionic complexes, and polymerization for \(\text{Pd}_2(\text{SO}_3\text{F})_6\).

In summary, the inability to obtain pure \(\text{Pd}(\text{SO}_3\text{F})_4\) may be attributed to its limited thermal stability, the lack of solubility of \(\text{Pd}_2(\text{SO}_3\text{F})_6\) in \(\text{HSO}_3\text{F}\), and the high oxidizing power of \(\text{Pd(IV)}\).

3.C.2 VIBRATIONAL SPECTRA

3.C.2.1 \(\text{Pd}(\text{SO}_3\text{F})_2\)

The i.r. and Raman data for \(\text{Pd}(\text{SO}_3\text{F})_2\) are listed in Table 3.1 and compared to the reported i.r. frequencies for \(\text{Ni}(\text{SO}_3\text{F})_2\) \(^{87}\). The spectra are assigned in terms of a \(\text{C}_3\text{v}\) symmetry for the \(\text{SO}_3\text{F}\) group except for the two low frequency bands. For \(\text{Ni}(\text{SO}_3\text{F})_2\), the 290 cm\(^{-1}\) band has been assigned to lattice modes \(^{87}\); for \(\text{Pd}(\text{SO}_3\text{F})_2\), the very weak band at 354 cm\(^{-1}\) could be due to impurities as it was not present in the i.r. The position of the S-F stretch at ~860 cm\(^{-1}\) implies a tridentate coordination mode for the anions rather than a true \(\text{SO}_3\text{F}^-\) ion. Thus, \(\text{Pd}(\text{SO}_3\text{F})_2\) is isostructural.
### TABLE 3.1: VIBRATIONAL FREQUENCIES OF Pd(SO$_3$F)$_2$

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<th>Pd(SO$_3$F)$_2$</th>
<th>Ni(SO$_3$F)$_2$</th>
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<tr>
<td>R 1231 m</td>
<td>IR 1240 s,b</td>
<td>$\nu_4$(E)</td>
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<tr>
<td>1111 ms</td>
<td>1090 ms</td>
<td>$\nu_1$(A$_1$)</td>
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<td>869 m</td>
<td>860 s</td>
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<tr>
<td>612 w</td>
<td>610 s</td>
<td>$\nu_5$(E)</td>
</tr>
<tr>
<td>552 w</td>
<td>565 m</td>
<td>$\nu_3$(A$_1$)</td>
</tr>
<tr>
<td>430 m</td>
<td>421 m</td>
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</tr>
<tr>
<td>354 vw</td>
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<td>impurity Lattice mode</td>
</tr>
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</table>

![PROPOSED STRUCTURE OF Pd(SO$_3$F)$_2$](image-url)
with a general class of bis(fluorosulfate)s which includes those of Ni, Mg, Ca, Zn, Cd, Hg, Fe and Co. This highly polymeric structure is also consistent with the observed physical properties of Pd(SO$_3$F)$_2$, discussed in the previous section. The absence of splittings for the three degenerate E modes suggests a regular octahedral environment for Pd(II), in contrast to the extensive splittings observed in the spectra for Cu(SO$_3$F)$_2$ and Mn(SO$_3$F)$_2$, which implies a distortion of the octahedral coordination spheres for the M(II) cations in these compounds. The proposed structure of Pd(SO$_3$F)$_2$, consistent also with its magnetic and electronic spectral information, is shown in Fig. 3.1.


Both i.r. and Raman spectra of the fluorosulfato complexes containing Pd(IV) were not easily obtainable for a number of reasons. The oxidizing ability of these compounds limited the use of i.r. window materials to BaF$_2$, with a transmission range down to only about 800 cm$^{-1}$. The dark colours of these compounds also interfered with the recording of Raman spectra at room temperature when the 514.4 nm line of the argon ion laser was used. Thus, sample cooling down to ~80K had to be employed in order to reduce laser induced decomposition. Alternatively, Raman spectra of rather low resolution were obtained on another spectrometer equipped with a He-Ne laser (632.8 nm).
For the two Pd[M(IV)(SO₃F)₆] complexes, with M = Pt, Sn, i.r. spectra down to 450 cm⁻¹ were obtained (AgCl plates). For Pd[Sn(SO₃F)₆], because of the presence of strong fluorescence, a Raman spectrum could not be obtained.

The Raman spectra for Pd₂(SO₃F)₆ and Pd[Pt(SO₃F)₆] are shown in Fig. 3.2 and Fig. 3.3, respectively. The observed vibrational frequencies for all the [Pd(SO₃F)₆]²⁻ complexes and the two Pd[M(IV)(SO₃F)₆] compounds are listed in Table 3.2 together with the literature values for K₂[Sn(SO₃F)₆]³². With the exception of Pd[Sn(SO₃F)₆], the Raman frequencies are reported, since they are generally of better resolution and extend to lower frequencies. The corresponding i.r. spectra show no major discrepancies in most of the band positions.

Except for a few additional features which will be discussed later, the spectra of these hexakis(fluorosulfato) complexes correlate well with each other and the main bands can be attributed to monodentate fluorosulfate groups in an anionic environment. A common, tentative assignment for these octahedral complexes is also attempted in Table 3.2.

As noted previously for the [Sn(SO₃F)₆]²⁻ cases, band proliferation, especially in the SO₃F stretching region (≥800 cm⁻¹) is found. This is due, presumably, to solid state splittings and, probably more importantly, to extensive vibrational couplings suggesting, in turn, strong covalent bondings to the central M(IV) atoms. This is particularly true for the [Pd(SO₃F)₆]²⁻
FIG. 3.2 RAMAN SPECTRUM OF Pd₂(SO₃F)₆

FIG. 3.3 RAMAN SPECTRUM OF Pd[Pt(SO₃F)₆]
**Table 3.2**

Vibrational Spectra of Ca₂[PO₄][SO₄]₄ₓ, (MO)₂[PO₄][SO₄]₂, (CaO₂)₄[PO₄][SO₄]₄ₓ, Ba[PO₄][SO₄]₄ₓ, Pb[PO₄][SO₄]₂, Pb[Pt(SO₄)₂] and Pb[Sn(SO₄)₂]

<table>
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<th>ν [cm⁻¹]</th>
<th>ν [cm⁻¹]</th>
<th>ν [cm⁻¹]</th>
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<td>1395 w, sh</td>
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<td>1240 vs</td>
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<td>1244 vs</td>
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<td></td>
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<td>1215 m</td>
<td>1214 m</td>
<td>1202 w, sh</td>
<td>1210 sh</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>1001 w</td>
<td>1024 vs</td>
<td>1013 vs</td>
<td>1034 s</td>
<td>1050 ms</td>
<td>1028 vs</td>
<td>O-SO₄²⁻ stretch</td>
</tr>
<tr>
<td></td>
<td>995 ms</td>
<td>1004 ms</td>
<td>1001 ms</td>
<td>1001 m</td>
<td>1015 w, b</td>
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<td></td>
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<tr>
<td></td>
<td>975 vs, sh</td>
<td>980 w, sh</td>
<td>981 w</td>
<td>996 ms</td>
<td>960 w</td>
<td></td>
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<tr>
<td></td>
<td>860 w</td>
<td>852 w</td>
<td>841 w</td>
<td>860 w</td>
<td>867 m</td>
<td>855 vs</td>
<td>SF stretch</td>
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<td></td>
<td>835 w</td>
<td>835 w</td>
<td>826 w</td>
<td>833 w</td>
<td>830 w</td>
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<tr>
<td></td>
<td>805 w</td>
<td>805 w</td>
<td>823 w</td>
<td>805 w</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>785 w</td>
<td></td>
<td>623 ms</td>
<td>630 ms</td>
<td>648, 632 ms</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>M-O stretch + M-O-S bend (see text)</td>
</tr>
<tr>
<td></td>
<td>618 ms</td>
<td>613 vs</td>
<td>612 s</td>
<td>579 w</td>
<td>590 s</td>
<td></td>
<td>SO₂ bend</td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>SO₂ rock</td>
</tr>
<tr>
<td></td>
<td>542 w</td>
<td>545 w</td>
<td>551 w</td>
<td>538 w</td>
<td>562, 531 m</td>
<td></td>
<td>M-O stretch + M-O-S bend</td>
</tr>
<tr>
<td></td>
<td>441 ms</td>
<td>444 ms</td>
<td>450 ms</td>
<td>446 ms</td>
<td>447 s</td>
<td></td>
<td>S-O wagging</td>
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<td>424 w</td>
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<tr>
<td></td>
<td>400 w</td>
<td>400 w</td>
<td>414 w</td>
<td>400 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>270 s</td>
<td>272 vs</td>
<td>272 vs</td>
<td>270 s</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>275 s</td>
<td>264 s</td>
<td>270 s</td>
<td>275 s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Spectrum recorded with sample at <80K.

b) Bands assigned to CaO₂⁺

---

70
derivatives, in which strong Raman bands at ~1240 cm\(^{-1}\) \((\nu\text{SO}_2 \text{ asym})\) and ~1020 cm\(^{-1}\) \((\nu\text{S-OPd})\) have weaker side bands at ~1210 and ~980 cm\(^{-1}\), respectively, with the intensities reversed in the i.r. spectra.

The spectra for the three Pd(II) containing compounds have bands at ~1170 to 1190 and ~1040 to 1050 cm\(^{-1}\) that are not present in the spectra of the other complexes, including Ba[Pd(SO\(_3\)F)\(_6\)]. Bands in these regions, also reported for Ag[Pt(SO\(_3\)F)\(_6\)] and Ag[Sn(SO\(_3\)F)\(_6\)] \(^{33}\), are usually associated with bidentate bridging fluorosulfate groups \(^{33}\). Their occurrence in the spectra of these particular compounds may be due to the strong polarizing abilities of the divalent transition metal cations. Ba\(^{2+}\), although being a divalent cation, is not expected to have as great a polarizing effect on the fluorosulfate groups because it lacks the necessary d-orbitals. Further evidence in support of the coordination of Pd(II) will be presented in subsequent sections. This type of coordination, shown in Fig. 3.4, in which the fluorosulfate ligands are bonded primarily to M(IV) and coordinated weakly to M(II), can be considered as bridging anisobidentate. Hence, the ionic formulation of these compounds as consisting of discrete M(II) and [M(IV)(SO\(_3\)F)\(_6\)]\(^{2-}\) units may be somewhat misleading. This highly polymerized structure is also inferred from the noted lack of solubility of these complexes, (Ba[Pd(SO\(_3\)F)\(_6\)] is slightly soluble).

Strong Raman bands at ~620 to 640, ~400 to 460 and ~270 to
280 cm\(^{-1}\), observed for all the anionic complexes are not assignable to absorptions due to the fluorosulfate groups alone. Their positions appear to show a slight dependence on the nature of both the M(IV) species and the counter-cations. These bands, occasionally split into doublets, are most likely due to M(IV)-O vibrations, possibly coupled with ligand deformation modes. The evidence for strong M(IV)-O bonds leading also to the coupling of S-O stretching modes has been discussed earlier.

For the complexes with polyatomic heterocations, additional bands due to the cations are observed and they compare favorably with previously reported data. For the NO\(^+\) complex, the N-O stretch is found at 2330 cm\(^{-1}\) in the i.r.; in (NO)\(_2\)[Sn(SO\(_3\)F)\(_6\)], the same vibration is found at 2325 cm\(^{-1}\) \(^{32}\). Bands due to ClO\(_2^+\) are found at 1293 cm\(^{-1}\) (split into 1300 and 1290 cm\(^{-1}\) for the
stronger i.r. band) and 1050 cm\(^{-1}\), consistent with literature values \(^{32,138}\). The bending mode for \(\text{ClO}_2^+\), expected to be only weakly Raman active, and usually found at \(\approx 520\) cm\(^{-1}\), is not observable in this case.

To summarize, the apparent spectral similarities indicate strong structural similarities in these compounds. The formulation of the tris(fluorosulfate) as the ternary compound, 
Pd(II)[Pd(IV)(SO\(_3\)F)\(_6\)] is supported by its vibrational spectra. The strong vibrational coupling between the fluorosulfate groups and the [M(IV)O\(_6\)] skeleton confirms the covalent character of the M(IV)-O bond.

3.C.2.3 [Pd(SO\(_3\)F)\(_4\)]\(^{2-}\)

Because of the light brown color of the samples containing [Pd(SO\(_3\)F)\(_4\)]\(^{2-}\), no Raman spectrum was obtainable. The i.r. frequencies are listed in Table 3.3. A good correlation can be made between the spectra of [Pd(SO\(_3\)F)\(_4\)]\(^{2-}\) and those from the presumably square planar, [Au(SO\(_3\)F)\(_4\)]\(^-\), suggesting structural similarities. The difference in the positions of a few diagnostic bands can be interpreted as being caused by the replacement of Au(III) by Pd(II). It has been hypothesized that the weakening of an S-O bond due to the coordination of the oxygen leads to the strengthening of the remaining S-F and S-O bonds \(^{92}\). The lowering of the S-F stretching frequency by about 20 cm\(^{-1}\) in the Pd(II) compound is significant, and must be attributed to a decrease in
<table>
<thead>
<tr>
<th></th>
<th>Ba[\text{Pd}(\text{SO}_3\text{F})_4]</th>
<th>(NO)_2[\text{Pd}(\text{SO}_3\text{F})_4]</th>
<th>Cs_2[\text{Pd}(\text{SO}_3\text{F})_4]</th>
<th>Cs[\text{Au}(\text{SO}_3\text{F})_4]</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>-2330 vW</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1340 vs</td>
<td>1350 vs</td>
<td>1340 vs</td>
<td>1440 vs</td>
<td>\nu_7 \text{asymSO}_3</td>
<td></td>
</tr>
<tr>
<td>1200 vs</td>
<td>1200 vs</td>
<td>1200 vs</td>
<td>1210 vs</td>
<td>\nu_1 \text{symSO}_3</td>
<td></td>
</tr>
<tr>
<td>1030 vs</td>
<td>1020 vs</td>
<td>1000 vs</td>
<td>930 vs</td>
<td>\nu_4 \text{asymSO}_3</td>
<td></td>
</tr>
<tr>
<td>800 s</td>
<td>800 s</td>
<td>795 s</td>
<td>-820 s</td>
<td>\nu_2 \text{S-F}</td>
<td></td>
</tr>
<tr>
<td>640 s</td>
<td>660 s</td>
<td>655 s,sh</td>
<td>675 s</td>
<td>\nu_3 \text{SO}_3\text{F rock} + \nu \text{MO sym}</td>
<td></td>
</tr>
<tr>
<td>580 s</td>
<td>580 s</td>
<td>575 s</td>
<td>585 s</td>
<td>\nu_5 \text{SO}_3\text{F def}</td>
<td></td>
</tr>
<tr>
<td>550 s</td>
<td>560 s</td>
<td>555 s</td>
<td>550 s</td>
<td>\nu_8 \text{SO}_3\text{F def}</td>
<td></td>
</tr>
<tr>
<td>450 m</td>
<td>-420 m</td>
<td>-420 w</td>
<td>460 m</td>
<td>\nu_9 \text{SO}_3\text{F rock} + \nu \text{MO asym}</td>
<td></td>
</tr>
</tbody>
</table>
covalent nature of the Pd-0 bond. This can also be illustrated by the decrease in the splitting in the asymmetric SO₃ stretch ($v_4$ and $v_7$) for [Pd(SO₃F)₄]²⁻. (For [Pd(SO₃F)₄]²⁻, $v_7$-$v_4$ = -340 cm⁻¹; for [Au(SO₃F)₄]²⁻, $v_7$-$v_4$ = -470 cm⁻¹). This seems to indicate that the three S-0 bonds are more similar in the [Pd(SO₃F)₄]²⁻ species than the ones in [Au(SO₃F)₄]²⁻, also not unexpected.

The colors of these Pd(II) complexes, together with evidence from vibrational spectroscopy, seem to indicate a square planar environment for the Pd(II). Magnetic susceptibility measurements, to be discussed later, support such a conclusion.

3.C.3 ELECTRONIC SPECTRA

The Pd(II) containing compounds of Pd(SO₃F)₂, Pd[Sn(SO₃F)₆] and Pd[Pt(SO₃F)₆] are purple, blue and green, respectively, quite in contrast to the usually brown colors of Pd(II) compounds with Pd(II) in a square planar environment. Similar blue or purple colors are also found for PdF₂, CsPdF₃₁⁰⁷, ZnPdF₄₁¹⁶, and Pd[M(IV)F₆]₁⁰³, with M = Ge, Sn, Pt, all with Pd(II) in an octahedral environment. However, a detailed analysis of their electronic spectra is not reported.

It is therefore not surprising that the magnetic results and the vibrational spectra also supported a regular octahedral environment for Pd(II) in Pd(SO₃F)₂ and Pd[M(IV)(SO₃F)₆].
Pd(SO₃F)₂ shows a three-band electronic spectrum that can be assigned as due to d-d transitions. Although no extinction coefficients to support the assignment were obtainable because of the insolubility of all the compounds in HSO₃F, it appears that all the bands are of about the same intensities and the D_q and B values obtained from such an assignment are very reasonable.

The electronic ground state for a d⁸ ion in an octahedral field is ⁳A₂g, and three d-d transitions are expected. The energy level diagram for a d⁸ ion in an octahedral field is shown in Fig 3.5. The band positions of the observed electronic spectra and the calculated ligand field parameters of Pd(SO₃F)₂, Pd[Sn(SO₃F)₆], Pd[Pt(SO₃F)₆] and Ni(SO₃F)₂ are listed in Table 3.4. There is generally a good correspondence between spectra obtained from mulls and those obtained by diffuse reflection. In the platinum compound, ν₃ is not observed because the strong charge transfer band due to Pt(IV), with λ_max at 245 nm and ε of ~1.5×10⁴ M⁻¹cm⁻¹, extends well into the visible region. This further substantiates the premise that the remaining bands are due to the d-d transitions with lower intensities.

The good agreement in band positions for the spectra for the three compounds suggests a similar environment for Pd(II) and an ⁳A₂g ground state in all cases. Although no splitting of any of the bands is observable, it does not confirm or deny the existence of distortion in the coordination sphere as the bands are quite broad. In any case, no distortion is evident from the vibrational
FIG. 3.5: ENERGY LEVEL DIAGRAM FOR A $d^8$ ION IN AN $O_h$ FIELD

\[ v_1 = 10Dq \]
\[ v_2 = \frac{1}{2}(15B + 30Dq) - \frac{1}{2}[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{\frac{1}{2}} \]
\[ v_3 = \frac{1}{2}(15B + 30Dq) + \frac{1}{2}[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{\frac{1}{2}} \]

TABLE 3.4: ELECTRONIC TRANSITIONS AND LIGAND FIELD PARAMETERS FOR SOME PALLADIUM (II) COMPOUNDS AND Ni(SO$_3$F)$_2$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$Dq$</th>
<th>$B$</th>
<th>$B/B^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd[Sn(SO$_3$F)$_6$]</td>
<td>11,050</td>
<td>11,950</td>
<td>26,850</td>
<td>1,105</td>
<td>717</td>
<td>0.863</td>
</tr>
<tr>
<td>Pd[Pt(SO$_3$F)$_6$]</td>
<td>11,400</td>
<td>16,950</td>
<td>26,480*</td>
<td>1,140</td>
<td>642</td>
<td>0.774</td>
</tr>
<tr>
<td>Pd(SO$_3$F)$_2$</td>
<td>11,770</td>
<td>17,400</td>
<td>27,030</td>
<td>1,177</td>
<td>633</td>
<td>0.763</td>
</tr>
<tr>
<td>Ni(SO$_3$F)$_2$</td>
<td>734</td>
<td>905</td>
<td>838</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Calculated value

Diffuse reflectance values for $v_2$ are 16,890 cm$^{-1}$ for Pd[Sn(SO$_3$F)$_6$] and 16,810 cm$^{-1}$ for Pd[Pt(SO$_3$F)$_6$].
FIG. 3.5: ENERGY LEVEL DIAGRAM FOR A $d^6$ ION IN AN $O_h$ FIELD

\[
\begin{align*}
\nu_1 &= 10Dq \\
\nu_2 &= \frac{1}{2}(15B + 30Dq) - \frac{1}{2}[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{\frac{1}{2}} \\
\nu_3 &= \frac{1}{2}(15B + 30Dq) + \frac{1}{2}[(15B - 10Dq)^2 + 12B \cdot 10Dq]^{\frac{1}{2}}
\end{align*}
\]

TABLE 3.4: ELECTRONIC TRANSITIONS AND LIGAND FIELD PARAMETERS FOR SOME PALLADIUM (II) COMPOUNDS AND Ni(SO$_3$F)$_2$ (in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$v_1$</th>
<th>$v_2$</th>
<th>$v_3$</th>
<th>$Dq$</th>
<th>$B$</th>
<th>$B/B^\circ$</th>
</tr>
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<tr>
<td>Pd[Sn(SO$_3$F)$_6$]</td>
<td>11,050</td>
<td>11,400</td>
<td></td>
<td>1,105</td>
<td>717</td>
<td>0.863</td>
</tr>
<tr>
<td>Pd[Pt(SO$_3$F)$_6$]</td>
<td>16,950</td>
<td>16,950</td>
<td>26,850</td>
<td>1,140</td>
<td>642</td>
<td>0.774</td>
</tr>
<tr>
<td>Pd(SO$_3$F)$_2$</td>
<td>11,770</td>
<td>17,400</td>
<td>27,030</td>
<td>1,177</td>
<td>633</td>
<td>0.763</td>
</tr>
<tr>
<td>Ni(SO$_3$F)$_2$</td>
<td></td>
<td></td>
<td></td>
<td>734</td>
<td>905</td>
<td>0.838</td>
</tr>
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</table>

*calculated value
Diffused reflectance values for $v_2$ are 16,890 cm$^{-1}$ for Pd[Sn(SO$_3$F)$_6$] and 16,810 cm$^{-1}$ for Pd[Pt(SO$_3$F)$_6$]
analysis of the compounds. By using Tanabe-Sugano diagrams as suggested by Lever, the positions of all the bands are confirmed, and $v_3$ for Pd[Pt(SO$_3$F)$_6$] is calculated using this method. The octahedral splitting — $10 D_q$ — and the interelectronic repulsion term — $B$ — are also obtained. The increase in $D_q$ and the decrease in $\beta$, (defined as the ratio of $B$ over $B^0$, the free ion value), in going from Ni(II), (3d$^8$), to Pd(II), (4d$^8$), are not unexpected in view of the higher nuclear charge and more spatially diffused 4d orbitals for palladium.

It appears that within the series of Pd(SO$_3$F)$_2$, Pd[Pt(SO$_3$F)$_6$] and Pd[Sn(SO$_3$F)$_6$], $10 D_q$ gradually decreases while $\beta$ increases, with $B$ approaching the $B^0$ value of 830 cm$^{-1}$. The presence of the M(IV) species, with their higher cationic charge, is expected to compete favorably for the coordination of the SO$_3$F ligands. A lessening of Pd-SO$_3$F interaction is expected to decrease $10 D_q$ and also increase the interelectronic repulsion as the orbitals are more confined to the metal. For the two complexes, the one that contains Sn(IV) has the lowest $10 D_q$ and the highest $\beta$ value. This cannot be due to structural dissimilarities, because this was not noted in the vibrational spectra, and must be attributed to a greater ability of Sn(IV) to bond to the SO$_3$F groups. This has also been observed in the following two complexes — Ag(II)[M(IV)(SO$_3$F)$_6$], with M = Pt, Sn.

(NO)$_2$[Pd(SO$_3$F)$_4$], Cs$_2$[Pd(SO$_3$F)$_4$] and Ba[Pd(SO$_3$F)$_4$] are light brown solids, and the bands of the diffuse reflectance spectra
of the latter two compounds are compared with those of \( \text{K}_2[\text{PdCl}_4] \) in Table 3.5. The energy level diagram for a \( d^8 \) ion in a square planar ligand field is shown in Fig. 3.6. As can be seen, a good comparison can be made between the spectra for the two types of compounds, suggesting the presence of species with similar electronic configuration. Strong absorptions are found for \( \text{K}_2[\text{PdCl}_4] \) at 278 and 223 nm, and are assigned to \( L \rightarrow M \) charge transfer bands. For \( [\text{Pd(SO}_3\text{F})_4]^2^- \), such absorptions were not observed as they are beyond the range of the instrument, but an extremely strong background was observed at the high energy end of the spectrum, giving rise to quite poor resolution for the two bands at \( \sim 450 \) nm. An assignment of the obtained spectra by analogy with \( \text{K}_2[\text{PdCl}_4] \) gives \( \Delta_1=15,400 \text{ cm}^{-1} \), \( \Delta_2=4600 \text{ cm}^{-1} \), and \( \Delta_3=2200 \text{ cm}^{-1} \). \( \Delta_1 \) is equivalent to \( 10 \, D_q \) if it can be assumed, (from a crystal field point of view at least), that a square planar structure is derived from the gradual elongation of an octahedron, and that the energy difference between \( d(x^2-y^2) \) and \( d(xy) \) remains \( 10 \, D_q \). A comparison to a \( \Delta_1 \) of \( \sim 16,700 \text{ cm}^{-1} \) for \( \text{K}_2[\text{PdCl}_4] \), is reasonable on the basis that the fluorosulfate group is generally known to produce a weaker ligand field than a chloro group.

Some generalizations concerning the relative ability of a \( \text{SO}_3\text{F} \) group to coordinate to a metal ion depending on how the other two oxygen atoms are bonded can be made. For the Pd(II)-fluorosulfate system, three types of coordination of a \( \text{SO}_3\text{F} \) group are evident from results obtained in this study:
FIG. 3.6: d-ORBITAL ENERGY LEVEL FOR A SQUARE PLANAR COMPLEX $^{142}$

\[
\begin{align*}
\Delta_1 & \quad d(x^2-y^2) \\
\Delta_2 & \quad d(xy) \\
\Delta_3 & \quad d(z^2) \\
\end{align*}
\]

d(xz), d(yz)

$\nu_1 = \Delta_1$
$\nu_2 = \Delta_1 + \Delta_2$
$\nu_3 = \Delta_1 + \Delta_2 + \Delta_3$

TABLE 3.5: ELECTRONIC SPECTRA AND LIGAND FIELD PARAMETERS FOR $^{142}$

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1, A_{1g} \rightarrow A_{2g}$</td>
<td>Cs$_2$Pd(SO$_3$F)$_4$</td>
<td>15,400 w</td>
<td>15,400 w</td>
</tr>
<tr>
<td>$\nu_2, A_{1g} \rightarrow B_{1g}$</td>
<td></td>
<td>-20,000 s,sh</td>
<td>-20,000 s,sh</td>
</tr>
<tr>
<td>$\nu_3, A_{1g} \rightarrow E_{1g}$</td>
<td></td>
<td>22,200 s</td>
<td>-22,700 s</td>
</tr>
<tr>
<td>Charge Transfer</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Charge Transfer</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| \$\Delta_1$ | | | |
| \$\Delta_2$ | 4,600 | 4,600 | 4,800 |
| \$\Delta_3$ | 2,200 | 2,500 | 1,800 |
a) monodentate, as in \([\text{Pd}(\text{SO}_3\text{F})_4]^{2-}\),
b) aniso-bidentate bridging between Pd(II) and a M(IV) cation, as in \(\text{Pd}[\text{M(IV)}(\text{SO}_3\text{F})_6]\), and
c) bridging tridentate to three equivalent Pd(II) in \(\text{Pd}(\text{SO}_3\text{F})_2\).

Most likely a result of less competition for ligand electrons from another metal centre, a monodentate SO\(_3\)F produces the strongest ligand field. The withdrawal of electron density from a SO\(_3\)F group due to its bonding to a highly charged M(IV) cation can drastically reduce the ligands' coordinating ability to Pd(II). In fact, the reduction can make the SO\(_3\)F ligand in the former coordination mode bind more weakly to Pd(II) than does a tridentate SO\(_3\)F group. By extrapolation, a bidentate SO\(_3\)F group bridging two Pd(II) should produce a ligand field splitting somewhat between the ones present in \([\text{Pd}(\text{SO}_3\text{F})_4]^{2-}\) and \(\text{Pd}(\text{SO}_3\text{F})_2\). Similar observations have been made for a number of transition metal tri-fluorides, MF\(_3\), with M = Ti, V, Cr, Mn, Fe and Co, and their mixed ternary salts of the general formula of M'\(_2\)M''[MF\(_6\)]. The fluorine atoms in the binary fluorides are shared by two M(III) cations while in the [MF\(_6\)]\(^{3-}\) complexes, the fluoride ligands are essentially coordinated to M(III) with weak interactions towards M'', an alkali metal ion. An increase in \(\Delta_0\) of \(-7\%\) is noted in going from MF\(_3\) to [MF\(_6\)]\(^{3-}\) \(^{144}\).

For the \([\text{Pd}(\text{SO}_3\text{F})_6]^{2-}\) containing compounds, less informative electronic spectra were obtained. \(\text{Pd}_2(\text{SO}_3\text{F})_6\) is a dark brown solid, and its u.v.-vis spectrum consists of a very intense,
featureless band which extends over most of the spectrum. This must be due to charge transfer because

a) the high cationic charge of Pd(IV) enhances L → M transfer, and

b) the mixed valency nature of the compound which can give rise to M → M' transfer.

As mentioned, the solution of (NO)₂[Pd(SO₃F)₆] in HSO₃F shows a single absorption peak at 320 nm with an extinction coefficient of 1.3×10⁴ M⁻¹cm⁻¹; charge transfer origin of the L → M type is also suggested here.

3.4.3 MAGNETIC SUSCEPTIBILITY

As mentioned in the introduction, most palladium compounds, regardless of the oxidation state of palladium, are diamagnetic. This is because

a) both Pd(II) and Pd(IV) are even-electron species,

b) Pd(IV) is invariably octahedral low spin with high 10 Dₑ values, and

c) Pd(II) is usually in a square planar, and thus diamagnetic, environment.

Octahedral Pd(II), d⁸, is expected to be paramagnetic, with two unpaired electrons corresponding to a ³A₂g ground state. Therefore, a direct orbital contribution to the magnetic moment
is not expected, but through spin-orbital coupling, which is expected to be quite large for 2nd and 3rd series transition metals, the observed magnetic moment should be in excess of the spin-only value of 2.83 $\mu_B$.

3.C.4.1 PARAMAGNETIC Pd(II) FLUOROSULFATES

Paramagnetism is found for Pd(SO$_3$F)$_2$, Pd$_2$(SO$_3$F)$_6$, Pd[Pt(SO$_3$F)$_6$] and Pd[Sn(SO$_3$F)$_6$], all with magnetic moments indicative of two unpaired electrons for Pd(II). As mentioned, the electronic spectra for these compounds have shown that a $^3A_{2g}$ ground state can best be assigned to Pd(II) in these compounds. The magnetic susceptibility of such a species can be represented by the following equation, according to Figgis $^{141}$:

$$
\chi_A = \chi_A^{s.o.}(1 - \frac{8k^2\lambda_0}{10D_q}) + \frac{8k^2N\beta^2}{10D_q}
$$

(3.24)

where $\chi_A^{s.o.}$ = spin only susceptibility,

$k$ = electron delocalization factor,

$\lambda_0$ = spin-orbit coupling constant = $-\xi/2$ for d$^8$,

$\beta$ = Bohr Magneton,

$N$ = Avogadro's Number

$10D_q$ = Ligand Field Splitting.

The first correction term involving $\lambda_0$, is due to the spin-orbital coupling, and the second (and much smaller) term arises from 2nd order Zeeman Effect and is usually called Temperature Independent Paramagnetism (T.I.P.). $\xi$, the spin-orbital coupling
parameter, has been estimated as $1460 \text{ cm}^{-1}$ for Pd(II) $^{145}$. Therefore, with $\lambda_0$ negative, the observed magnetic susceptibility should be higher than the spin only value.

The magnetic susceptibilities of the four paramagnetic Pd(II) compounds are listed in Tables 3.6 to 3.9 and their Curie-Weiss Law dependence is represented diagrammatically in Fig 3.7. A comparison of these results with the corresponding fluoride system is made in Table 3.10. Having obtained the ligand field splitting parameter, $D_q$, from the electronic spectra of some of these compounds, it is possible to estimate the electron delocalization factor, $k$, and also to verify the value of the spin orbital coupling constant $-\lambda_0$.

As can be seen, the four paramagnetic compounds all obey the Curie-Weiss Law in the temperature range of the investigation with very small Weiss constants as extrapolated from $\sim 80 \text{ K}$. This suggests the presence of magnetically dilute systems in these cases, in contrast to the antiferromagnetic couplings observed in the fluoride system $^{104,108,116}$. It is not expected that such couplings via the superexchange mechanism $^{115,146}$ can occur effectively through the polyatomic fluorosulfate ligands. The experimentally obtained magnetic susceptibilities and moments are very close to the ones calculated from the Curie-Weiss Law relationship. Small temperature dependence of the susceptibilities as a result of positive Weiss constants, can be decreased by applying T.I.P. to the two complexes containing Sn(IV) and Pt(IV).
<table>
<thead>
<tr>
<th>T</th>
<th>$\chi_m^c$</th>
<th>$1/\chi_m^c$</th>
<th>$1/\chi_m^c$ (calc)</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\mu_{\text{eff}}$ (calc)</th>
<th>$\mu_{\text{eff}}$ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>103</td>
<td>1.462x10^-2</td>
<td>68.40</td>
<td>67.43</td>
<td>3.47</td>
<td>3.50</td>
<td>3.45</td>
</tr>
<tr>
<td>125</td>
<td>1.163x10^-2</td>
<td>85.18</td>
<td>83.32</td>
<td>3.43</td>
<td>3.46</td>
<td>3.41</td>
</tr>
<tr>
<td>150</td>
<td>9.678x10^-3</td>
<td>102.2</td>
<td>101.4</td>
<td>3.43</td>
<td>3.44</td>
<td>3.40</td>
</tr>
<tr>
<td>183</td>
<td>8.119x10^-3</td>
<td>121.7</td>
<td>125.2</td>
<td>3.47</td>
<td>3.42</td>
<td>3.44</td>
</tr>
<tr>
<td>207</td>
<td>7.083x10^-3</td>
<td>139.1</td>
<td>142.5</td>
<td>3.45</td>
<td>3.41</td>
<td>3.42</td>
</tr>
<tr>
<td>225</td>
<td>6.313x10^-3</td>
<td>155.8</td>
<td>155.5</td>
<td>3.40</td>
<td>3.40</td>
<td>3.36</td>
</tr>
<tr>
<td>250</td>
<td>5.655x10^-3</td>
<td>173.6</td>
<td>173.6</td>
<td>3.39</td>
<td>3.39</td>
<td>3.35</td>
</tr>
<tr>
<td>274</td>
<td>5.067x10^-3</td>
<td>193.3</td>
<td>190.9</td>
<td>3.37</td>
<td>3.39</td>
<td>3.32</td>
</tr>
<tr>
<td>299</td>
<td>4.668x10^-3</td>
<td>209.5</td>
<td>209.0</td>
<td>3.38</td>
<td>3.38</td>
<td>3.33</td>
</tr>
</tbody>
</table>

$K$  
cgs  
cgs  
cgs  
$\mu_B$  
$\mu_B$  
$\mu_B$  
units

$1/\chi_m^c$ (calc) = $(T - 10)/1.38$

TIP = 140x10^-6 cgs units

$k \approx 0.89$

---

<table>
<thead>
<tr>
<th>T</th>
<th>$\chi_m^c$</th>
<th>$1/\chi_m^c$</th>
<th>$1/\chi_m^c$ (calc)</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\mu_{\text{eff}}$ (calc)</th>
<th>$\mu_{\text{eff}}$ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>334</td>
<td>4.419x10^-3</td>
<td>226.3</td>
<td>224.3</td>
<td>3.44</td>
<td>3.45</td>
<td>3.38</td>
</tr>
<tr>
<td>302</td>
<td>4.926x10^-3</td>
<td>203.0</td>
<td>202.2</td>
<td>3.45</td>
<td>3.46</td>
<td>3.40</td>
</tr>
<tr>
<td>279</td>
<td>5.410x10^-3</td>
<td>184.8</td>
<td>186.3</td>
<td>3.48</td>
<td>3.46</td>
<td>3.43</td>
</tr>
<tr>
<td>253</td>
<td>5.987x10^-3</td>
<td>167.0</td>
<td>168.3</td>
<td>3.48</td>
<td>3.47</td>
<td>3.44</td>
</tr>
<tr>
<td>229</td>
<td>6.616x10^-3</td>
<td>151.1</td>
<td>151.7</td>
<td>3.48</td>
<td>3.48</td>
<td>3.44</td>
</tr>
<tr>
<td>204</td>
<td>7.472x10^-3</td>
<td>133.8</td>
<td>134.4</td>
<td>3.49</td>
<td>3.48</td>
<td>3.46</td>
</tr>
<tr>
<td>179</td>
<td>8.621x10^-3</td>
<td>116.0</td>
<td>117.1</td>
<td>3.51</td>
<td>3.50</td>
<td>3.48</td>
</tr>
<tr>
<td>153</td>
<td>9.985x10^-3</td>
<td>100.2</td>
<td>99.12</td>
<td>3.50</td>
<td>3.51</td>
<td>3.47</td>
</tr>
<tr>
<td>131</td>
<td>1.185x10^-2</td>
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<td>83.91</td>
<td>3.52</td>
<td>3.53</td>
<td>3.50</td>
</tr>
<tr>
<td>107</td>
<td>1.468x10^-2</td>
<td>68.13</td>
<td>67.30</td>
<td>3.54</td>
<td>3.57</td>
<td>3.53</td>
</tr>
</tbody>
</table>

$K$  
cgs  
cgs  
cgs  
$\mu_B$  
$\mu_B$  
$\mu_B$  
units

$1/\chi_m^c$ (calc) = $(T - 10)/1.45$

TIP ~ 150x10^-6 cgs units

$k \approx 0.92$ to 0.95
### TABLE 3.8  MAGNETIC PROPERTIES OF Pd\(\text{[Pt(SO}_3\text{F)}]_6\)}

<table>
<thead>
<tr>
<th>(T)</th>
<th>(x_m)</th>
<th>(1/x_m)</th>
<th>(1/x_m) (calc)</th>
<th>(\mu_{\text{eff}})</th>
<th>(\mu_{\text{eff}}) (calc)</th>
<th>(\mu_{\text{eff}} T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>89</td>
<td>1.447x10(^{-2})</td>
<td>69.09</td>
<td>69.82</td>
<td>3.21</td>
<td>3.19</td>
<td>3.20</td>
</tr>
<tr>
<td>119</td>
<td>1.106x10(^{-2})</td>
<td>90.41</td>
<td>90.95</td>
<td>3.24</td>
<td>3.24</td>
<td>3.23</td>
</tr>
<tr>
<td>142</td>
<td>9.350x10(^{-3})</td>
<td>107.0</td>
<td>107.1</td>
<td>3.26</td>
<td>3.26</td>
<td>3.24</td>
</tr>
<tr>
<td>167</td>
<td>7.975x10(^{-3})</td>
<td>125.4</td>
<td>124.8</td>
<td>3.26</td>
<td>3.27</td>
<td>3.24</td>
</tr>
<tr>
<td>193</td>
<td>6.895x10(^{-3})</td>
<td>145.0</td>
<td>143.1</td>
<td>3.26</td>
<td>3.29</td>
<td>3.23</td>
</tr>
<tr>
<td>222</td>
<td>6.122x10(^{-3})</td>
<td>163.3</td>
<td>163.5</td>
<td>3.30</td>
<td>3.30</td>
<td>3.27</td>
</tr>
<tr>
<td>246</td>
<td>5.544x10(^{-3})</td>
<td>180.4</td>
<td>180.4</td>
<td>3.30</td>
<td>3.30</td>
<td>3.27</td>
</tr>
<tr>
<td>278</td>
<td>4.934x10(^{-3})</td>
<td>202.7</td>
<td>202.9</td>
<td>3.31</td>
<td>3.31</td>
<td>3.27</td>
</tr>
<tr>
<td>302</td>
<td>4.565x10(^{-3})</td>
<td>219.1</td>
<td>219.8</td>
<td>3.32</td>
<td>3.32</td>
<td>3.28</td>
</tr>
</tbody>
</table>

\(K\)  cgs   cgs   cgs  \(\mu_B\)  \(\mu_B\)  \(\mu_B\) units

\(1/x_m\) (calc) = \((T + 10)/1.42\)

TIP = 121x10\(^{-6}\) cgs units

\(k \approx 0.81\)

### TABLE 3.9  MAGNETIC PROPERTIES OF Pd\(\text{[Sn(SO}_3\text{F)}]_6\)}

<table>
<thead>
<tr>
<th>(T)</th>
<th>(x_m) (C)</th>
<th>(1/x_m)</th>
<th>(1/x_m) (calc)</th>
<th>(\mu_{\text{eff}})</th>
<th>(\mu_{\text{eff}}) (calc)</th>
<th>(\mu_{\text{eff}} T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1.829x10(^{-2})</td>
<td>54.69</td>
<td>55.41</td>
<td>3.42</td>
<td>3.40</td>
<td>3.40</td>
</tr>
<tr>
<td>107</td>
<td>1.407x10(^{-2})</td>
<td>71.09</td>
<td>72.09</td>
<td>3.47</td>
<td>3.45</td>
<td>3.45</td>
</tr>
<tr>
<td>129</td>
<td>1.171x10(^{-2})</td>
<td>85.38</td>
<td>85.68</td>
<td>3.48</td>
<td>3.47</td>
<td>3.45</td>
</tr>
<tr>
<td>154</td>
<td>9.833x10(^{-3})</td>
<td>101.7</td>
<td>101.1</td>
<td>3.48</td>
<td>3.49</td>
<td>3.45</td>
</tr>
<tr>
<td>178</td>
<td>8.522x10(^{-3})</td>
<td>117.3</td>
<td>116.0</td>
<td>3.48</td>
<td>3.50</td>
<td>3.45</td>
</tr>
<tr>
<td>203</td>
<td>7.564x10(^{-3})</td>
<td>132.2</td>
<td>131.4</td>
<td>3.50</td>
<td>3.52</td>
<td>3.46</td>
</tr>
<tr>
<td>229</td>
<td>6.784x10(^{-3})</td>
<td>147.4</td>
<td>147.5</td>
<td>3.53</td>
<td>3.52</td>
<td>3.48</td>
</tr>
<tr>
<td>252</td>
<td>6.121x10(^{-3})</td>
<td>163.4</td>
<td>161.7</td>
<td>3.51</td>
<td>3.53</td>
<td>3.46</td>
</tr>
<tr>
<td>280</td>
<td>5.609x10(^{-3})</td>
<td>178.3</td>
<td>179.0</td>
<td>3.54</td>
<td>3.54</td>
<td>3.49</td>
</tr>
<tr>
<td>306</td>
<td>5.172x10(^{-3})</td>
<td>193.3</td>
<td>195.0</td>
<td>3.56</td>
<td>3.54</td>
<td>3.49</td>
</tr>
</tbody>
</table>

\(K\)  cgs   cgs   cgs  \(\mu_B\)  \(\mu_B\)  \(\mu_B\) units

\(1/x_m\) (calc) = \((T + 10)/1.62\)

TIP = 185x10\(^{-6}\) cgs units

\(k \approx 0.99\)
FIG 3.7 CURIE-WEISS PLOT FOR Pd(II)-FLUROUSULFATE DERIVATIVES

- Pd[Pt(SO$_3$F)$_6$]
- Pd(SO$_3$F)$_2$
- Pd[Pd(SO$_3$F)$_6$]
- Pd[Sn(SO$_3$F)$_6$]
<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^3 \chi_m$</th>
<th>$\mu_{\text{eff}}$</th>
<th>Temperature dependence</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdF$_2$</td>
<td>1.28</td>
<td>1.75</td>
<td>antiferromagnetic coupling</td>
<td>108,151</td>
</tr>
<tr>
<td>Pd[PdF$_6$]</td>
<td>3.31</td>
<td>2.81</td>
<td>$\theta = -28$K</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pd[PtF$_6$]</td>
<td>3.10</td>
<td>2.72</td>
<td>$\theta = -1$K</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pd[GeF$_6$]</td>
<td>3.34</td>
<td>2.82</td>
<td>$\theta = -31$K</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pd[SnF$_6$]</td>
<td>3.37</td>
<td>2.83</td>
<td>$\theta = -28$K</td>
<td>&quot;</td>
</tr>
<tr>
<td>Pd(SO$_3$F)$_2$</td>
<td>4.80</td>
<td>3.38</td>
<td>$\chi_m^c = 1.38/(T-10)$</td>
<td></td>
</tr>
<tr>
<td>Pd[Pd(SO$_3$F)$_6$</td>
<td>5.01</td>
<td>3.46</td>
<td>$\chi_m^c = 1.45/(T-10)$</td>
<td></td>
</tr>
<tr>
<td>Pd[Pt(SO$_3$F)$_6$</td>
<td>4.61</td>
<td>3.32</td>
<td>$\chi_m^c = 1.42/(T+10)$</td>
<td></td>
</tr>
<tr>
<td>Pd[Sn(SO$_3$F)$_6$</td>
<td>5.26</td>
<td>3.54</td>
<td>$\chi_m^c = 1.62/(T+10)$</td>
<td></td>
</tr>
</tbody>
</table>
For the two compounds with negative Weiss constants, no improvements could be expected from the T.I.P. adjustments, but still, the deviations are very small. No great significance should be attached to these small Weiss constants because they are extrapolated over a temperature range of close to 100 K. Magnetic orderings, should they occur, cannot be inferred from these measurements; ferromagnetic orderings have been found for $\text{Pd}_2\text{F}_6$ and $\text{Pd}[\text{PtF}_6]$ below 13 K and 21 K, respectively\(^\text{147}\).

However, the similarity in the magnetic moments for all the four fluorosulfate-containing compounds indicates a similar environment for Pd(II) in all cases. It also shows, conclusively, that the tris(fluorosulfate) should be formulated as containing high spin, paramagnetic Pd(II), and low spin, diamagnetic, Pd(IV), in a mixed-valency configuration.

At first, the magnetic moments of these fluorosulfates appear to be much higher than the spin only value for Pd(II); however, an investigation into the isoelectronic nickel (II) system shows that even Ni(II), with a spin orbit coupling parameter — $\xi$, of only $\sim 630 \text{ cm}^{-1}\text{145}$, can have magnetic moments as high as $3.5 \mu_B$. Some representative $\mu_{\text{eff}}$ values at 298 K are listed in Table 3.11.

As mentioned, although the magnetic moment of PdF\(_2\) is lowered by antiferromagnetic exchange, at infinite dilution of the fluoride by ZnF\(_2\), an extrapolated moment of 3.2 $\mu_B$ is obtained\(^\text{116}\), quite close to the values for the fluorosulfate-
Table 3.11 MAGNETIC PROPERTIES OF SOME Ni(II) COMPOUNDS

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$</th>
<th>Temperature Dependence</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(SO$_3$F)$_2$</td>
<td>3.49</td>
<td>Curie-Weiss</td>
<td>148</td>
</tr>
<tr>
<td>(NH$_4$)$_2$NiF$_4$$\cdot$2H$_2$O</td>
<td>3.24</td>
<td>Curie-Weiss, $\theta = -13$ K</td>
<td>149</td>
</tr>
<tr>
<td>NiF$_2$$\cdot$4H$_2$O</td>
<td>3.16</td>
<td>Curie-Weiss, $\theta = -19$ K</td>
<td>149</td>
</tr>
<tr>
<td>LiNiF$_4$</td>
<td>3.19</td>
<td>Curie-Weiss, $\theta \sim 0$ K</td>
<td>149</td>
</tr>
<tr>
<td>NiF$_2$</td>
<td>2.85</td>
<td>Antiferromagnetic</td>
<td>149,150</td>
</tr>
<tr>
<td>NiF$_2$/MgF$_2$, 5.48 mol%Ni</td>
<td>3.04</td>
<td>Curie-Weiss, $\theta \sim -17$ K</td>
<td>150</td>
</tr>
<tr>
<td>NiCl$_2$</td>
<td>2.91</td>
<td>Ferromagnetic</td>
<td>150</td>
</tr>
<tr>
<td>NiCl$_2$/MgCl$_2$, 3.88 mol%Ni</td>
<td>3.20</td>
<td>Curie-Weiss, $\theta \sim 6$ K</td>
<td>150</td>
</tr>
</tbody>
</table>

The increase in the $\mu_{\text{eff}}$ at room temperature in the order of Pd(SO$_3$F)$_2$ < Pd[Pt(SO$_3$F)$_6$] < Pd$_2$(SO$_3$F)$_6$ < Pd Sn(SO$_3$F)$_6$ parallels a similar trend observed in the fluoride system $^{108,151}$. Referring to equation (3.24), the only factors expected to have a dependence on individual Pd(II) compounds are $10 D_q$ — the ligand field splitting, and $k$ — the electron delocalization factor which leads to an effective reduction of $\lambda$ from the free ion value, $\lambda_0$. Although no ligand field parameters can be obtained from the electronic spectrum of Pd$_2$(SO$_3$F)$_6$, the similarity of its magnetic moment to those of the other compounds justifies using the known $10 D_q$'s for the three compounds to arrive at an estimate for $k$ for Pd(II) in Pd$_2$(SO$_3$F)$_6$. The values of $k$ obtained appear to increase in a similar trend as does $\mu_{\text{eff}}$, approaching the free ion value of 1 for the Sn(IV) compound.

However, these differences which are obtained from small deviations in the magnetic measurements from Curie-Weiss Law
should not be overemphasized quantitatively since:

a) they are derived from values that test the limit of accuracy of the Gouy method, and

b) a purely Russell-Saunders coupling scheme, although assumed to apply in the calculations, may not accurately describe the behavior in heavy metal ions $^{141}$. Nevertheless, the magnetic result from these Pd(II) compounds confirms the conclusions arrived at from electronic and vibrational spectroscopy. The Sn(IV) complex has the smallest $10D_q$, and both $\beta$ and $k$ are almost equal to 1, suggesting that of the four compounds, it most closely approaches a free-ion environment for Pd(II). An octahedral coordination for Pd(II), evident from vibrational spectroscopy, is also substantiated by these measurements.

3.C.4.2 DIAMAGNETIC FLUOROSULFATO COMPLEXES OF PALLADIUM

As expected, Pd(IV) was found to be diamagnetic, suggesting a $^{1}A_{1g}$ ground state. For $[\text{Pd(SO}_3\text{F)}_4]^2-$, diamagnetism was also observed, indicating a square planar coordination sphere — the type usually encountered for Pd(II). The magnetic susceptibility results are listed in Table 3.12.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_g$</th>
<th>$\chi_m$</th>
<th>$\Sigma\chi_{\text{dia}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$[\text{Pd(SO}_3\text{F)}_6]$</td>
<td>$-3.15\pm0.27 \times 10^{-7}$</td>
<td>$-264\pm23 \times 10^{-6}$</td>
<td>$-202 \times 10^{-6}$</td>
</tr>
<tr>
<td>Cs$_2[\text{Pd(SO}_3\text{F)}_4]$</td>
<td>$-2.78\pm0.24 \times 10^{-7}$</td>
<td>$-214\pm18 \times 10^{-6}$</td>
<td>$-247 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
3.C.5 SOLUTION STUDIES IN HSOF

Due to the observed lack of any appreciable solubility of most of the fluorosulfate-containing palladium compounds in HSOF, solution studies in these systems were rather limited.

Although Cs$_2$[Pd(SO$_3$F)$_4$] and (NO)$_2$[Pd(SO$_3$F)$_4$] are soluble in HSOF, the resulting solutions are very unstable, with a precipitation of Pd(SO$_3$F)$_2$ forming almost immediately upon the addition of the compounds. Pd(SO$_3$F)$_2$ was identified by i.r. spectroscopy as the only solid left after a filtration of the mixture. Presumably, the high lattice energy of the extensively polymerized Pd(SO$_3$F)$_2$ favored its formation and subsequent removal from the equilibrium of:

$$[\text{Pd(SO}_3\text{F)}_4]^{2-} \xrightarrow{\text{HSOF}} \text{Pd(SO}_3\text{F)}_2 + 2\text{SO}_3\text{F}^{-}. \quad (3.25)$$

This is also consistent with the observation that no reversal of equation (3.25) takes place when alkali metal fluorosulfates are mixed with Pd(SO$_3$F)$_2$.

In order to provide further evidence for the existence of [Pd(SO$_3$F)$_6$]$^{2-}$ as an ionic entity, electrical conductivity measurements for solutions of Cs$_2$[Pd(SO$_3$F)$_6$] in HSOF were undertaken. The results, shown in Fig 3.8, agree quite well with the literature values for an analogous compound, K$_2$[Sn(SO$_3$F)$_6$] $^{32}$. The basic dissociation for the anions [M(SO$_3$F)$_6$]$^{2-}$, where M = Pd, Pt, Ir, Sn, will be discussed in detail in Chapters 5 and 9. An ionization scheme, at least in a first approximation, can be
FIG. 3.8  CONDUCTIVITY OF Cs$_2$[Pd(SO$_3$F)$_6$] IN HSO$_3$F
represented by:

\[ \text{Cs}_2\text{[Pd(SO}_3\text{F})_6]} \xrightarrow{\text{HSO}_3\text{F}} 2\text{Cs}^+ (\text{solv}) + [\text{Pd(SO}_3\text{F})_6]^{2-} (\text{solv}) \quad (3.26) \]

<table>
<thead>
<tr>
<th>m (mol.kg(^{-1}))</th>
<th>(\kappa (10^{-4}\Omega^{-1}\text{cm}^{-1}))</th>
</tr>
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<td>0.0000</td>
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<tr>
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<td>23.00</td>
</tr>
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<td>0.0140</td>
<td>25.14</td>
</tr>
</tbody>
</table>

units
3.D CONCLUSION

The study into the fluorosulfates of palladium yielded a number of new compounds with the metal in the +2 and the +4 oxidation states. Two binary fluorosulfates, Pd(SO$_3$F)$_2$, and the mixed valency compound, Pd(II)Pd(IV)(SO$_3$F)$_6$, were obtained and characterized.

Pd(SO$_3$F)$_2$ has the metal in the rather uncommon octahedral and thus paramagnetic environment. Dilute magnetic systems are also encountered for Pd(II)[M(IV)(SO$_3$F)$_6$], where M = Pd, Pt, Sn. Ligand field parameters have also been determined for all the above compounds, except for Pd$_2$(SO$_3$F)$_6$, by electronic spectroscopy. Diamagnetic complexes containing the presumably square planar [Pd(SO$_3$F)$_4$]$^{2-}$ can also be obtained.

While a number of [Pd(SO$_3$F)$_6$]$^{2-}$ complexes can be synthesized and characterized, the parent compound — Pd(SO$_3$F)$_4$ has thus far eluded all attempts. Indirect evidence seems to indicate its existence in S$_2$O$_6$F$_2$/HSO$_3$F and that it has a strong fluorosulfate-accepting ability.
CHAPTER 4  GOLD-FLUOROSULFATE

4.A  INTRODUCTION

Although gold is a member of the copper triad — copper, silver and gold —, unlike in most other groups, there is little resemblance between the chemistry of the three metals. While both the noble metals can exist in the monovalent state, Au(III) is the only commonly found high oxidation state. Both Ag(II) and Ag(III) are extremely strongly oxidizing and cannot be obtained easily. Compounds have frequently appeared in the literature in which gold has formally the oxidation number of +2. Most of them, however, are actually mixed valency compounds containing Au(I) and Au(III) because they are diamagnetic. A true Au(II) compound should be paramagnetic because of the presence of a d⁹ electronic configuration for the metal. The few truly Au(II) compounds contain dithiolate-type ligands which are very effective in electron delocalization. These compounds are paramagnetic, as studied by bulk magnetic susceptibility measurements and e.s.r.¹³³,¹⁵².

The first example of a +5 oxidation state for gold is the [AuF₆]⁻ complexes, formed by the fluorination/complexation reaction of AuF₃ according to¹⁵³,¹⁵⁴:

\[ 2\text{XeF}_2 + \text{AuF}_3 + 5\text{F}_2 \rightarrow [\text{Xe}_2\text{F}_{11}]^+ [\text{AuF}_6]^- \]  

The pentafluoride, AuF₅, can be prepared by the pyrolysis of O₂[AuF₆]⁻¹⁵⁵. These fluorine coordinated compounds of Au(V) represent a frequent observation in transition metal chemistry
that the highest possible oxidation state of a metal is usually found in such systems.

The general chemistry of gold has been reviewed in a number of recent publications \(^{156-159}\). Again, some brief comments on the halide system of gold can provide some pertinent background information to the corresponding fluorosulfate system.

The monohalides, Au-Hal, with Hal=Cl, Br, I, the trihalides, Au-Hal\(_3\), with Hal=F, Cl, Br, and the previously mentioned AuF\(_5\), are known. All of these binary halides, because of their unsaturated coordination spheres, can exhibit Lewis acidity towards halide ions or other suitable donor ligands to form complexes. For examples, neutral adducts of the types Au(I)-Hal·L, and Au(III)-Hal\(_3\)·L, where L=neutral ligands, and anionic complexes of the types of \([\text{Au(I)}-\text{Hal}_2]^-\), \([\text{Au(III)}-\text{Hal}_4]^-\) and \([\text{AuF}_6]^-\), can readily be prepared. The chemistry of the monohalides, by virtue of its similarities to those of Ag(I) and Cu(I), will not be discussed here.

The three trihalides are polymeric to varying degrees: Au\(_2\)Cl\(_6\) and Au\(_2\)Br\(_6\) are the species present in vapor, solid state and solutions in covalent solvents. AuF\(_3\), on the other hand, is extensively polymerized, and consists of chains of fluorine-bridged [AuF\(_4\)] units packed in a helical manner \(^{160}\). The tetrahalo-complexes, similar to the binary trihalides, are square planar and therefore diamagnetic \(^{161}\). Actually, all gold compounds, except for the very few that contains Au(II), are diamagnetic;
the rationale generally invoked to explain the diamagnetism of most Pd(II) compounds is even more applicable to Au(III) because of the latter's larger ligand field splitting.

Au(SO₃F)₃, first reported by Cady in 1972⁸², appears to be the only well documented binary oxyacid salt of Au(III). While the existence of the nitrate is questionable, its anionic complex, K[Au(NO₃)₄], can be prepared and crystallographic results indicate the compound has monodentate nitrate group in a square planar configuration around Au(III)¹⁶².

Au(SO₃F)₃ may behave as an ansolvo acid in the HSO₃F solvent system for the following reasons:

a) The reaction of gold metal with BrSO₃F, as reported by Cady et al⁸², resulted in the formation of a solution. Since BrSO₃F is an ionizing solvent, the solvation of the product indicates some type of dissociation process of the solvent taking place with Au(SO₃F)₃.

b) The product isolated from the reaction mixture described above is a solid of the approximate composition of Au(SO₃-F)₃·2BrSO₃F. This could be a donor-acceptor adduct, and since BrSO₃F is not known to be a strong SO₃F acceptor, Au(SO₃F)₃ could be the acceptor, with the formation of a species which may be formulated as [Br₂SO₃F]⁺[Au(SO₃F)₄]⁻.

c) Solutions of AuF₃ in HSO₃F have been reported by Woolf to show acid behavior, although the actual nature of the species present in solution was not identified¹⁶⁴.
Therefore, a full investigation into the chemistry and solution behavior of \( \text{Au(} \text{SO}_3\text{F)}_3 \) in \( \text{HSO}_3\text{F} \) was undertaken, in the hope of establishing its existence as a novel superacid system \(^{165,166}\). The gold-trifluoromethylsulfate system was also studied for possible superacid behavior in \( \text{HSO}_3\text{CF}_3 \); the results are described in Appendix B.
4.B EXPERIMENTAL

4.B.1 SYNTHESIS OF Au(SO$_3$F)$_3$

4.B.1.1 OXIDATION OF GOLD METAL BY S$_2$O$_6$F$_2$/HSO$_3$F

$$2\text{Au} + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} 2\text{Au(SO}_3\text{F)}_3$$ (4.2)

In a typical reaction, S$_2$O$_6$F$_2$ (~2 mL) and HSO$_3$F (~3 mL) were distilled into a reactor containing gold powder (579 mg, 2.940 mmol). The reaction proceeded slowly at room temperature, with the metal dissolving over a period of about 6 hours to give a yellow to orange solution. The removal of all volatile materials yielded Au(SO$_3$F)$_3$, (1.460 g, 2.955 mmol).

Au(SO$_3$F)$_3$ is a yellow to orange, hygroscopic, crystalline solid. It is sublimable at ~120°C in vacuo and melts with decomposition at ~140°C to a dark red liquid. It is very soluble in HSO$_3$F, with concentrations of up to ~7 m having been obtained. The elemental analysis of Au(SO$_3$F)$_3$ was reported by Cady et al $^8_2$.

4.B.1.2 SOLVOLYSIS OF AuCl$_3$ IN BrSO$_3$F

$$2\text{AuCl}_3 + 6\text{BrSO}_3\text{F} \rightarrow 2\text{Au(SO}_3\text{F)}_3 + 3\text{Br}_2 + 3\text{Cl}_2$$ (4.3)

AuCl$_3$, (168 mg, 0.554 mmol), dissolved in BrSO$_3$F, (~6 mL), with gas evolution. The vapor had the appearance of Cl$_2$, which could be in equilibrium with BrCl. To ensure a complete reaction, the solution was heated at 60°C for 4 hours. After the removal of all volatile materials, Au(SO$_3$F)$_3$ was obtained, (276 mg, 0.599 mmol).
Au(SO₃F)₃ can also be obtained from,

a) the reaction of Au₂O₃ with S₂O₆F₂/HSO₃F:

\[ \text{Au}_2\text{O}_3 + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} 2\text{Au(SO}_3\text{F)}_3 + 3\text{O}_2 \quad (4.4) \]

or b) the reaction of gold metal with BrSO₃F followed by the thermal decomposition of the intermediate as reported by Cady et al. ⁸²

### 4.B.2 SYNTHESIS OF IONIC [Au(SO₃F)₄]⁻ COMPLEXES

\[
\text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{HCl} \quad (4.5)
\]

\[
2\text{CsSO}_3\text{F} + 2\text{Au} + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} 2\text{Cs[Au(SO}_3\text{F)}_4] \quad (4.6)
\]

HSO₃F (−3 mL) was added to a mixture of CsCl (142 mg, 0.843 mmol) and gold powder (166 mg, 0.843 mmol). The HCl formed was removed by evacuating all the solvent. S₂O₆F₂, (−2 mL) and HSO₃F, (−4 mL), were then added to the solid mixture and the reactor was subsequently heated at ~60°C for 12 hours. After which time all the metal had reacted. The removal of all volatile materials yielded Cs[Au(SO₃F)₄], (622 mg, 0.844 mmol).

An alternative synthetic route involves solvolysis/oxidation in BrSO₃F according to:

\[
\text{CsCl} + \text{Au} + 4\text{BrSO}_3\text{F} \rightarrow \text{Cs[Au(SO}_3\text{F)}_4] + 2\text{Br}_2 + \frac{1}{2}\text{Cl}_2 \quad (4.7)
\]

The equimolar mixture of CsCl and gold metal was heated in an excess amount of BrSO₃F at ~60°C for 2 days, followed by the removal
of all volatile materials.

Cs[Au(SO$_3$)$_4$] is a yellow, crystalline, hygroscopic solid. It is soluble in both HS$_3$F and BrSO$_3$F, and melts at 105°C into a deep orange liquid which decomposes at ~300°C.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Cs</th>
<th>Au</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
<td>18.30</td>
<td>27.13</td>
<td>10.47</td>
</tr>
<tr>
<td>Found %</td>
<td>18.14</td>
<td>26.98</td>
<td>10.30</td>
</tr>
</tbody>
</table>

4.B.2.2 PREPARATION OF K[Au(SO$_3$)$_4$]

KCl + HS$_3$F $\rightarrow$ KSO$_3$F + HCl

2KSO$_3$F + 2Au + 3S$_2$O$_6$F$_2$ $\xrightarrow{HSO_3 F}$ 2Cs[Au(SO$_3$)$_4$] (4.9)

In an analogous manner to the preparation of the corresponding Cs$^+$ salt, KCl (78 mg, 1.05 mmol) and gold powder (206 mg, 1.05 mmol) were reacted with a mixture of S$_2$O$_6$F$_2$ and HS$_3$F to yield K[Au(SO$_3$)$_4$], (692 mg, 1.09 mmol).

Similarly, K[Au(SO$_3$)$_4$] can also be obtained from the cosolvolysis of KCl and AuCl$_3$ in an excess of BrSO$_3$F, followed by the removal of all volatile materials.

K[Au(SO$_3$)$_4$] is a yellow, crystalline, hygroscopic solid. It is soluble in both HS$_3$F and BrSO$_3$F; it melts with decomposition at ~230°C.

<table>
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<tr>
<th>Analysis</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
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<td>12.02</td>
</tr>
<tr>
<td>Found %</td>
<td>6.22</td>
<td>30.80</td>
<td>12.28</td>
</tr>
</tbody>
</table>
4.B.2.3 PREPARATION OF Li[Au(SO₃F)₄]

\[ \text{Li}_2\text{CO}_3 + \text{S}_2\text{O}_6\text{F}_2 \rightarrow 2\text{LiSO}_3\text{F} + \text{CO}_2 + \frac{3}{2}\text{O}_2 \]  \hspace{1cm} (4.10)

\[ 2\text{LiSO}_3\text{F} + 2\text{Au} + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} 2\text{Li}[\text{Au(SO}_3\text{F)}_4] \]  \hspace{1cm} (4.11)

An excess of \( \text{S}_2\text{O}_6\text{F}_2 \) (~1 mL) was added to a mixture of \( \text{Li}_2\text{CO}_3 \) (25 mg, 0.68 mmol) and gold powder (132 mg, 0.67 mmol). After the gas evolution from the first reaction had ceased, all volatile materials were removed and a mixture of \( \text{S}_2\text{O}_6\text{F}_2 \) (~2 mL) and \( \text{HSO}_3\text{F} \) (~2 mL) was distilled into the reactor. A slow reaction occurred, and the reactor had to be kept at 100°C for 2 days in order for all the metal to react. A precipitate formed, and the removal of all volatile materials yielded \( \text{Li}[\text{Au(SO}_3\text{F)}_4] \), (406 mg, 0.68 mmol).

\( \text{Li}[\text{Au(SO}_3\text{F)}_4] \) is a yellow, crystalline, hygroscopic solid which does not melt below 280°C. It is only slightly soluble in \( \text{HSO}_3\text{F} \) at room temperature.

\begin{tabular}{lccc}
Analysis & Li & Au & F \\
Calculated % & 1.16 & 32.87 & 12.66 \\
Found % & 1.21 & 32.59 & 12.51 \\
\end{tabular}

4.B.2.4 PREPARATION OF (ClO₂)[Au(SO₃F)₄]

\[ \text{ClO}_2\text{SO}_3\text{F} + \text{Au(SO}_3\text{F)}_3 \rightarrow (\text{ClO}_2)[\text{Au(SO}_3\text{F)}_4] \]  \hspace{1cm} (4.12)

\( \text{Au(SO}_3\text{F)}_3 \), (224 mg, 0.453 mmol), was dissolved in an excess of \( \text{ClO}_2\text{SO}_3\text{F} \) (~2 mL). The subsequent removal of all excess \( \text{ClO}_2\text{-SO}_3\text{F} \) yielded \( (\text{ClO}_2)[\text{Au(SO}_3\text{F)}_4] \), (288 mg, 0.436 mmol).
The above compound can also be obtained from a reaction of gold metal with a ClO₂SO₃F/S₂O₆F₂ mixture, according to:

\[ 2\text{ClO}_2\text{SO}_3\text{F} + 2\text{Au} + 3\text{S}_2\text{O}_6\text{F}_2 \rightarrow 2(\text{ClO}_2)[\text{Au(SO}_3\text{F})_4] \]  

(4.13)

(\text{ClO}_2)[\text{Au(SO}_3\text{F})_4] \text{ is a yellow, crystalline, hygroscopic solid. It is soluble in ClO}_2\text{SO}_3\text{F at 25°C to give a light orange solution. It melts at 101 - 103°C to an orange liquid which decomposes at ~170°C.}

Analysis  
Calculated % | Cl | Au | S  
--- | --- | --- | ---  
5.23 | 29.81 | 19.41  
Found %  
5.23 | 30.00 | 19.24

4.8.2.5 PREPARATION OF (NO)[Au(SO₃F)₄]

\[ 2\text{Au} + 3\text{Br}_2 \rightarrow 2\text{AuBr}_3 \]  

(4.14)

\[ 4\text{NOCl} + \text{AuBr}_3 \rightarrow (\text{NO})[\text{AuCl}_4] + 3\text{NOBr} \]  

(4.15)

\[ (\text{NO})[\text{AuCl}_4] + 4\text{BrSO}_3\text{F} \rightarrow (\text{NO})[\text{Au(SO}_3\text{F})_4] + 2\text{Br}_2 + 2\text{Cl}_2 \]  

(4.16)

Gold powder (112 mg, 0.569 mmol) was reacted with Br₂ at 80°C for 12 hours to give AuBr₃ (247 mg, 0.565 mmol), which was reacted with an excess of NOCl (~5 mL) at 80°C for ½ day. The insoluble, light brown, powder was identified as (NO)[AuCl₄], (209 mg, 0.567 mmol), by its Raman spectrum which had bands at 2205 and 2183 cm⁻¹, (νN=O), and also at 345 and 321 cm⁻¹, (ν[Au-Cl₄]). (NO)[Au(SO₃F)₄], (348 mg, 0.558 mmol) was prepared by reacting the (NO)[AuCl₄] with an excess of BrSO₃F, (~2 mL), and heating the reaction mixture at 80°C for ½ hour. The product was
isolated after the removal of all volatile materials.

(NO)[Au(SO$_3$F)$_4$] is a yellow, crystalline, hygroscopic solid. It is soluble in both BrSO$_3$F and HSO$_3$F. It melts at 192 - 195°C to an orange liquid which decomposes at ~260°C.

\[
\begin{array}{ccc}
\text{Analysis} & \text{N} & \text{Au} & \text{F} \\
\text{Calculated \%} & 2.25 & 31.61 & 12.19 \\
\text{Found \%} & 2.10 & 31.85 & 12.32 \\
\end{array}
\]

4.B.3 SYNTHESIS OF [Au(SO$_3$F)$_4$] COMPLEXES CONTAINING HALOGENOFLUOROSULFATO CATIONS

4.B.3.1 PREPARATION OF [Br(SO$_3$F)$_2$][Au(SO$_3$F)$_4$]

\[
\begin{align*}
\text{Br}_2 + 3\text{S}_2\text{O}_6\text{F}_2 & \rightarrow 2\text{Br(SO}_3\text{F)}_3 \\
2\text{Br(SO}_3\text{F)}_3 + 2\text{Au} + 3\text{S}_2\text{O}_6\text{F}_2 & \rightarrow 2[\text{Br(SO}_3\text{F)}_2][\text{Au(SO}_3\text{F)}_4]
\end{align*}
\]

Br$_2$, (37 mg, 0.231 mmol) and gold powder (90 mg, 0.457 mmol) were reacted with S$_2$O$_6$F$_2$ (~3 mL) at 70°C for ½ day. The oxidation of Br$_2$ proceeded quickly, as evident by the formation of a yellow solution. Soon afterwards, the gold metal dissolved to form two immiscible, light yellow layers, with the top layer presumably containing mostly S$_2$O$_6$F$_2$. The bottom layer crystallized when the mixture was cooled at 0°C for 3 days. The removal of all volatile materials at room temperature yielded [Br(SO$_3$F)$_2$][Au(SO$_3$F)$_4$], (408 mg, 0.468 mmol).

[Br(SO$_3$F)$_2$][Au(SO$_3$F)$_4$] is a light yellow, hygroscopic, cry-
stalline solid that has a tendency towards supercooling at room
temperature. It melts at 52 - 55°C.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Br</th>
<th>Au</th>
<th>S</th>
<th>F</th>
</tr>
</thead>
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<td>Found %</td>
<td>9.26</td>
<td>22.45</td>
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<td>13.13</td>
</tr>
</tbody>
</table>

4.B.3.2 PREPARATION OF \([I(SO_3F)_2][Au(SO_3F)_4]\)

\[
I_2 + 3S_2O_6F_2 \longrightarrow I(SO_3F)_3 \quad (4.19)
\]

\[
2I(SO_3F)_3 + 2Au + 3S_2O_6F_2 \longrightarrow 2[I(SO_3F)_2][Au(SO_3F)_4] \quad (4.20)
\]

In a manner similar to the last preparation, \(I_2\) (92 mg, 0.363 mmol) and gold powder (143 mg, 0.726 mmol) were allowed to react with \(S_2O_6F_2\) (~3 mL) at ~80°C for 12 hours. After all the metal had reacted, crystalline \([I(SO_3F)_2][Au(SO_3F)_4]\) was formed upon cooling the mixture to room temperature (650 mg, 0.708 mmol).

\([I(SO_3F)_2][Au(SO_3F)_4]\) is a light orange to yellow, hygroscopic crystalline solid. It has a melting range of 70 - 73°C.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>I</th>
<th>Au</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
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</tr>
<tr>
<td>Found %</td>
<td>14.04</td>
<td>21.61</td>
<td>12.67</td>
</tr>
</tbody>
</table>

4.B.4.1 PREPARATION OF (Br$_3$)[Au(SO$_3$F)$_4$]

\[
\text{Au} + 4\text{BrSO}_3\text{F} \longrightarrow (\text{Br}_3)[\text{Au(SO}_3\text{F)}_4] + \frac{1}{2}\text{Br}_2 \quad (4.21)
\]

An excess of BrSO$_3$F (~3 mL) was distilled onto gold powder, (293 mg, 1.488 mmol), contained in a reaction vial. A vigorous, exothermic reaction occurred at room temperature. To ensure a complete reaction, the mixture was heated at 60°C for 6 hours. The removal of all volatile materials at room temperature yielded a compound that analyzed as (Br$_3$)[Au(SO$_3$F)$_4$], (1.239 g, 1.488 mmol).

(Br$_3$)[Au(SO$_3$F)$_4$] is a dark brown, hygroscopic, polycrystalline solid. It decomposes at 105°C to form Au(SO$_3$F)$_3$. It is soluble in BrSO$_3$F and HS$_2$O$_3$F.

**Analysis**

<table>
<thead>
<tr>
<th></th>
<th>Br</th>
<th>Au</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
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<td>23.65</td>
<td>9.12</td>
</tr>
<tr>
<td>Found</td>
<td>28.64</td>
<td>23.89</td>
<td>9.15</td>
</tr>
</tbody>
</table>

4.B.4.2 PREPARATION OF (Br$_5$)[Au(SO$_3$F)$_4$]

\[
(\text{Br}_3)[\text{Au(SO}_3\text{F)}_4] + \text{Br}_2 \longrightarrow (\text{Br}_5)[\text{Au(SO}_3\text{F)}_4] \quad (4.22)
\]

Gold powder (175 mg, 0.888 mmol) was converted into (Br$_3$)-[Au(SO$_3$F)$_4$] as described above. Br$_2$ (~5 mL) was distilled onto the intermediate and the mixture was heated at 70°C for 6 hours. The removal of all volatile materials at room temperature yielded (Br$_5$)[Au(SO$_3$F)$_4$], (875 mg, 0.882 mmol).
The same compound can also be obtained by

a) the addition of excess Br\textsubscript{2} to a 2:1 mixture of Au(SO\textsubscript{3}F\textsubscript{3}) and S\textsubscript{2}O\textsubscript{6}F\textsubscript{2}, according to:

\[ 5\text{Br}_2 + 2\text{Au(SO}_3\text{F)}_3 + \text{S}_2\text{O}_6\text{F}_2 \longrightarrow 2\text{(Br}_5\text{)[Au(SO}_3\text{F)}\text{]}_4 , \quad (4.23) \]

or b) the addition of excess Br\textsubscript{2} to \([\text{Br(SO}_3\text{F)}_2]\)[\text{Au(SO}_3\text{F)}_4]:

\[ \text{(Br}_5\text{)[Au(SO}_3\text{F)}_4] + 3\text{Br}_2 \longrightarrow [\text{Br(SO}_3\text{F)}_2]\text{[Au(SO}_3\text{F)}_4] + 2\text{BrSO}_3\text{F} \]. \quad (4.24) \]

\((\text{Br}_5\text{)[Au(SO}_3\text{F)}_4]\) is a dark brown, polycrystalline, hygroscopic solid. It is insoluble in Br\textsubscript{2}, and melts with decomposition at \(\sim 65^\circ\text{C}\). The compound shows a slight decomposition pressure at room temperature in vacuo but is stable if kept in 1 atm nitrogen.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Br</th>
<th>Au</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>40.25</td>
<td>19.84</td>
<td>7.66</td>
</tr>
<tr>
<td>Found</td>
<td>40.20</td>
<td>20.07</td>
<td>7.79</td>
</tr>
</tbody>
</table>
4.C DISCUSSION

4.C.1 SYNTHESIS AND GENERAL DISCUSSION

4.C.1.1 Au(SO₃F)₃

For the intended solution study on Au(SO₃F)₃ in HSO₃F, a convenient and fast synthetic route to very pure samples of the compound was needed. The original synthesis, described by Cady et al.⁸², involved the oxidation of the metal with BrSO₃F followed by the pyrolysis of the intermediate with the reported composition of Au(SO₃F)₃·2BrSO₃F, led to slightly impure products. Samples of Au(SO₃F)₃ obtained by this method were found to be slightly paramagnetic, with a magnetic moment of ~0.5 μB and displaying Curie-Weiss law behavior from ~300 to ~100K. Interestingly, the original synthesis of AuF₃ by an almost parallel method, represented below:

\[
\begin{align*}
\text{Au} + 2\text{BrF}_3 & \rightarrow \text{AuF}_3\cdot\text{BrF}_3 + \frac{3}{2}\text{Br}_2 \\
\text{AuF}_3\cdot\text{BrF}_3 & \xrightarrow{\Delta} \text{AuF}_3 + \text{BrF}_3
\end{align*}
\]

(4.25) \hspace{1cm} (4.26)

also produced weakly paramagnetic materials¹⁶⁷, while pure AuF₃ obtained from the direct fluorination of AuCl₃ is diamagnetic¹⁶⁰,¹⁶⁸. Although the presence of Au(II) or paramagnetic bromine-containing species such as Br₂⁺ may be the cause of the observed paramagnetism, a detailed investigation was considered beyond the intent of this study.

The reaction of gold metal with S₂O₆F₂ resulted in only a slow surface attack and required a reaction temperature of ~160°C for ~14 days. The addition of HSO₃F as the solvent allows the
synthesis of pure and diamagnetic Au(SO₃F)₃ in a fast and efficient manner. As an added advantage, this method allows the direct preparation of solutions of S₂O₆F₂ in HSO₃F because the excess S₂O₆F₂ can be removed readily. As shown by Raman spectroscopy of the resulting solutions, for an initial 1:1 S₂O₆F₂/HSO₃F mixture, no trace of S₂O₆F₂ (detected by νO-O at 900 cm⁻¹) was left after about 70% of the solution was removed by vacuum.

The alternative synthetic route to Au(SO₃F)₃ by the solvolysis of AuCl₃ in BrSO₃F offers no distinct advantage over the S₂O₆F₂/HSO₃F method. The attempted solvolysis of AuCl₃ in HSO₃F did not proceed even at ~110°C.

4.C.1.2 IONIC [Au(SO₃F)₄]⁻ COMPLEXES

The preparation of these complexes utilizes the various synthetic methods described in Chapter 3 for the preparation of Pd(IV) complexes. Due to the lack of reactivity of gold metal towards HSO₃F, stoichiometric mixtures of gold and an alkali metal chloride can be solvolysed to give the corresponding M(I)(SO₃F). The addition of S₂O₆F₂/HSO₃F results in the oxidation of gold and the formation of the alkali metal tetrakis(fluorosulfato) aurate(III) salts. Because of the deliquescent nature of LiCl, the carbonate was used instead; but because the solvolysis of CO₃²⁻ in HSO₃F would lead to water being one of the products, according to:

\[ \text{CO}_3^{2-} + 2\text{HSO}_3^- \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{SO}_3^{2-} \].

(4.27)
S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} was used as the fluorosulfonating agent. These pseudo-one-step reactions are very reliable synthetic routes which exclude the handling of hygroscopic intermediates.

NO[AuCl\textsubscript{4}] is usually prepared by the reaction between NOCl and AuCl\textsubscript{3} in the presence of a solvent such as diethyl ether or THF\textsuperscript{169}. To avoid having to dry and use such hygroscopic solvents, an alternative synthetic method was chosen, involving the solvolysis and subsequent complexation of AuBr\textsubscript{3} in NOCl.

A very interesting trend can be noted in the melting points of a few of these complexes: ClO\textsubscript{2}\textsuperscript{+}, (~102°C), Cs\textsuperscript{+}, (~105°C), NO\textsuperscript{+}, (~193°C), K\textsuperscript{+}, (~230°C), Li\textsuperscript{+}, (~280°C).

This may be due to lattice energy effects which depend on the size of the cation, and anion-polarization by the cation resulting in anion-cation interactions. The effect of NO\textsuperscript{+} is very similar to that of K\textsuperscript{+}; this is consistent with crystallographic results from other studies which have shown that the two cations have almost identical effective ionic radii in the solid state\textsuperscript{94}.

4.C.1.3 COMPLEXES CONTAINING POLYBROMINE CATIONS

In order to characterize the intermediate of Au(SO\textsubscript{3}F)\textsubscript{3}.2BrSO\textsubscript{3}F from the Au + BrSO\textsubscript{3}F reaction, thought to contain a [Br\textsubscript{2}(SO\textsubscript{3}F)]\textsuperscript{+} ion, the published formation reaction was reinvestigated\textsuperscript{82}. While interhalogen cations such as Br\textsubscript{2}Cl\textsuperscript{+}, I\textsubscript{2}Cl\textsuperscript{+} and I\textsubscript{2}Br\textsuperscript{+}\textsuperscript{85} are known, such an analogy does not exist in the form of
\[
\text{[Br}_2(\text{SO}_3\text{F})\text{]}^+. \text{ Although the auto-ionization of BrSO}_3\text{F has been postulated as}\]
\[
3\text{BrSO}_3\text{F} \rightleftharpoons [\text{Br}_2(\text{SO}_3\text{F})]^+ + [\text{Br(SO}_3\text{F)}_2]^-, \tag{4.28}
\]
only thermally unstable salts containing [Br(SO$_3$F)$_2$]$^-$ are known 80,81,163.

The oxidation of gold with an excess of BrSO$_3$F did yield a dark brown polycrystalline material; however, its chemical analysis revealed its composition as Br$_3$Au(SO$_3$F)$_4$, suggesting a formulation as Br$_3^+$[Au(SO$_3$F)$_4$]$^-$. The Br$_3^+$ cation has been identified in solid compounds of the type of Br$_3^+$EF$_n^-$, where EF$_n^-$ = AsF$_6^-$ 170, BF$_4^-$ and SbF$_6^-$ 171, and in solutions of strong protonic acids 25,28,55. The addition of Br$_2$ to BrSO$_3$F giving Br$_3^+$ was also shown by low temperature i.r. spectroscopy 172.

The formation of Br$_3^+$ in the reaction of gold with BrSO$_3$F may proceed via the following reaction scheme:

\[
\text{Au + 3BrSO}_3\text{F} \rightarrow \text{Au(SO}_3\text{F)}_3 + \frac{3}{2}\text{Br}_2 \tag{4.29}
\]

\[
\text{Br}_2 + \text{BrSO}_3\text{F} \rightarrow \text{Br}_3^+ + \text{SO}_3\text{F}^- \tag{4.30}
\]

\[
\text{Br}_3^+ + \text{SO}_3\text{F}^- + \text{Au(SO}_3\text{F)}_3 \xrightarrow{\text{BrSO}_3\text{F}} \text{Br}_3^+\text{[Au(SO}_3\text{F)}_4]^-}, \tag{4.31}
\]
with the precipitation of the final product a necessary driving force to its formation. Evidence for reaction (4.30) has been found in superacid solutions 28 and low temperature i.r. study 172. Unlike the previously reported Br$_3^+$-containing compounds, which all show appreciable decomposition pressures at 25°C, Br$_3^+$[Au-(SO$_3$F)$_4$]$^-$ is found to be thermally stable at room temperature,
with no decomposition evident in a dynamic vacuum at 25°C.

The thermal decomposition of \( \text{Br}_3^+\left[\text{Au(SO}_3\text{F)}_4\right]^- \) at \( \sim100^\circ\text{C} \) in vacuo to give slightly paramagnetic \( \text{Au(SO}_3\text{F)}_3 \) may proceed via a \( \text{Br}_2^+ \)-containing species. The \( \text{^2}\Pi_3/2g \) ground state would give rise to the observed paramagnetism. Therefore, attempts were made to synthesize \( \text{Br}_2^+\left[\text{Au(SO}_3\text{F)}_4\right]^- \), by reacting \( \text{Br}_2 \) with stoichiometric amounts of \( \text{BrSO}_3\text{F} \) or \( \text{S}_2\text{O}_6\text{F}_2 \) and \( \text{Au(SO}_3\text{F)}_3 \), according to:

\[
\frac{1}{2}\text{Br}_2 + \text{BrSO}_3\text{F} + \text{Au(SO}_3\text{F)}_3 \rightarrow \text{Br}_2^+\left[\text{Au(SO}_3\text{F)}_4\right]^- \quad (4.32)
\]
\[
\text{Br}_2 + \frac{1}{2}\text{S}_2\text{O}_6\text{F}_2 + \text{Au(SO}_3\text{F)}_3 \rightarrow \text{Br}_2^+\left[\text{Au(SO}_3\text{F)}_4\right]^- \quad (4.33)
\]

However, both these reactions led to the formation of rather inhomogeneous products, even when \( \text{C}_8\text{F}_{17}\text{SO}_2\text{F} \) was used as the inert reaction medium for \( \text{Br}_2 \). The observation of a strong resonance Raman spectrum of \( \text{Br}_2^+ \), with the principle band at \( 360 \text{ cm}^{-1} \), indicates the cation was present \( ^{25,28} \), but an analytically pure product of the desired composition was not isolable.

The further addition of bromine to \( \text{Br}_3\left[\text{Au(SO}_3\text{F)}_4\right] \) resulted in the formation of \( \text{Br}_5\left[\text{Au(SO}_3\text{F)}_4\right] \), a compound of relatively low thermal stability (although the decomposition at room temperature is rather slow, thus allowing its isolation). A formulation invoking the hitherto unknown \( \text{Br}_5^+ \) ion is possible. In the iodine system, \( \text{I}_5^+ \) has been reported in solid \( \text{I}_5\text{AlCl}_4 \) \( ^{173} \) as well as in \( \text{HSO}_3\text{F} \) solution together with \( \text{I}_7^+ \) \( ^{56} \). The limited thermal stability of \( \text{Br}_5^+ \) is not unexpected, and the compound can only be formed in a large excess of \( \text{Br}_2 \), whether the starting material is \( \text{Br}_3\left[\text{Au(SO}_3\text{F)}_4\right] \) or \( \left[\text{Br(SO}_3\text{F)}_2\right]\left[\text{Au(SO}_3\text{F)}_4\right] \). Being an easily oxidiz-
able species, with a formal oxidation number of +1/5 for bromine, Br$_5^+$ is unstable in the presence of any significant quantities of BrSO$_3$F; for example, when gold is reacted with a mixture of Br$_2$/BrSO$_3$F of approximately 1:1 by volume, the only product isolated is the tribromine species.

4.C.1.4 COMPLEXES CONTAINING HALOGENO-FLUOROSULFATO CATIONS

There is only one precedent reported for complexes containing [Hal(SO$_3$F)$_2$]$^+$ cations, with Hal = Br and I, — those of [Sn(SO$_3$F)$_6$]$_2$ $^{2-}$ 31. The synthesis of the corresponding [Au(SO$_3$F)$_4$]$^-$ containing complexes was undertaken to gain more insights into this group of compounds and to compare the SO$_3$F$^-$ acceptor abilities of Au(SO$_3$F)$_3$ and Hal(SO$_3$F)$_3$. The successful synthesis of [Hal(SO$_3$F)$_2$]$^+$/[Au(SO$_3$F)$_4$]$^-$. would establish Au(SO$_3$F)$_3$ as the stronger ansolvo acid and confirm the amphoteric behavior of the halogen trifluorosulfates.

The reaction of stoichiometric amounts of bromine or iodine and gold with an excess of S$_2$O$_6$F$_2$ resulted in the formation of the corresponding [Hal(SO$_3$F)$_2$][Au(SO$_3$F)$_4$], with the formulation supported by a characterization of the compounds. S$_2$O$_6$F$_2$ acts as both the oxidizing agent and the solvent in these reactions by dissolving the halogen tris(fluorosulfate) formed in the initial reactions. The reaction can be viewed as between a Lewis acid and a Lewis base, according to:

\[
\text{Hal(SO}_3\text{F)}_3 + \text{Au(SO}_3\text{F)}_3 \rightarrow \text{[Hal(SO}_3\text{F)}_2][\text{Au(SO}_3\text{F)}_4] \quad (4.34)
\]
The alternative reaction scheme involving \( \text{Au(SO}_3\text{F)}_3 \) as the base is not supported by vibrational spectroscopy.

As the compound originally thought to be a 2:1 adduct between \( \text{BrSO}_3\text{F} \) and \( \text{Au(SO}_3\text{F)}_3 \) turned out to contain the \( \text{Br}_3^+ \) cation instead, attempts were made to synthesize the adduct by alternate methods. Although \( \text{Au(SO}_3\text{F)}_3 \) was found to be soluble in \( \text{BrSO}_3\text{F} \), the only product isolated upon the removal of all volatile materials was \( \text{Au(SO}_3\text{F)}_3 \). It therefore appears that the \([\text{Br}_2(\text{SO}_3\text{F})]^+\) cation has very limited stability with respect to dissociation in vacuo at room temperature.

4.C.1.5 REACTION OF \( \text{Au(SO}_3\text{F)}_3 \) WITH NEUTRAL DONOR MOLECULES

\[
\text{Au(SO}_3\text{F)}_3 + :L \rightarrow \text{Au(SO}_3\text{F)}_3\cdot L \quad (4.35)
\]

Although many attempts were made to synthesize adducts of the type of \( \text{Au(SO}_3\text{F)}_3\cdot L \) according to equation (4.35), no stable products could be isolated.

\( \text{Au(SO}_3\text{F)}_3 \) was found to be slightly soluble in \( \text{SO}_2 \), and the resulting solution was investigated by Raman spectroscopy, but the removal of all \( \text{SO}_2 \) at 0°C yielded only unreacted \( \text{Au(SO}_3\text{F)}_3 \). The use of other Lewis bases such as pyridine, dimethylsulfoxide, and acetonitrile all led to the reduction of \( \text{Au(SO}_3\text{F)}_3 \) to gold metal.

It therefore appears that:

a) With the formation of \( \text{SbF}_5\cdot \text{SO}_2 \) \(^{17} \), \( \text{SbF}_5 \) is a stronger Lewis acid towards \( \text{SO}_2 \) than \( \text{Au(SO}_3\text{F)}_3 \) is, although this could be
due to the inability of SO₂ to compete favorably against the bridging SO₃F groups in the Au(SO₃F)₃ polymer. In any case, SO₂ is a very weak Lewis base; SbF₅·SO₂ has only limited thermal stability and SO₂ has been used effectively as a diluent in superacid systems.

b) The observed reduction of Au(SO₃F)₃ by the ligands with stronger Lewis basicity may proceed by the displacement of the coordinating SO₃F group followed by a reductive decomposition of the Au(III) species to Au(0). The substitution of SO₃F groups in transition metal bis(fluorosulfate)s by pyridine and bipyridine to form ionic fluorosulfates have been reported.

4.C.1.6 ATTEMPTS TO STABILIZE OTHER POLYHALOGEN AND INTERHALOGEN CATIONS

The only reported example for a polychlorine cation is Cl₃⁺, found in thermally unstable complexes with [AsF₆]⁻ or [SbF₆]⁻ as the counter-anion. The reasonable thermal stability of Br₃[Au(SO₃F)₄] suggests that the chlorine analogue may exist as well. Also, interhalogen cations formed between bromine and chlorine are uncommon, with BrCl₂⁺ and Br₂Cl⁺ identifiable only in SbF₅ solutions; the interaction of Br₃⁺ and Br₅⁺ with Cl₂ may be a possible synthetic route to such compounds.

Unfortunately, both Br₃[Au(SO₃F)₄] and Br₅[Au(SO₃F)₄], when reacted with chlorine gas at room temperature, or with liquid chlorine at −78°C, resulted in the formation of a product with
the characteristics of AuCl$_3$ as followed by weight and i.r. spectroscopy. No compounds containing mixed chloro-bromo cations were isolated from these reactions. AuCl$_3$ reacted with ClSO$_3$F to give a mixture identified by Raman spectroscopy as consisting of ClO$_2$[Au(SO$_3$F)$_4$] and Au(SO$_3$F)$_3$, with the former arising as a result of ClSO$_3$F's reaction with traces of moisture in the quartz reactor. The attempted reductive replacement of (ClO$_2$)$^+$ in ClO$_2$[Au(SO$_3$F)$_4$] with Cl$_3^+$ by reaction with liquid chlorine was unsuccessful; an analogous reaction using Br$_2$ yielded Br$_3$[Au(SO$_3$F)$_4$]. No reaction was evident either when AuCl$_3$ was mixed with a ~1:3 mixture of ClSO$_3$F/Cl$_2$ at ~-23°C. Therefore, the basicity of the [Au(SO$_3$F)$_4$]$^-$ anion may not be low enough for the stabilization of Cl$_3^+$, BrCl$_2^+$ or Br$_2$Cl$^+$; all of them are expected to be more electrophilic than Br$_3^+$. The borderline stability of Br$_2^+$ in the Au(III)-SO$_3$F system may be due to a similar explanation.

4.C.1.7 ATTEMPTED FURTHER OXIDATION OF GOLD

Although the most common oxidation state of gold is Au(III), Au(V) can be found in the fluoride system. Considering the strong similarity between fluorides and fluorosulfates, the possibility of such an analogy in the fluorosulfate system was explored.

Neither Au(SO$_3$F)$_3$ nor Cs[Au(SO$_3$F)$_4$], when exposed to unfiltered u.v. radiation from a Hg-discharge lamp in the presence of S$_2$O$_6$F$_2$ at temperatures up to ~100°C, was found to react. The
addition of O₂ to the above reactor containing Au(SO₃F)₃ and S₂O₆F₂ did not yield any O₂⁺ containing products. FSO₃F, a very powerful oxidant, was added to Cs[Au(SO₃F)₄] and warmed up to room temperature; no fluoride-fluorosulfate of Au(V) was obtained from the reaction.

4.C.2 VIBRATIONAL SPECTRA

4.C.2.1 IONIC [Au(SO₃F)₄]⁻-COMPLEXES AND Au(SO₃F)₃

The Raman spectra of K[Au(SO₃F)₄] and (ClO₂)[Au(SO₃F)₄] are shown in Fig. 4.1 and 4.2, respectively. As can be illustrated in the figures, these complexes are excellent Raman scatterers, and spectra of extremely high signal to noise ratio and good resolution are generally obtained even with laser powers of ~15 mW. The Raman frequencies of M[Au(SO₃F)₄], with M = Cs, K, Li, NO, and ClO₂, are listed in Table 4.1 and are compared with those of K[I(SO₃F)₄]⁻³⁵. The i.r. frequencies of Cs[Au(SO₃F)₄] are also included in the table to illustrate the intensity difference between the two types of spectra.

Except for occasional small splittings, identical spectra are obtained for all the complexes discussed here. Both band positions and relative intensities agree well with the previously reported spectra for [I(SO₃F)₄]⁻ and [Br(SO₃F)₄]⁻, suggesting some structural similarities and similar vibrational mode assign-
FIG. 4.1

Raman Spectrum of $K[Au(SO_3F)_4]$
FIG. 4.2

Raman Spectrum of $\text{ClO}_2^+ [\text{Au(SO}_3\text{F}_4)]^-$
**TABLE 4.1: VIBRATIONAL FREQUENCIES OF M[Ag(SO$_3$F)$_4$]**

<table>
<thead>
<tr>
<th>M</th>
<th>M = CsO$_2$ R</th>
<th>M = NO R</th>
<th>M = Li R</th>
<th>M = K R</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>1423 m</td>
<td>1443 w</td>
<td>1434 w</td>
<td>1430 w</td>
<td>1404 m</td>
<td>v$_{NO}^+$</td>
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<tr>
<td>1416 m</td>
<td>1417 m</td>
<td>1409 w,sh</td>
<td>1415 m</td>
<td>1380 w,sh</td>
<td>v$_{as}$SO$_3$</td>
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<tr>
<td>1375 w</td>
<td>1399 m</td>
<td>1400 w</td>
<td>1398 m</td>
<td></td>
<td>v$_{as}$C$_2$O$_2^+$</td>
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<tr>
<td>1300 vw</td>
<td>1228 vs</td>
<td>1231 vs</td>
<td>1242 vs</td>
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<td>1250 s</td>
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<td>1210 w,sh</td>
<td>1205 w,sh</td>
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</tr>
<tr>
<td>1222 w,sh</td>
<td>1050 m</td>
<td></td>
<td></td>
<td></td>
<td>v$_s$SO$_3$</td>
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<tr>
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<td>1018 s</td>
<td>1029 s</td>
<td>999 s</td>
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<td>239 vs</td>
<td>162 w</td>
<td>150 w,sh</td>
<td>151 w</td>
<td>179 w</td>
<td>150 m</td>
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<tr>
<td>125 w</td>
<td>133 m</td>
<td>146 s</td>
<td>127 m</td>
<td></td>
<td>Lattice Modes</td>
</tr>
</tbody>
</table>

**Assignment**

v$_N$O$^+$

v$_{as}$SO$_3$

v$_{as}$C$_2$O$_2^+$

v$_s$SO$_3$

v$_s$C$_2$O$_2^+$

v$_{MO}$ + def

v$_{SO}_2$ bend

v$_{SO}_2$

v$_{C}_2$O$_2^+$

v$_{MO}$ + def

v$_{SO}_2$
The position of the $\text{SO}_3^-$ stretching modes at ~1400, ~1220, and ~1000 cm$^{-1}$ indicate monodentate $\text{SO}_3\text{F}$ groups in an overall anionic environment $^{32,35}$. The reversal of the intensities of these bands in the i.r. and Raman spectra, best illustrated by the two groups at ~(1240, 1200 cm$^{-1}$) and ~(1010, 950 cm$^{-1}$), are presumably due to vibrational couplings between identical $\text{SO}_3\text{F}$ groups through the $[\text{AuO}]$ skeleton to produce in-phase and out-of-phase vibrations, as discussed in Chapter 3.

An extreme case of intensity reversal in the two types of spectra can be found in the 640-680 cm$^{-1}$ region, where internal fluorosulfate modes are commonly not expected for monodentate $\text{SO}_3\text{F}$ groups. Strong contributions from $[\text{AuO}]$ stretching vibrations coupled to ligand deformation modes may explain the mutual exclusion of i.r. and Raman bands in this region. In addition, strong Raman bands are found at ~450 and ~280 cm$^{-1}$ for all the complexes; they may have their origins in the same sort of vibrational couplings discussed for the ~650 cm$^{-1}$ band, not entirely unexpected for such a complex molecule with a cation of +3 charge.

A Raman spectrum was taken of the melt of Cs$[\text{Au(SO}_3\text{F)}_4]$ at ~150°C; except for the presence of line broadening, the spectrum obtained was identical to that at room temperature. Depolarization ratio measurements revealed all the stronger bands, for which $\rho$, the depolarization ratio, could be obtained, have a large contribution from asymmetric vibrations, with all $\rho$ values of the order of 0.1 (for a totally symmetric vibration $\rho$ should be close to
zero). This is expected for a molecule with such a low symmetry \( \text{C}_s \) and supports the argument for the presence of strong vibrational couplings.

An interesting comparison of the [AuO\(_4\)] vibrations can be made with the vibrational spectrum of K[Au(NO\(_3\))\(_4\)], which has an extremely intense and depolarized Raman band at 360 cm\(^{-1}\) assignable to \([v_S-\text{AuO}_4]\)\(^{177}\). Furthermore, the splittings in the NO\(_3\)-stretching modes can best be explained as due to solid state effects since the intensities after splitting are very similar. On the contrary, as previously mentioned, in the fluorosulfate system, some of the bands are split into strong/weak pairs, evident of strong vibrational couplings. The crystal structure of K[Au(NO\(_3\))\(_4\)]\(^{162}\) indicates a significant lengthening of the AuO-NO\(_2\) bond to 1.37 Å from 1.25 Å in Ni(NO\(_3\))\(_2\)-4H\(_2\)O\(^{178}\), in which NO\(_3^-\) is uncoordinated. The other two N-O bond lengths are \((1.20\pm0.03)\) Å, shorter than that found in free nitrates. As a comparison, in \((\text{CH}_3)_2\text{Sn(SO}_3\text{F})_2\), in which the SO\(_3\)F groups are bidentate bridging, all the SnO-S bond lengths are equivalent within experimental error\(^{97}\). Therefore, as far as vibrational analysis is concerned, [Au(NO\(_3\))\(_4\)]\(^-\) may be viewed as consisting of [AuO\(_4\)]---[NO\(_2\)], whereas in [Au(SO\(_3\)F)\(_4\)]\(^-\), a much closer association between the two units is evidently present, giving rise to the observed extensive vibrational couplings.

For the complexes containing the alkali metal ions, the additional splittings observed in the SO\(_3\)-stretching region are most
likely due to anion-cation interaction, which can be a form of solid state effects; the degree of splitting appears to increase with decreasing cation sizes, suggesting an increase in the polarizing power of the cation. The manifestation of these effects in producing splittings in the $\text{SO}_3$ stretching modes rather than in producing any significant frequency shifts provides further evidence for a very stable $[\text{Au} (\text{SO}_3\text{F})_4]$ unit.

The presence of ionic species in all the complexes is supported by the almost invariable band position of the anion and the agreement of the vibrational frequencies for the two heterocations, $\text{ClO}_2^+$ and $\text{NO}^+$, with published values. The fundamentals for the chloronium cation are found at 1300, 1050 and 518 cm$^{-1}$; similarly, the N-O stretching frequency is found at 2331 cm$^{-1}$, compared to ~2300 cm$^{-1}$ for $\text{NOSO}_3\text{F}^+$. Splittings in the vibrational spectra due to the aspherical nature of these two multiatomic cations are not unexpected.

Finally, the similarities in the vibrational spectra extend also to $\text{Au} (\text{SO}_3\text{F})_3$ and the halogen tris(fluorosulfate)s, $\text{Br} (\text{SO}_3\text{F})_3$ and $\text{I} (\text{SO}_3\text{F})_3$, illustrated in Table 4.2. The spectra contain contributions from both monodentate and bridging bidentate fluorosulfate groups. The diagnostic band for the bidentate bridging $\text{SO}_3\text{F}$ ligand is found at 1135 cm$^{-1}$, and also in the $\text{SO}_3$-stretching, a strong doublet is present at 1442 and 1425 cm$^{-1}$ in the i.r. spectrum, indicating two types of $\text{SO}_3$ coordinations. The splittings in the $[\text{AuO}_4]$ related vibrational modes at (682, 670 cm$^{-1}$),
Table 4.2  VIBRATIONAL FREQUENCIES OF Au(SO₃F)₃

<table>
<thead>
<tr>
<th>Au(SO₃F)₃</th>
<th>Au(SO₃F)₃</th>
<th>I(SO₃F)₃³⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IR</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1449 m</td>
<td>1442 vs</td>
<td>1469 m</td>
</tr>
<tr>
<td>1423 m,sh</td>
<td>1425 s,sh</td>
<td>1381 w</td>
</tr>
<tr>
<td>1227 vs</td>
<td>1240 s</td>
<td>1233 vs</td>
</tr>
<tr>
<td></td>
<td>1220 s,sh</td>
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</tr>
<tr>
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<td>1076 w,sh</td>
</tr>
<tr>
<td>1053 m</td>
<td>1055 s</td>
<td>1050 m</td>
</tr>
<tr>
<td>955 m,sh</td>
<td>960 s,b</td>
<td>963 s</td>
</tr>
<tr>
<td>936 s</td>
<td>920 s,sh</td>
<td></td>
</tr>
<tr>
<td>899 s</td>
<td>895 s,b</td>
<td></td>
</tr>
<tr>
<td>873 m,sh</td>
<td>820 s</td>
<td>869 s</td>
</tr>
<tr>
<td>822 w</td>
<td></td>
<td>826 w</td>
</tr>
<tr>
<td>650 vs</td>
<td>682 s</td>
<td>642 vs</td>
</tr>
<tr>
<td>610 w</td>
<td>670 s,sh</td>
<td>619 w</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>546 m</td>
<td>550 s</td>
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<tr>
<td>465 m</td>
<td>460 m</td>
<td>457 s</td>
</tr>
<tr>
<td>444 w</td>
<td></td>
<td>430 w</td>
</tr>
<tr>
<td></td>
<td></td>
<td>412 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>386 m</td>
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<tr>
<td>348 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>327 w,sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>292 vs</td>
<td></td>
<td>290 vs</td>
</tr>
<tr>
<td>285 s</td>
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<tr>
<td>189</td>
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<td>181 m</td>
</tr>
<tr>
<td>170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>149</td>
<td></td>
<td>148 m</td>
</tr>
</tbody>
</table>
(465, 444 cm\(^{-1}\)) and (292, 285 cm\(^{-1}\)) are most likely the result of the presence of non-identical SO\(_3\)F groups around Au(III) and the coupling of AuO\(_4\) vibrations of adjacent [AuO\(_4\)] units through bridging SO\(_3\)F ligands. While splittings previously assigned to solid state effects are observed in the Raman spectra of some [Au(SO\(_3\)F)\(_4\)] complexes in the same regions, they are of much smaller magnitudes and are not present in their i.r. spectra. The proliferation of low frequency bands for Au(SO\(_3\)F)\(_3\), especially in the i.r. spectrum, must be a result of structural complexities leading to a reduced local symmetry for the [AuO\(_4\)] unit. A band of medium intensity at 348 cm\(^{-1}\) in the Raman spectrum of Au(SO\(_3\)F)\(_3\) may be assigned as due to \(\nu\)Au-O, which, because of the distortion in the AuO\(_4\) skeleton from square planar geometry, becomes a separate vibration in addition to those that are coupled to ligand deformations.

Thus, it can be concluded that Au(SO\(_3\)F)\(_3\) contains both bridging- and terminal-fluorosulfate groups, in possibly a polymerized structure with a distorted square planar environment for Au(III).

4.C.2.2 [X(SO\(_3\)F)\(_2\)][Au(SO\(_3\)F)\(_4\)], X=Br, I

Both the title compounds are excellent Raman scatterers when sample cooling to ~80 K is employed; the spectra thus obtained are of extremely high resolution. They were found to either melt or decompose at room temperature upon their exposure to laser radiation. Their vibrational frequencies are compared with those
of \([\text{Br(SO}_3\text{F)}_2][\text{Sn(SO}_3\text{F)}_6]\)^{31} and Cs[\text{Au(SO}_3\text{F)}_4]\) in Table 4.3. As can be seen, both new compounds give rather complex vibrational spectra, and a complete band assignment is therefore not possible.

It is evident that the strong characteristic Raman bands for \([\text{Au(SO}_3\text{F)}_4]^-\) are present in the spectra of the two compounds; on the other hand, referring to the spectrum of \(K[\text{I(SO}_3\text{F)}_4]\) listed in Table 4.1, bands due to \([\text{I(SO}_3\text{F)}_4]^-\) could not be found in the iodine-containing complex discussed here. For example, the strong \([\text{I(SO}_3\text{F)}_4]^-\) bands at 1250, 1002, 620, 442, 260 and 239 cm\(^{-1}\) are absent in the gold-containing complex. This argues against the alternative formulation for these compounds as \([\text{Au(SO}_3\text{F)}_2][\text{X(SO}_3\text{F)}_4]\), with \(\text{Au(SO}_3\text{F)}_3\) formally acting as the \(\text{SO}_3\text{F}\)-donor. This is also consistent with the observation that while both halogen fluorosulfates — \(\text{I(SO}_3\text{F)}_3\)^{36} and \(\text{Br(SO}_3\text{F)}_3\), are weak electrolytes in \(\text{HSO}_3\text{F}\), \(\text{Au(SO}_3\text{F)}_3\) forms highly conducting solutions in \(\text{HSO}_3\text{F}\) and as will be discussed in the following section, has been found to be a strong \(\text{SO}_3\text{F}\) acceptor.

Further supporting evidence for the suggested formulation can be found in the bromine-containing complex. By comparison to the reported spectra for \(\text{Br(SO}_3\text{F)}_3\)^{35} and \([\text{Br(SO}_3\text{F)}_2][\text{Sn(SO}_3\text{F)}_6]\)^{31}, characteristic bands due to \([\text{Br(SO}_3\text{F)}_2]^+\) are readily recognized in the \([\text{Au(SO}_3\text{F)}_4]^-\) complex. In particular, the pair of bands at 1050 and 1491 cm\(^{-1}\), assigned to an asymmetric \(\text{SO}_3\text{-stretch}\), are found in other cases at such a high frequency only for volatile \(\text{SO}_3\text{F}\)-derivatives such as \(\text{S}_2\text{O}_6\text{F}_2\)^{95}, \(\text{S}_2\text{O}_5\text{F}_2\) and \(\text{S}_3\text{O}_8\text{F}_2\)^{181}. It
<table>
<thead>
<tr>
<th>R</th>
<th>X = Br</th>
<th>X = I</th>
<th>X = I</th>
<th>Cs[Au(SO₃F)₄]</th>
</tr>
</thead>
<tbody>
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<td>1505 ms</td>
<td>1476 w</td>
<td>1458 w,sh</td>
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<tr>
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<td>1440 w,sh</td>
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<tr>
<td>1420 mw</td>
<td>1425 ms</td>
<td>1413 ms</td>
<td>1410 s,sh</td>
<td>1404 ms</td>
</tr>
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<td>1389 mw</td>
<td>1388 wv</td>
<td>1388 s</td>
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<td>1235 s</td>
<td>1237 m,sh</td>
<td>1239 vs</td>
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<td></td>
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</tr>
<tr>
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<td>1025 w</td>
<td>1011 s</td>
</tr>
<tr>
<td>985 m</td>
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<td>964 ms</td>
<td>960 s,b</td>
<td>960 mw,b</td>
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<tr>
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<td>864 m</td>
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<td>830 mw</td>
</tr>
<tr>
<td>830 w</td>
<td>817 w,b</td>
<td>830 vw</td>
<td></td>
<td></td>
</tr>
<tr>
<td>745 s</td>
<td>745 ms</td>
<td>813 ms</td>
<td>815 vs</td>
<td>814 w</td>
</tr>
<tr>
<td>640 s</td>
<td>648 vs</td>
<td>651 vs</td>
<td>670 m,sh</td>
<td>649 vs</td>
</tr>
<tr>
<td>596 mw</td>
<td>581 w</td>
<td>589 w</td>
<td>579 s</td>
<td>580 w</td>
</tr>
<tr>
<td>558 m</td>
<td>549 w</td>
<td>553 mw</td>
<td>555 m,sh</td>
<td>550 w</td>
</tr>
<tr>
<td>530 m</td>
<td>530 vw</td>
<td>540 w,sh</td>
<td>542 s</td>
<td></td>
</tr>
<tr>
<td>464 s</td>
<td>452 s</td>
<td>453 s</td>
<td>452 s</td>
<td></td>
</tr>
<tr>
<td>430 vw</td>
<td></td>
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</tr>
<tr>
<td>414 ms</td>
<td>410 vw</td>
<td>399 vw</td>
<td>405 w</td>
<td></td>
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<tr>
<td>386 m</td>
<td>390 vw</td>
<td>390 vw</td>
<td>391 w</td>
<td></td>
</tr>
<tr>
<td>309 s</td>
<td>308 vs</td>
<td>298 s,sh</td>
<td>282 vs</td>
<td>282 vs</td>
</tr>
<tr>
<td>264 ms</td>
<td>281 vs</td>
<td>278 vs</td>
<td>213 w</td>
<td>205 w</td>
</tr>
<tr>
<td>181 w</td>
<td></td>
<td></td>
<td>205 w</td>
<td></td>
</tr>
<tr>
<td>151 m</td>
<td></td>
<td></td>
<td>150 m</td>
<td></td>
</tr>
<tr>
<td>100 w,sh</td>
<td></td>
<td></td>
<td>127 m</td>
<td></td>
</tr>
</tbody>
</table>
also appears that the increase in positive charge on the bromine atom increases the frequency of this vibrational mode, as can be illustrated below for the three compounds:

\[
\begin{align*}
[\text{Br}(\text{SO}_3\text{F})_2]^+ \text{[Au(}\text{SO}_3\text{F})_4], \quad \text{Br}(\text{SO}_3\text{F})_3 \quad 35, \quad K[\text{Br}(\text{SO}_3\text{F})_4] \quad 35 \\
\nu = \quad 1505 \quad , \quad 1490 \quad , \quad 1424
\end{align*}
\]

A speculation as to the cause of this trend could be the strengthening of the Br-0 bond upon the removal of a SO$_3$F group as the positive charge becomes more concentrated on the bromine atom.

Nevertheless, an ionic formulation of these compounds consisting of [X(SO$_3$F)$_2$]$^+$ and [Au(SO$_3$F)$_4$]$^-$ moieties may be an oversimplification. Prominent bands in the region of ~1150 cm$^{-1}$, characteristic for bidentate bridging fluorosulfate groups, indicate the presence of covalent cation-anion interaction in both the [Au(SO$_3$F)$_4$]$^-$ and [Sn(SO$_3$F)$_6$]$^{2-}$-derivatives. Such an interaction is not unexpected between these large anions and cations; in the molecular structure of the related interhalogen cation complexes of [BrF$_2$][SbF$_6$] and [ICl$_2$][SbCl$_6$], short interionic distances suggest the presence of strong interactions, but not to the extent that the compounds could be classified as covalent solids.

4.2.3 \( \text{Br}_n[\text{Au(}\text{SO}_3\text{F})_4], \ n=3, 5 \)

Because of their dark colors, both polybromine-containing complexes gave rather poorly resolved Raman spectra, even when the samples were cooled to ~80 K. Their i.r. spectra at room
temperature show a band pattern typical of \([\text{Au(SO}_3\text{F})_4]^-\), with no cation bands observable down to \(~450\ \text{cm}^{-1}\). Low temperature i.r. spectra using CsI windows allowed the extension of the transmission range down to \(~200\ \text{cm}^{-1}\); but because the sample could only be deposited as a powder, the spectra have peaks with broad contours due to the Christiansen effect. The vibrational frequencies of the two polybromine complexes are compared with the Raman frequencies of Cs[\text{Au(SO}_3\text{F})_4] in Table 4.4.

As mentioned previously, it becomes evident from the vibrational spectra that the only fluorosulfate-containing species is \([\text{Au(SO}_3\text{F})_4]^-\). The band positions of the spectra from the two compounds are very similar, consistent with the almost invariant spectra observed for the ionic \([\text{Au(SO}_3\text{F})_4]^-\)-complexes. Unfortunately, a clear identification and assignment of bands due to the two polybromine cations are rather difficult. The low frequency range expected for \(\nu\ \text{Br-Br} (<300\ \text{cm}^{-1})\) presented an instrumentation problem combined with the possible confusion of bands observed at such low frequencies with lattice modes. Furthermore, the very intense Raman band at \(~282\ \text{cm}^{-1}\) observed for the \([\text{Au(SO}_3\text{F})_4]^-\) ion is in the same region where the stretching fundamentals for \(\text{Br}_3^+\) are expected. (In superacid solutions, only one peak at \(~290\ \text{cm}^{-1}\) was reported for \(\text{Br}_3^+\), attributed to a coincidence of the two stretching modes)\(^{55,183}\). A relatively strong Raman band at \(~220\ \text{cm}^{-1}\) observed for \(\text{Br}_3[\text{Au(SO}_3\text{F})_4]\) may be due to the bending mode of \(\text{Br}_3^+\). Two other weak bands are found at 188 and 178 cm\(^{-1}\).
<table>
<thead>
<tr>
<th>Br₃[Au(SO₃F)₄]</th>
<th></th>
<th>Br₅[Au(SO₃F)₄]</th>
<th></th>
<th>Cs[Au(SO₃F)₄]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>R, ~80 K</td>
<td>IR, ~80 K</td>
<td>R, ~298 K</td>
</tr>
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<td>1392 m</td>
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<td>1224 s</td>
<td>1200 s,b</td>
<td>1239 vs</td>
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<td>1201 mw</td>
<td></td>
<td>1205 w</td>
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</tr>
<tr>
<td>960 vw</td>
<td>955 vs,sh</td>
<td>1014 m</td>
<td>920 s,b</td>
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<td>800 s</td>
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</tr>
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<td>405 w</td>
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<tr>
<td>167 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>150 w</td>
<td></td>
<td></td>
<td></td>
<td>150 m</td>
</tr>
</tbody>
</table>
in the Raman spectrum, with a band at 300 cm\(^{-1}\) observable also in the i.r. spectrum. The assignment of these weak bands is most likely lattice modes.

\(\text{Br}_5^+\), because of its low symmetry (C\(_2\) or even C\(_1\)), is expected to have nine vibrational modes, all i.r. and Raman active. (VSEPR predicts a linear Br\(_3\) unit with bent terminal bromine attachments at each end free to rotate). For Br\(_5\)[Au(SO\(_3\)F)\(_4\)], bands that may be due to Br\(_5^+\) are found at 304, 295, 267 and 205 cm\(^{-1}\) in the Raman spectrum, and at 305, 295 and 260 cm\(^{-1}\) in the i.r. spectrum. It is noteworthy that the Raman spectrum does not provide any evidence for the presence of free Br\(_2\), with \(\nu(\text{Br}-\text{Br})\) expected at 320 cm\(^{-1}\) \(^{28}\).

Therefore, the presence of Br\(_5^+\) can best be arrived at by default of all the other possibilities that the five bromine atoms can exist in, especially since there is no evidence for a breakdown of the [Au(SO\(_3\)F)\(_4\)]\(^-\) anion and an involvement of bromine in the formation of Au-Br bonds. Unfortunately, both the polybromine-containing complexes are polycrystalline and all attempts at a crystal structure determination have been unsuccessful.

4.C.3 MAGNETIC SUSCEPTIBILITY

Except for a paramagnetic contaminant present in samples of Au(SO\(_3\)F)\(_3\) prepared by the pyrolysis of Br\(_3\)[Au(SO\(_3\)F)\(_4\)], the
tris(fluorosulfate) is diamagnetic. Diamagnetism is also observed for the two polybromine-containing complexes, further confirming the presence of a square planar low-spin electronic configuration for Au(III). The magnetic susceptibility results are listed below in Table 4.5.

Table 4.5 MAGNETIC SUSCEPTIBILITIES OF Au(SO$_3$F)$_3$ AND Br$_n$[Au(SO$_3$F)$_4$]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$x_g$ (cgs units)</th>
<th>$x_m$ (cgs units)</th>
<th>$\Sigma x_{dia}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(SO$_3$F)$_3$</td>
<td>-(2.94±0.03)$\times 10^{-7}$</td>
<td>-(147±2)$\times 10^{-6}$</td>
<td>-152$\times 10^{-6}$</td>
</tr>
<tr>
<td>Br$_3$[Au(SO$_3$F)$_4$]</td>
<td>-(2.88±0.03)$\times 10^{-7}$</td>
<td>-(240±3)$\times 10^{-6}$</td>
<td>-284$\times 10^{-6}$</td>
</tr>
<tr>
<td>Br$_5$[Au(SO$_3$F)$_4$]</td>
<td>-(3.34±0.15)$\times 10^{-7}$</td>
<td>-(331±15)$\times 10^{-6}$</td>
<td>-345$\times 10^{-6}$</td>
</tr>
</tbody>
</table>

4.C.4 SOLUTION STUDIES IN HSO$_3$F

With the exception of Li[Au(SO$_3$F)$_4$], all complexes containing [Au(SO$_3$F)$_4$]$^-$ are very soluble in HSO$_3$F at room temperature. As expected for a polymeric material, Au(SO$_3$F)$_3$ dissolves only very slowly; but when the initially produced suspension is allowed to stand for several hours at room temperature, or if heating is applied at ~100°C for ~1 h, clear solutions can be formed. In addition, when Au(SO$_3$F)$_3$ is prepared from S$_2$O$_6$F$_2$/HSO$_3$F, the removal of all S$_2$O$_6$F$_2$ results in the formation of very concentrated solutions of Au(SO$_3$F)$_3$ in HSO$_3$F (~7 m) and these can be easily diluted for solution studies.
4.C.4.1 ELECTRONIC SPECTRA

With the exception of the polybromine complexes, all solutions containing the gold-fluorosulfato species are yellow to deep orange in color, depending on the concentration. Both Au-(SO$_3$F)$_3$ and Cs[Au(SO$_3$F)$_4$] give rise to identical absorption spectra in HS$_3$O$_3$F, with $\lambda_{\text{max}}$ at 278 nm and $\varepsilon$ of $1.5 \times 10^4$ M$^{-1}$cm$^{-1}$. This rather broad band, best interpreted as due to charge transfer, extends well into the visible region and obscures any band which may be due to d-d transitions (the half-width of the band is about 120 nm).

In [Pd(SO$_3$F)$_4$]$^{2-}$, the charge transfer bands are higher in energy, presumably due to the lower effective nuclear charge on the metal, and therefore bands arising from d-d transitions are observed.

Solutions of the polybromine-cation-containing complexes, although reddish brown in color when they are concentrated, gave identical spectra with $\lambda_{\text{max}}$=278 nm. Bands due to bromine containing species, (Br$_3^+$ at 375 nm, Br$_2$ at 410 nm, and Br$_2^+$ at 510 nm) $^{28,58}$, all with $\varepsilon$ of the order of $\sim$1600 M$^{-1}$cm$^{-1}$, could not be detected.

4.C.4.2 CONDUCTIVITY MEASUREMENTS

The results of electrical conductivity measurements on dilute solutions of K[Au(SO$_3$F)$_4$] and Au(SO$_3$F)$_3$ in HS$_3$O$_3$F are shown
in Fig. 4.3 and 4.4 respectively. While both solutes behave as strong electrolytes in HSO$_3$F, as indicated by the almost linear concentration dependence of the specific conductance, their effects on the dissociation equilibrium of the solvent are quite different.

It appears that the ionization of K[Au(SO$_3$F)$_4$] in HSO$_3$F can best be described according to:

$$K[Au(SO_3F)_4] \xrightarrow{HSO_3F} K^+(solv) + [Au(SO_3F)_4]^- (solv) \quad (4.36)$$

Although the basic dissociation of [Au(SO$_3$F)$_4$]$^-$ according to:

$$[Au(SO_3F)_4]^- (solv) \xleftrightarrow{} Au(SO_3F)_3(solv) + SO_3F^- (solv) \quad (4.37)$$

is possible, the conductometric titration of Au(SO$_3$F)$_3$ with KSO$_3$F, (the reverse of the above reaction) giving a minimum conductance at a mole ratio of 1:1, does not provide any supporting evidence for such a dissociation occurring to any great extent; furthermore, the equilibrium constant for equation (4.37) thus calculated is of the order of $10^{-6}$.

On the other hand, Au(SO$_3$F)$_3$ exhibits a much higher conductivity in HSO$_3$F, and as can be seen from Fig 4.4, it approaches the conductivity observed for solutions of SbF$_2$(SO$_3$F)$_3$ $^{24}$. Since this can only be due to the presence of large amounts of either H$_2$SO$_3$F$^+$ or SO$_3$F$^-$, as they possess very high ionic mobilities in HSO$_3$F $^{11}$, Au(SO$_3$F)$_3$ is therefore either a strong acid or a strong base. With preliminary information concerning the Lewis acidity of Au(SO$_3$F)$_3$ obtained from the synthesis of complexes containing
FIG. 4.3 CONDUCTIVITY OF [Au(SO₃F)₄]-COMPLEXES IN HSO₃F

\[ \kappa \text{ (10}^{-4} \text{S}\cdot\text{cm}^{-1} \text{)} \]

- \( K[Au(SO₃F)₄] \)
- \( Br₅[Au(SO₃F)₄] \)
- \( Br₃[Au(SO₃F)₄] \)

\[ m \text{ (mol} \cdot \text{kg}^{-1} \text{)} \]
FIG. 4.4 CONDUCTIVITY OF $\text{Au}(\text{SO}_3\text{F})_3$ IN $\text{HSO}_3\text{F}$
[Au(SO₃F)₄], it is not surprising therefore to find that Au(SO₃F)₃ behaves as a strong acid by its conductometric titration with KSO₃F solutions, shown in Fig. 4.5 and Table 4.6. As expected for the titration of a strong acid (the only other example of such a moiety in HSO₃F being SbF₂(SO₃F)₃) ²⁴, with a strong base, the conductance decreases gradually upon the addition of KSO₃F, until the endpoint at the KSO₃F/Au(SO₃F)₃ ratio of 1 is reached. The coincidence of the endpoint with the point of lowest conductance is typical for a strong, monoprotic acid in a protonic solvent. In comparison, SbF₅, a weaker acid, reaches its minimum conductance in a titration at a KSO₃F/SbF₅ ratio of ~0.4, and the region of low conductance is broad and ill-defined ²⁴.

The titration can be formulated as the neutralization of a strong acid — H[Au(SO₃F)₄] or its equivalent, with a strong base — KSO₃F, according to:

\[ \text{KSO}_3\text{F} + \text{H}[\text{Au(SO}_3\text{F)}_4] \rightarrow \text{K}[\text{Au(SO}_3\text{F)}_4] + \text{HSO}_3\text{F} \]  \hspace{1cm} (4.38)

Whether H[Au(SO₃F)₄] or solvated Au(SO₃F)₃ is actually the acid present in solution is immaterial to this discussion, since they are both nonconducting species.

Since KSO₃F solutions were used in the titration instead of solid KSO₃F, the total concentration of the system decreased as the titration proceeded. This is the major factor contributing to the curvature of the conductivity plot; a correction, although not entirely theoretically justified, can be made and is also shown in Fig. 4.5. It can be seen that this second curve, in
The conductometric titration of \( \text{Au}(\text{SO}_3\text{F})_3 \) with \( \text{KSO}_3\text{F} \) in \( \text{HSO}_3\text{F} \) at 25 °C

\[ 10^4 \kappa (\Omega^{-1}/\text{cm}) \]

- \( \kappa \) adjusted to initial volume
TABLE 4.6  CONDUCTOMETRIC TITRATION OF Au(SO$_3$F)$_3$ WITH KSO$_3$F IN HSO$_3$F

| R  | $\kappa_{\text{obs}}$ | $\kappa_{\text{calc}}$ | $|\kappa_{\text{obs}} - \kappa_{\text{calc}}|$ | I (calc) |
|----|----------------------|------------------------|--------------------------|---------|
| 0  | 99.92                | 99.92                  | 0                        | 0.031   |
| 0.1| 86.82                | 86.72                  | 0.01                     | 0.030   |
| 0.2| 75.21                | 75.04                  | 0.16                     | 0.030   |
| 0.3| 64.84                | 64.64                  | 0.20                     | 0.030   |
| 0.4| 55.52                | 55.30                  | 0.22                     | 0.030   |
| 0.5| 47.09                | 46.88                  | 0.21                     | 0.030   |
| 0.6| 39.43                | 39.23                  | 0.16                     | 0.030   |
| 0.7| 32.42                | 32.26                  | 0.16                     | 0.029   |
| 0.8| 25.99                | 25.88                  | 0.11                     | 0.029   |
| 0.9| 20.07                | 20.01                  | 0.06                     | 0.029   |
| 1.0| 15.60                | 15.60                  | 0                        | 0.029   |

$10^4 \Omega^{-1} \text{cm}^{-1} \quad 10^{-4} \Omega^{-1} \text{cm}^{-1} \quad 10^{-4} \Omega^{-1} \text{cm}^{-1} \quad \text{mol.kg}^{-1}$
which the conductance has been corrected to correspond to the initial concentration of Au(SO$_3$F)$_3$, is almost a straight line, especially at the initial points.

The fact that the concentration corrected curve is not a straight line can be caused by:

a) the polymerization of Au(SO$_3$F)$_3$,

b) the dependence of molal conductivity, $\lambda^*$, with respect to concentration, and/or
c) the incomplete ionization of the superacid in solution.

The polymerization of the ansolvo acid, found in SbF$_5$ and SbF$_2$-(SO$_3$F)$_3$$_2U$, does not seem to occur in the HS$_3$F-Au(SO$_3$F)$_3$ system, at least not in the dilute solution (~0.04 m) range that the titration was performed in.

For an ionic electrolyte in dilute solutions, the molal conductivity is expected to decrease as the ionic strength, I, which can be approximated by molality for a 1:1 electrolyte ($I = \frac{1}{2}m_{1}\zeta_1^2$, where $\zeta$ is the ionic charge), increases. This relationship, which is really only applicable at ionic strengths of less than 10$^{-3}$ m, can be represented below:

$$\lambda^* = \lambda_0^* - kI^{1/2}$$

where $\lambda_0^* = \lambda^*$ as $I \to 0$

and $k = \text{func}(\lambda_0^*, \epsilon, T, n, z)$.

At higher ionic strengths, $\lambda^*$ decreases much faster than can be described by the above equation. In this particular titration, by coincidence, the ionic strength remains relatively constant.
throughout the titration, and therefore the variation of $\lambda^*$ due to changes in $I$ is not very serious.

Assuming $K^+$ and $[\text{Au} (\text{SO}_3 \text{F})_4]^-$ are the only conducting species in solution at the endpoint, (this is not entirely correct and a solvent conductivity of $1 \times 10^{-4}$ $\Omega^{-1}\text{cm}^{-1}$ has been subtracted from the interpolated $\kappa$ of $1.56 \times 10^{-3}$ $\Omega^{-1}\text{cm}^{-1}$ at the endpoint), some estimates concerning the $\lambda^*$ values and the equilibrium constant for the acid dissociation of $\text{H}[\text{Au} (\text{SO}_3 \text{F})_4]$ according to:

$$\text{H}[\text{Au} (\text{SO}_3 \text{F})_4] + \text{HSO}_3 \text{F} \xrightarrow{K_a} \text{H}_2\text{SO}_3 \text{F}^+ + [\text{Au} (\text{SO}_3 \text{F})_4]^-, \quad (4.40)$$

can be made. Using the literature value of 320 for $\lambda^*_0(\text{H}_2\text{SO}_3 \text{F}^+)$ and a value of 30 for $\lambda^*_0(K^+) \text{21}$, and applying the $\lambda^*$ correction procedure described in Appendix A, a value of 24 is obtained for $\lambda^*_0([\text{Au} (\text{SO}_3 \text{F})_4]^-$), together with $K_a$ of 0.051 mol/kg. The $\lambda^*_0$ value for the anion is in a reasonable range for a singly charged ion in $\text{HSO}_3 \text{F}$; by comparison, $\lambda^*([\text{SbF}_2 (\text{SO}_3 \text{F})_4]^-$) is -13 at 0.086 $\text{m}^2$. This latter low value may be attributed to it having been obtained from a solution of much higher ionic strength and perhaps, more importantly, the larger degree of solvent-solute interaction in the antimony system, as illustrated by its tendency towards dimerization.

The correspondence between the calculated conductance, using the above parameters, and the experimentally obtained data is quite good, considering the crude adjustments made to the $\lambda^*$ values. The remaining deviations, which are also listed in Table 4.6, are quite small and can be rationalized in terms of non-
idealities in the solution behavior of the species.

An earlier conductometric titration of AuF$_3$ in HSO$_3$F with KSO$_3$F gave a conductivity minimum at a KSO$_3$F/AuF$_3$ ratio of $\sim$0.4 $^{164}$. It is likely that the titration is not between KSO$_3$F and AuF$_3$, but between KSO$_3$F and a series of mixed fluoride-fluorosulfate of Au(III) formed by the solvolysis of AuF$_3$ in HSO$_3$F:

$$\text{AuF}_3 + \text{HSO}_3\text{F} \rightleftharpoons \text{AuF}_2(\text{SO}_3\text{F}) + \text{HF}, \text{ etc.}$$

(4.41)

The HF formed, being a base in HSO$_3$F $^{21}$, would increase the basicity of the solution according to:

$$\text{HF} + \text{HSO}_3\text{F} \rightleftharpoons \text{H}_2\text{F}^+ + \text{SO}_3\text{F}^-.$$ 

(4.42)

The conductivity result on the Br$_n^+\,[\text{Au(}\text{SO}_3\text{F}])$ species is also shown in Fig. 4.3. As can be seen, they have an almost identical conductance/concentration dependence as K[\text{Au(}\text{SO}_3\text{F}]) in HSO$_3$F. This observation is not totally unexpected for either of the two complexes, if they ionize as 1:1 electrolytes; for Br$_3^-[\text{Au(}\text{SO}_3\text{F}])$, the following dissociation is most likely:

$$\text{Br}_3[\text{Au(}\text{SO}_3\text{F}])_{(s)} \rightleftharpoons \text{Br}_3^+[\text{solv}] + [\text{Au(}\text{SO}_3\text{F}])]^-_{(\text{solv})}.$$ 

(4.43)

However, for Br$_5^+[\text{Au(}\text{SO}_3\text{F}])$, although a similar dissociation is consistent with the observed conductivity, it is not expected to occur for a number of reasons. Firstly, Br$_5^+$ has never been observed in solution, and excess Br$_2$ can be reportedly removed from superacid solutions containing Br$_3^+$ by evacuation $^{28}$. Secondly, when Br$_5^+[\text{Au(}\text{SO}_3\text{F}])$ is dissolved in HSO$_3$F, the evolution of Br$_2$ is evident from the color of the gas phase above the solution. This suggests a dissociation of Br$_5^+$ into Br$_3^+$ and Br$_2$,.
the latter being a non-electrolyte, would give rise to a similar conductivity as \( \text{Br}_3[\text{Au} (\text{SO}_3\text{F})_4] \) solutions:

\[
\text{Br}_5[\text{Au} (\text{SO}_3\text{F})_4] (s) \xrightarrow{\text{HSO}_3\text{F}} \text{Br}_2 (\text{solv}) + \text{Br}_3^+ (\text{solv}) + [\text{Au} (\text{SO}_3\text{F})_4]^-(\text{solv}). \tag{4.44}
\]

4.C.4.3 N.M.R. SPECTRA

The \(^{19}\text{F-}\)n.m.r. spectra of solutions of \( \text{Au} (\text{SO}_3\text{F})_3 \) and \( \text{Cs}[\text{Au} - (\text{SO}_3\text{F})_4] \) are shown in Fig. 4.6. All spectra show the presence of two resonances: the strong one at \(-40\) ppm due to \( \text{HSO}_3\text{F} \) and a weaker one slightly downfield assigned to \( \text{Au(III)-fluorosulfate-containing species} \).

The spectrum for the \( \text{Cs}[\text{Au} (\text{SO}_3\text{F})_4] \) solution is very straightforward, with the weaker peak due to \( [\text{Au} (\text{SO}_3\text{F})_4]^- \) arising as a result of a dissociation similar to the type of equation (4.36). The presence of two very sharp signals indicates negligible exchange in the system. This is most likely a consequence of the formation of a coordinatively saturated species with little or no dissociation giving rise to other \( \text{SO}_3\text{F}\)-containing moieties. This hypothesis is also supported by the observation that the solvent peak at \(-40.8\) ppm is not shifted from that of pure \( \text{HSO}_3\text{F} \) \((-40.6\) ppm) within experimental errors.

For \( \text{Au} (\text{SO}_3\text{F})_3 \), the n.m.r. spectra of its solutions in \( \text{HSO}_3\text{F} \) also show two resonances, but they seem to indicate a much more complex solution behavior. The spectrum for the dilute solution already shows line broadening for both resonances. When the con-
FIG 4.6  $^{19}$F-N.M.R. SPECTRA OF $\text{Au(SO}_3\text{F)}_3$ AND $\text{Cs[Au(SO}_3\text{F)}_4]$ IN HSO$_3$F

- **CsAu(SO$_3$F)$_4$**
  - Concentration: 0.1 m
  - Temperature: 310 K

- **CFC$_3$**

- **Au(SO$_3$F)$_3$**
  - Concentration: 0.3 m
  - Temperature: 290 K

- **Au(SO$_3$F)$_3$**
  - Concentration: 0.6 m
  - Temperature: 310 K
centration is increased the position of the solute resonance becomes increasingly uncertain due to line broadening, and ~2 m, the peaks are found at -41.2 and ~-46.5 ppm.

For a more concentrated solution (~7 m), the two resonances collapse into a single, extremely broad, (half width of ~5 ppm) and asymmetric peak. Although this concentration dependence is also partly due to viscosity effects, the presence of two separate resonances for dilute solutions and the asymmetric single resonance in the concentrated solution argues against a rapid exchange rate for equation (4.40). Since it is not expected that the exchange of a proton would drastically alter the magnetic environment for fluorine in a fluorosulfate group, its effect on line broadening is not as great as that obtained if a SO$_3$F group actually dissociates from [Au(SO$_3$F)$_4$]$^\text{+}$. The latter process presumably takes place rapidly in the HSO$_3$F-I(SO$_3$F)$_3$ system, as a single resonance was observed in its $^{19}$F-n.m.r. spectrum even at -90°C $^{36}$.

The appearance of a single $^{19}$F-resonance for the solute in the HSO$_3$F-Au(SO$_3$F)$_3$ is consistent with the presence of a monomeric species (at least in dilute solutions), rather than SO$_3$F bridged species. Again, due to line broadening, combined with the expectation that the chemical environment for the fluorine atoms in both configurations should not be very different, such a conclusion may not be warranted from these results alone.

In addition, a downfield shift of the solvent resonance to
10.30 ppm was observed in the $^1$H-n.m.r. spectrum of the concentrated solutions, while for dilute solutions, the resonance remains unchanged at 9.93 ppm. Since the resonance for the pure solvent is already broad due to extensive hydrogen bonding, no further broadening was discernable. The downfield shift of the resonance, however, has a precedence in the $\text{H}_2\text{SO}_3\text{F}-\text{H}[\text{B}(\text{SO}_3\text{H})_4]$ superacid system $^{185}$.

4.C.4.4 VIBRATIONAL SPECTRA

Raman spectra were obtained on solutions of $\text{Au(SO}_3\text{F)}_3$ and $\text{Cs[Au(SO}_3\text{F)}_4]$ in $\text{HSO}_3\text{F}$. The observed Raman shifts are listed in Table 4.7.

As expected for solution spectra, the bands are rather broad, and since the fluorosulfate group is common to both the solvent and solute, some overlap is encountered. However, the Au-SO$_3$F species in solution is found to be an excellent Raman scatterer, allowing the observation of bands at quite low concentrations. For more concentrated solutions, suppression of the solvent bands occurs, leading to the observed trend in relative intensities.

The spectra of $\text{Au(SO}_3\text{F)}_3$ in solution are very similar to that obtained for $\text{Cs[Au(SO}_3\text{F)}_4]$ in both the solid state and $\text{HSO}_3\text{F}$ solution. This suggests a breakdown of the binary fluorosulfate's polymeric structure once it becomes solvated. Any polymeric fluorosulfate bridged species, observed in the solid state vibrational spectra of $\text{Au(SO}_3\text{F)}_3$, are not evident in even very
Table 4.7: Raman Frequencies for Cs[Au(SO$_3$F)$_4$], Br$_3$[Au(SO$_3$F)$_4$] and Au(SO$_3$F)$_3$ in HS$_3$F

<table>
<thead>
<tr>
<th>HSO$_3$F</th>
<th>Cs[Au(SO$_3$F)$_4$]</th>
<th>Br$_3$[Au(SO$_3$F)$_4$]*</th>
<th>Au(SO$_3$F)$_3$</th>
<th>Au(SO$_3$F)$_3$</th>
<th>Au(SO$_3$F)$_3$</th>
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<tr>
<td></td>
<td>-1 m</td>
<td>-1 m</td>
<td>-0.15 m</td>
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<td>1440 ms</td>
<td>1440 m,b</td>
<td>1430 ms</td>
<td>1412 m,b</td>
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<td>1417 w</td>
<td>1420 m,sh</td>
<td></td>
<td>-1360 m,b</td>
<td>-1360 vw</td>
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<tr>
<td>1230 ms,b</td>
<td>1232 s</td>
<td>1230 vw</td>
<td>1228 vs</td>
<td>1227 vs</td>
<td>1226 vs</td>
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<td>1178 m</td>
<td>1190 m,sh</td>
<td>1175 s</td>
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<td>1020 w</td>
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<td>958 m</td>
<td>960 vw</td>
<td>960 w,b</td>
<td>960 m</td>
<td>997 m,sh</td>
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<td>910 vw</td>
<td>910 w,b</td>
<td>912 m</td>
<td></td>
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<td>850 ms</td>
<td>846 m</td>
<td>840 m</td>
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<tr>
<td>-820 m,sh</td>
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<td>718 w</td>
<td>830 m,sh</td>
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<td></td>
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<td>652 ms</td>
<td>647 vs</td>
<td>647 vs</td>
<td>647 vs</td>
<td></td>
</tr>
<tr>
<td>560 vs</td>
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<td>580</td>
<td>-570 m,sh</td>
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<td>555 sh</td>
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<td>278 vs</td>
<td>284 vs</td>
<td>276 vs</td>
<td>276 vs</td>
<td>-350 vw,b</td>
</tr>
<tr>
<td>150 m</td>
<td>156 m</td>
<td>150 mw</td>
<td>151 mw</td>
<td>148 mw</td>
<td>δ,Br$_3^+$</td>
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</tbody>
</table>

*Frozen solution at ~80K
highly concentrated solutions of Au(SO$_3$F)$_3$ in HSO$_3$F. Very weak new bands at $\sim$1360, $\sim$1090 and 350 cm$^{-1}$ for the almost saturated ($\sim$7 m) solution may be due to combination bands, the presence of small amounts of bridged species or laser induced decomposition products. It should also be mentioned that the most prominent bands at $\sim$645, $\sim$450 and $\sim$275 cm$^{-1}$, previously assigned to modes containing Au-O vibrations, are all present in the solution spectra as single bands with no noticeable splittings. Overall, the solution spectra of HSO$_3$F/Au(SO$_3$F)$_3$ can best be regarded as the composite of HSO$_3$F and [Au(SO$_3$F)$_4$].

The concentration range covered by the Raman experiment overlaps well with those used to obtain n.m.r. spectra. However, more dilute solutions were used to obtain conductivity measurements. Nevertheless, it seems rather unlikely that polymerization of Au(SO$_3$F)$_3$ should exist at such low concentrations, evidence for such a process can hardly be detected in very concentrated solutions. The results presented here suggest that the species in solution can best be described as H[Au(SO$_3$F)$_4$] in equilibrium with [Au(SO$_3$F)$_4$].

Finally, as previously reported for pure HSO$_3$F, bands due to the O-H stretching vibration could not be detected in the solution Raman spectra obtained here. I.R. spectra, obtained by using Teflon films between BaF$_2$ plates, show a shift of the solvent band from 3125 cm$^{-1}$ to $\sim$2950 cm$^{-1}$ for a 2.3 m solution. However, the extreme broadness of the band (half width $\sim$700 cm$^{-1}$)
makes it difficult to attach much significance to the frequency shift.

For the two polybromine-containing species, only Br$_3^+$[Au-(SO$_3$F)$_4$]$^-$ was found to be stable in HS$_3$O$_3$F solutions, and even for this solution, the sample had to be cooled to ~80 K in order to obtain a Raman spectrum. The Raman frequencies are also listed in Table 4.7. The peaks are generally quite broad, like in a typical solution spectrum. All the bands due to [Au(SO$_3$F)$_4$]$^-$ and HS$_3$O$_3$F can be distinguished, along with a series of resonance Raman bands originating at 362 cm$^{-1}$, and assignable to Br$_2^+$. The concentration of Br$_2^+$ must be very low, as bands due to this species are extremely intense due to the resonance Raman effect. The source of Br$_2^+$ may be due to the dissociation of Br$_3^+$ according to:

$$
\text{Br}_3^+(\text{solv}) \rightleftharpoons \text{Br}_2^+(\text{solv}) + \frac{1}{2}\text{Br}_2(\text{solv}),
$$

with the equilibrium lying mostly to the left.

The strong band at 284 cm$^{-1}$, usually found at 276 cm$^{-1}$ for other [Au(SO$_3$F)$_4$] complexes, may contain some contribution from Br$_3^+$ vibrations, expected at ~290 cm$^{-1}$ $^{28}$. This upward shift in band position is also noted in its solid state spectrum. Finally, the weak band at 206 cm$^{-1}$ may be due to δ Br$_3^+$, which, because of the solvation of the cation by HS$_3$O$_3$F, becomes shifted to a lower frequency from 220 cm$^{-1}$ in the solid.
4.C.5 RAMAN STUDIES OF Au(SO$_3$F)$_3$ IN LIQUID SO$_2$

Sulfur dioxide, owing partly to its low Lewis acidity and basicity, is commonly used as a solvent in superacid systems, since it is a relatively poor ionizing solvent which can dissolve organic compounds. It was originally thought that because of the observed high Lewis acidity of Au(SO$_3$F)$_3$ towards SO$_3$F$^-$, adduct-formation according to:

$$\text{Au(SO}_3\text{F)}_3 + \text{SO}_2 \rightarrow \text{[Au(SO}_3\text{F)}_3\cdot\text{SO}_2]} \quad (4.46)$$
may be possible. Although no such adduct could be isolated, it was hoped that Raman spectroscopy may provide some evidence for its existence in \(\iota\)-SO$_2$ solutions. The spectra were recorded in high pressure capillaries containing saturated solutions of Au(SO$_3$F)$_3$ in \(\iota\)-SO$_2$ at room temperature. The solubility of Au(SO$_3$F)$_3$ in \(\iota\)-SO$_2$ is quite low, but solute peaks with intensities comparable to the two weaker solvent peaks at 1337 and 521 cm$^{-1}$ can be obtained. The Raman frequencies for such a solution are listed in Table 4.8.

Most compounds containing SO$_2$ as a ligand are very unstable with respect to SO$_2$ elimination $^{187}$. The Lewis acid-Lewis base adduct of SbF$_5$·SO$_2$, with an oxygen-bonded SO$_2$ ligand, is only thermally stable up to ~50°C $^{188}$. The i.r. spectrum of this complex has bands at 1625(w), 1323(s), 1145(w, sh), 1100(m), 696(s), and 480 cm$^{-1}$(w) $^{174}$. It has also been detected in the HSO$_3$F-SbF$_5$-SO$_2$ superacid system by the presence of a band at 1106 cm$^{-1}$ in the Raman spectrum $^{22}$. It seems that in the presence
<table>
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<td>s</td>
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<td>s</td>
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<tr>
<td>285 s</td>
<td>272 vs</td>
<td>s</td>
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</table>
of liquid SO₂ as the solvent, the only diagnostic Raman band for O-bonded SO₂ is a band at ~1100 cm⁻¹.

Most transition metal -SO₂ complexes are S-bonded, for [Ru(NH₃)₄(SO₂)Cl]Cl, the SO₂ vibrations are found at 1301(s), 1278(s), 1110(s), and 555 cm⁻¹(m), in the i.r. ¹⁸⁹.

A comparison of the Raman frequencies of solid Au(SO₃F)₃ and its solution in ε-SO₂ reveals that except for some small shifts in band positions, the spectra are almost identical. The band at 1122 cm⁻¹ is due to the isotope effect of S¹⁶O¹⁸O and is confirmed by its presence in the Raman spectrum of pure ε-SO₂. This band, although expected to be ~10⁻³ times as intense as the band due to the more abundant S¹⁶O₂, arises because this symmetric mode is ~10³ times more intense than the bands in the rest of the spectrum.

Some increased splittings in the [AuO₄] related vibrations are observed and may be interpreted in two opposite ways:

a) In the formation of smaller oligomers such as Au₂(SO₃F)₆, the coupling between the [AuO₄] vibrations in adjacent [Au(SO₃F)₄] units via SO₃F bridging groups may be stronger than in the solid state where increased cross-linkage serves to diffuse the coupling.

b) If Au(SO₃F)₃·SO₂ is formed, the replacement of a bidentate SO₃F group by SO₂ will lead to a greater distortion in the AuO₄ unit from D₄h symmetry, leading to an increased splitting in the bands.

The band at 365 cm⁻¹ can conceivably be due to νAu-OSO or
vAu-SO$_2$, but the position of vAu-(SO$_3$F bridging) at 348 cm$^{-1}$ in Au(SO$_3$F)$_3$ makes such an assignment rather ambiguous. In the SO$_3$-stretching region for bridging SO$_3$F group at ~1000 cm$^{-1}$, the relative intensity of the three bands at 1031, 970, and 915 cm$^{-1}$ is very similar to that found for solid Au(SO$_3$F)$_3$; quite unlike that observed for monodentate SO$_3$F groups such as [Au(SO$_3$F)$_4$]$^-$. Therefore, it does not appear that the relative proportion of monodentate/bidentate SO$_3$F groups changes upon the dissolution of Au(SO$_3$F)$_3$ in $\lambda$-SO$_2$.

With direct evidence supporting the formation of an adduct absent, it must be concluded that if it does exist, it must be present in quite a low concentration. The species most likely to be present in $\lambda$-SO$_2$ are smaller oligomers of Au(SO$_3$F)$_3$, such as Au$_2$(SO$_3$F)$_6$. 
4.D CONCLUSION

Au(SO$_3$F)$_3$ has been shown to act as a strong ansolvo-acid in HSO$_3$F, giving rise to a new superacid system. From conductivity measurements and the conductometric titration of H[Au(SO$_3$F)$_4$] with KSO$_3$F, the acidity of the new superacid is found to be comparable to that of H[SbF$_2$(SO$_3$F)$_4$]. However, unlike the antimony system, no extensive polymerization of the ansolvo-acid is evident in solution, although Au(SO$_3$F)$_3$ itself is a polymer, with bridging SO$_3$F groups.

A series of ionic salts containing the [Au(SO$_3$F)$_4$]$^-$ anion can be synthesized with alkali metal ions, NO$^+$ and ClO$_2^+$. These have been characterized using vibrational spectroscopy.

The Lewis acidity of Au(SO$_3$F)$_3$ with respect to SO$_3$F abstraction can be demonstrated in its reaction with the halogen tris-(fluorosulfate)s of Br(SO$_3$F)$_3$ and I(SO$_3$F)$_3$, to give the corresponding [Hal(SO$_3$F)$_2$]$^+$ cations; in this system, extensive anion-cation interaction is evident from the proliferation of bands in the vibrational spectra, suggesting the presence of bridging SO$_3$F groups.

The low oxidizing power of Au(SO$_3$F)$_3$ is illustrated by the successful synthesis of polybromine cations-Br$_3^+$ and Br$_5^+$, stabilized by [Au(SO$_3$F)$_4$]$^-$. The stability of Br$_3^+$ in the gold complex with respect to dissociation is higher than all previously reported examples of Br$_3^+$ complexes, and the Br$_5^+$ cation is the only such example so far. The stability of solutions of Br$_3$[Au(SO$_3$F)$_4$]
in HSO$_3$F also points to the low basicity of the [Au(SO$_3$F)$_4$]$^-$ anion in solution, a property essential to any further attempts in the stabilization of other novel cations.

Au(SO$_3$F)$_3$, [Au(SO$_3$F)$_4$]$^-$, and the two polybromine cations are all diamagnetic, suggesting a square planar coordination of SO$_3$F for Au(III) giving rise to a $^1A_{1g}$ electronic ground state.
5.A INTRODUCTION

The chemistry of platinum has been studied extensively in the past and is one of the earliest systems investigated in coordination chemistry. The principle oxidation states of platinum are +2 and +4; the higher states of +5 and +6 occur only in fluorine-containing compounds. The investigation into the chemistry of PtF$_6$, one of the most powerful oxidizing and fluorination agents, led to the discovery of the first noble gas compound.

Platinum forms a wide variety of complexes with platinum in both very high and very low oxidation states. Simple anionic complexes containing [Pt-Hal$_4$]$^{2-}$ and [Pt-Hal$_6$]$^{2-}$, together with [PtF$_6$]$^{-}$ and [Pt$_2$F$_{11}$]$^{-}$ are known and can be easily obtained. Their existence suggests halide ion accepting properties of the binary platinum halides.

In contrast to palladium, the relative ease with which the +4 oxidation state can be accessed is illustrated by the existence of PtBr$_4$ and PtI$_4$, formed by direct halogenation of the metal. The reaction takes place even when neither Br$_2$ nor I$_2$ are usually considered to be strong oxidizing agents$^{190}$. Some structural aspects and some principle features of the halides of platinum will be reviewed briefly.

As mentioned before, most of the compounds in the series of Pt-Hal$_2$, Pt-Hal$_3$ and Pt-Hal$_4$ are known but in keeping with the
trend observed for palladium, the trivalent oxidation state of platinum is very uncommon and the trihalides are best regarded as mixed valency compounds of Pt(II)Pt(IV)-Hal₆. Not unexpected, the di- and tetra-halides are all diamagnetic, implying a square planar d⁸ electronic configuration for Pt(II) and an octahedral low-spin d⁶ configuration for Pt(IV). In general, Pt(IV) compounds are diamagnetic because of the high ligand field splitting possible with the 5d metal in such a high oxidation state. The 'trihalides', with the exception of Pt₂F₆, only recently synthesized \(^{191}\), are also diamagnetic, providing one the most conclusive evidence for the mixed valency nature of the compounds (Pt(III), d⁷, with an odd number of electron, must be paramagnetic). Pt₂F₆, a black solid whose existence was suggested at a very early time in fluorine chemistry by Moissan, is the only example for Pt(II) in an octahedral environment with a ³A₂g electronic ground state and a magnetic moment of 3.05 μₜ. PtF₂ has not been successfully synthesized so far, and it has been suggested that this fluoride may not be stable with respect to a disproportionation into platinum metal and PtF₄ \(^{192}\).

The two higher-valent fluorides, [PtF₅]₄ and PtF₆, are obtained by the fluorination of platinum, or lower-valent platinum halides, at different conditions \(^{192,193}\). Both have found use as fluorinating agents in the synthesis and stabilization of easily reduced and novel cations such as O₂⁺, XeF⁺ and ClF₆⁺ \(^{122,194}\). Fluorination reactions involving PtF₆ usually lead to the forma-
tion of \([\text{PtF}_6]^–\) or \([\text{Pt}_2\text{F}_{11}]^–\), both are anions of low basicity.

The solution behavior of PtF\(_4\) in HS\(_3\)O\(_3\)F, like that of AuF\(_3\), was studied by Woolf; however, due to the extremely low solubility of PtF\(_4\) in HS\(_3\)O\(_3\)F, no quantitative results were obtained, even though acidic behavior was suggested\(^{164}\). The only known fluoro-
sulfate of platinum, Pt(SO\(_3\)F)\(_4\), was synthesized in a method ana-
logous to the preparation of Au(SO\(_3\)F)\(_3\) — from a reaction betwe-
en the metal and BrSO\(_3\)F\(^{82}\). The initial product from the above
reaction with BrSO\(_3\)F is likewise reported to give an adduct of
the approximate composition of Pt(SO\(_3\)F)\(_4\)·4BrSO\(_3\)F. These rather
preliminary results raise the possibility that Pt(SO\(_3\)F)\(_4\) may act
as a SO\(_3\)F\(^–\) acceptor, leading to the formation of \([\text{Pt(SO}_3\text{F})_6]^{2–}\)
and therefore a superacid system in HS\(_3\)O\(_3\)F.
5.B EXPERIMENTAL

5.B.1 PREPARATION OF Pt(SO$_3$F)$_4$

Pt + S$_2$O$_6$F$_2$ $\xrightarrow{HSO_3F}$ Pt(SO$_3$F)$_4$  \hspace{1cm} (5.1)

In a typical reaction, platinum powder (233 mg, 1.19 mmol) was reacted with a mixture of S$_2$O$_6$F$_2$/HSO$_3$F at 120°C for 2 days. The orange colored solution gave, after the removal of all volatile materials, dark yellow crystals of Pt(SO$_3$F)$_4$, (692 mg, 1.07 mmol).

Pt(SO$_3$F)$_4$ is a deep yellow to light orange crystalline, hygroscopic solid. It melts with decomposition at 220°C and is very soluble in HSO$_3$F. The micro-analysis of the compound had been reported previously.

Pt(SO$_3$F)$_4$ can also be prepared by the reaction of platinum metal with BrSO$_3$F followed by the pyrolysis of the intermediate as reported earlier by Cady et al.

5.B.2 SYNTHESIS OF COMPLEXES CONTAINING [Pt(SO$_3$F)$_6$]$^{2-}$

5.B.2.1 PREPARATION OF Cs$_2$[Pt(SO$_3$F)$_6$]

CsCl + HSO$_3$F $\rightarrow$ CsSO$_3$F + HCl  \hspace{1cm} (5.2)

2CsSO$_3$F + Pt + 2S$_2$O$_6$F$_2$ $\xrightarrow{HSO_3F}$ Cs$_2$[Pt(SO$_3$F)$_6$]  \hspace{1cm} (5.3)

CsSO$_3$F, formed by the solvolysis of CsCl (302 mg, 1.80 mmol) in HSO$_3$F, was mixed with a stoichiometric amount of platinum metal powder (175 mg, 0.897 mmol) and reacted with S$_2$O$_6$F$_2$ (~3 mL)
and HSO₃F (5 mL). The reaction required heating at 80°C for 3 days, after which time a light yellow solution had formed. The evacuation of all volatile materials yielded crystalline Cs₂[Pt(SO₃F)₆].

Cs₂[Pt(SO₃F)₆] is a light yellow, crystalline, hygroscopic solid. It is soluble in HSO₃F and melts with decomposition at ~260°C.

Analysis

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<th>Cs</th>
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<th>S</th>
<th>F</th>
</tr>
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</tbody>
</table>

5.B.2.2 PREPARATION OF (C₁₀₂)₂[Pt(SO₃F)₆]

\[2\text{C}_1\text{O}_2\text{SO}_3\text{F} + \text{Pt(SO}_3\text{F)}_4 \rightarrow (\text{C}_1\text{O}_2)_2[\text{Pt(SO}_3\text{F)}_6]\] (5.4)

C₁₀₂SO₃F (~1 mL) was added to a sample of Pt(SO₃F)₄ (828 mg, 1.400 mmol). A portion of Pt(SO₃F)₄ was found to dissolve in the liquid which was heated at ~60°C for 1 day. The removal of all volatile materials at ~70°C gave (C₁₀₂)₂[Pt(SO₃F)₆].

The compound can also be prepared by the reaction of platinum metal with a mixture of S₂O₆F₂ and C₁₀₂SO₃F according to:

\[\text{Pt} + 2\text{C}_1\text{O}_2\text{SO}_3\text{F} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow (\text{C}_1\text{O}_2)_2[\text{Pt(SO}_3\text{F)}_6]\] (5.5)
at 160°C for 2 days followed by the removal of all volatile materials at 70°C.

(C₁₀₂)₂[Pt(SO₃F)₆] is a light yellow, crystalline, hygroscopic solid. It is soluble in HSO₃F and melts with decomposition at ~195-200°C.
Analysis | Cl | Pt | F  
--- | --- | --- | ---  
Calculated % | 7.67 | 21.11 | 12.33  
Found % | 7.60 | 21.24 | 12.42  

5.B.2.3 PREPARATION OF Ba[Pt(SO₃F)₆]

\[
\text{BaCl}_2 + 2\text{HSO}_3\text{F} \rightarrow \text{Ba(SO}_3\text{F)}_2 \quad (5.6)
\]
\[
\text{Ba(SO}_3\text{F)}_2 + \text{Pt} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{Ba[Pt(SO}_3\text{F)}_6] } \quad (5.7)
\]

Anhydrous BaCl₂ (88 mg, 0.423 mmol) was converted into the fluorosulfate by the reaction with HSO₃F (~5 mL). After the removal of the HCl evolved, S₂O₆F₂ (~2 mL) was distilled onto the equimolar mixture of Ba(SO₃F)₂ and platinum metal powder (82 mg, 0.420 mmol) in HSO₃F. After heating at 140°C for 3 days, all the metal had dissolved and a light yellow precipitate had formed. The removal of all volatile materials yielded Ba[Pt(SO₃F)₆].

Ba[Pt(SO₃F)₆] is a light yellow, hygroscopic powder. It is only sparingly soluble in HSO₃F and melts with decomposition at ~190°C.

Analysis | Ba | Pt | F  
--- | --- | --- | ---  
Calculated % | 14.82 | 21.05 | 12.03  
Found % | 14.83 | 21.03 | 12.27  

5.B.2.4 PREPARATION OF (Br₃)₂[Pt(SO₃F)₆]

\[
\text{Pt} + 6\text{BrSO}_3\text{F} \rightarrow (\text{Br}_3)_2[\text{Pt(SO}_3\text{F)}_6] \quad (5.8)
\]

Platinum metal powder (157 mg, 0.805 mmol) was reacted with a large excess of BrSO₃F (~10 mL) at 140°C for 7 days. About 1 mL
of Br₂ was added into the mixture which was heated at ~70°C for about 5 minutes. The subsequent removal of all volatile materials at room temperature yielded a compound analyzed as (Br₃)₂[Pt(SO₃F)₆] (998 mg, 0.787 mmol).

(Br₃)₂[Pt(SO₃F)₆] is a dark brown, polycrystalline, and hygroscopic solid. Prolonged standing at room temperature in vacuo causes the slow evolution of Br₂, but the compound is reasonably stable in an atmosphere of nitrogen where it decomposes at ~90°C.

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5.B.3 PREPARATION OF CsPt(SO$_3$F)$_5$

\[
\text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{HCl} \quad (5.9)
\]

\[
\text{CsSO}_3\text{F} + \text{Pt} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{CsPt(SO}_3\text{F)}_5 \quad (5.10)
\]

Stoichiometric amounts of CsCl (102 mg, 0.606 mmol) and platinum metal powder (118 mg, 0.605 mmol) are mixed in a reactor. HSO$_3$F (~2 mL) is added to solvolyze the CsCl, and the resultant solution evacuated to remove all HSO$_3$F. A mixture of S$_2$O$_6$F$_2$/HSO$_3$F (~4 mL) is then added and the reaction vial held at 80°C for 3 days, after which time all the metal had dissolved and a light orange solution had formed. The removal of all volatile materials yielded a compound which analyzed as CsPt(SO$_3$F)$_5$ (503 mg, 0.608 mmol).

CsPt(SO$_3$F)$_5$ is a light yellow crystalline solid, soluble in HSO$_3$F. It melts with decomposition at ~154°C to an orange liquid.

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5.C DISCUSSION

5.C.1 SYNTHESIS AND GENERAL DISCUSSION

5.C.1.1 PLATINUM TETRAKIS(FLUOROSULFATE)

Pt(SO\textsubscript{3}F\textsubscript{4}) can be prepared, in a manner analogous to the synthesis of Au(SO\textsubscript{3}F\textsubscript{3}), by the reaction of platinum metal with a) S\textsubscript{2}O\textsubscript{6}F\textsubscript{2}/HSO\textsubscript{3}F, or b) BrSO\textsubscript{3}F followed by the subsequent decomposition of the bromine-containing intermediate. Method a) is the preferred synthetic route as Pt(SO\textsubscript{3}F\textsubscript{4}) is formed directly. Samples of the compound obtained via b) were always darker in color (Cady reported the color of Pt(SO\textsubscript{3}F\textsubscript{4} as being dark brown) and contained paramagnetic impurities. It seems that the high temperature (~120\degree C) involved in the pyrolysis of the intermediate (although the intermediate show signs of decomposition at ~90\degree C, a higher temperature was needed in order to shorten the time for the reaction), may also lead to the thermal decomposition of the desired product. This intermediate, again similar to the Au(SO\textsubscript{3}F\textsubscript{3}-BrSO\textsubscript{3}F system, is best regarded as (Br\textsubscript{3})\textsubscript{2}[Pt(SO\textsubscript{3}F\textsubscript{6}] instead of an adduct between Pt(SO\textsubscript{3}F\textsubscript{4}) and BrSO\textsubscript{3}F.

There are, however, a few major differences between the synthesis of Pt(SO\textsubscript{3}F\textsubscript{4}) and Au(SO\textsubscript{3}F\textsubscript{3}). While both metals can be synthesized by the same methods, platinum displays a much lower degree of reactivity towards either BrSO\textsubscript{3}F or S\textsubscript{2}O\textsubscript{6}F\textsubscript{2}/HSO\textsubscript{3}F. Furthermore, the removal of HSO\textsubscript{3}F from solutions containing Pt(SO\textsubscript{3}F\textsubscript{4}) proceeds only with difficulties at room temperature, suggesting possibly a greater degree of solvent-solute interac-
tion in the platinum system.

5.C.1.2 COMPLEXES CONTAINING \([\text{Pt} (\text{SO}_3 \text{F})_6]^{2-}\)

The synthesis of the three ionic complexes containing Ba\(^{2+}\), ClO\(_2^+\) and Cs\(^+\) follows a general scheme to the preparation of transition metal fluorosulfato complexes. Their synthesis provides the first evidence for the fluorosulfate-accepting property of \(\text{Pt} (\text{SO}_3 \text{F})_4\). Complexes of a less ionic nature, exemplified by \(\text{Pd} [\text{Pt} (\text{SO}_3 \text{F})_6]\), discussed in Chapter 3, and \(\text{Ag} [\text{Pt} (\text{SO}_3 \text{F})_6]\ \)\(^{84}\), can also be readily prepared.

The reaction of \(\text{BrSO}_3 \text{F}\) with platinum metal leads to the formation of a complex containing the \(\text{Br}_3^+\) cation. Although this reaction supposedly proceeds via an analogous mechanism as the corresponding reaction in the gold system, some differences exist. The formation of \((\text{Br}_3)_2 [\text{Pt} (\text{SO}_3 \text{F})_6]\) according to equation (5.8) requires that all the bromine formed from the reduction of \(\text{BrSO}_3 \text{F}\) be used up, while in the reaction involving gold metal, and excess of half a mole of \(\text{Br}_2\) is left per mole of gold reacted. Since \(\text{Br}_3^+\) is not expected to be very stable in the presence of \(\text{BrSO}_3 \text{F}\), a strong oxidizing agent, the complete conversion of all \(\text{Br}_2\) into the complex may not occur. Experimentally, yields corresponding to as low as a 1:1 mixture of \(\text{Pt} (\text{SO}_3 \text{F})_4\) and \((\text{Br}_3)_2 [\text{Pt} (\text{SO}_3 \text{F})_6]\) have been obtained for reactions involving large excess of \(\text{BrSO}_3 \text{F}\). The situation is further aggravated by the observed low thermal stability of the complex in vacuo. The synthesis of analytically
pure (Br$_3$)$_2$[Pt(SO$_3$F)$_6$] therefore requires the introduction of a small quantity of Br$_2$ (~1 mL) into the reaction mixture after all the metal had dissolved. The preparation can also be accomplished by the in situ synthesis of BrSO$_3$F in the reaction vial using S$_2$O$_6$F$_2$ and a slight excess of Br$_2$. This latter method eliminates the initial vacuum distillation of BrSO$_3$F, which has a low vapor pressure at room temperature.

The thermal stability of (Br$_3$)$_2$[Pt(SO$_3$F)$_6$] is comparable to that of Br$_5$Au(SO$_3$F)$_4$, both showing signs of decomposition, giving off Br$_2$, at room temperature in vacuo. It is therefore not surprising that further addition of bromine to Br$_3^+$, forming longer chained polybromine cations, does not occur in this system. It is possible that the large number of bromine atoms, already six in (Br$_3$)$_2$[Pt(SO$_3$F)$_6$], will drastically reduce the lattice energy in a complex such as (Br$_5$)$_2$[Pt(SO$_3$F)$_6$]. If this postulation is correct, then the lower thermal stability of (Br$_3$)$_2$[Pt(SO$_3$F)$_6$] as compared to Br$_3$[Au(SO$_3$F)$_4$] is not necessarily a consequence of the lower Lewis acidity of Pt(SO$_3$F)$_4$.

5.C.1.3 SYNTHESIS OF CsPt(SO$_3$F)$_5$

The synthesis of CsPt(SO$_3$F)$_5$ was sought as supporting evidence for the polymerization of Pt(SO$_3$F)$_4$ as inferred from the conductometric titration of the fluorosulfate with KSO$_3$F solutions. Being a SO$_3$F$^-$ acceptor, forming [Pt(SO$_3$F)$_6$]$^{2-}$ in the presence of an excess of SO$_3$F$^-$, CsPt(SO$_3$F)$_5$ is made in a reaction
essentially between CsSO$_3$F and Pt(SO$_3$F)$_4$, all the HCl formed in the initial solvolysis of CsCl in HSO$_3$F having been removed by evacuating the CsSO$_3$F solution to dryness (the formation of a mixture of complexes containing Cs$^+$ and ClO$_2^+$ is a likely occurrence if any chlorine-containing substance was present). This complex appears to be a dimeric species from an analysis of its vibrational spectra.

5.C.1.4 ATTEMPTED SYNTHESIS OF FLUOROSULFATES CONTAINING PLATINUM IN OTHER OXIDATION STATES

The ease with which Pt(IV) could be obtained suggests that Pt(V) fluorosulfate or fluorosulfato complexes might be obtainable. This was found not to be the case, and no reaction was observed when Pt(SO$_3$F)$_4$ was heated at 100°C with S$_2$O$_6$F$_2$. It seems logical to assume that, with the reactivity of S$_2$O$_6$F$_2$ greatly enhanced when it is dissolved in HSO$_3$F, the oxidation of a transition metal in S$_2$O$_6$F$_2$/HSO$_3$F should lead to the highest oxidation state attainable in the metal-fluorosulfate system.

The attempted synthesis of Pt(SO$_3$F)$_2$ by the solvolysis of PtCl$_2$ in HSO$_3$F, consistent with attempted reactions involving other noble metal chlorides examined in this study, with or without the presence of KSO$_3$F, did not give rise to any reaction product. The heating of a sample of K$_2$PtCl$_4$ in HSO$_3$F at ~80°C for 2 days led to the decomposition of the sample, although an ionic fluorosulfate, probably KSO$_3$F, identified by its i.r. spectrum,
was the only fluorosulfate-containing species present. The residue gave a positive chloride ion test. Furthermore, the extremely polymeric nature of PtCl₂ can be illustrated by an unsuccessful chloride abstraction reaction with Sn(SO₃F)₄, which shows no signs of any reaction after 3 days at ~90°C.

While the reduction of Pd₂(SO₃F)₆ with Br₂ gave rise to Pd(SO₃F)₂, such an analogous reaction involving Pt(SO₃F)₄ or any of its complexes may not be too likely. The formation of (Br₃)₂-[Pt(SO₃F)₆], containing bromine in the +1/3 formal oxidation state and in the presence of an excess of bromine, seems to indicate that the fluorosulfate of Pt(IV), likewise Au(III), is compatible with Br₂, and therefore no reduction should be expected to take place.

5.C.2 VIBRATIONAL SPECTRA
5.C.2.2 PLATINUM TETRAKIS(FLUOROSULFATE)

Due to the low Raman scattering efficiency of Pt(SO₃F)₄ coupled with its limited stability in the laser beam, only poorly resolved Raman spectra could be obtained. The vibrational frequencies of Pt(SO₃F)₄ are compared to the i.r. frequencies of Au(SO₃F)₃ in Table 5.1.

As can be seen, a good correspondence between the major bands in the spectra of the two compounds can be made, indicating
<table>
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<th>I.R.</th>
<th>R.</th>
<th>Assignment</th>
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<td>-1400 vs,b</td>
<td>1442 vs</td>
<td>1431 s</td>
<td>$\nu_{\text{asSO}_3}$</td>
</tr>
<tr>
<td></td>
<td>1425 s,sh</td>
<td>1420 s,sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1230 vs</td>
<td>1225 vs</td>
<td>1240 s</td>
<td>1233 s</td>
<td>$\nu_S\text{SO}_2$</td>
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<td></td>
<td>1220 s,sh</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1060 w</td>
<td>-1150 s,vb</td>
<td>1135 ms</td>
<td>1124 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1070 vs,vb</td>
<td>1055 s</td>
<td>1075 s</td>
<td>$\nu_{\text{asSO}_3}$</td>
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<tr>
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<td>960 s,b</td>
<td>986 w</td>
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<td></td>
<td>920 s,sh</td>
<td>911 m</td>
<td></td>
</tr>
<tr>
<td>900 s,b</td>
<td>-900 vs,vb</td>
<td>895 s,b</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-820 s,vb</td>
<td>820 s,b</td>
<td>845 m</td>
<td>$\nu_{\text{S-F}}$</td>
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<td></td>
<td></td>
<td>827 m</td>
<td></td>
</tr>
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<td>-670 s,b</td>
<td>682 s</td>
<td></td>
<td>$\nu_{\text{SM-0 + MO-S def.}}$</td>
</tr>
<tr>
<td></td>
<td>-640 s,b</td>
<td>670 s,sh</td>
<td>640 w,sh</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-615 w,sh</td>
<td>610 w</td>
<td>632 s</td>
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</tr>
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<td>580 s</td>
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<td>590 s</td>
<td>589 s</td>
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<tr>
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<td></td>
<td>582 s</td>
<td></td>
<td></td>
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<td>540 m</td>
<td>550 s</td>
<td>552 m</td>
<td>$\nu_{\text{asM-0 + MO-S def.}}$</td>
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<tr>
<td>454 m</td>
<td>460 m</td>
<td>427 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>293 s</td>
<td>320 w</td>
<td></td>
<td></td>
<td>$\nu_{\text{S-M-0 + SO}_3\text{F rock}}$</td>
</tr>
<tr>
<td>268 s</td>
<td></td>
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the presence of similar bonding modes for SO\textsubscript{3}F groups in them. In the i.r. spectrum of Pt(SO\textsubscript{3}F)\textsubscript{4}, a very strong and broad peak extends from ~800 to ~1150 cm\textsuperscript{-1}; some minor features are discernible only when very thin film samples are used. This is in contrast to Au(SO\textsubscript{3}F)\textsubscript{3}, for which relatively well resolved bands can be observed in this same region. This complexity in the S-O and S-F stretching modes of Pt(SO\textsubscript{3}F)\textsubscript{4} may not be totally unexpected. If the coordination of Pt(IV) is octahedral, for each Pt(IV), there will be two monodentate and two bridging bidentate SO\textsubscript{3}F groups. By comparison, Au(SO\textsubscript{3}F)\textsubscript{3} would have only two monodentate and one bridging bidentate SO\textsubscript{3}F groups for each Au(III). This increased proportion of bridging SO\textsubscript{3}F groups would give rise to a proliferation of vibrational modes, in particular in the S-O stretching region, unless their local symmetry is identical, as in Sn(SO\textsubscript{3}F)\textsubscript{4}. 

In contrast to Pt(SO\textsubscript{3}F)\textsubscript{4}, Sn(SO\textsubscript{3}F)\textsubscript{4} has relatively well-resolved bands in the ~800 to ~1100 cm\textsuperscript{-1} region in its i.r. spectrum\textsuperscript{33}, while both compounds are expected to give the same monodentate to bidentate SO\textsubscript{3}F ligand ratio. The reason may lie in the proposed structure for Sn(SO\textsubscript{3}F)\textsubscript{4}, which has trans-monodentate SO\textsubscript{3}F groups and a square planar arrangement for the bridging SO\textsubscript{3}F groups. This would mean that all the bridging SO\textsubscript{3}F groups are well ordered and in relatively similar structural arrangements. Conversely, in Pt(SO\textsubscript{3}F)\textsubscript{4}, the bridging may not lead to the formation of such a well ordered polymeric structure. This may be
illustrated by a difference in the physical properties of two
tetrakis(ﬂuorosulfates). While Sn(SO₃F)₄ is virtually insoluble
in HSO₃F, Pt(SO₃F)₄ is extremely soluble, although the break down
of the polymer in the latter case is very slow.

5.C.2.2 COMPLEXES CONTAINING [Pt(SO₃F)₆]²⁻

Unlike the parent compound, the three ionic complexes con­
taining the [Pt(SO₃F)₆]²⁻ anion were found to be excellent Raman
scatterers, giving rise to well resolved spectra. (Br₃)₂[Pt(SO₃F)₆],
however, presented a similar problem as the analogous Au(III)
complex; as a result of its dark color and low Raman-scattering
efficiency, only poorly resolved Raman spectra could be obtained,
even when the sample was cooled to ~80 K. The Raman frequencies
of the four [Pt(SO₃F)₆]²⁻ complexes are listed in comparison with
those of Cs₂[Pd(SO₃F)₆] in Table 5.2. The i.r. spectrum of
(CIO₂)₂[Pt(SO₃F)₆] is shown in Fig. 5.1. The vibrational spectra
of Pd[Pt(SO₃F)₆] have already been discussed in Chapter 3, and
are consistent with the presence of anisobidentate bridging SO₃F
groups spanning Pd(II) and Pt(IV), both in octahedral coordina­
tion spheres.

A comparison of the vibrational spectra of [Pt(SO₃F)₆]²⁻ and
[Pd(SO₃F)₆]²⁻ reveals that the compounds both contain monoden­
tate SO₃F groups, and that they appear to be isostructural.
Slight shifts at ~630, ~450 and ~280 cm⁻¹ are presumably due to
the different M(IV) cations, supporting the assignment of these
**TABLE 5.2: RAMAN FREQUENCIES OF [Pt(SO₃F)₆]²⁻ COMPLEXES**

<table>
<thead>
<tr>
<th></th>
<th>X = (CsO₂)₂</th>
<th>X = Cs₂</th>
<th>X = Ba</th>
<th>X = (Br₃)₂</th>
<th>Cs₂[Pd(SO₃F)₈]</th>
<th>Assignment</th>
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<tr>
<td>1406 m</td>
<td>1416 w,sh</td>
<td>1397 w</td>
<td>~1400 vw</td>
<td>1405 w</td>
<td></td>
<td>νₐsSO₂</td>
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<tr>
<td>1375 m</td>
<td>1410 m</td>
<td>1386 m</td>
<td>~1377 w</td>
<td>1395 vw,sh</td>
<td></td>
<td>νₐC₂O₂⁺</td>
</tr>
<tr>
<td>1300 vw</td>
<td>1250 vs</td>
<td>1258 vs</td>
<td>1229 m</td>
<td>1236 vs</td>
<td></td>
<td>νₛSO₂</td>
</tr>
<tr>
<td>1220 vw,sh</td>
<td>1219 m</td>
<td>1218 m</td>
<td>1199 w</td>
<td>1212 m</td>
<td></td>
<td>νₛC₂O₂⁺</td>
</tr>
<tr>
<td>1045 s</td>
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<td>1045 w</td>
<td>1020 vs</td>
<td></td>
<td>νₐsSO₂</td>
</tr>
<tr>
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<td>1010 m</td>
<td>1012 w</td>
<td>~1005 vw</td>
<td>995 ms</td>
<td></td>
<td>νₛSO₂</td>
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<tr>
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<td>857 w</td>
<td>835 vw</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>826 vw</td>
<td>838 vw</td>
<td>805 vw</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>807 vw</td>
<td>~800 w,b</td>
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<td>785 w</td>
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<td></td>
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</tr>
<tr>
<td>631 s</td>
<td>634 vs</td>
<td>629 vs</td>
<td>634 w</td>
<td>618 ms</td>
<td>νₛM-O + SO₃F def</td>
<td></td>
</tr>
<tr>
<td>580 vw</td>
<td>579 vw</td>
<td>583 vw</td>
<td>~585 vw,sh</td>
<td>542 w</td>
<td>def SO₃F</td>
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</tr>
<tr>
<td>546 vw</td>
<td>550 vw</td>
<td>549 vw</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>517 w</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>411 w</td>
<td>~400 vw</td>
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<td>Br₃⁺</td>
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<td>283 s</td>
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<td>283 vs</td>
<td>272 m</td>
<td>270 s</td>
<td>νₛM-O + SO₃F</td>
<td></td>
</tr>
<tr>
<td>273 s</td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>
The infrared spectrum of $(\text{ClO}_2)_2[\text{Pt(SO}_3\text{F)}_6]$ between 1500 and 400 cm$^{-1}$. 
vibrational modes as having substantial contributions from the [MO$_6$] skeletal vibrations. The i.r. spectrum of (ClO$_2$)$_2$[Pt(SO$_3$F)$_6$] shows almost a mutual exclusion of the SO$_3$F stretching modes and the MO vibrations with the Raman frequencies listed, especially in the 1050 to 900 cm$^{-1}$ region. Extensive couplings within the same vibrational modes between different SO$_3$F groups must be present to account for the intensity differences.

For the ClO$_2^+$-containing complex, $v_{as}$ ClO$_2^+$ are found at 1298 and 1285 cm$^{-1}$ in the i.r. spectrum, split by the two naturally occurring isotopes of $^{37}$Cl and $^{35}$Cl. $v_s^-$ and $\delta^-$ ClO$_2^+$ are found at 1045 and 517 cm$^{-1}$ respectively, supporting an ionic formulation for the compound.

The i.r. spectrum of (Br$_3$)$_2$[Pt(SO$_3$F)$_6$], down to the low frequency limit of 400 cm$^{-1}$ for the AgCl windows used, indicates the presence of bands due only to the [Pt(SO$_3$F)$_6$]$^{2-}$ anion. In the low temperature Raman spectrum, all the major bands due to the anion are also present, together with new features at 295, 355 and 700 cm$^{-1}$. The two higher frequency bands show an intensity difference that may be due to the Resonance Raman effect of Br$_2^+$, and the peak at 295 cm$^{-1}$ compares well with the value of 290 cm$^{-1}$ in superacid solutions and the band at 280 cm$^{-1}$ in Br$_3$[Au(SO$_3$F)$_4$], both assigned as due to Br$_3^+$. The presence of Br$_2^+$ seems to be suggested in all the Raman spectra of Br$_3^+$-containing complexes studied here; it may be a decomposition product or in equilibrium with Br$_3^+$ in these systems.
5.C.2.3 CsPt(SO₃F)₅

Both the Raman and i.r. spectra of this compound have features that can be ascribed to the presence of both monodentate and bidentate SO₃F groups. The vibrational frequencies of CsPt-(SO₃F)₅ are listed in Table 5.3 together with those of CsSn(SO₃F)₅ and CsRu(SO₃F)₅.

It is evident from the Table that the characteristic strong Raman band at 900 cm⁻¹ for Pt(SO₃F)₄ is missing from the Raman spectrum of CsPt(SO₃F)₅, and a general simplification of the S-O stretching region in the i.r. spectrum of the latter compound is also noticed. This argues against the possibility that the compound is simply a mixture of Pt(SO₃F)₄ and Cs₂[Pt(SO₃F)₆]. Not surprisingly, the spectra are still quite complex, as even for a dimeric [Pt₂(SO₃F)₁₀]²⁻ species, there exists three different types of SO₃F groups — equatorial bridging, equatorial monodentate and terminal monodentate.

A good agreement between the vibrational frequencies of the compounds listed in Table 5.3 suggests the presence of similar SO₃F groups in all three cases. The i.r. active asymmetric SO-stretching vibration for CsSn(SO₃F)₅ is at ~1000 cm⁻¹, almost 80 cm⁻¹ higher than that found for the other complexes. An analogous observation is also found for [Sn(SO₃F)₆]²⁻ ³²; whereas in [M(SO₃F)₆]²⁻, with M=Pd, Pt, Ir, and [Au(SO₃F)₄]⁻, the band is shifted to ~930 cm⁻¹. A slightly different mode of electronic interaction may take place in the complexes involving transition
### Table 5.3: Vibrational Frequencies of CsPt(SO$_3$F)$_5$ and Related Compounds

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<th>CsPt(SO$_3$F)$_5$</th>
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<th>CsSn(SO$_3$F)$_5$</th>
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<td><strong>IR</strong></td>
<td><strong>IR</strong></td>
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<td>-1400 vs, b</td>
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<td>v$_s$SO$_2$ bridge</td>
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<td>-1002 vw</td>
<td></td>
<td>v$_s$SO$_2$ bridge</td>
</tr>
<tr>
<td>980 w, b</td>
<td>950 vs, b</td>
<td>925 vs, b</td>
<td>-1000 vs, b</td>
</tr>
<tr>
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<td></td>
<td>920 vs, b</td>
<td></td>
</tr>
<tr>
<td>930 w</td>
<td></td>
<td>925 vs, b</td>
<td>v$_s$SO$_2$ bridge</td>
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<td>850 w</td>
<td>-830 w, sh</td>
<td>vSF</td>
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<tr>
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<td>810 s, b</td>
<td>820 w</td>
<td></td>
</tr>
<tr>
<td>658 w</td>
<td>670 w, sh</td>
<td>650 m, b</td>
<td>v$_s$M-0 + SO$_3$F def</td>
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<tr>
<td>635 s</td>
<td>660 m</td>
<td>630 m</td>
<td>625 m, b</td>
</tr>
<tr>
<td>605 w</td>
<td>605 vw</td>
<td></td>
<td>v$_s$M-0 + SO$_3$F def</td>
</tr>
<tr>
<td>590 vw</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>580 vw</td>
<td>580 m</td>
<td>580 ms</td>
<td>585 w</td>
</tr>
<tr>
<td>547 w</td>
<td>540 m</td>
<td>550 ms</td>
<td>560 w</td>
</tr>
<tr>
<td>510 vw</td>
<td>515 vw, sh</td>
<td></td>
<td>587 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>v$_{as}$SO$_3$F def</td>
</tr>
<tr>
<td>447 m</td>
<td>-400 w, sh</td>
<td>440 mw</td>
<td>-450 vw, sh</td>
</tr>
<tr>
<td>410 vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>275 s</td>
<td></td>
<td></td>
<td>v$_s$M-0 + SO$_3$ bend</td>
</tr>
</tbody>
</table>
metals. The vibrational spectra of CsSn(SO$_3$F)$_5$ will be discussed in more detail in Chapter 9.

Therefore, it appears that the existence of monomeric [Pt-(SO$_3$F)$_5$]$^-$ with monodentate SO$_3$F groups is not supported by the vibrational spectra of the compound. A polymeric structure, containing [Pt(SO$_3$F)$_5$]$^-$, must therefore be present, as there is no evidence that the compound is a mixture of Pt(SO$_3$F)$_4$ and [Pt-(SO$_3$F)$_6$]$^{2-}$. A dimer would have two [Pt(SO$_3$F)$_6$] octahedra joined by a common edge, a trimer or high oligomers would be a cyclic structure joined via cis-corners of the octahedra. The exact structure cannot be elucidated by vibrational spectroscopy alone and an X-ray diffraction study is required.

5.C.3 MAGNETIC SUSCEPTIBILITY

All the Pt(IV)-SO$_3$F compounds investigated in this study are diamagnetic, suggesting a low-spin octahedral ligand field for the d$^6$ Pt(IV) and a $^1A_g$ electronic ground state. The experimentally obtained susceptibilities at room temperature are listed in Table 5.4. As it was required for a dilution experiment in Chapter 6, the temperature dependence of the magnetic susceptibility of (ClO$_2$)$_2$[Pt(SO$_3$F)$_6$] was investigated from 300 to 81 K. The diamagnetic susceptibility of -(250 ± 15)×10$^{-6}$ cgs units was found to have no discernable temperature dependence. The sum
of the Pascal constant for $\text{ClO}_2^+$ and the diamagnetic correction for $[\text{Pt(SO}_3\text{F)}_6]^{2-}$ is $-320 \times 10^{-6}$ cgs units. Therefore, $(70 \pm 15) \times 10^{-6}$ cgs units of paramagnetic susceptibility must be due to Temperature Independent Paramagnetism, expected to be only about $50 \times 10^{-6}$ cgs units for Pt(IV)\textsuperscript{141}. The presence of T.I.P. is also evident for the other compounds listed in Table 5.4.

Table 5.4 DIAMAGNETIC SUSCEPTIBILITY FOR SOME Pt(IV)-FLUOROSULFATE COMPOUNDS (IN cgs UNITS) AT ROOM TEMPERATURE

<table>
<thead>
<tr>
<th></th>
<th>$\chi_g$</th>
<th>$\chi_m$</th>
<th>$\Sigma \chi_{dia}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Pt(SO}_3\text{F)}_4$</td>
<td>$-(1.52 \pm 31) \times 10^{-7}$</td>
<td>$-(81 \pm 17) \times 10^{-6}$</td>
<td>$-188 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{Ba}[\text{Pt(SO}_3\text{F)}_6]$</td>
<td>$-(2.95 \pm 7) \times 10^{-7}$</td>
<td>$-(271 \pm 6) \times 10^{-6}$</td>
<td>$-292 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{(ClO}_2)_2[\text{Pt(SO}_3\text{F)}_6]$</td>
<td>$-(2.70 \pm 16) \times 10^{-7}$</td>
<td>$-(250 \pm 15) \times 10^{-6}$</td>
<td>$-320 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\text{(Br}_3)_2[\text{Pt(SO}_3\text{F)}_6]$</td>
<td>$-(3.47 \pm 16) \times 10^{-7}$</td>
<td>$-(440 \pm 20) \times 10^{-6}$</td>
<td>$-454 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

* $81 \leq T \leq 300$ K

5.C.4 SOLUTION STUDIES IN HS0$_3$F

5.C.4.1 ELECTRONIC SPECTRA

Solutions of $\text{Pt(SO}_3\text{F)}_4$ and $\text{Cs}_2[\text{Pt(SO}_3\text{F)}_6]$ have identical absorption spectra when dissolved in HS0$_3$F, supporting the presence of similar Pt(IV)-fluorosulfate species. The spectrum consists of a strong broad peak at 245 nm (half width of $\sim 70$ nm), $\varepsilon=1.5 \times 10^4$ M$^{-1}$cm$^{-1}$. This band must be of charge transfer origin; no other absorptions due to d-d transition could be observed.
5.C.4.2 ELECTRICAL CONDUCTIVITIES

Both \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6]\) and \(\text{Pt(SO}_3\text{F})_4\) dissolve in \(\text{HSO}_3\text{F}\) to give conducting solutions, and, as in the \(\text{HSO}_3\text{F-Au(SO}_3\text{F})_3\) system, the binary fluorosulfate gives rise to strongly conducting solutions. \(\text{CsPt(SO}_3\text{F})_5\) also dissolves in \(\text{HSO}_3\text{F}\) to give solutions with conductivities slightly higher than those of \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6]\), when the conductivities are calculated for equivalents of cations, i.e. \(\text{Cs}^+\) and \(\text{C}_\text{10}_2^+\). The conductivities of solutions of \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6]\) and \(\text{CsPt(SO}_3\text{F})_5\) are shown in Fig.5.2 and listed in Table 5.5. Those of \(\text{Pt(SO}_3\text{F})_4\) are shown in Fig.5.3 and Table 5.6.

The conductivities of solutions of \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{M(\text{SO}_3\text{F})}_6]\), where \(\text{M} = \text{Pt, Sn}^{32}, \text{Ir}, \text{Pd}\), are all very similar, indicating a similar dissociative process in \(\text{HSO}_3\text{F}\). A qualitative titration using small amounts of \(\text{KSO}_3\text{F}\) indicates no acidic property for \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6]\).

If \((\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6]\) undergoes a simple ionic dissociation in solution, like \(\text{K[Au(SO}_3\text{F})_4]\), according to:

\[
(\text{C}_\text{10}_2\text{H}_{18})_2[\text{Pt(\text{SO}_3\text{F})}_6] + \text{HSO}_3\text{F} \rightarrow 2\text{C}_\text{10}_2^+(\text{solv}) + [\text{Pt(\text{SO}_3\text{F})}_6]^{2-}(\text{solv})
\]

the conductivity of the resultant solution should be about 1.5 times that of a solution of \(\text{K[Au(SO}_3\text{F})_4]\) at the same concentration. This is expected because

a) \(\lambda_o^*(\text{K}^+) = 30\), while \(\lambda_o^*([\text{Au(SO}_3\text{F})_4]^-) = 24\),

b) \(\lambda_o^*(\text{K}^+)\) seems to be slightly higher than \(\lambda_o^*(\text{C}_\text{10}_2^+)\) to 9, and,
The electrical conductivity of $\text{Cs}_2\text{Pt}_2(\text{SO}_3\text{F})_{10}$ and $(\text{ClO}_2)_2\text{Pt}(\text{SO}_3\text{F})_6$ in HSO$_3$F at 25°C
<table>
<thead>
<tr>
<th>m*</th>
<th>(ClO₂)₂[Pt(SO₃F)₆]</th>
<th>[Cs(Pt(SO₃F)₅]</th>
</tr>
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<tbody>
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<td>1.148</td>
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<td>0.002</td>
<td>5.185</td>
<td>5.925</td>
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<td>14.64</td>
</tr>
<tr>
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<td>13.54</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>15.54</td>
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<td>17.82</td>
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<tr>
<td>0.026</td>
<td>34.10</td>
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</tr>
</tbody>
</table>

mol·kg⁻¹ | 10⁻⁴Ω⁻¹cm⁻¹ | 10⁻⁴Ω⁻¹cm⁻¹ | units

* For comparison purposes, the molality of CsPt(SO₃F)₅ is calculated for two cations, i.e., [CsPt(SO₃F)₅]₂
FIG 5.3 CONDUCTIVITY OF Pt(SO₃F)₄ IN HSO₃F

10⁴ \kappa (\Omega^{-1} \text{cm})

m (mol/kg)
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<th>m</th>
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<th>κ(calc)</th>
</tr>
</thead>
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<td>1.100</td>
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</table>

mol·kg⁻¹  10⁻⁴Ω⁻¹cm⁻¹  10⁻⁴Ω⁻¹cm⁻¹  units
c) $\lambda^*_0 [\text{Pt(SO}_3\text{F)}_6]^{2-}$ should be less than $\lambda^*_0 ([\text{Au(SO}_3\text{F)}_4]^-)$ due to its double negative charge which may result in more extensive solution. This, however, is not found for $(\text{ClO}_2)_2[\text{Pt(SO}_3\text{F)}_6]$ or any of the $[\text{M(SO}_3\text{F)}_6]^{2-}$ complexes; on the contrary, the conductivity of these solutions is about twice that of $K[\text{Au(SO}_3\text{F)}_4]$, at the same concentration. Furthermore, whereas the molal conductivity of $K[\text{Au(SO}_3\text{F)}_4]$ remains relatively constant with respect to concentration, the same is not true for the $[\text{M(SO}_3\text{F)}_6]^{2-}$ complexes; these seem to decrease much faster as the concentration increases.

The high conductivity, the large concentration dependence of the molal conductivity and the lack of acidic behavior for the solutions seem to suggest the existence of an equilibrium giving rise to SO$_3$F$^-$ in the process, i.e., a basic dissociation for $[\text{M(SO}_3\text{F)}_6]^{2-}$. Further evidence for this will be presented in the titration of $\text{Pt(SO}_3\text{F)}_4$ with $K\text{SO}_3\text{F}$.

As can be seen from Fig 5.3, the conductivity of $\text{Pt(SO}_3\text{F)}_4$ in $\text{HSO}_3\text{F}$ is comparable to that of $\text{Au(SO}_3\text{F)}_3$, which has been shown to be a superacid in $\text{HSO}_3\text{F}$; but being a solute that can conceivably give rise to two acidium ions per mole of $\text{Pt(SO}_3\text{F)}_4$ dissolved, the conductivity appears quite low, or about a half as expected for a complete dissociation.

As with any diprotic acid, $H_2[\text{Pt(SO}_3\text{F)}_6]$, the hypothetical solvated acid in $\text{HSO}_3\text{F}$, should undergo the following two-step deprotonation reaction:

$$\text{HSO}_3\text{F} + H_2[\text{Pt(SO}_3\text{F)}_6] \xrightleftharpoons{K_1} H_2\text{SO}_3\text{F}^+ + H[\text{Pt(SO}_3\text{F)}_6]^- \quad (5.12)$$
\[
\text{HSO}_3\text{F} + \text{H}[\text{Pt(SO}_3\text{F)}_6]^- \xrightleftharpoons{K_2} \text{H}_2\text{SO}_3\text{F}^+ + [\text{Pt(SO}_3\text{F)}_6]^{2-} \quad (5.13)
\]

\(K_1\) should also be expected to be much larger than \(K_2\), by analogy with multiprotic acids in the aqueous system, such as \(\text{H}_2\text{SO}_4\) and \(\text{H}_3\text{PO}_4\). With the high conductivity of solutions of \(\text{HSO}_3\text{F-Pt(SO}_3\text{F)}_4\), \(\text{H}_2[\text{Pt(SO}_3\text{F)}_6]\) must be almost completely dissociated via equation (5.12), and the almost identical conductivity of \(\text{HSO}_3\text{F-Pt(SO}_3\text{F)}_4\) with that of \(\text{HSO}_3\text{F-Au(SO}_3\text{F)}_3\) suggests an almost monoprotic system, or \(K_1 \gg K_2\).

The conductometric titration of \(\text{H}_2[\text{Pt(SO}_3\text{F)}_6]\) with \(\text{KSO}_3\text{F}\), a typical plot of which is shown in Fig 5.4, supports both the above suggestions. In the beginning of the titration, and up to a \(K/\text{Pt}\) ratio of about 1, the conductance decreases almost linearly with the addition of \(\text{KSO}_3\text{F}\), indicating that a strong acid is present. But further into the titration, a gradual increase in the slope of the titration curve occurs, and a broad conductivity minimum is found at a \(K/\text{Pt}\) ratio of ~1.5. The titration curve crosses the equivalent point of 2 without any changes in the slope that would suggest that it is reached. This indicates a very weakly acidic solution, and \(K_2[\text{Pt(SO}_3\text{F)}_6]\), the empirical formula of the species present at the endpoint, is a base in \(\text{HSO}_3\text{F}\). The titration was repeated 6 times, using both weight- and volume-buret addition of \(\text{KSO}_3\text{F}\), and the result is reproducible.

Using the procedure described in Appendix A, a theoretical titration curve was calculated; this is shown in Fig 5.4 and
The conductometric titration of
$\text{Pt} \left( \text{SO}_3 \text{F} \right)_4$ with $\text{KSO}_3 \text{F}$
in $\text{HSO}_3 \text{F}$

$10^4 \kappa$  
($\Omega^{-1}/\text{cm}$)

$K/\text{Pt}$
listed in Table 5.7. The following parameters were used:

\[
\begin{align*}
\lambda^*_o (H_2SO_3F^+) &= 320, \\
\lambda^*_o (SO_3F^-) &= 227, \\
\lambda^*_o (K^+) &= 29, \\
\lambda^*_o (H[Pt(SO_3F)_6])^- &= 29, \\
\lambda^*_o ([Pt(SO_3F)_6]^{2-}) &= 32, \\
K_1 &= 6.3 \times 10^{-2} \text{ mol/kg,} \\
K_2 &= 5.0 \times 10^{-5} \text{ mol/kg, and} \\
K_{ap} &= [H_2SO_3F^+] \cdot [SO_3F^-] = 3.8 \times 10^{-8} \text{ mol/kg.}
\end{align*}
\]

This would give a basic dissociation, \( K_{-2} \), for \([Pt(SO_3F)_6]^{2-}\) in HSO_3F, according to:

\[
[Pt(SO_3F)_6]^{2-} + HSO_3F \xrightleftharpoons[K_{-2}]{} H[Pt(SO_3F)_6]^- + SO_3F^- , \quad (5.14)
\]

of 1.2 \(10^{-3}\) mol/kg, i.e., \([Pt(SO_3F)_6]^{2-}\) is a reasonably strong base when dissolved in HSO_3F. This is consistent with the high conductivity of solutions of \([Pt(SO_3F)_6]^{2-}\) and the basic behavior of the solution near the endpoint of the Pt(SO_3F)_4/KSO_3F titration. By analogy, the other \([M(SO_3F)_6]^{2-}\), where \(M=Sn, Pd, Ir\), because of the similarity in the conductivity of their solutions, should have very similar \( K_{-2} \) values and thus are strong bases in HSO_3F.

The fit between the calculated and observed titration points is acceptable at the ratios \( K/Pt \) at \(-0 \) and at \(-2 \), the deviation increases quite rapidly as \( K/Pt \) approximates 1, a higher acidity than can be accounted for by equations (5.12) and (5.13) was observed. The \( \lambda^*_o \) values are in the range expected for the various species, although the apparently high mobility of \([Pt(SO_3F)_6]^{2-}\).
Table 5.7  CONDUCTOMETRIC TITRATION OF Pt(SO₃F)₄ WITH KSO₃F IN HSO₃F

<table>
<thead>
<tr>
<th>R</th>
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<th>(\kappa(\text{calc})^*)</th>
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\(\Omega^{-1}\)cm\(^{-1}\) \(\Omega^{-1}\)cm\(^{-1}\) mol\cdot kg\(^{-1}\) units

* calculated using the following parameters:

\[ \lambda_o^*(H_2SO_3F^+) = 320 \]
\[ \lambda_o^*(SO_3F^-) = 227 \]
\[ \lambda_o^*(K^+) = 29 \]
\[ \lambda_o^*(H[Pt(SO_3F)_6]^-) = 29 \]
\[ \lambda_o^*([Pt(SO_3F)_6]^{2-}) = 32 \]
\[ [H_2SO_3F^+][SO_3F^-] = 3.8 \times 10^{-8} \text{ mol}^2\cdot\text{kg}^{-2} \]
\[ K_1 = 0.063 \text{ mol}\cdot\text{kg}^{-1} \]
\[ K_2 = 5.0 \times 10^{-5} \text{ mol}\cdot\text{kg}^{-1} \]
should require some explanation. Although one would normally expect that a doubly charged ion would have a less mobility than its singly charged counterpart because of the increased size of the former's solvation sphere, such a phenomenon may not be very important when the ion itself is already very large, like the $[\text{M(SO}_3\text{F)}_6]^{2-}$ studied here, and the charge can be delocalized more efficiently than a point charge such as $\text{K}^+$. $\text{K}^+$ may be extensively solvated in HSO$_3$F since $\lambda^*(\text{Ba}^{2+})$ is about 35 in Ba(SO$_3$F)$_2$ solutions ($\lambda^*(\text{K}^+) = 29$) $^{21}$. For similarly solvated ions of different charges, the higher the charge on the ion, the higher its mobility should be, since it would experience an increased force from the electric field.

At the intermediate K/Pt ratios during the titration, the excess acidium ion may be indirectly due to a dimerization of [Pt(SO$_3$F)$_6$]-containing species according to:

\[
\begin{align*}
H_2[\text{Pt(SO}_3\text{F)}_6] & \xrightleftharpoons{Kd_1} \frac{1}{2}H_2[\text{Pt}_2(\text{SO}_3\text{F)}_{10}] + \text{HSO}_3\text{F} \\
H[\text{Pt(SO}_3\text{F)}_6]^{-} & \xrightleftharpoons{Kd_2} \frac{1}{2}H_2[\text{Pt}_2(\text{SO}_3\text{F)}_{10}] + \text{SO}_3\text{F}^{-} \\
[\text{Pt(SO}_3\text{F)}_6]^{2-} & \xrightleftharpoons{Kd_3} \frac{1}{2}[\text{Pt}_2(\text{SO}_3\text{F)}_{10}]^{2-} + \text{SO}_3\text{F}^{-}
\end{align*}
\]

All these dimerization reactions have the result of decreasing the acidity of the system; two also have a strong dependence on [SO$_3$F$^-$] and conversely [H$_2$SO$_3$F$^+$]. At the initial conditions of high acidity, if the hypothesis is correct, dimerization or even higher oligomer formation is favored. But as the titration proceeds (by the addition of KSO$_3$F solution which also dilutes the system), the initially formed oligomers will gradually depoly-
merize, and increase the acidity of the solution by the reverse reaction which can be represented by:

\[
\frac{1}{2}H_2[Pt_2(SO_3F)_{10}] + 3HSO_3F \xrightleftharpoons[K_1^{-1}]{} [Pt(SO_3F)_6]^{2-} + 2H_2SO_3F^+. \tag{5.18}
\]

The net effect of this extra quantity of $H_2SO_3F^+$ would contribute to an increase in conductivity of the system. Furthermore, the actual $K_1$ would be higher than the one calculated here and the actual $K_2$ would be lower. This is because of the calculation procedure used; also because of this, $\lambda_0^*(\text{[Pt(SO}_3F)_6]^{2-})$ would be lowered, but since the calculated value is so high to start with, this should not be a problem. This extra set of equilibria serves to buffer the system when the acidity is not very high, and the observed broad conductivity minimum seems to be consistent with this. It is possible to include equations (5.15) to (5.17) into the calculation, but the procedure outlined in Appendix A already involves four variables and the addition of three more is certainly beyond the intent of this study. Qualitatively, the addition of equations (5.15) to (5.17) appears to be able to shift the calculated curve closer to the observed one.

It is now necessary to present some evidence for polymerization in the platinum(IV)-fluorosulfate system. $\text{Pt(SO}_3F)_4$ is a polymer in the solid state, much like $\text{Au(SO}_3F)_3$ is, and both dissolve in $\text{HSO}_3F$ only with difficulties, although very concentrated solutions can be formed. $\text{Pt(SO}_3F)_4$ shows a much greater reluctance to dissolve, and this has been discussed in the vibrational
spectra section. Solutions of Pt(SO$_3$)$_4$ obtained in this manner all show lower conductivity than those obtained without first isolating Pt(SO$_3$)$_4$ as a solid (i.e., formed from platinum metal and S$_2$O$_6$F$_2$/HSO$_3$F). The complete removal of all S$_2$O$_6$F$_2$ in the latter case is shown by Raman spectroscopy for one such sample. It therefore appears that oligomers, possibly of a much higher degree of polymerization than 2, may be present when solid Pt-(SO$_3$)$_4$ is dissolved in HSO$_3$F. Furthermore, as mentioned before, the apparent molal conductivity of (ClO$_2$)$_2$[Pt(SO$_3$)$_6$], and also those of CsPt(SO$_3$)$_5$, CsSn(SO$_3$)$_5$ and Pt(SO$_3$)$_4$ all show a large concentration dependence. This is especially evident for CsSn-(SO$_3$)$_5$, for which a larger concentration range was investigated. A detailed discussion on the conductivity of CsM(SO$_3$)$_5$ and [M-(SO$_3$)$_6$]$^{2-}$, M=Pt, Sn, will be presented in Chapter 9. All these observations suggest the occurrence of polymerization in solutions containing these species.

Supporting evidence can also be found in the vibrational spectra of CsPt(SO$_3$)$_5$ (also CsSn(SO$_3$)$_5$), which indicate the presence of both monodentate and bidentate SO$_3$F groups. It can be visualized that CsPt(SO$_3$)$_5$ is the compound isolated at K/Pt=1 during the titration, and that it is formed either by the desolvation-dimerization of H[Pt(SO$_3$)$_6$]$^-$ according to:

$$2H[Pt(SO_3F)_6]^- \rightarrow [Pt_2(SO_3F)_{10}]^{2-} + 2HSO_3F,$$

(5.19)

or, if [Pt$_2$(SO$_3$F)$_{10}$]$^{2-}$ is the predominant species present at that condition, by a desolvation process. The n.m.r. and vibrational
spectra evidence to be presented later seem to indicate quite a low extent of polymerization in solution, and favors equation (5.19) (this does not negate its contribution to the conductivity though, because the deviation between the two curves in Fig 5.4 is quite small).

CsPt(SO$_3$F)$_5$ dissolves in HSO$_3$F to give a solution which shows acidic conductivity. Its higher conductivity than solutions of (ClO$_2$)$_2$[Pt(SO$_3$F)$_6$] (Fig 5.2) is consistent with H$_2$SO$_3$F$^+$ having a greater ionic mobility than SO$_3$F$^-$.  

5.C.4.3 SOLUTION VIBRATIONAL SPECTRA

It was hoped that Raman spectra of solutions of Pt(SO$_3$F)$_4$ would show signs of polymerization. This, however, was not observed up to a concentration of about 0.12 mol/kg. Actually, the only bands that are definitely due to Pt(SO$_3$F)$_4$ are at 638, 455 and 276 cm$^{-1}$, as all other bands are overlapped by broad solvent bands. This suggests that solutions of Pt(SO$_3$F)$_4$ are not as efficient Raman scatterers as those of Au(SO$_3$F)$_3$. In addition, because of the broadness of the peaks, splittings observed in the solid state spectra of CsPt(SO$_3$F)$_5$ are not evident here.

5.C.4.4 SOLUTION N.M.R.

All three species, Pt(SO$_3$F)$_4$, CsPt(SO$_3$F)$_5$ and Cs$_2$[Pt(SO$_3$F)$_6$] gave identical $^{19}$F-n.m.r. spectra in HSOS$_3$F solutions. This is
in sharp contrast to what was observed in the \text{Au(SO}_3\text{F})_3-\text{HSO}_3\text{F} system. A typical \textsuperscript{19}F-n.m.r. spectrum of \text{Pt(SO}_3\text{F})_4-\text{HSO}_3\text{F} is shown in Fig. 5.5.

One of the natural occurring isotope of platinum, \textsuperscript{195}Pt, has a nuclear spin of \( \frac{3}{2} \), and its coupling to \textsuperscript{19}F supposedly gives rise to the splitting of the fluorine resonance with \( J(\text{Pt-F}) = 31 \text{ Hz} \). Since \textsuperscript{195}Pt is present in only 33.8% natural abundance, about \( \frac{2}{3} \) of the fluorine signal should not be affected, and this was shown by an integration of the peaks. Therefore, the coupling occurs via a sulfur and an oxygen atom. \text{[PtF}_6\text{]}^{2-} on the other hand, presumably due to the proximity of the two atoms, has a large \( J(\text{Pt-F}) \) coupling constant of \( \sim 2000 \text{ Hz} \). \textsuperscript{195}

For the species \text{[Pt}_2(\text{SO}_3\text{F})_{10}]^{2-}, the coupling scheme for that ion alone will be a 1:8:2:8:1 pattern, each separated by \( \sim 15 \text{ Hz} \). This is expected since the chemical environment for a fluorosulfate group should not be very different whether the \text{SO}_3\text{F} ligand is monodentate or bidentate. However, no satellites on either side of the triplet was observed, at concentrations up to \( \sim 0.12 \text{ mol/kg} \). This indicates that even if the dimer is present, it must be in quite a low concentration.

The sharpness of the resonances does not necessarily mean a lack of exchange between the platinum-fluorosulfate-containing solute (at -47.8 ppm) and the solvent (at -40.8 ppm), as these resonances are 7 ppm apart, and proton exchange evidently does occur in this system.
F-19 nmr of $\text{Cs}_2[\text{Pt}(\text{SO}_3\text{F})_6]$ in $\text{HSO}_3\text{F}$ (conc. = 0.11 m)

-47.75 ppm

$J = 31 \text{ Hz}$

-40.77 ppm

$\text{HSO}_3\text{F}$
These $^{19}$F-n.m.r. results show that identical species containing platinum and fluorosulfate groups are present in solution, whether the starting solid is the binary fluorosulfate or either of its two types of complexes.

Since $^{195}$Pt is a nucleus accessible by n.m.r. spectroscopy, attempts were made to obtain $^{195}$Pt-n.m.r. spectra of these solutions. For the spectrum of $[\text{Pt(SO}_3\text{F})_6]^{2-}$, a septet of the relative intensity of 1:6:15:20:15:6:1 and separated by $J(\text{Pt-F})=31$ Hz is expected, while for $[\text{Pt}_2(\text{SO}_3\text{F})_{10}]^{2-}$, two groups of septets separated by $J(\text{Pt-Pt})$ should be present if Pt-Pt coupling occurs. The observation of the latter group of peaks should provide the most conclusive evidence for the existence of the dimer in solution.

This, unfortunately, did not occur, and no $^{195}$Pt-n.m.r. spectra was obtainable for any one of the fluorosulfates, even when solutions of up to $\sim$1 mol/kg concentration were used, although a resonance from a $[\text{PtCl}_6]^{2-}$ test solution was obtained. The wide range of chemical shifts possible in $^{195}$Pt-n.m.r. spectra ($\sim$7000 ppm from $[\text{PtF}_6]^{2-}$ to $[\text{PtCl}_6]^{2-}$) combined with its low sensitivity (only $\sim$0.3 % that of proton when natural abundance is included) probably contributed to this experiment's demise.
5.D CONCLUSION

HSO₃F-Pt(SO₃F)₄ has been found to be a superacid in the HSO₃F solvent system. In a per-mole basis, its acidity is comparable to that of HSO₃F-Au(SO₃F)₃ and slightly less than that of HSO₃F-SbF₂-(SO₃F)₃. The decrease in acidity in the system, similar to other diprotic acids, is due to the low equilibrium constant for the dissociation of the second proton. In addition, the oligomer-formation of the [Pt(SO₃F)₆]-containing species is also a contributing factor. These have been shown by conductometric titrations of the superacid with KSO₃F.

As expected, complexes containing [Pt(SO₃F)₆]²⁻ can readily be formed, including one which contains the tribromine cation — (Br₃)₂[Pt(SO₃F)₆]. The anion dissociates in HSO₃F to give basic conducting solutions, and appears to be isostructural with a general class of [M(IV)(SO₃F)₆]²⁻ anions. A complex with the empirical formula of CsPt(SO₃F)₅ can also be synthesized this is a weak acid in HSO₃F and is not monomeric in the solid state.

The Pt(IV)-fluorosulfate system investigated here is diamagnetic, thus indicating a ¹A₁g, low-spin electronic ground state for the d⁶ metal ion in an octahedral ligand field.
6.A INTRODUCTION

Iridium is one of the rarest members of the platinum metals, but because of its possible role in homogeneous catalysis, especially with Ir in the lower oxidation states, the chemistry of iridium has been a field of active research \(^{198,196}\). Iridium can exist in a variety of oxidation states, from -1 to +6, the possible exception being Ir(II), which is isoelectronic with Pd(III) and Pt(III). As far as the halogen chemistry of iridium is concerned, it is much like that of platinum, with IrF\(_6\), [IrF\(_5\)]\(_4\) and Ir-Hal\(_3\), Hal=F, Cl, Br, I, all having been synthesized. Although the binary tetrahalides of iridium are unknown, it forms many very stable [Ir-Hal\(_6\)]\(^{2-}\) complexes \(^{190}\). The instability of Ir-Hal\(_4\), at least in the case of IrF\(_4\), cannot be attributed to the lack of oxidative ability of the halogen, and may be due to the more favorable formation of either IrF\(_3\) or [IrF\(_5\)]\(_4\). The normal product of the fluorination of iridium metal, depending on the reaction condition, is IrF\(_6\) or [IrF\(_5\)]\(_4\); IrF\(_3\) can only be obtained by the reduction of the higher fluorides.

While the gold and the platinum systems discussed in previous chapters provided some interesting solution chemistry, and novel superacid systems in HS\(_2\)O\(_3\)F, they are lacking in having any paramagnetic compounds. One of the most easily accessible oxidation states of iridium, at least in anionic complexes, is Ir(IV), which
is $d^5$. So regardless of whether the ion is high spin or low spin, this should provide a paramagnetic species.

The high ligand field splitting expected for Ir(IV) would almost certainly force the electronic state to be $^2T_{2g}$, low-spin. Although this would imply quite complicated temperature dependent magnetic behavior for Ir(IV), this is sometimes not very noticeable due to the inherent small magnitude of the magnetic susceptibility itself. However, antiferromagnetic coupling is prevalent in this system, and $[\text{Ir-Hal}_6]^{2-}$ complexes, with Hal=Cl, Br, have low moments of about 1.5 $\mu_B$ at room temperature. It was of interest to see if the replacement of a halide ion with a $\text{SO}_3\text{F}$ group would lead to a drastic increase in the magnetic moment of the species, as was observed in the palladium system.

Therefore, the investigation into iridium-fluorosulfate is not so much in terms of solution studies, but rather as a study into the magnetic behavior of fluorosulfates containing a transition metal in a high oxidation state and to collect more information as to the coordination properties of the fluorosulfate group.
6.B EXPERIMENTAL

6.B.1 SYNTHESIS OF IRIDIUM TRIS(FLUOROSULFATE)

\[
\text{Ir} + 2\text{S}_2\text{O}_5\text{F}_2 + \text{HSO}_3\text{F} \xrightarrow{\text{HSO}_3\text{F}} \text{Ir(SO}_3\text{F})_4
\]  
\[
\text{Ir(SO}_3\text{F})_4 \xrightarrow{\Delta} \text{Ir(SO}_3\text{F})_3 + \frac{1}{2}\text{S}_2\text{O}_5\text{F}_2 + \frac{3}{4}\text{O}_2
\]

In a typical reaction, iridium metal (158 mg, 0.822 mmol) was reacted with an excess of \(\text{S}_2\text{O}_5\text{F}_2/\text{HSO}_3\text{F}\) (10 mL) at ~140°C. Parts of the metal initially dissolved to form a brown solution containing \(\text{Ir(SO}_3\text{F})_4\); after 3 days of heating, a deep purple solution together with unreacted metal was formed. After the removal of most of the \(\text{S}_2\text{O}_5\text{F}_2\) and oxygen formed from the reaction, more \(\text{S}_2\text{O}_5\text{F}_2\) (~3 mL) was added to the mixture which was subsequently reheated at ~140°C. After 3 days, all metal had dissolved and the solution again changed back into having a deep purple color. All volatile materials were removed in vacuo and a solid which analyzed as \(\text{Ir(SO}_3\text{F})_3\) was obtained (398 mg, 0.813 mmol). \(\text{Ir(SO}_3\text{F})_3\) can also be obtained by the thermal decomposition of \(\text{Ir(SO}_3\text{F})_4\) at ~120°C in vacuo according to equation (6.2). In a typical pyrolysis experiment, \(\text{Ir(SO}_3\text{F})_4\) (294 mg, 0.500 mmol) was converted into \(\text{Ir(SO}_3\text{F})_3\) (239 mg, 0.488 mmol) after 12 hours of heating.

\(\text{Ir(SO}_3\text{F})_3\) is a very deep bluish purple, hygroscopic solid. It is soluble in \(\text{HSO}_3\text{F}\) and decomposes at ~200°C with the evolution of a colorless gas which was not identified.

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<th>F</th>
</tr>
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<td>Found %</td>
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<td>11.48</td>
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6.B.2 SYNTHESIS OF IRIDIUM TETRAKIS(FLUOROSULFATE)

\[
\text{Ir(SO}_3\text{F)}_3 + \frac{1}{2}\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{Ir(SO}_3\text{F)}_4
\]

(6.3)

Ir(SO\(_3\)F\(_4\)) can be prepared in a reaction similar to that discussed for Ir(SO\(_3\)F\(_3\)). Iridium metal (198 mg, 1.030 mmol), was reacted with S\(_2\)O\(_6\)F\(_2\)/HSO\(_3\)F (~4 mL) and was taken through the same cycles of S\(_2\)O\(_6\)F\(_2\) addition. When all the metal had dissolved and most of the S\(_2\)O\(_5\)F\(_2\) had been removed, S\(_2\)O\(_6\)F\(_2\) (~2 mL) was added to the solution of essentially Ir(SO\(_3\)F\(_3\)) in HSO\(_3\)F. This was heated at ~60°C for 6 hours, after which time a deep brown solution had formed. The removal of all volatile materials by the usual method yielded Ir(SO\(_3\)F\(_4\)) with traces of the blue Ir(SO\(_3\)F\(_3\)) (the weight of the product was slightly lower than expected for Ir(SO\(_3\)F\(_4\)) also). More S\(_2\)O\(_6\)F\(_2\) (~2 mL) was added to the impure product which was heated at ~60°C for another 6 hours. The removal of all excess S\(_2\)O\(_6\)F\(_2\) (and traces of S\(_2\)O\(_5\)F\(_2\) and oxygen) at room temperature yielded pure \(\text{Ir(SO}_3\text{F)}_4\) (607 mg, 1.032 mmol).

Ir(SO\(_3\)F\(_4\)) is a deep brown, almost black, hygroscopic solid which is very soluble in HSO\(_3\)F. It decomposes into Ir(SO\(_3\)F\(_3\)) according to equation (6.2) at ~100°C in vacuo but is stable up to ~150°C in an atmosphere of N\(_2\).

Analysis

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<th></th>
<th>Ir</th>
<th>S</th>
<th>F</th>
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6.B.3 SYNTHESIS OF [Ir(SO$_3$F)$_6$]$^{2-}$ COMPLEXES

6.B.3.1 PREPARATION OF (C$_{10}$)$_2$[Ir(SO$_3$F)$_6$]

$$2\text{C}_{10}\text{S}_3\text{F} + \text{Ir} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{HS}_3\text{F} (\text{C}_{10})_2[\text{Ir(SO}_3\text{F})_6] \quad (6.4)$$

A mixture of C$_{10}$S$_3$F (~1 mL), and S$_2$O$_6$F$_2$/HSO$_3$F (~6 mL) was allowed to react with iridium metal (289 mg, 1.505 mmol) at ~120°C for 3 days. All the metal by that time had dissolved and the solution took on a dark brown color. The removal of all volatile materials at ~70°C yielded a compound which analyzed as (C$_{10}$)$_2$-[Ir(SO$_3$F)$_6$] (1.362 g, 1.478 mmol).

(C$_{10}$)$_2$[Ir(SO$_3$F)$_6$] can also be prepared by:

a) replacing C$_{10}$S$_3$F with C$_{11}$SO$_3$F in equation (6.4) and performing the reaction under the same conditions, or

b) a reaction between IrCl$_3$ and S$_2$O$_6$F$_2$/HSO$_3$F at ~120°C for 4 days.

In both these alternative synthetic routes, the required C$_{10}$S$_3$F is generated by an attack of C$_{11}$SO$_3$F (formed from the reaction of IrCl$_3$ with S$_2$O$_6$F$_2$ in (b)) on the glass reactor.

(C$_{10}$)$_2$[Ir(SO$_3$F)$_6$] is a dark orange-brown, hygroscopic solid. It is soluble in HSO$_3$F and melts with decomposition at ~190°C to form a dark brown liquid.

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</thead>
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<td>Found %</td>
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6.B.3.2 PREPARATION OF Cs$\textsubscript{2}$[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$]

$$\text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsCl} + \text{HCl} \quad (6.5)$$

$$2\text{CsSO}_3\text{F} + \text{Ir} + 2\text{S}_2\text{O}_6\text{F}_2 \xrightleftharpoons{\text{HSO}_3\text{F}} \text{Cs}_2\text{[Ir(SO}_3\text{F)}_6] \quad (6.6)$$

Cs$\textsubscript{2}$[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$] was prepared by the oxidation of iridium metal (398 mg, 2.071 mmol) with S$\textsubscript{2}$O$\textsubscript{6}$F$_2$/HSO$\textsubscript{3}$F (~10 mL) in the presence of CsCl (798 mg, 4.146 mmol) at ~150°C for 10 days. The removal of all volatile materials at ~70°C yielded a product with a weight corresponding to that expected for Cs$\textsubscript{2}$[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$], (2.121 g, 2.015 mmol).

Cs$\textsubscript{2}$[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$] is a pale orange, hygroscopic solid. It is soluble in HSO$\textsubscript{3}$F and melts with decomposition at ~150°C.

6.B.3.3 PREPARATION OF Ba[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$]

$$\text{BaCl}_2 + 2\text{HSO}_3\text{F} \rightarrow \text{Ba(SO}_3\text{F)}_2 \quad (6.7)$$

$$\text{Ba(SO}_3\text{F)}_2 + \text{Ir} + 2\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{Ba[Ir(SO}_3\text{F)}_6] \quad (6.8)$$

A mixture of dried BaCl$_2$ (198 mg, 0.951 mmol) and iridium metal (183 mg, 0.952 mmol) was reacted with S$\textsubscript{2}$O$\textsubscript{6}$F$_2$/HSO$\textsubscript{3}$F (~10 mL) at ~100°C for 2 weeks and, after replenishing the largely decomposed S$\textsubscript{2}$O$\textsubscript{6}$F$_2$, at ~160°C for another 2 weeks. The removal of all volatile materials at ~70°C yielded a product with a weight suggesting the composition of Ba[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$] (788 mg, 0.853 mmol). The low yield is due to the visually evident etching of the glass reactor by the solution.

Ba[Ir(SO$\textsubscript{3}$F)$\textsubscript{6}$] is a light orange, hygroscopic solid. It appears to be almost insoluble in HSO$\textsubscript{3}$F, and decomposes at ~200°C.
6.C DISCUSSION

6.C.1 SYNTHESIS AND GENERAL DISCUSSION

6.C.1.1 BINARY FLUOROSULFATES

Iridium was found to be much less reactive than platinum towards fluorosulfonation, whether the starting material is the metal itself or IrCl$_3$. Although, as pointed out in previous chapters, these noble metal chlorides are not susceptible to displacement reactions in HSO$_3$F, they are usually quite reactive towards S$_2$O$_6$F$_2$/HSO$_3$F.

All the preparative reactions described could take up to 1 month for completion, while some had actually been aborted eventually. The preparation of the binary fluorosulfates has one of the most serious difficulties that a synthetic reaction could encounter — the decomposition of both the reactant (S$_2$O$_6$F$_2$) and the product (Ir(SO$_3$F)$_4$). Since S$_2$O$_6$F$_2$ is not known to decompose into S$_2$O$_5$F$_2$ and O$_2$ at a temperature of only ~120°C, the path that it takes must be via Ir(SO$_3$F)$_4$, in a catalytic manner. A higher reaction temperature was not feasible since it was found that the decomposition took place much faster than the conversion of the metal to either Ir(III) or Ir(IV). The S$_2$O$_5$F$_2$ formed, identified by i.r. spectroscopy, had to be removed before the S$_2$O$_6$F$_2$ could be replenished because its presence would reduce the ionizing ability of the solvent. Because of the extremely dark colors of the solutions, the addition of the oxidant was usually repeated.
at least twice after all the metal had reacted, to ensure a complete reaction.

The decomposition of \( \text{Ir(SO}_3\text{F})_4 \) to form \( \text{S}_2\text{O}_5\text{F}_2 \) and oxygen is unlike that found for \( \text{Pd}_2(\text{SO}_3\text{F})_6 \), \( \text{Au(SO}_3\text{F})_3 \) or \( \text{Pt(SO}_3\text{F})_4 \). While the latter two compounds break down completely to form \( \text{SO}_2\text{F}_2 \), the decomposition of palladium tris(fluorosulfate) giving \( \text{S}_2\text{O}_6\text{F}_2 \) has been used as an evidence for Pd(IV)'s strong oxidizing ability. It therefore appears that Ir(IV) is not a very strong oxidizing agent. Although the compound is not very thermally stable, it is one of the few examples of binary Ir(IV) compounds, another example of which is \( \text{IrO}_2 \).\(^{199}\)

6.C.1.2 \( [\text{Ir(SO}_3\text{F})_6]^2^- \) COMPLEXES

As with the synthesis of the binary fluorosulfates of iridium, these reactions are very time consuming. Although the thermal stability of the anionic Ir(IV) complexes appears to be greater than that of \( \text{Ir(SO}_3\text{F})_4 \), the formation of the complexes, for some inexplicable reasons, is very slow. An attempt to synthesize \( \text{Na}_2[\text{Ir(SO}_3\text{F})_6] \) was terminated after six months, at which time the reactor had become badly etched. The above reaction was actually thought to proceed quickly by the following reasonings.

a) The decomposition of \( [\text{Ir(SO}_3\text{F})_6]^2^- \) is faster when it is solvated, and for the almost insoluble \( \text{Ba[Ir(SO}_3\text{F})_6] \), a higher reaction temperature of \( -160^\circ \text{C} \) could be used, but, because of the insolubility of the product, the reaction
proceeded slowly.

b) An inspection of the solubility of the various alkali metal hexachloroplatinates(IV) reveals that Na$_2$[PtCl$_6$] has a very low solubility and Na$_2$[Ir(SO$_3$F)$_6$] may be expected to behave similarly. This was later found to be the case during the course of the reaction, but the formation of the complex was exceedingly slow, and it more than compensated for the presumably slower decomposition of the product.

6.C.2 VIBRATIONAL SPECTRA

For both the binary fluorosulfates, vibrational spectroscopy had been of very limited help in their investigation. Being deeply colored compounds, no Raman spectra could be obtained, even at ~80 K. The i.r. spectra obtained were of extremely poor resolution. Using a variety of mulling agents such as fluorolube oil, hexachlorobutadiene and silicone oil, separate regions of the spectrum could be 'pieced' together for Ir(SO$_3$F)$_3$. The i.r. frequencies of Ir(SO$_3$F)$_3$ and Ir(SO$_3$F)$_4$ are listed in Table 6.1 and compared to those of Pt(SO$_3$F)$_4$. All three spectra are very similar, especially in the region of ~800 - 1200 cm$^{-1}$, where the large number of bands probably leads to overlaps and thus the observed unresolvability. This suggests that the two iridium
<table>
<thead>
<tr>
<th></th>
<th>Ir(SO₃F)₃</th>
<th>Ir(SO₃F)₄</th>
<th>Pt(SO₃F)₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1400 s</td>
<td></td>
<td>1390 s</td>
<td>~1400 vs,b</td>
</tr>
<tr>
<td>1210 s</td>
<td>1210 s</td>
<td></td>
<td>~1225 vs</td>
</tr>
<tr>
<td>1100 vs,</td>
<td>1070 s,sh</td>
<td></td>
<td>~1150 s, vb</td>
</tr>
<tr>
<td>1020 vs,sh</td>
<td>1020 s,b</td>
<td></td>
<td>~1000 vs,vb</td>
</tr>
<tr>
<td>950 s,vb</td>
<td>870 s,b</td>
<td></td>
<td>~900 vs,vb</td>
</tr>
<tr>
<td>800 s,vb</td>
<td>820 s,b</td>
<td></td>
<td>~820 s,vb</td>
</tr>
<tr>
<td>630 s</td>
<td>640 m,b</td>
<td></td>
<td>~640 s,b</td>
</tr>
<tr>
<td>575</td>
<td>580 m</td>
<td></td>
<td>580 s</td>
</tr>
<tr>
<td>540</td>
<td>540 m</td>
<td></td>
<td>540 m</td>
</tr>
<tr>
<td>450</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
fluorosulfates are extensively $SO_3F$-bridged species. Because of the increased complexity of the i.r. spectrum of $Ir(SO_3F)_3$ over that of $Au(SO_3F)_3$, the former may not be square planar, but rather octahedral. This may be resolved with the synthesis of anionic complexes of either $[Ir(SO_3F)_4]^-_2$ or $[Ir(SO_3F)_6]^{3-}$, although this was not pursued. In the halide system, the trihalides contain octahedrally coordinated $Ir(III)$ with, as expected, a low spin $d^6$ electronic configuration.

For the $[Ir(SO_3F)_6]^{2-}$ complexes, i.r. spectra of reasonable resolution could be obtained, but due to the samples' deep yellow color, Raman spectra of only relatively poor quality was recorded at ~80 K. The vibrational frequencies of these compounds are listed in Table 6.2 in comparison with the Raman frequencies of $Cs_2[Pt(SO_3F)_6]$. The three iridium complexes all have spectra that are similar to that of $Cs_2[Pt(SO_3F)_6]$, suggesting a similar type of metal-ligand interaction and a monodentate coordination of the $SO_3F$ groups. The positions of the three vibrational modes of $ClO_2^+$ at (1310, 1295), 1060 and 522 cm$^{-1}$ in the i.r. spectrum also indicate an ionic formulation for the compound can be made.

In summary, it appears that all the iridium species involved in this study have octahedral coordination for iridium, with bidentate $SO_3F$ groups evident for the two binary fluorosulfates.
<table>
<thead>
<tr>
<th>Compound</th>
<th>IR</th>
<th>R&lt;sup&gt;+&lt;/sup&gt;</th>
<th>IR</th>
<th>R</th>
<th>IR</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₂O₂)₂[Ir(SO₃F)₆]</td>
<td>1400s,b</td>
<td>1400,1380w</td>
<td>1390s,b</td>
<td>1415w</td>
<td>1390s</td>
<td>1416w,sh</td>
</tr>
<tr>
<td>Cs₂[Ir(SO₃F)₆]</td>
<td>1250vs</td>
<td>1255m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba[Ir(SO₃F)₆]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs₂[Pt(SO₃F)₆]</td>
<td>950vs,vb</td>
<td>950s,b</td>
<td>978w</td>
<td>950s,b</td>
<td>1057m</td>
<td>1043s</td>
</tr>
<tr>
<td>820s</td>
<td>840,810w</td>
<td>~800s,b</td>
<td>~802w,b</td>
<td>820s</td>
<td>~800w,b</td>
<td></td>
</tr>
<tr>
<td>660s</td>
<td>640w</td>
<td>645m</td>
<td>630w</td>
<td>630w</td>
<td>634vs</td>
<td></td>
</tr>
<tr>
<td>590s</td>
<td>580w</td>
<td>570s</td>
<td>575w</td>
<td>575m</td>
<td>579vw</td>
<td></td>
</tr>
<tr>
<td>550s</td>
<td>548w</td>
<td>540s</td>
<td>550w</td>
<td>540m</td>
<td>550vw</td>
<td></td>
</tr>
<tr>
<td>522m&lt;sup&gt;*&lt;/sup&gt;</td>
<td>520w&lt;sup&gt;*&lt;/sup&gt;</td>
<td>460w</td>
<td>460vw</td>
<td>460w,sh</td>
<td>440m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>443w</td>
<td>440m</td>
<td>440vw</td>
<td>447m</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>286m</td>
<td>287w</td>
<td>280vs</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>268m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>*</sup> denotes bands due to C₂O₂<sup>+</sup>

<sup>†</sup> obtained at -80K
6.C.3 MAGNETIC SUSCEPTIBILITY

According to Figgis, the magnetic susceptibility of Ir(IV), a d⁵ low spin system with a ²T₂g electronic ground state can be represented by the following equation

\[ \mu^2 = \frac{8 + (3x - 8)\exp(-3x/2)}{x[2 + \exp(-3x/2)]} \]  

(6.9)

where \( x = \lambda/kT \)

\[ \lambda = -\xi = -5000 \text{ cm}^{-1} \text{ for Ir(IV)} \]

\[ k = \text{Boltzmann's constant} = 0.6950 \text{ cm}^{-1} \]

Therefore, as \( x \to -\infty \) (for large \( |\lambda| \) or low temperature), \( \mu \to \sqrt{3} \), and as \( x \to 0 \), \( \mu \to \sqrt{5} \). In the temperature range accessible in this study (~100 - 330 K), \( \mu \) should have values from 1.76 \( \mu_B \) at 100 K to 1.84 \( \mu_B \) at 330 K. For the hexachloro- and hexabromo-complexes of Ir(IV), \( \mu_{\text{eff}} \) was found to generally decrease with temperature, but in most cases they were lower than \( \sqrt{3} \), the minimum value predicted by equation (6.9). The moments also showed marked drops at temperatures below ~150 K to ~1.3 \( \mu_B \); this had been attributed to antiferromagnetic couplings in the system.

The magnetic susceptibility results on \((\text{ClO}_2)_2[\text{Ir(SO}_3\text{F})_6] \), \( \text{Cs}_2[\text{Ir(SO}_3\text{F})_6] \) and \( \text{Ir(SO}_3\text{F})_4 \) are listed in Tables 6.3 to 6.5, respectively. The temperature dependence of their \( \mu_{\text{eff}} \) is shown in Fig 6.1.

In all three cases, the observed magnetic moments are lower than the expected values (the estimated uncertainty in \( \mu \) is about \( \pm 0.02 \mu_B \), contributions from temperature and weighing errors considered). \( \mu_{\text{eff}} \) ranges from 1.55 to 1.71 \( \mu_B \) for \( \text{Cs}_2[\text{Ir(SO}_3\text{F})_6] \).
### TABLE 6.3  MAGNETIC PROPERTIES OF \((\text{C}\text{C}_2\text{O}_2)_2[\text{Ir(SO}_3\text{F)}_6]\)

<table>
<thead>
<tr>
<th>T</th>
<th>(\chi_m^c)</th>
<th>(1/\chi_m^c)</th>
<th>(1/\chi_m^c) (calc'd)</th>
<th>(\mu_{\text{eff}})</th>
<th>(\mu_{\text{eff}}) (calc'd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>4.348x10^{-3}</td>
<td>230</td>
<td>234</td>
<td>1.64</td>
<td>1.63</td>
</tr>
<tr>
<td>108</td>
<td>3.236x10^{-3}</td>
<td>309</td>
<td>314</td>
<td>1.67</td>
<td>1.66</td>
</tr>
<tr>
<td>130</td>
<td>2.653x10^{-3}</td>
<td>377</td>
<td>371</td>
<td>1.66</td>
<td>1.67</td>
</tr>
<tr>
<td>155</td>
<td>2.294x10^{-3}</td>
<td>436</td>
<td>436</td>
<td>1.68</td>
<td>1.68</td>
</tr>
<tr>
<td>178</td>
<td>2.000x10^{-3}</td>
<td>500</td>
<td>498</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>203</td>
<td>1.770x10^{-3}</td>
<td>565</td>
<td>563</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>227</td>
<td>1.585x10^{-3}</td>
<td>631</td>
<td>626</td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>251</td>
<td>1.447x10^{-3}</td>
<td>691</td>
<td>689</td>
<td>1.70</td>
<td>1.71</td>
</tr>
<tr>
<td>276</td>
<td>1.326x10^{-3}</td>
<td>754</td>
<td>755</td>
<td>1.71</td>
<td>1.71</td>
</tr>
<tr>
<td>300</td>
<td>1.238x10^{-3}</td>
<td>808</td>
<td>816</td>
<td>1.72</td>
<td>1.71</td>
</tr>
</tbody>
</table>

\(K = \text{cgs cgs cgs } \mu_B \)  \(\mu_B \) units

\(1/\chi_m^c\) (calc'd) = \((T + 12)/0.382\)

### TABLE 6.4  MAGNETIC PROPERTIES OF \(\text{Cs}_2[\text{Ir(SO}_3\text{F)}_6]\)

<table>
<thead>
<tr>
<th>T</th>
<th>(\chi_m^c)</th>
<th>(1/\chi_m^c)</th>
<th>(1/\chi_m^c) (calc)</th>
<th>(\mu_{\text{eff}})</th>
<th>(\mu_{\text{eff}}) (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>3.831x10^{-3}</td>
<td>261</td>
<td>269</td>
<td>1.55</td>
<td>1.52</td>
</tr>
<tr>
<td>106</td>
<td>3.003x10^{-3}</td>
<td>333</td>
<td>339</td>
<td>1.59</td>
<td>1.58</td>
</tr>
<tr>
<td>129</td>
<td>2.494x10^{-3}</td>
<td>401</td>
<td>399</td>
<td>1.60</td>
<td>1.61</td>
</tr>
<tr>
<td>154</td>
<td>2.141x10^{-3}</td>
<td>467</td>
<td>462</td>
<td>1.62</td>
<td>1.63</td>
</tr>
<tr>
<td>179</td>
<td>1.880x10^{-3}</td>
<td>532</td>
<td>524</td>
<td>1.64</td>
<td>1.65</td>
</tr>
<tr>
<td>203</td>
<td>1.681x10^{-3}</td>
<td>595</td>
<td>586</td>
<td>1.65</td>
<td>1.66</td>
</tr>
<tr>
<td>229</td>
<td>1.536x10^{-3}</td>
<td>651</td>
<td>651</td>
<td>1.68</td>
<td>1.68</td>
</tr>
<tr>
<td>252</td>
<td>1.410x10^{-3}</td>
<td>709</td>
<td>709</td>
<td>1.68</td>
<td>1.68</td>
</tr>
<tr>
<td>277</td>
<td>1.290x10^{-3}</td>
<td>775</td>
<td>773</td>
<td>1.69</td>
<td>1.69</td>
</tr>
<tr>
<td>302</td>
<td>1.214x10^{-3}</td>
<td>824</td>
<td>836</td>
<td>1.71</td>
<td>1.70</td>
</tr>
</tbody>
</table>

\(K = \text{cgs cgs cgs } \mu_B \)  \(\mu_B \) units

\(1/\chi_m^c\) (calc) = \((T + 28)/0.395\)
### TABLE 6.5  MAGNETIC PROPERTIES OF Ir(SO$_3$F)$_4$

<table>
<thead>
<tr>
<th>T</th>
<th>$x_m^c$</th>
<th>$1/x_m^c$</th>
<th>$1/x_m^c$ (calc)</th>
<th>$\mu_{\text{eff}}$</th>
<th>$\mu_{\text{eff}}$ (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>284</td>
<td>9.06x10^{-4}</td>
<td>1104</td>
<td>1155</td>
<td>1.43</td>
<td>1.40</td>
</tr>
<tr>
<td>254</td>
<td>9.63x10^{-4}</td>
<td>1039</td>
<td>1040</td>
<td>1.40</td>
<td>1.40</td>
</tr>
<tr>
<td>230</td>
<td>1.028x10^{-3}</td>
<td>972.9</td>
<td>948.9</td>
<td>1.38</td>
<td>1.39</td>
</tr>
<tr>
<td>205</td>
<td>1.102x10^{-3}</td>
<td>907.7</td>
<td>853.5</td>
<td>1.34</td>
<td>1.39</td>
</tr>
<tr>
<td>177</td>
<td>1.320x10^{-3}</td>
<td>757.5</td>
<td>746.7</td>
<td>1.37</td>
<td>1.38</td>
</tr>
<tr>
<td>154</td>
<td>1.556x10^{-3}</td>
<td>642.8</td>
<td>659.0</td>
<td>1.38</td>
<td>1.37</td>
</tr>
<tr>
<td>130</td>
<td>1.758x10^{-3}</td>
<td>569.1</td>
<td>567.5</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>107</td>
<td>2.044x10^{-3}</td>
<td>489.3</td>
<td>479.8</td>
<td>1.32</td>
<td>1.34</td>
</tr>
<tr>
<td>78</td>
<td>2.963x10^{-3}</td>
<td>337.5</td>
<td>369.1</td>
<td>1.36</td>
<td>1.30</td>
</tr>
</tbody>
</table>

$K$  

\[
1/x_m^c \text{ (calc)} = (T + 19) / 0.262
\]
FIG 6.1 MAGNETIC MOMENTS OF \((\text{ClO}_2)_2\text{[Ir(SO}_3\text{F)}_6]\) AND \(\text{Cs}_2\text{[Ir(SO}_3\text{F)}_6]\)
1.64 to 1.72 $\mu_B$ for $(\text{ClO}_2)_2[\text{Ir(SO}_3\text{F)}_6]$ and 1.32 to 1.43 $\mu_B$ for \text{Ir(SO}_3\text{F)}_4$. At high temperature, the moments remain relatively constant and appear to obey the Curie-Weiss Law. This suggests either the presence of antiferromagnetic coupling in these systems, or perhaps, a slight departure of the coordination sphere around \text{Ir(IV)} from cubic symmetry.

Jahn-Teller distortion in a low-spin $d^5$ system is predicted from theory, and results in an axial elongation of the coordination sphere. However, since the splitting occurs in the orbitals not directly facing the ligands, a distortion of this type is usually very small compared to that present in species such as \text{Cu}^{2+}, d^9, which can give rise to severe axial elongations leading to the formation of square planar complexes. For \text{Ti}^{3+}, d^1, which has a $^2T_{2g}$ electronic ground state but with a positive spin-orbital coupling constant, $\lambda$, (resulting in a drop of $\mu_{\text{eff}}$ from $\sqrt{5}$ as $x \rightarrow 0$ to zero as $x \rightarrow \infty$, i.e., a larger range of variation in the moment as compared to a $d^5$ system), the magnetic behavior of \text{CsTi(SO}_4\text{)}\cdot12\text{H}_2\text{O} has been interpreted in terms of a large distortion of about 3.6 times the magnitude of the spin-orbital coupling $^{141}$. Because the effect of low symmetry on the magnetic moment of a compound is inversely proportional to $\lambda$, the spin orbital coupling constant, Jahn-Teller distortion may not be explicit in \text{Ir(IV)}, which has a $\lambda_0$ value almost 33 times that of \text{Ti(III)}. In any case, a distortion would lead to an increase of the magnetic moment, at the temperature of this study, to about
1.8 \mu_B, and this is certainly not observed here. Besides, the vibrational spectra do not offer any suggestion that a large distortion from \(O_h\) symmetry occurs. Therefore, it must be concluded that Jahn-Teller distortion, although it should be present in the iridium compounds studied here, does not appear to contribute to the observed lowering of the magnetic moment to below 1.73 \mu_B.

The other likely alternative — antiferromagnetic coupling, was therefore investigated. As the vibrational spectra of the \([\text{Ir}(\text{SO}_3\text{F})_6]^2^-\) and \([\text{Pt}(\text{SO}_3\text{F})_6]^2^-\) complexes show great similarities, and it is not really expected that they would be structurally very different, a dilution experiment involving a mixture of \((\text{ClO}_2)_2\text{[M(SO}_3\text{F})_6]\), M=Ir, Pt, was undertaken.

Starting with a mixture of metal powders containing 8.85 mole % of iridium, the mixed chloronium salt was prepared by reacting the metals with \(\text{ClO}_2\text{SO}_2\text{F}\) and \(\text{S}_2\text{O}_6\text{F}_2/\text{HSO}_3\text{F}\). The resulting product corresponded to the expected weight and had the appearance of \((\text{ClO}_2)_2\text{[Pt(SO}_3\text{F})_6]\). The result of a bulk magnetic susceptibility measurement on the mixture is listed in Table 6.6 and shown in Fig 6.2.

The \text{ClO}_2-containing complexes were used because, in the case of \([\text{Ir}(\text{SO}_3\text{F})_6]^2^-\), it is the only iridium complex that can be prepared comparatively easily. The presence of an excess reactant — \text{ClO}_2\text{SO}_3\text{F}, also ensure the formation of a product of high purity. The diamagnetic correction of \((250\pm15)\times10^{-6}\) cgs units, obtained for \((\text{ClO}_2)_2\text{[Pt(SO}_3\text{F})_6]\) over a temperature range of 81 to
<table>
<thead>
<tr>
<th>T</th>
<th>$\chi^C_m$</th>
<th>$1/\chi^C_m$</th>
<th>$1/\chi^C_m$ (calc)</th>
<th>$\mu_{\text{eff}}$ (calc)</th>
<th>$\mu_{\text{eff}}$ (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>1.506</td>
<td>664</td>
<td>728</td>
<td>1.91</td>
<td>1.82</td>
</tr>
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<td>1.515</td>
<td>660</td>
<td>675</td>
<td>1.83</td>
<td>1.81</td>
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<td>251</td>
<td>1.435</td>
<td>697</td>
<td>621</td>
<td>1.70</td>
<td>1.80</td>
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<td>1.616</td>
<td>619</td>
<td>575</td>
<td>1.72</td>
<td>1.78</td>
</tr>
<tr>
<td>204</td>
<td>1.911</td>
<td>523</td>
<td>523</td>
<td>1.77</td>
<td>1.76</td>
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<tr>
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<td>2.201</td>
<td>454</td>
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<td>1.74</td>
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<td>2.416</td>
<td>414</td>
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<td>1.73</td>
<td>1.71</td>
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<tr>
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<td>2.745</td>
<td>364</td>
<td>369</td>
<td>1.68</td>
<td>1.67</td>
</tr>
<tr>
<td>106</td>
<td>3.073</td>
<td>325</td>
<td>320</td>
<td>1.61</td>
<td>1.62</td>
</tr>
<tr>
<td>78</td>
<td>4.049</td>
<td>247</td>
<td>263</td>
<td>1.59</td>
<td>1.54</td>
</tr>
</tbody>
</table>

$K \times 10^{-3} \text{cgs} \quad \text{cgs} \quad \text{cgs} \quad \mu_B \quad \mu_B \quad \text{UNITS}$

$1/\chi^C_m\text{(calc)} = (T + 49)/0.484$
FIG 6.2  MAGNETIC MOMENT OF (ClO$_2$)$_2$[Ir(SO$_3$F)$_6$] DILUTED IN (ClO$_2$)$_2$[Pt(SO$_3$F)$_6$] (8.85 mol% Ir)
300 K, was used for both the complexes. Any Temperature Independent Paramagnetism present in these systems, estimated to be of the order of only 50×10^{-6} cgs units, should be compensated for by this procedure.

Although the accuracy of the measurements is greatly reduced by the introduction of (ClO_2)_2[Pt(SO_3F)_6], a diamagnetic species, as the majority constituent (the estimated uncertainty, arising mainly from weight measurements, ranges from ±0.12 μB at ~300 K to ±0.05 μB at ~80 K), it can be seen that the μ_{eff} obtained agree quite well with those calculated from equation (6.9), and in general, are consistently higher than those of pure (ClO_2)_2-[Ir(SO_3F)_6]. This shows that antiferromagnetic coupling does occur in the Ir(IV) fluorosulfate system, and is the most likely cause contributing to a lowering of μ_{eff} in these compounds. A similar explanation has been invoked for the hexahalo-complexes of Ir(IV), although in this latter class of compounds, a much more extensive coupling must be present as their magnetic moments are much lower than what is found here. This is consistent with the conclusion arrived at in Chapter 3 on the paramagnetic Pd(II) compounds that SO_3F is a much poorer medium for the superexchange to occur than monatomic ligands such as the halide ions.

For Ir(SO_3F)_3, diamagnetism is observed, with x_m of -(80±30) ×10^{-6} cgs units, compared to a sum of diamagnetic correction of -154×10^{-6} cgs units. It therefore appears that Ir(III) in the fluorosulfate is a spin-paired, d^8 system, not surprising in
of the high 10 $D_Q$ expected for a 5d metal in the +3 oxidation state. The coordination for Ir(III) in Ir(SO$_3$F)$_3$ can either be octahedral or square planar in order to explain the diamagnetism, but there appears to be no reason why a square planar geometry should prevail over an octahedral one for a d$^6$ system, unless by stereochemical restrictions which should not be present here. Therefore, the ligand configuration for Ir(SO$_3$F)$_3$ is most likely octahedral, or conversely, all fluorosulfate groups present in the compound must be bidentate, leading to the great complexity observed in the S-O stretching region in the i.r. spectrum.

6.C.4 SOLUTION STUDIES IN HSO$_3$F

6.C.4.1 CONDUCTIVITY MEASUREMENTS

Iridium-fluorosulfate was not intended to be investigated for its possible use as a superacid system in HSO$_3$F, although there exist indications that it may be one, at least for Ir(SO$_3$F)$_4$.

The conductivity measurements of solutions of (ClO$_2$)$_2$[Ir(SO$_3$-F)$_6$] in HSO$_3$F were undertaken to further establish its similarity to the corresponding platinum complex, and to provide evidence for the existence of [Ir(SO$_3$F)$_6$]$^{2-}$-containing species in solution. The results are shown in Fig 6.3 and listed in Table 6.7. From
FIG 6.3 CONDUCTIVITY OF (ClO₂)₂[Ir(SO₃F)₆] IN HSO₃F
TABLE 6.7  CONDUCTIVITY OF \( (C_2O_2)_2[\text{Ir(SO}_3\text{F)}_6] \) IN HSO\(_3\)F*

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\(10^{-2}\text{mol.kg}^{-1}\)  \(10^{-4}\Omega^{-1}\text{cm}^{-1}\)  unit

* interpolated
the plot, it becomes evident that the ionization of $(\text{ClO}_2)_2[\text{Ir}-(\text{SO}_3\text{F})_6]$ in $\text{HSO}_3\text{F}$ is very similar to that of the other $[\text{M}($\text{SO}_3\text{F}$)_6]^{2-}$ complexes, $\text{M}=$Pd, Pt, Ir, Sn, and a similar solution behavior must be present for all these solutes, i.e., $[\text{Ir}($\text{SO}_3\text{F}$)_6]^{2-}$ undergoes a basic dissociation in $\text{HSO}_3\text{F}$ according to:

$$[\text{Ir}($\text{SO}_3\text{F}$)_6]^{2-} + \text{HSO}_3\text{F} \rightleftharpoons \text{H}[\text{Ir}($\text{SO}_3\text{F}$)_6]^- + \text{SO}_3\text{F}^-,$$  \hspace{1cm} (6.10)

with an equilibrium constant of the order of $10^{-3}$, by comparison with the conductivity of the other hexafluorosulfato-complexes, described in detail in Chapters 5 and 9.

6.C.4.2 ELECTRONIC SOLUTION SPECTRA

All the compounds, with the exception of the insoluble Ba-$[\text{Ir}($\text{SO}_3\text{F}$)_6]$, form deeply colored solutions in $\text{HSO}_3\text{F}$. $\text{Ir}($\text{SO}_3\text{F}$)_3$ dissolves to form a bluish purple solution with an absorption maximum at 563 nm, $\epsilon=1\times10^4$ $\text{M}^{-1}\text{cm}^{-1}$. Both $\text{Ir}($\text{SO}_3\text{F}$)_4$ and $(\text{ClO}_2)_2-[\text{Ir}($\text{SO}_3\text{F}$)_6]$, although they are differently colored in the solid state, form solutions with an identical $\lambda_{\text{max}}$ at 200 nm, $\epsilon=1\times10^4$ $\text{M}^{-1}\text{cm}^{-1}$, suggesting the presence of similar species in solution. The high $\epsilon$ values imply that these absorptions must be due to charge transfer, most likely from $\text{L} \rightarrow \text{M}$. 
6.D CONCLUSION

The Ir(IV)-fluorosulfate system has been shown to be a paramagnetic analogue of the Pt(IV)-fluorosulfate system, although no attempts were made to test the iridium fluorosulfates' possible acidity in HSO₃F. The d⁵ low-spin electronic configuration of Ir(IV) resulted in some very interesting magnetic properties. From a dilution experiment involving the presumably isomorphous compounds of (ClO₂)₂[M(SO₃F)₆], M=Ir, Pt, antiferromagnetic exchange has been shown to be present in (ClO₂)₂[Ir(SO₃F)₆], although to a lesser extent than in the halide system. The contention that the superexchange mechanism cannot operate effectively through a fluorosulfate ligand, first suggested in the Pd(II)-fluorosulfate system, is supported by the results here.

Ir(SO₃F)₃ is diamagnetic, and therefore, most likely octahedral. This system was not investigated in much detail as it was not the original intention of studying iridium chemistry.
CHAPTER 7  MOLYDENUM(VI)-FLUOROSULFATE

7.A  INTRODUCTION

The investigation into the molydenum-fluorosulfate system is guided mostly by interests on synthetic and structural aspects. For a binary or ternary metal fluorosulfate, all previous work indicates that the highest oxidation state obtainable by the metal appears to be +4, although the coordination sphere around the central metal ion may be octahedral. This may be due to the limited oxidizing power of $\text{S}_2\text{O}_5\text{F}_2$, the strongest oxidant in the fluorosulfate system, or due to the steric crowding in the coordination sphere if a highly charged M(V) or M(VI) species is present.

For molydenum, as well as tungsten, the +6 oxidation state is readily attainable, even when relatively weak oxidizing agents are used. $\text{Mo(VI)}$ and $\text{W(VI)}$ are found in binary halides, $\text{MX}_6$, and their complexes, as well as in oxyhalides mainly of the two types $\text{MOX}_4$ and $\text{MO}_2\text{X}_2$, with $\text{X}=$F and Cl. With the possible exception of $\text{MoO}_2\text{F}_2$ and $\text{MF}_8^{2-}$, which are octa-coordinated, and $\text{MF}_7^{-}$, which is seven-coordinated, these compounds have octahedral structures. In most of the oxyhalides, an octahedral geometry is obtained by using bridging oxygen to form highly polymerized compounds, whereas $\text{MoOF}_4$ and $\text{WOF}_4$ appear to have bridging fluorine.

Complexes containing terminal M=O bonds generally show
strong Raman and i.r. absorptions in the region of 900-1100 cm\(^{-1}\), which can be assigned to metal oxygen stretching.\(^{200,205,206}\)

With the absence of detailed crystallographic data, vibrational spectra of the oxyhalides have been used frequently to elucidate structures. The substitution of a fluorosulfate group for a halide ligand in the oxyhalides introduces a potential bridging group and diminishes the importance of oxygen bridging. The reason for this expectation is the larger SO\(_3\)F ligand would increase the distance between intermolecular M=O groups and make bridging via the smaller oxygen atoms more difficult. Vibrational spectroscopy should be very helpful in this case because \(\nu\) M-O is readily detected and the conformation of the SO\(_3\)F group is also evident from vibrational spectroscopy.

Previously published work in this area is represented by the synthesis of WO(SO\(_3\)F)\(_4\) and a report on its \(^{19}\)F-n.m.r. and Raman spectra.\(^{211}\) The compound is a clear liquid at room temperature and appears to be polymeric with both bridging and terminal SO\(_3\)F groups; bands at \(~960\) cm\(^{-1}\) in its Raman spectrum has been assigned to the terminal W=O stretch. The reaction of Mo or Mo(CO)\(_6\) with S\(_2\)O\(_6\)F\(_2\) is reported to give rise to two products: MoO\(_2\)(SO\(_3\)F)\(_2\), a white solid, and a red liquid that analyzed as MoO(SO\(_3\)F)\(_2\).\(^{90}\)

Since the chemistries of Mo(VI) and W(VI) are very similar, it was decided to characterize the two previously reported molydenum oxyfluorosulfates and to attempt complex formation reactions on these compounds.
7.B EXPERIMENTAL

7.B.1 PREPARATION OF MoO₂(SO₃F)₂

\[ \text{Mo} + \text{xsS}_2\text{O}_6\text{F}_2 \rightarrow \text{MoO}_2(\text{SO}_3\text{F})_2 + \text{MoO}(\text{SO}_3\text{F})_4 + \text{S}_2\text{O}_5\text{F}_2 \]  

(7.1)

MoO₂(SO₃F)₂ was prepared by a method based on the original synthesis described by Shreeve and Cady. Molydenum metal (~0.5 g) was allowed to react with an excess of S₂O₆F₂ (~5 mL) in the temperature range from ~25 to ~70°C, resulting in the formation of a white solid and a red liquid. The mixture was vacuum filtered and washed with S₂O₆F₂. The removal of all volatile materials from the solid residue yielded MoO₂(SO₃F)₂.

MoO₂(SO₃F)₂ is an extremely hygroscopic white solid which decomposes at ~230°C into a blue solid.

Analysis

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MoO₂(SO₃F)₂ can also be conveniently prepared by reacting Mo metal with ClSO₃F in a quartz reactor at ~40°C. In a typical reaction, Mo metal powder (386 mg, 4.02 mmol) was reacted with ClSO₃F (~4 mL) for 2 weeks, giving MoO₂(SO₃F)₂ (1.315 g, 4.03 mmol) without contamination from MoO(SO₃F)₄.

\[ \text{Mo} + 6\text{ClSO}_3\text{F} \rightarrow \text{MoO}_2(\text{SO}_3\text{F})_2 + 2\text{S}_2\text{O}_6\text{F}_2 + 3\text{Cl}_2 \]  

(7.2)

S₂O₆F₂ was detected by its i.r. spectrum.
7.B.2 PREPARATION OF MoO(SO₃F)₄

The red filtrate from the reaction of Mo with S₂O₆F₂ was subjected to a dynamic vacuum with the sample held at ~40°C. After 12 hours, an orange-red liquid of very high viscosity was obtained. The sample analyzed as MoO(SO₃F)₄.

MoO(SO₃F)₄ appears to show a large range of miscibility with S₂O₆F₂ at room temperature. Upon heating at ~100°C, MoO(SO₃F)₄ decomposes according to:

\[ \text{MoO(SO}_3\text{F)}_4 \rightarrow \text{MoO}_2(\text{SO}_3\text{F)}_2 + \text{S}_2\text{O}_5\text{F}_2 \]  

with S₂O₅F₂ detected by its i.r. spectrum.

Analysis

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7.C DISCUSSION

7.C.1 SYNTHESIS AND GENERAL DISCUSSION

The reaction of molydenum metal with $\text{S}_2\text{O}_6\text{F}_2$ resulted in the formation of two Mo(VI)-containing compounds—a white solid, and a red liquid which analyzed as MoO(SO$_3$F)$_4$, instead of the previously reported Mo(IV)-containing species. Different ratios of the two oxyfluorosulfates seem to be obtainable under different reaction temperatures. If the reaction is performed at room temperature, most of the product is MoO(SO$_3$F)$_4$, but if the reaction temperature is raised to ~70°C, MoO$_2$(SO$_3$F)$_2$ is the main product. Furthermore, the thermal decomposition of MoO(SO$_3$F)$_4$ giving MoO$_2$-(SO$_3$F)$_2$, although this does not constitute a viable synthetic route, because of relatively high volatility of MoO(SO$_3$F)$_4$, also suggests a similar thermal stability trend. A scheme of formation of the two compounds, consistent with the above observations, may be presented:

\[
\begin{align*}
\text{Mo} + 3\text{S}_2\text{O}_6\text{F}_2 & \rightarrow '\text{Mo(SO}_3\text{F)}_6' \quad \text{(7.4)} \\
'\text{Mo(SO}_3\text{F)}_6' & \rightarrow \text{MoO(SO}_3\text{F)}_4 + \text{S}_2\text{O}_5\text{F}_2 \quad \text{(7.5)} \\
\text{MoO(SO}_3\text{F)}_4 & \rightarrow \text{MoO}_2(\text{SO}_3\text{F)}_2 + \text{S}_2\text{O}_5\text{F}_2 \quad \text{(7.6)}
\end{align*}
\]

The formation of molydenum hexakis(fluorosulfate) as the initial oxidation product is followed by the elimination of S$_2$O$_5$F$_2$, giving the two oxyfluorosulfates. The energetically favorable formation of a Mo=O bond, coupled with the resulting reduction in the steric crowding around Mo(VI), are most likely the contributing factors. This is also consistent with the general reaction
chemistry of $S_2O_6F_2$, where the initial reaction of -OSO$_2$F radicals leads to the formation of a fluorosulfate. The ability of moly­
denum to form Mo=O bonds with $p_n$-$d_n$ donation from filled oxygen orbitals probably promotes the decomposition.

Whereas WO(SO$_3$F)$_4$ was reported to be obtainable by the reac­tion of the metal with $S_2O_6F_2$ at ~100°C, it appeared to be the sole product $^{27}$. When the synthesis was repeated in this study, the removal of all volatile materials yielded a small amount of white precipitate. This could possibly be WO$_2$(SO$_3$F)$_2$, but no attempts were made to identify this solid or to increase its yield.

In order to test the complex formation ability of the Mo(VI)-oxyfluorosulfate, a slight excess of CIO$_2$SO$_3$F was added to a mix­ture of MoO$_2$(SO$_3$F)$_2$ and MoO(SO$_3$F)$_4$ in $S_2O_6F_2$. The removal of all volatile materials at ~50°C did not lead to any weight increase and therefore, no complex formation was evident. If a complex was formed, it must have been of a rather low thermal stability.

7.C.2 VIBRATIONAL SPECTRA

7.C.2.1 MoO$_2$(SO$_3$F)$_2$

The vibrational spectra of MoO$_2$(SO$_3$F)$_2$ show a distinct pair of sharp peaks at ~994 and 955 cm$^{-1}$, with inverted intensities in the Raman and i.r.. These vibrations are assigned to stretching
vibrations of the \( \text{O}=\text{M}=\text{O} \) group, and their positions compare well with those found for liquid or gaseous \( \text{MoO}_2\text{Cl}_2 \), in which terminal \( \text{Mo}=\text{O} \) bonds have been postulated \(^{200}\). Therefore, it appears that terminal \( \text{Mo}=\text{O} \) bonds are present, and the relatively high intensity of the symmetric mode at 994 cm\(^{-1}\) in the i.r. spectrum is consistent with a non linear \( \text{O}=\text{Mo}=\text{O} \) arrangement. The vibrational frequencies for \( \text{MoO}_2(\text{SO}_3\text{F})_2 \) are shown in Table 7.1 in comparison with those of \( \text{SnCl}_2(\text{SO}_3\text{F})_2 \) \(^{33}\).

There are three possible geometries for the compound:

a) tetrahedral with monodentate \( \text{SO}_3\text{F} \) groups,

b) trigonal bipyramidal with one monodentate-and one bridging \( \text{SO}_3\text{F} \) group, or,

c) octahedral with only bridging \( \text{SO}_3\text{F} \) groups and cis-\( \text{M}=\text{O} \) bonds.

The vibrational spectra indicate the absence of monodentate \( \text{SO}_3\text{F} \) groups, thus ruling out the first two possibilities. The observed spectra are most consistent with the presence of bidentate \( \text{SO}_3\text{F} \) groups in the compound, as indicated by the characteristically strong asymmetric \( \text{SO}_2 \) stretch at \( \sim 1170 \text{ cm}^{-1} \) in the i.r. spectrum.

Strong vibrational couplings within the \( \text{MoO}_2(\text{SO}_3\text{F})_2 \) moiety and best reflected in the \( \text{SO}_2 \) stretching vibrations at \( \sim 1000 \) and \( \sim 1200 \text{ cm}^{-1} \), and between \( \nu \text{ M}=\text{O} \) and \( \delta \text{ O}-\text{SO}_2\text{F} \) vibrations producing Raman intensity enhancements at \( \sim 650, \sim 450 \) and \( \sim 280 \text{ cm}^{-1} \), as found in anions of the type \([\text{M(}\text{SO}_3\text{F})_n]\)^{\text{M}^-}, seem to be absent. The position of \( \nu \text{ SF} \) is found at 873-885 cm\(^{-1}\), indicating a strong
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Table 7.1 VIBRATIONAL FREQUENCIES OF MoO$_2$(SO$_3$F)$_2$
Mo(VI)-OSO₂F interaction. In general, the vibrational bands assigned to the SO₃F group correspond closely to a pattern shown by SnCl₂(SO₃F)₂, also listed in Table 7.1; however, in the latter case, a linear Cl-Sn-Cl grouping is evident from both vibrational and ¹¹⁹Sn Mössbauer spectroscopy. For this compound, the presence of bidentate bridging SO₃F groups has been proposed.

For MoO₂(SO₃F)₂, an arrangement consisting of two oxygen atoms on one side of the molecule and four bridging SO₃F groups on the other side of the distorted octahedron can be proposed here.

7.C.2.2 MoO₂(SO₃F)₄

The vibrational frequencies of MoO₂(SO₃F)₄ are listed in comparison with Raman data of WO₂(SO₃F)₄ in Table 7.2 (the relative intensities of the Raman bands of WO₂(SO₃F)₄ were not given in the reference). As can be seen, a good correspondence can be made between the spectra of the two compounds, suggesting structural similarities. The terminal Mo=O stretch is assigned to a sharp Raman band at 933 cm⁻¹. The presence of both bridging and terminal SO₃F groups is indicated by the band positions. The band at ~700 cm⁻¹, present also in the spectrum of WO₂(SO₃F)₄, is presumably due to bridging SO₃F groups in a specific conformational mode. Again, strong vibrational couplings are not observed for MoO₂(SO₃F)₄.
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7.C.3 $^{19}$F-n.m.r. SPECTRA OF MoO(SO$_3$F)$_4$

Since MoO(SO$_3$F)$_4$ is very soluble in S$_2$O$_6$F$_2$, solution $^{19}$F-n.m.r. spectra of the compound were obtained. The spectrum of a ~10 mol% solution in S$_2$O$_6$F$_2$ consists of a single broad peak at -42.3 ppm (Fig 7.1). The peak is highly asymmetric, with a shoulder definitely present on the low-field side. When the concentration of MoO(SO$_3$F)$_4$ is increased to almost 100%, with only a trace of S$_2$O$_6$F$_2$ as the reference, two definite resonances become evident at -42.0 and -41.4 ppm, although they are extremely broad and overlapping.

**FIG. 7.1**

[Diagram showing F-19 nmr spectra of MoO(SO$_3$F)$_4$]
A dilution of MoO(SO$_3$F)$_4$ with S$_2$O$_6$F$_2$ is expected to lead to a break down of the polymer and thus a decrease in the number of bridging SO$_3$F groups. Therefore, the resonance at -42.0 ppm can be assigned as due to monodentate SO$_3$F groups while the one at -41.4 ppm must be due to bridging SO$_3$F groups. The extreme broadness of the peaks indicates an exchange process involving the inter-convertion of the two types of SO$_3$F groups or possibly a random polymerization process.

The broadness of the peaks also prevented any attempts at quantitative measurements on the relative abundance of the two types of SO$_3$F groups, but it appears that in almost pure MoO(SO$_3$F)$_4$, the resonance due to the bridging species is slightly more prominent. If the coordination around Mo(VI) is octahedral, the ratio of bridging to terminal SO$_3$F groups should be 1:3. The observation here implies an almost equal population for both types of ligands, or an increase in the coordination number. Octa-coordination for Mo(VI) has been suggested for MoO$_2$F$_2$ \cite{200} and MoF$_8^2-$ \cite{201}. It is also likely, from the broadness of the resonance and the lack of appreciable vibrational couplings between $\nu$ Mo-O and $\nu$ SO$_3$F, that dynamic species with possibly various coordination numbers from six to eight, or even higher, may be present.
7.D CONCLUSION

Two Mo(VI) oxyfluorosulfates have been characterized mainly by vibrational spectroscopy. For MoO$_2$(SO$_3$F)$_2$, a white solid, hexa-coordination of molydenum with a cis-0=Mo=0 bond and bridging SO$_3$F groups is suggested. For MoO(SO$_3$F)$_4$, both bridging and terminal SO$_3$F groups are present, with a terminal Mo=0 bond evident. From $^{19}$F-n.m.r., MoO(SO$_3$F)$_4$ appears to undergo intermolecular exchange reactions between the two types of differently bonded SO$_3$F ligands, possible resulting in the compound's existence as a liquid at room temperature.

The presence of Mo(SO$_3$F)$_6$ as a possible intermediate in the synthesis of these two compounds is suggested, although it could not be isolated. Neither oxyfluorosulfates appear to have any tendency towards accepting SO$_3$F$^-$ to form anionic complexes.
CHAPTER 8  GERMANIUM- AND TIN- FLUOROSULFATE

8.A  INTRODUCTION

The group IV halides are potential halide ion acceptors because of the possibility of the expansion of their coordination spheres to six (carbon is an exception due to its lack of available low energy d-orbitals). The covalency of the bond between the element and electronegative atoms such as oxygen and the halogens increases as the element becomes more non-metallic, with the result that the lighter halides are volatile whereas PbF₄ is a high-melting crystal. The fluorosulfates of C(IV)⁷⁹, Sn(IV)³³ and Pb(IV)²⁰⁷, and the adduct of Si(SO₃F)₄·2CH₃CN⁹⁶ have been reported, but only Sn(SO₃F)₄ is known to form anionic complexes.³² The other fluorosulfates are either unstable at room temperature or dissociate in HSO₃F solutions.

During the investigation into the palladium-fluorosulfate system, described in Chapter 3, it became apparent that Sn(SO₃F)₄ could have a SO₃F-accepting ability comparable to that of Pt(SO₃F)₄. Unfortunately, Sn(SO₃F)₄ reportedly is insoluble in HSO₃F³³, thus ruling out its usefulness as a superacid in that solvent system. As Pb(SO₃F)₄ was reported to exhibit basic behavior in HSO₃F²⁰⁷, it was decided to investigate the hitherto unknown germanium-fluorosulfate system as possibly an easily obtainable superacid in HSO₃F.

Sn(SO₃F)₄ is similar to Pt(SO₃F)₄ in that in both systems,
the hexakis(fluorosulfato)-complexes can be synthesized. A complex of the empirical formula of CsPt(SO₃F)₅ was used as an illustration of the polymerization of the platinum-fluorosulfate system in solution, although little structural information could be obtained from vibrational spectra analysis other than that it was polymeric in the solid state. By using $^{119}$Sn Mössbauer spectroscopy, which had been applied to the study of Sn(SO₃F)₄ and [Sn-(SO₃F)₄]²⁻, it may be possible to provide more insights into the structure of the analogous [Sn(SO₃F)₅]ₓ⁻ complex, if it can be synthesized. The solution behavior of the tin-fluorosulfate system will also be investigated and compared to those of other M(IV)-fluorosulfates.
8.B  EXPERIMENTAL

8.B.1  Sn(IV)-FLUOROSULFATE

8.B.1.1  PREPARATION OF Sn(SO$_3$F)$_4$

Sn + 2S$_2$O$_6$F$_2$ $\xrightarrow{HSO_3F}$ Sn(SO$_3$F)$_4$  \hspace{3em} (8.1)

In a typical reaction, tin metal granules (121 mg, 1.019 mmol) were reacted with a mixture of S$_2$O$_6$F$_2$ (~3 mL) and HSO$_3$F (~2 mL) at room temperature. A rapid reaction occurred and after 3 days, all of the metal had reacted and a white precipitate had formed. The removal of all volatile materials yielded a product identified by vibrational spectroscopy as Sn(SO$_3$F)$_4$ (530 mg, 1.029 mmol).

8.B.1.2  PREPARATION OF KSn(SO$_3$F)$_5$

KCl + HSO$_3$F $\rightarrow$ KSO$_3$F + HCl  \hspace{3em} (8.2)

KSO$_3$F + Sn + 2S$_2$O$_6$F$_2$ $\xrightarrow{HSO_3F}$ KSn(SO$_3$F)$_5$  \hspace{3em} (8.3)

Tin metal granules (402 mg, 3.387 mmol) were added to a reactor containing solid KSO$_3$F obtained from the solvolysis of KCl (251 mg, 3.366 mmol) in HSO$_3$F. After a mixture of S$_2$O$_6$F$_2$/HSO$_3$F (~3 mL) was distilled into the reactor, a violent reaction occurred at room temperature. The reaction mixture was subsequently kept at ~50°C for 12 hours to ensure completion. The removal of all volatile materials yielded a glass-like material which has a weight corresponding to that of KSn(SO$_3$F)$_5$ (2.201 g, 3.370 mmol).

KSn(SO$_3$F)$_5$ is a clear, hygroscopic crystalline solid which
may be a supercooled glass at room temperature. It is very soluble in HSO₃F.

8.B.1.3 PREPARATION OF CsSn(SO₃F)₅

\[
\text{CsCl} + \text{HSO}_3\text{F} \rightarrow \text{CsSO}_3\text{F} + \text{HCl} \quad (8.4)
\]

\[
\text{CsSO}_3\text{F} + \text{Sn} + 2\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{CsSn(SO}_3\text{F)}_5 \quad (8.5)
\]

In a manner analogous to the preparation of KSn(SO₃F)₅, tin metal granules (566 mg, 4.769 mmol) were allowed to react with CsSO₃F formed from the solvolysis of CsCl (802 mg, 4.764 mmol) in HSO₃F, giving a white, crystalline, hygroscopic product which analyzed as CsSn(SO₃F)₅ (3.492 g, 4.675 mmol).

CsSn(SO₃F)₅ is soluble in HSO₃F.

Analysis

<table>
<thead>
<tr>
<th></th>
<th>S</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
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<td>12.72</td>
</tr>
<tr>
<td>Found %</td>
<td>21.11</td>
<td>12.39</td>
</tr>
</tbody>
</table>

8.B.1.4 PREPARATION OF Cs₂[Sn(SO₃F)₆]

\[
2\text{CsCl} + \text{Sn} + 3\text{S}_2\text{O}_6\text{F}_2 \xrightarrow{\text{HSO}_3\text{F}} \text{Cs}_2[\text{Sn(SO}_3\text{F)}_6] + \text{Cl}_2 \quad (8.6)
\]

A mixture of dried CsCl (839 mg, 4.983 mmol) and tin metal granules (296 mg, 2.494 mmol) is reacted with S₂O₆F₂/HSO₃F (~5 mL) at ~90°C for 1 day. After the removal of all volatile materials from the solution at 90°C, a white solid which corresponds to Cs₂[Sn(SO₃F)₆] (2.444 g, 2.497 mmol) was obtained.

K₂[Sn(SO₃F)₆] can be prepared similarly.
8.B.2 GERMANIUM-FLUOROSULFATE

8.B.2.1 PREPARATION OF GeF$_2$(SO$_3$F)$_2$

Ge + 2S$_2$O$_6$F$_2$ $\xrightarrow{\text{HSO}_3F}$ GeF$_2$(SO$_3$F)$_2$ + 2SO$_3$ \hspace{1cm} (8.7)

Germanium metal powder (129 mg, 1.777 mmol) was reacted with a mixture of S$_2$O$_6$F$_2$/HSO$_3$F (~2 mL) at ~80°C for 3 days. A white sublimate formed on the cooler parts of the reactor and the product was vacuum filtered, washed with S$_2$O$_6$F$_2$ and dried by evacuation at room temperature for 30 minutes. A white powder which analyzed as GeF$_2$(SO$_3$F)$_2$ (428 mg, 1.386 mmol) was obtained; the yield was very low due to the loss of the product by removal in vacuo.

GeF$_2$(SO$_3$F)$_2$ can also be obtained by the reaction of germanium metal powder with S$_2$O$_6$F$_2$ at ~150°C for 1 week. This method, although takes longer to complete, eliminates the filtration process.

GeF$_2$(SO$_3$F)$_2$ is a white, hygroscopic, flaky solid which is insoluble in HSO$_3$F. It is sublimable at room temperature in vacuo.

Analysis

<table>
<thead>
<tr>
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<th>Ge</th>
<th>S</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
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<td>20.77</td>
<td>24.62</td>
</tr>
<tr>
<td>Found %</td>
<td>21.06</td>
<td>18.68</td>
<td>22.12</td>
</tr>
</tbody>
</table>

Although the analytical result appears to be low, the calculated mole ratio for Ge:S:F is 1.000:2.009:4.014, an excellent comparison with the expected 1:2:4 ratio.
8.B.2.2 PREPARATION OF $(\text{C1O}_2)_2[\text{Ge(SO}_3\text{F)}_6]$ 

$$2\text{C1O}_2\text{SO}_3\text{F} + \text{Ge} + 2\text{S}_2\text{O}_6\text{F}_2 \rightarrow \text{H}_2\text{SO}_3\text{F} (\text{C1O}_2)_2[\text{Ge(SO}_3\text{F)}_6] \quad (8.8)$$

A mixture of $\text{C1O}_2\text{SO}_3\text{F} (~1 \text{ mL})$ and $\text{S}_2\text{O}_6\text{F}_2 (~4 \text{ mL})$ was distilled into a reactor containing germanium metal powder (130 mg, 1.791 mmol). An exothermic reaction occurred at room temperature, and the metal dissolved into the deep red $\text{C1O}_2\text{SO}_3\text{F}$ layer. After keeping the reaction mixture at $\sim 50^\circ \text{C}$ for 1 day to ensure a complete reaction, the excess liquid reactants were removed by pumping at $\sim 80^\circ \text{C}$ for 12 hours. A light yellow solid, which analyzed as $(\text{C1O}_2)_2[\text{Ge(SO}_3\text{F)}_6]$ (126 mg, 0.157 mmol) was obtained; again, the low yield was caused by the volatility of the product.

$(\text{C1O}_2)_2[\text{Ge(SO}_3\text{F)}_6]$ is a light yellow, hygroscopic solid. It is sublimable in vacuo at room temperature, but melts at $\sim 145^\circ \text{C}$ under an atmosphere of nitrogen, giving off a $\text{C1O}_2\text{SO}_3\text{F}$-like gas.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Ge</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated %</td>
<td>9.05</td>
<td>14.22</td>
</tr>
<tr>
<td>Found %</td>
<td>8.75</td>
<td>14.22</td>
</tr>
</tbody>
</table>
8.C DISCUSSION

8.C.1 SYNTHESIS AND GENERAL DISCUSSION

The synthesis of Sn(SO$_3$F)$_4$, using the medium of S$_2$O$_6$F$_2$/HSO$_3$F, is an improvement over the original synthesis using SnCl$_4$, both in terms of speed and purity of the product. Because of the possibility of HSO$_3$F being reduced by tin metal, a larger than normal ratio of S$_2$O$_6$F$_2$ (~75 \%) was used as a precaution, and the reaction mixture had to be shaken from time to time to ensure no local depletion of S$_2$O$_6$F$_2$. When S$_2$O$_6$F$_2$ was omitted from the reaction, the glass reactor became badly etched and the solution took on a blue color, most likely due to sulfur cations. For the same reason, the solvolysis of CsCl or KCl in HSO$_3$F cannot be performed in the presence of metallic tin, which must be added to the alkali-metal fluorosulfate in the dry-box. Although Sn(SO$_3$F)$_4$ is insoluble in HSO$_3$F, the reactivity of tin metal towards S$_2$O$_6$F$_2$ is greatly enhanced by the addition of the acid, suggesting a very slight solubility, combined with the energetically highly favorable formation of Sn(SO$_3$F)$_4$ from Sn.

CsSn(SO$_3$F)$_5$ does not precipitate Sn(SO$_3$F)$_4$ in solutions in HSO$_3$F; this argues against the complex as being a mixture of Sn-(SO$_3$F)$_4$ and Cs$_2$[Sn(SO$_3$F)$_6$]. Furthermore, highly concentrated solutions can be obtained at room temperature (~1.3 mol/kg). KSn(SO$_3$F)$_5$ is extremely soluble in HSO$_3$F, and at high concentrations, results in the formation of a glass-like material which
loses HS\textsubscript{3}F very slowly.

The attempted synthesis of Ge(SO\textsubscript{3}F)\textsubscript{4} resulted in the formation of a compound that analyzed as GeF\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2}. The systematic lowering of the analytical results for the compound seems to suggest the presence of an inert impurity in the sample; small fragments of glass in the germanium metal powder could be the source of such an error. Mixed halide-fluorosulfate compounds of Sn(IV) such as SnF\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2} \textsuperscript{208} and SnCl\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{3} \textsuperscript{33} are known; \textsuperscript{119}Sn Mössbauer and vibrational spectroscopy suggest the presence of terminal halide ligands and bridging SO\textsubscript{3}F groups in these compounds. SnF\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2} can be prepared by the replacement of chlorine in SnF\textsubscript{2}Cl\textsubscript{2} by S\textsubscript{2}O\textsubscript{6}F\textsubscript{2} or ClSO\textsubscript{3}F \textsuperscript{208}, and SnCl\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2} can be obtained by a ligand redistribution reaction involving SnCl\textsubscript{4} and Sn(SO\textsubscript{3}F)\textsubscript{4} \textsuperscript{33}. The existence of GeF\textsubscript{2}(SO\textsubscript{3}F)\textsubscript{2} instead of Ge(SO\textsubscript{3}F)\textsubscript{4} as a stable compound at room temperature provides a transition between the Si-SO\textsubscript{3}F and the Sn-SO\textsubscript{3}F systems. Due to the preferential formation of a Si-F covalent bond over a Si-OSO\textsubscript{2}F bond, the product obtained from the fluorosulfonation of silicon compounds is invariably SiF\textsubscript{4}, and the compound Si(SO\textsubscript{3}F)\textsubscript{4}·2CH\textsubscript{3}CN requires stabilization by the two coordinated nitriles \textsuperscript{66}. Sn(SO\textsubscript{3}F)\textsubscript{4}, on the other hand, is a crystalline solid stable up to 216°C \textsuperscript{33}. In view of this, and the expectation that the electronegativity of germanium is between that of silicon and tin, it is not surprising to find the observed stability of the Ge-OSO\textsubscript{2}F bond with respect to replacement by a Ge-F bond.
Ge(SO$_3$F)$_4$, however, can be stabilized by the formation of [Ge(SO$_3$F)$_6$]$^{2-}$ complexes, but these also exhibit quite low thermal stabilities, subliming or decomposing in vacuo at room temperature. Attempts to prepare Cs$_2$[Ge(SO$_3$F)$_6$] resulted in the formation of a CsSO$_3$F-rich product, as shown by Raman and i.r. spectroscopy. (ClO$_2$)$_2$[Ge(SO$_3$F)$_6$] could be obtained as a pure product because the ClO$_2$SO$_3$F formed from the decomposition is also volatile, but in order to ensure the complete removal of the excess ClO$_2$SO$_3$F used in the reaction, a large quantity of the desired product was also lost. An alternative method may be to use filtration instead of evacuation as a means of removing excess reactants, followed by washing with liquid SO$_2$ which can be evaporated at room temperature without the application of a vacuum.

8.C.2 VIBRATIONAL SPECTRA

8.C.2.1 CsSn(SO$_3$F)$_5$

As mentioned in Chapter 5, the vibrational spectra of CsSn-(SO$_3$F)$_5$ are very similar to those of KRu(SO$_3$F)$_5$ and CsPt(SO$_3$F)$_5$, suggesting structural similarities. Only a relatively poorly resolved Raman spectrum could be obtained for CsSn(SO$_3$F)$_5$ due to the sample's fluorescence in the laser radiation. The Raman frequencies of CsSn(SO$_3$F)$_5$ are compared to the literature values
Table 8.1  RAMAN FREQUENCIES OF CsSn(SO$_3$F)$_5$

<table>
<thead>
<tr>
<th>CsSn(SO$_3$F)$_5$</th>
<th>Sn(SO$_3$F)$_4$</th>
<th>$K_2[Sn(SO_3F)_6]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1430 w</td>
<td>1431 s</td>
<td>1407 m</td>
</tr>
<tr>
<td>1406 w</td>
<td>1420 s,sh</td>
<td>1390 m</td>
</tr>
<tr>
<td>1265 m</td>
<td></td>
<td>1278 ms</td>
</tr>
<tr>
<td>1220 w</td>
<td>1233 s</td>
<td>1228 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1208 w</td>
</tr>
<tr>
<td>1130 w</td>
<td>1124 s</td>
<td></td>
</tr>
<tr>
<td>1112 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1060 w</td>
<td>1075 s</td>
<td>1096 s</td>
</tr>
<tr>
<td>1055 w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 w</td>
<td>986 w, 911 m</td>
<td>1002 m</td>
</tr>
<tr>
<td>850 w</td>
<td>845 m</td>
<td>859 m</td>
</tr>
<tr>
<td>820 w</td>
<td>827 m</td>
<td>836 m</td>
</tr>
<tr>
<td></td>
<td>640 w,sh</td>
<td>823 m</td>
</tr>
<tr>
<td>630 m</td>
<td>632 s</td>
<td>625 s</td>
</tr>
<tr>
<td>605 vw</td>
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</tr>
<tr>
<td>585 w</td>
<td>589 s</td>
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</tr>
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<td>560 w</td>
<td>552 m</td>
<td>560 m</td>
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<td>430 w</td>
<td>427 s</td>
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<tr>
<td></td>
<td>320 w</td>
<td>360 m</td>
</tr>
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<td>266 w</td>
</tr>
</tbody>
</table>
for Sn(SO$_3$F)$_4$ and K$_2$[Sn(SO$_3$F)$_6$] in Table 8.1

It appears that the Raman spectrum of CsSn(SO$_3$F)$_5$ contains bands from both the other two compounds' spectra, but some very intense bands have been shifted, indicating the existence of not merely a mixture of the two known compounds. For example, the strong SO$_2$ symmetric stretch is shifted to 1220 cm$^{-1}$; similarly, a downward shift of the band at $\sim$1060 cm$^{-1}$ is also evident.

The similarities between the three spectra are not unexpected because [Sn(SO$_3$F)$_6$]$^{2-}$ contains only monodentate SO$_3$F groups, Sn-(SO$_3$F)$_4$ has an equal number of monodentate and bidentate SO$_3$F groups, and for CsSn(SO$_3$F)$_5$, there should be one bidentate SO$_3$F group for every four monodentate SO$_3$F groups. The presence of the diagnostic band at $\sim$1130 cm$^{-1}$ in both the i.r. and Raman spectra of CsSn(SO$_3$F)$_6$ confirms the existence of bidentate bridging SO$_3$F groups.

8.C.2.2 GeF$_2$(SO$_3$F)$_2$ AND (CIO$_2$)$_2$[Ge(SO$_3$F)$_6$]

Again because of the fluorescence of the sample when it is irradiated by the laser, only a rather poorly resolved Raman spectrum could be obtained for GeF$_2$(SO$_3$F)$_2$. The i.r. spectrum of the compound has a broad absorption from $\sim$1000 to $\sim$1150 cm$^{-1}$, indicating the presence of bridging SO$_3$F ligands. The vibrational frequencies of GeF$_2$(SO$_3$F)$_2$ are listed in Table 8.2 and compared to the i.r. frequencies of SnF$_2$(SO$_3$F)$_2$.

The absence of the strongly Raman active symmetric SO$_3$
<table>
<thead>
<tr>
<th>I.R.</th>
<th>R.</th>
<th>I.R.</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1390 vs</td>
<td>1426 w</td>
<td>1420 m,sh</td>
<td>$\nu_{SO_3}$</td>
</tr>
<tr>
<td>~1100 vs,sh</td>
<td>1095 w</td>
<td>1115 vs,b</td>
<td>$\nu_{SO_3}$</td>
</tr>
<tr>
<td>~1050 vs, vb</td>
<td>1064 w</td>
<td>1103 s,sh</td>
<td>$\nu_{SO_3}$</td>
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<tr>
<td>880 vs</td>
<td>880 vs</td>
<td>855 vs</td>
<td>$\nu_{SF}$</td>
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<tr>
<td>770 vs</td>
<td></td>
<td></td>
<td>$\nu_{Ge-F \text{ asym}}$</td>
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<td>660 s</td>
<td>656 w,sh</td>
<td>628 ms</td>
<td>$SO_3$ \text{ bend}$</td>
</tr>
<tr>
<td>570 s</td>
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<td>$SO_3$ \text{ bend}$</td>
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<tr>
<td>555s</td>
<td>560 w</td>
<td>548 vs</td>
<td>$SO_3$ \text{ bend}$</td>
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<td>495 s</td>
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<td>$\nu_{Ge-OSO_2F}$</td>
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<td>420 m</td>
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<td>~350 m</td>
<td></td>
<td></td>
<td>$\nu_{Sn-OSO_2F}$</td>
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<td>280 w</td>
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</table>
stretch at ~1220 cm\(^{-1}\) in the spectrum of \(\text{GeF}_2(\text{SO}_3\text{F})_2\) denotes the absence of monodentate, tridentate and ionic \(\text{SO}_3\text{F}\) groups. Therefore, together with the feature noted in the \(\text{SO}_2\) stretching region in the i.r. spectrum, it can be concluded that the fluorosulfate is present in a bidentate form. A good comparison can be made with the i.r. spectrum of \(\text{SnF}_2(\text{SO}_3\text{F})_2\) \(^{208}\), suggesting similarities in the structure and bonding of the two compounds. A strong band at 770 cm\(^{-1}\) in the i.r. spectrum of \(\text{GeF}_2(\text{SO}_3\text{F})_2\), not observed in its Raman spectrum, is assigned to the asymmetric stretching of the Ge-F bonds. A relatively strong Raman band at 648 cm\(^{-1}\) is most likely the \(\nu\text{Ge-F sym}\) (this assignment is based on the fact the band at ~650 cm\(^{-1}\) is usually not very strongly Raman active relative to the bands at ~450 and ~280 cm\(^{-1}\)). For the tin compound, the analogous vibrations are found at 691 and 612 cm\(^{-1}\). The mutual exclusion of the two Ge-F stretching vibrations indicates a linear or nearly linear configuration for the [F-Ge-F] unit; a similar conclusion has been reached for the chlorine \(^{33}\), fluorine \(^{208}\) and methyl \(^{96}\) derivatives of tin(IV), thus indicating that all four compounds are closely related structurally.

Assuming a linearity in the [Hal-M-Hal] bonds, a comparison can be made on the approximate stretching force constants of \(\text{GeF}_2(\text{SO}_3\text{F})_2\), \(\text{SnF}_2(\text{SO}_3\text{F})_2\) and \(\text{SnCl}_2(\text{SO}_3\text{F})_2\) \(^{206}\) (stretch-bend interactions are ignored):
\[ v_1(A_{1g}) = \left( \frac{\mu_h(k + k_i)}{5.889 \times 10^{-7}} \right)^{1/2} \]  
(8.9)

\[ v_2(A_{2u}) = \left( \frac{(\mu_h + 2\mu_m)(k + k_i)}{5.889 \times 10^{-7}} \right)^{1/2} \]  
(8.10)

where \( v \) is the frequency in cm\(^{-1}\),

\( \mu \) is the reciprocal of the atomic masses of the halogen or metal atoms in a.m.u., and

\( k, k_i \) are the stretching and stretch-stretch interaction force constants in m dynes/Å, respectively.

By using \( v_1(\text{Ge-F}) = 648 \) cm\(^{-1}\), \( v_2(\text{Ge-F}) = 770 \) cm\(^{-1}\),

\( v_1(\text{Sn-F}) = 612 \) cm\(^{-1}\), \( v_2(\text{Sn-F}) = 691 \) cm\(^{-1}\) \text{208},

\( v_1(\text{Sn-Cl}) = 356 \) cm\(^{-1}\), \( v_2(\text{Sn-Cl}) = 411 \) cm\(^{-1}\) \text{33},

the following force constants are obtained:

\[
\begin{align*}
   k(\text{Ge-F}) &= 4.53 & k_i(\text{Ge-F}) &= 0.17 \\
   k(\text{Sn-F}) &= 4.12 & k_i(\text{Sn-F}) &= 0.07 \\
   k(\text{Sn-Cl}) &= 2.43 & k_i(\text{Sn-Cl}) &= 0.22
\end{align*}
\]

Stretch-stretch interaction can also arise from the involvement of \( \pi \) orbitals in the bonding; as one M-Hal bond stretches, lessening the interaction of the \( d_\pi \) orbitals on the metal to the halogen, these \( \pi \) orbitals will become more available to the halogen on the other side, and \( \pi \) bonding to them will become stronger. Consequently, this would result in \( k_i \) having a positive sign \text{206}. The degree of \( \pi \)-bonding in the chlorine-containing compound is large, as can be seen from the relative values of \( k_i \) and \( k \). This is consistent with chlorine having \( d \)-orbitals of lower energy.
than fluorine has. In spite of the increase in \( \pi \)-bonding, the Sn-Cl bond is weaker than the Sn-F bond, presumably due to an increase in covalent character in the latter. For the same reason, the Ge-F bond is shown by these calculations to be much stronger than the Sn-F bond, and supports the contention that this may be an important factor contributing to the preferential formation of \( \text{GeF}_2(\text{SO}_3\text{F})_2 \) instead of \( \text{Ge}(\text{SO}_3\text{F})_4 \). By extending the force constant calculations to the literature values for the vibrational frequencies of the tetrahedral fluorides of \( \text{CF}_4, \text{SiF}_4 \) and \( \text{GeF}_4^{210} \), using the formulae given in reference 206, a comparison can be made in Table 8.3.

Table 8.3 STRETCHING FORCE CONSTANTS OF SOME GROUP IV ELEMENT-FLUORINE BONDS (in mdyne/Å)

<table>
<thead>
<tr>
<th></th>
<th>( \nu(A_{1g}) )</th>
<th>( \nu(F_2) )</th>
<th>( \nu(A_{2u}) )</th>
<th>( k )</th>
<th>( k_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CF}_4^{210} )</td>
<td>908</td>
<td>1281</td>
<td>—</td>
<td>6.73</td>
<td>0.83</td>
</tr>
<tr>
<td>( \text{SiF}_4^{210} )</td>
<td>800</td>
<td>1010</td>
<td>—</td>
<td>6.29</td>
<td>0.29</td>
</tr>
<tr>
<td>( \text{GeF}_4^{210} )</td>
<td>738</td>
<td>800</td>
<td>—</td>
<td>5.50</td>
<td>0.20</td>
</tr>
<tr>
<td>( \text{GeF}_2(\text{SO}_3\text{F})_2 )</td>
<td>648</td>
<td>—</td>
<td>770</td>
<td>4.53</td>
<td>0.17</td>
</tr>
<tr>
<td>( \text{SnF}_2(\text{SO}_3\text{F})_2^{208} )</td>
<td>612</td>
<td>—</td>
<td>691</td>
<td>4.12</td>
<td>0.07</td>
</tr>
</tbody>
</table>

It can be seen that the element-fluorine bond strengthens as the element becomes more electronegative. The substitution of a fluorine atom with two bridging fluorosulfate groups tends to weaken the covalent Ge-F bond by possibly a delocalization of the electron density away from germanium. The increase in the stretch-and-stretch interaction for \( \text{CF}_4 \) is most likely a result of steric
effects in the small molecule. For example, the stretching of one C-F bond would decrease the crowding for the remaining three fluorine atoms, leading to an increase in the strength of the other C-F bonds.

In the vibrational spectrum of GeF$_2$(SO$_3$F)$_2$, vS-F is found at 880 cm$^{-1}$, an unusually high frequency, suggesting the presence of a strong Ge-O bond. This is not unexpected since the Ge-F bond is strong and the electronegativities of oxygen and fluorine are similarly high.

(CIO$_2$)$_2$[Ge(SO$_3$F)$_6$] is an excellent Raman scatterer, and a good comparison can be made with the Raman frequencies of (CIO$_2$)$_2$-[Sn(SO$_3$F)$_6$] in Table 8.3.

The ionic nature of the complex is shown by the presence of the three vibrational modes for CIO$_2^+$ at ~1300, 1063 and 526 cm$^{-1}$ in the Raman spectrum. The rest of the spectrum is essentially that of a monodentate SO$_3$F group coordinated in a manner similar to other hexakis(fluorosulfato) complexes. It appears that the coordination of six SO$_3$F groups reduces the polarizing ability of Ge(IV), as can be shown by a lowering of the stretching frequency of the Ge-OSO$_2$F vibration to 461 cm$^{-1}$ from 495 cm$^{-1}$ in GeF$_2$(SO$_3$F)$_2$. Furthermore, vS-F is lowered to the normal range at ~820 to ~850 cm$^{-1}$ from 380 cm$^{-1}$ in GeF$_2$(SO$_3$F)$_2$. These observations are not surprising in view of the increased delocalizing ability of a SO$_3$F group as compared to a fluorine atom.
Table 8.4  VIBRATIONAL FREQUENCIES OF (CIO\textsubscript{2})\textsubscript{2}[Ge(SO\textsubscript{3}F)\textsubscript{6}]  

<table>
<thead>
<tr>
<th></th>
<th>(CIO\textsubscript{2})\textsubscript{2}[Ge(SO\textsubscript{3}F)\textsubscript{6}]</th>
<th>(CIO\textsubscript{2})\textsubscript{2}[Sn(SO\textsubscript{3}F)\textsubscript{6}]</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.</td>
<td>I.R.</td>
<td>R.</td>
<td>Assignment</td>
</tr>
<tr>
<td>1414 w</td>
<td>1390 m</td>
<td>1412 w</td>
<td>vSO\textsubscript{2} asym.</td>
</tr>
<tr>
<td>1390 m</td>
<td>1385 vs</td>
<td>1386 s</td>
<td>vSO\textsubscript{2} asym.</td>
</tr>
<tr>
<td>1380 m</td>
<td>1305 s</td>
<td>1308 m</td>
<td>v\textsubscript{3}(CIO\textsubscript{2})\textsuperscript{+}</td>
</tr>
<tr>
<td>1307 w</td>
<td>1295 vw</td>
<td>1295 w</td>
<td>vSO\textsubscript{2} asym.</td>
</tr>
<tr>
<td>1295 vw</td>
<td>~1200 vs,b</td>
<td>1206 s</td>
<td>vSO\textsubscript{2} sym.</td>
</tr>
<tr>
<td>1272 m</td>
<td>1215 s</td>
<td>1265 ms</td>
<td>v\textsubscript{1}(CIO\textsubscript{2})\textsuperscript{+}</td>
</tr>
<tr>
<td>1205 s</td>
<td>1098 m</td>
<td>1092 m</td>
<td>v\textsubscript{O}-SO\textsubscript{2}F</td>
</tr>
<tr>
<td>1098 m</td>
<td>1063 vs</td>
<td>1062 vw</td>
<td>vS-F</td>
</tr>
<tr>
<td>1001 w</td>
<td>1020 vs,b</td>
<td>1030 s</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>985 vw</td>
<td>965 vw</td>
<td>990 sh</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>985 vw</td>
<td></td>
<td>990 sh</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>847 w</td>
<td>820 vs,b</td>
<td>842 m</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>821 w</td>
<td></td>
<td>820 m</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>821 w</td>
<td></td>
<td>820 m</td>
<td>v\textsubscript{S}-F</td>
</tr>
<tr>
<td>631 m</td>
<td>640 s</td>
<td>624 s</td>
<td>SO\textsubscript{2} bend</td>
</tr>
<tr>
<td>591 w</td>
<td>580 s</td>
<td>582 m</td>
<td>SO\textsubscript{2} bend</td>
</tr>
<tr>
<td>567 w</td>
<td>550 s</td>
<td>555 m</td>
<td>SO\textsubscript{2} bend</td>
</tr>
<tr>
<td>554 w</td>
<td>520 m</td>
<td>526 m</td>
<td>v\textsubscript{2}(CIO\textsubscript{2})\textsuperscript{+}</td>
</tr>
<tr>
<td>526 m</td>
<td>520 m</td>
<td>526 m</td>
<td>v\textsubscript{2}(CIO\textsubscript{2})\textsuperscript{+}</td>
</tr>
<tr>
<td>461 w</td>
<td>432 w,sh</td>
<td>429 m</td>
<td>vGe-OSO\textsubscript{2}F</td>
</tr>
<tr>
<td>436 m</td>
<td></td>
<td>429 m</td>
<td>vGe-OSO\textsubscript{2}F</td>
</tr>
<tr>
<td>436 m</td>
<td></td>
<td>429 m</td>
<td>vGe-OSO\textsubscript{2}F</td>
</tr>
<tr>
<td>274 m</td>
<td>255 m</td>
<td>264 m</td>
<td>vSn-OSO\textsubscript{2}F</td>
</tr>
<tr>
<td>274 m</td>
<td></td>
<td>264 m</td>
<td>vSn-OSO\textsubscript{2}F</td>
</tr>
</tbody>
</table>
Neither GeF$_2$(SO$_3$F)$_2$ nor Sn(SO$_3$F)$_4$ show any appreciable solubility in HSO$_3$F, and thus solution studies on the systems are limited to the anionic complexes. In the previous chapters, the conductivities of solutions of [M(SO$_3$F)$_6$]$^{2-}$, where M=Pd, Pt, Ir, Sn, have been found to be almost identical, suggesting a similar ionization scheme for all the complexes. From solution studies of the platinum(IV)-fluorosulfate system, [Pt(SO$_3$F)$_6$]$^{2-}$ has been shown to undergo a basic dissociation in HSO$_3$F.

A conductometric titration of KSn(SO$_3$F)$_5$ with KSO$_3$F was undertaken to investigate the acid-base behavior of the complex in HSO$_3$F. KSn(SO$_3$F)$_5$ is potentially a SO$_3$F acceptor according to:

$$\text{KSn(SO}_3\text{F)}_5 + \text{KSO}_3\text{F} \rightarrow \text{K}_2[\text{Sn(SO}_3\text{F)}_6] . \quad (8.11)$$

But by analogy with [Pt(SO$_3$F)$_6$]$^{2-}$, the reverse reaction may be appreciable. The result of such a titration is shown in Fig 8.1 and Table 8.5. The procedure involved in the calculation is described in detail in Appendix A but will be briefly explained here.

Since there is no reason for the polymeric units of KSn(SO$_3$F)$_5$ to remain intact in the relatively dilute solution in which the titration was performed in, the species most likely present under such a condition is the solvated monomeric species, H[Sn(SO$_3$F)$_6$]$^-$. The titration is therefore the neutralization of this 'acid' by SO$_3$F$^-$ according to:

$$\text{H[Sn(SO}_3\text{F)}_6]^- + \text{SO}_3\text{F}^- \rightleftharpoons \frac{K_1}{\text{[Sn(SO}_3\text{F)}_6]^-} + \text{HSO}_3\text{F} . \quad (8.12)$$
FIG 8.1

The conductometric titration of K\(\text{Sn(SO}_3\text{F)}_5\) with KSO\(_3\text{F}\) in HSO\(_3\text{F}\)
### Table 8.5

**CONDUCTOMETRIC TITRATION OF KSn(SO$_3$F)$_5$ WITH KSO$_3$F**

IN HSO$_3$F

<table>
<thead>
<tr>
<th>R</th>
<th>$\kappa$(obs)</th>
<th>$\kappa$(calc)*</th>
<th>I(calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>48.52</td>
<td>48.52</td>
<td>0.090</td>
</tr>
<tr>
<td>0.1</td>
<td>46.69</td>
<td>43.90</td>
<td>0.100</td>
</tr>
<tr>
<td>0.2</td>
<td>45.99</td>
<td>43.12</td>
<td>0.112</td>
</tr>
<tr>
<td>0.3</td>
<td>45.76</td>
<td>42.83</td>
<td>0.123</td>
</tr>
<tr>
<td>0.4</td>
<td>45.98</td>
<td>42.73</td>
<td>0.133</td>
</tr>
<tr>
<td>0.5</td>
<td>46.35</td>
<td>42.80</td>
<td>0.143</td>
</tr>
<tr>
<td>0.6</td>
<td>46.86</td>
<td>43.09</td>
<td>0.152</td>
</tr>
<tr>
<td>0.7</td>
<td>47.46</td>
<td>43.72</td>
<td>0.160</td>
</tr>
<tr>
<td>0.8</td>
<td>48.13</td>
<td>44.94</td>
<td>0.167</td>
</tr>
<tr>
<td>0.9</td>
<td>49.16</td>
<td>47.29</td>
<td>0.173</td>
</tr>
<tr>
<td>1.0</td>
<td>51.50</td>
<td>51.50</td>
<td>0.178</td>
</tr>
</tbody>
</table>

* Calculated using the following parameters:

- $\lambda_0^*(H_2SO_3F^+) = 320$
- $\lambda_0^*(SO_3F^-) = 227$
- $\lambda_0^*(K^+) = 29$
- $\lambda_0^*(H[Sn(SO_3F)_6]^-) = 28$
- $\lambda_0^*([Sn(SO_3F)_6]^{2-}) = 29$
- $K_1 = 5.1 \times 10^{-5}$ mol$\cdot$kg$^{-1}$
By fixing the initial \( (R=0) \), and the last points \( (R=1) \) in the titration curve, \( \lambda_0^*([\text{Sn}(\text{SO}_3\text{F})_6]^{2-}) \) and \( K_1 \) can be obtained for each set of the other four variables listed in Table 8.5. In addition, the mobility of \( \text{H}_2\text{SO}_3\text{F}^+ \) is fixed at \( 320 \, \text{m}^2/\text{V} \cdot \text{s} \cdot \text{cm}^{-1} \) and those of \( \text{SO}_3\text{F}^- \) and \( \text{K}^+ \) are related. Because the system is only weakly acidic, the autoprotolysis of \( \text{HSO}_3\text{F} \) must also be taken into account. A reasonable fit with the experimental curve is obtained with the parameters listed in Table 8.5. The ionic mobilities and the value for \( K_1 \) compare quite well with those obtained for the platinum-fluorosulfate system, described in Chapter 5. Again, \( [\text{Sn-} \,(\text{SO}_3\text{F})_6]^{2-} \) has about the same ionic mobility as \( \text{K}^+ \) and \( \text{H}[\text{Sn}(\text{SO}_3\text{F})_6]^+ \), and can be attributed to the opposing effects of it being a doubly charged ion and the resulting increased solvation.

The equilibrium constant for the solvolysis of \( [\text{Sn}(\text{SO}_3\text{F})_6]^{2-} \) in \( \text{HSO}_3\text{F} \) according to:

\[
[\text{Sn}(\text{SO}_3\text{F})_6]^{2-} + \text{HSO}_3\text{F} \rightleftharpoons \text{H}[\text{Sn}(\text{SO}_3\text{F})_6]^+ + \text{SO}_3\text{F}^- , \quad (8.13)
\]

is about \( 7.5 \times 10^{-4} \, \text{mol/kg} \), indicating a weakly basic behavior for the solute.

In general, the two curves in Fig 8.1 deviates from each other by less than 8 %, this can be caused by:

a) the dependence of \( \lambda^* \) on \( I \) used in the calculation is not a good approximation, and

b) the average concentration of all ionic species during the titration is about 0.1 mol/kg, which cannot be strictly defined as being dilute. Polymerization according to:
\[ 2H[Sn(SO_3F)_6]^- \rightarrow [Sn_2(SO_3F)_{10}]^{2-} + 2HSO_3F \quad (8.14) \]

and
\[ 2[Sn(SO_3F)_6]^{2-} \rightarrow [Sn_2(SO_3F)_{10}]^{2-} + 2SO_3F^- \quad (8.15) \]

etc., would serve to increase the basicity of the solution, and since \( H[Sn(SO_3F)_6]^- \) is only a very weak acid, the conductivity for the most part of the titration (from \( R \) slightly greater than 0) would be increased.

The validity of the calculated \( K_1 \) and \( \lambda_0^* \) values is tested by calculating the conductivity of CsSn(SO_3F)\(_5\) and \( K_2[Sn(SO_3F)_6]^{32}\) solutions in HSO_3F, shown in Fig 8.2. The concentration range covered is quite large, and the approximation in \( \lambda^* \) is not expected to adequately describe the real system, especially when the \( \lambda \)'s were extrapolated from concentrated solutions in which solutions do not behave ideally. In any case, the calculated curves fit the experimental curves better at higher concentrations, and no further attempts were made to modify the dependence of \( \lambda^* \) on \( I \).

In summary, the conductometric studies on solutions of KSn-(SO_3F)\(_5\) in HSO_3F suggest a complicated behavior, involving both polymer-formation and weak proton-accepting properties. N.m.r. results, to be discussed later, also support such a hypothesis. The series of \([M(SO_3F)_6]^{2-}\), where \( M=Sn, Pd, Pt, Ir \), all appear to ionize in a similar manner in HSO_3F, forming weakly basic solutions.

\((ClO_2)_2[Ge(SO_3F)_6]\) dissolves in HSO_3F to give light yellow solutions, suggesting the presence of solvated \( ClO_2^+^{32} \). The
The electrical conductivity of KSn(SO$_3$F)$_5$ in HSO$_3$F at 25°C

$10^4 \kappa$ ($\Omega^{-1}$/cm)

$K\text{Sn(SO}_3\text{F)}_5$

$K_2[\text{Sn(SO}_3\text{F)}_6]$ (calculated)*

$K_2[\text{Sn(SO}_3\text{F)}_6]$ (calculated)*

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conductivity of \((\text{ClO}_2)_2[\text{Ge(SO}_3\text{F})_6]\) in \(\text{H}2\text{SO}_3\text{F}\) is shown in Fig. 8.3 and Table 8.6. In comparing these results with those of the corresponding platinum species, it is evident that the latter system has a higher conductivity of about 30\%. The high conductivity of \([\text{Pt(SO}_3\text{F})_6]^{2-}\) and related solutes in \(\text{H}2\text{SO}_3\text{F}\) has been attributed to solvolysis reactions, giving rise to \(\text{SO}_3\text{F}^-\), which, like \(\text{H}2\text{SO}_3\text{F}^+\), has a high mobility in the solvent. It may also be inferred from this that in the solutions containing \([\text{Ge(SO}_3\text{F})_6]^{2-}\), the protonation according to:

\[
[\text{Ge(SO}_3\text{F})_6]^{2-} + \text{H}2\text{SO}_3\text{F} \quad \leftrightarrow \quad \text{H}[\text{Ge(SO}_3\text{F})_6]^+ + \text{SO}_3\text{F}^-,
\]

occurs to a lesser extent. By assuming \(X^2([\text{Ge(SO}_3\text{F})_6]^{2-}) = 30\), and \(X^2(\text{ClO}_2^+) = 25\), for a 0.01 mol/kg solution of \((\text{ClO}_2)_2[\text{Ge(SO}_3\text{F})_6]\) that undergoes a dissociation giving rise to only \(\text{ClO}_2^+\) and \([\text{Ge(SO}_3\text{F})_6]^{2-}\), the conductance of the solution should be about \(9 \times 10^{-4} \ \Omega^{-1} \text{cm}^{-1}\), when solvent conductivity is included. With \(X^2(\text{SO}_3\text{F}^-) = 230\), it can be calculated that the equilibrium constant for equation (8.16) is about 25\% that of the other \([\text{M(SO}_3\text{F})_6]^{2-}\) complexes in solutions, or of the order of the solvent dissociation constant.

Therefore, solutions of \([\text{Ge(SO}_3\text{F})_6]^{2-}\) are anomalous when compared to those of the other \([\text{M(SO}_3\text{F})_6]^{2-}\) complexes investigated in this study, displaying a much less conductivity. It is also not expected that the other \([\text{M(SO}_3\text{F})_6]^{2-}\) complexes, where \(\text{M}=\text{Pd, Pt, Ir, Sn}\), should have identical equilibrium constants in solution but slight variations in them are masked by the autoprotonolysis of \(\text{H}2\text{SO}_3\text{F}\) because the amount of \(\text{SO}_3\text{F}^-\) derived from both
FIG 8.3 CONDUCTIVITY OF $(\text{ClO}_2)_2[\text{Ge(SO}_3\text{F})_6]$ IN HSO$_3$F
Table 8.6  CONDUCTIVITY OF (ClO$_2$)$_2$[Ge(SO$_3$F)$_6$] IN HSO$_3$F *

<table>
<thead>
<tr>
<th>m</th>
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<tbody>
<tr>
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<td>3.699</td>
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<td>21.96</td>
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</tbody>
</table>

mol·kg$^{-1}$  10$^{-4}$Ω$^{-1}$cm$^{-1}$

* interpolated
equilibria are of about the same order of magnitude.

8.C.4 N.M.R. STUDIES IN HSO$_3$F

Both $^{119}$Sn- and $^{19}$F-n.m.r. spectroscopy were applied to the study of the Sn(IV)-fluorosulfate system in HSO$_3$F solution. The $^{119}$Sn-n.m.r. spectra of CsSn(SO$_3$F)$_5$ and Cs$_2$[Sn(SO$_3$F)$_6$] are shown in Fig 8.4.

Of all the naturally occurring isotopes of tin, two have nuclear spins of $\frac{1}{2}$, they are $^{117}$Sn with an abundance of 7.61% and $^{119}$Sn with an abundance of 8.58%. $^{119}$Sn- n.m.r. has a relative sensitivity of 5.18$\times$10$^{-2}$ compared to $^1$H-n.m.r., and for an 80 MHz spectrometer, the resonance for $^{119}$Sn is at about 29.88 MHz. Both of the $^{119}$Sn-n.m.r. spectra consist of a single resonance, with that of CsSn(SO$_3$F)$_5$ shifted 41 Hz down-field from that of Cs$_2$[Sn(SO$_3$F)$_6$] (the frequency indicated on the spectra is simply for use as a reference). It becomes evident that the resonance for CsSn(SO$_3$F)$_5$ is broad (~25 Hz at half-height as compared to ~9 Hz for Cs$_2$[Sn(SO$_3$F)$_6$]). The same is also found for the $^{19}$F-n.m.r. spectra; even at a concentration of 0.12 m, much lower than used for the $^{119}$Sn-n.m.r. spectra, a single relatively broad peak occurs at -41.00 ppm. As an excess of KSO$_3$F was added to the solution, two sharp resonances appeared, a low intensity one at -41.75 ppm assigned to [Sn-SO$_3$F] species and a solvent reso-
FIG 8.4 \(^{119}\text{Sn-N.M.R. SPECTRA IN HSO}_3\text{F}\)

0.63\text{m }\text{Cs}_2\text{Sn}_2(\text{SO}_3\text{F})_{10}\n-5104.4\text{Hz}

0.68\text{m }\text{Cs}_2\text{Sn}(\text{SO}_3\text{F})_6\n-5145.6\text{Hz}
nance at -40.75 ppm. The solvent peak is hardly changed from that of pure HSO$_3$F, and the solute peak compares well with that reported for [Sn(SO$_3$F)$_6$]$^{2-}$ solutions. For more concentrated solutions of KSn(SO$_3$F)$_5$, such as at 0.88 mol/kg, the single resonance is shifted to -41.42 ppm (close to that for other [Sn-SO$_3$F] species) and the resonance is noticeably broadened (~24 Hz at half-height). A 'titration' of KSn(SO$_3$F)$_5$ monitored by $^{19}$F-n.m.r. is shown in Fig. 8.5; the sharpening and splitting of the resonance upon the addition of KSO$_3$F are well illustrated.

It therefore appears that an exchange process, involving SO$_3$F groups, must be present in MSn(SO$_3$F)$_5$, where M=K, Cs, as proton exchange in species such as H[Sn(SO$_3$F)$_6$]$^-$ is not expected to give rise to the observed broadening in the spectra. The dimerization of H[Sn(SO$_3$F)$_6$]$^-$ according to:

$$2H[Sn(SO_3F)_6]^- \leftrightarrow [Sn_2(SO_3F)_{10}]^{2-} + 2HSO_3F,$$  

(8.17)

could produce such an effect. The dimerization of [Sn(SO$_3$F)$_6$]$^{2-}$ according to:

$$[Sn(SO_3F)_6]^{2-} \leftrightarrow [Sn_2(SO_3F)_{10}]^{2-} + 2SO_3F^-,$$  

(8.18)

may not occur as readily because of its strong dependence on the acidity of the solution. This is especially true when an excess of KSO$_3$F is added, resulting in the reduction of the solvolysis of [Sn(SO$_3$F)$_6$]$^{2-}$ to form H[Sn(SO$_3$F)$_6$]. The small difference in the chemical environments of the fluorine atoms when the SO$_3$F group is bound as a terminal or a bridging ligand can also lead to the broadening in the $^{19}$F-n.m.r. spectrum of KSn(SO$_3$F)$_5$. 
FIG. 8.5

F-19 nmr of $[\text{Sn}(\text{SO}_3\text{F})_x]^{z-}$ in HSO$_3$F

$[\text{K Sn}(\text{SO}_3\text{F})_5]$  
conc. = 0.88 m

-41.42 ppm  
41.00 ppm

KSO$_3$F

10 ppm  10 ppm
In summary, it appears that the species present in HSO$_3$F solutions of $^{11}$Sn(SO$_3$F)$_5$ are dynamically exchanging SO$_3$F-containing moieties with the solvent, leading to a broadening and coalescence of the $^{19}$F resonance; this is supported also by the $^{119}$Sn-n.m.r. results.

Some differences exist between the n.m.r. studies described here and those involving platinum:

a) There was no Sn-F coupling observed. For the $^{19}$F spectra, the low natural abundance of $^{117}$Sn and $^{119}$Sn may be a factor here. For the $^{119}$Sn spectra, in which a septet is expected for [Sn(SO$_3$F)$_6$]$^{2-}$, the relatively sharp resonance suggests that either no Sn-F coupling occurs, or J(Sn-F) is very small ($\leq 5$ Hz).

b) In the $^{19}$F-n.m.r. spectra of the platinum compounds, no shifting or broadening in the resonance was observed. This is most likely due to the large separation between the solvent resonance and the [Pt-SO$_3$F] resonance, and does not rule out the occurrence of exchange reactions.
8.D CONCLUSION

Complexes of the type of $\text{M}_2\text{Sn(SO}_3\text{F)}_5$, where M=Cs, K, have been prepared and characterized by vibrational spectroscopy and solution studies involving conductometry and n.m.r. spectroscopy. These complexes are similar to those containing Pt(IV); the analogy also extends to the hexakis(fluorosulfato)-complexes of Pt(IV), Ir(IV) and Pd(IV) in terms of their structures and solution behaviors. Unlike $\text{K[Au(SO}_3\text{F)}_4]$, $\text{KSn(SO}_3\text{F)}_5$ is weakly acidic, and $\text{K}_2[\text{Sn(SO}_3\text{F)}_6]$ is weakly basic, when dissolved in HS$_3$O$_3$. Using n.m.r. spectroscopy, exchange reactions involving the transfer of SO$_3$F groups seem to be prevalent in solutions of $\text{KSn(SO}_3\text{F)}_5$; this has been attributed to a dimerization or polymerization in solution. Unfortunately, no $^{119}\text{Sn}$ Mössbauer studies could be performed on the complexes, as a suitable source was not available.

This study confirms the conclusion arrived in the palladium-fluorosulfate system that Sn(SO$_3$F)$_4$ is a strong fluorosulfate acceptor, and it would have been a practical superacid in the HS$_3$O$_3$ solvent system if not for its insolubility.

In the germanium-fluorosulfate system, the tetrakis(fluorosulfate) was not obtainable; instead, GeF$_2$(SO$_3$F)$_2$ was obtained as the product from the oxidation of germanium metal with S$_2$O$_6$F$_2$. From vibrational spectroscopy, the fluoride-fluorosulfate seems to be isostructural with SnF$_2$(SO$_3$F)$_2$. Although Ge(SO$_3$F)$_4$ could not be successfully prepared, an anionic complex containing $[\text{Ge-(SO}_3\text{F)}_6]^{2-}$ could be isolated, but it too displays limited thermal
CHAPTER 9  CONCLUSION

From a synthetic point of view, this study has provided a very versatile preparative reagent for the synthesis of metal fluorosulfates and their anionic complexes. The mixture of $S_2O_6F_2/HSO_3F$ combines the strong oxidizing ability of $S_2O_6F_2$ with the ionic solvating property of $HSO_3F$, and can be used from below room temperature up to almost 200°C. The usefulness of this oxidizing mixture is in its adaptability to most of the synthetic reactions described in this thesis, giving rise to compounds containing the highest oxidation state of the metal in the fluorosulfate system. Fluorosulfonation reactions using $S_2O_6F_2/HSO_3F$ do not result in the formation of a reactive by-product, like the halogen-monofluorosulfates do, and in cases where by-products are formed, they usually come from the decomposition of the metal fluorosulfate.

Of the systems investigated here, $Au(SO_3F)_3$ and $Pt(SO_3F)_4$ have been found to be superacids in $HSO_3F$, with acidities comparable to that of $SbF_2(SO_3F)_3$, the strongest superacid in the solvent system. Novel polybromine cations, $Br_3^+$ and $Br_5^+$ can be stabilized by $[Au(SO_3F)_4]^-$, illustrating the low basicity and low oxidizing ability of the anion. The two ansolvo acids are polymerized in the solid state, and, in the platinum system, also in solution, as illustrated by conductivity results and the synthesis of $CsPt(SO_3F)_5$-type complexes.
Although being a strong acceptor of \( SO_3F^- \) is the first requirement for a superacid, too strong an acceptor property also seems to lead to its demise. This can be illustrated in the Sn-SO\(_3\)F system, for which evidence from electronic spectra of Pd(II)-fluorosulfato complexes seems to suggest an extremely strong SO\(_3\)F-accepting property. It is perhaps because of this reason that Sn(SO\(_3\)F)\(_4\) is highly polymeric and insoluble in HSO\(_3\)F.

The study into the palladium system provided the first interpretation of the ligand field parameters of Pd(II) in an octahedral ligand field. The magnetic susceptibility of Pd(II) in various fluorosulfato complexes was found to have Curie-Weiss Law behavior in magnetically dilute systems. The iridium-fluorosulfate system is essentially a paramagnetic analogue of platinum's.

**SUGGESTIONS FOR FURTHER WORK IN THIS AREA**

a) A quantitative measure of acidity, the Hammett coefficients, should be applied to H[Au(SO\(_3\)F)\(_4\)] and H\(_2\)[Pt(SO\(_3\)F)\(_6\)]. It may also be useful to investigate the n.m.r. technique of measurement \(^{51,52}\).

b) The application of the two superacids is a definite possibility, especially in view of their high acidity, high thermal stability and low oxidizing power. The catalytic polymerization of small organic molecules such as CH\(_4\) should serve
as a comparison with the HSO₃F-SbF₅ superacid system.

c) Since [Au(SO₃F)₄]⁻ can stabilize Br₅⁺, other similarly large novel cations may be synthesized, containing the same counter-anion.

d) The application of ¹¹⁹Sn Mössbauer to the study of [Sn(SO₃F)₅]X⁻, and ¹⁹⁵Pt-n.m.r. to the platinum-fluorosulfate system should provide insights into the polymerization and bonding in these compounds.

e) The group IVB halides such as TiCl₄, TiF₄, are also strong Lewis acids; their corresponding fluorosulfates may provide economical alternatives to the noble metal superacids.

f) The group VB and VIB oxyfluorosulfates appear to be complicated, multicomponent systems; some preliminary results from this study seem to indicate exchange reactions resulting in the formation of metal-fluorine bonds and weakly acidic behavior in the tantalum system. These may merit further investigations.

g) The HSO₃CF₃ solvent system is more tolerant to water than HSO₃F is. Although Au(SO₃CF₃)₃ is insoluble in HSO₃CF₃, and Pt(SO₃CF₃)₄ appears to behave likewise, this may be the next solvent system to expand into, especially since it is also a very strongly acidic medium.
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119) Ref. 110, p. 1031.
140) Ref. 110, p. 998.


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198) Ref. 110, p. 772.
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INTRODUCTION

In this study, a theoretical treatment of the conductivity results is applied to three systems in HSO₃F — Au(SO₃F)₃, Pt(SO₃F)₄, and KSn(SO₃F)₅. The purpose of these calculations is to attempt to describe the solution behavior of these species in a semi-quantitative manner, to have a comparison of their acidities with other systems, and to obtain ionic mobility values for ions hitherto unknown. As with any treatment of this type, a few assumptions have been made.

a) The equilibrium constants are set to be invariant throughout the range of a particular experiment. This is not entirely valid as they do have a dependence on the ionic strength of the solution.

b) The autoprotolysis constant for HSO₃F, i.e., [H₂SO₃F⁺] [SO₃F⁻] is 3.8×10⁻⁸ mol·kg⁻¹, although this has only been approximately determined. This is not expected to have a large contribution to the conductivity of solutions in HSO₃F except at or near neutrality conditions.

c) The molal conductivity of H₂SO₃F⁺ at infinite dilution, λₚ⁰(H₂SO₃F⁺), is set at 320. Also the sum of λₚ⁰(SO₃F⁻) and λₚ⁰(K⁺) is set at 256, using the value of KSO₃F²¹.

d) A dependence of λ* on the ionic strength, I, is approximated as follows:
\[ \lambda^* = \lambda_0^* \exp(-1.567 \times I). \]  \hspace{1cm} (A.1)

The Limiting Law predicts a decrease of \( \lambda^* \) with respect to \( I^5 \), but this is seldom obeyed in solutions with concentrations greater than \( \sim 10^{-3} \text{ mol} \cdot \text{kg}^{-1} \). An empirical fit was attempted on the published data on solutions of \( M^I\text{SO}_3F \) and \( \text{M}^{II}(\text{SO}_3F)_2 \), where \( M^I=\text{Li, Na, K, NH}_4, \text{Rb} \), and \( M^{II}=\text{Sr, Ba} \). Although polynomials, usually of less than the 3rd degree, were found to provide the best least-square fit within the range of the data, as is usually found for curve fitting of this type, extrapolations outside the limits are extremely unreliable. Furthermore, the coefficients of the polynomials obtained for different solutions vary from solution to solution. The best compromise between the ability to extrapolate (required for the concentrated solutions in the \( \text{KSn-} (\text{SO}_3F)_5 \) system), and the degree of fit with the experimental data was obtained for an exponential relationship of the form of equation (A.1). The coefficient of \(-1.567\) was obtained by taking an average of all the different solutions' values (these range from \(-1.4\) to \(-1.7\)). In general, a difference of less than 2\% was encountered for solutions of concentrations higher than \( \sim 0.01 \text{ mol} \cdot \text{kg}^{-1} \), when equation (A.1) was applied to the solutions in reference 21. While it may be an over-simplification to expect other ions to behave as the alkali and alkali earth cations, and \( \text{SO}_3F^- \), equation(A.1) does provide a crude means of adjustment, and it improves the fit of the calculation performed here. It must also be stated that the equation has no theoretical impli-
cations, and is simply the result of a quantitative fit. To illustrate the degree of variation in the ionic strength during a titration, it is included in the appropriate tables.

A.1 HSO₃F-Au(SO₃F)₃

H[Au(SO₃F)₄] is a strong acid in HSO₃F, as can be illustrated by its titration with KSO₃F. The autoprotolysis of HSO₃F can be ignored for the most part of the calculation except at the end of the titration, at which point the solution is essentially neutral. In order to adjust for the solvent conductance without involving the autoprotolysis equilibrium constant into the calculation, a quantity of 1.0×10⁻⁴ Ω⁻¹cm⁻¹ is subtracted from the conductance at the end point.

For the titration, the calculation for a strong acid-strong base is applied. The titration can be represented by:

\[ \text{H[Au(SO₃F)₄]} + \text{HSO}_₃\text{F} \xrightarrow{\text{K}_1} \text{H}_₂\text{SO₃F}⁺ + \text{[Au(SO₃F)₄]}⁻ \]  \hspace{1cm} (A.2)

\[ \text{m-x-z} \]

\[ \text{x} \]

\[ \text{x+z} \]

\[ \text{K}_1 = \frac{(x)(x+z)}{(m-x-z)} \]  \hspace{1cm} (A.3)

and

\[ \kappa = \lambda^*_{\text{H}} x(x) + \lambda^*_{\text{Au}} x(x+z) + \lambda^*_{\text{K}} x(z) \]  \hspace{1cm} (A.4)

where \( m \)=total concentration of all Au-species

\[ x = \text{dissociation of H[Au(SO₃F)₄]} \]
\( z = \text{amount of KSO}_3 F \text{ added, } z = r \times m \)

\( r = K / Au \)

\( \lambda^*_{H} = \lambda^*(H_2SO_3F^+) \)

\( \lambda^*_{Au} = \lambda^*([Au(SO_3F)_4]^-) \)

\( \lambda^*_{K} = \lambda^*(K^+) \)

a) For each value of \( \lambda^*_K \), \( \lambda^*_{Au} \) is obtained from \( \kappa \) at \( r = 1 \) and converted into \( \lambda^*_0 \) Au.

b) \( \lambda^* \)'s are found at \( r = 0 \) by letting \( I = m \).

\( x \) is obtained from \( \kappa \) at \( r = 0, z = 0 \).

\( I \) is obtained from \( x \).

\( \lambda^* \)'s are recalculated using the new \( I \).

This procedure is repeated a total of 3 times to get a good approximation for \( I \).

\( K_1 \) is calculated from equation (A.3).

c) For each value of \( r, m, \) and \( z \) are calculated (\( m \) changes because of dilution).

d) By solving equation (A.3) for \( x \), the following can be obtained — \( I, \lambda^*, \kappa \).

e) Likewise, the conductivity of solutions of pure \( Au(SO_3F)_3 \) can be found by doing procedure d at \( r = z = 0 \) for the required concentration, \( m \).
A.2 HSO₃F- KSn(SO₃F)₅

The titration of KSn(SO₃F)₅ with KSO₃F indicates the former's weak acidity in HSO₃F, and therefore the autoprotolysis of HSO₃F has to be taken into account. For reasons discussed in Chapter 8, polymerization in solution is ignored in a first approximation. The titration can be represented by the following two equilibria and equations:

\[
\begin{align*}
H[Sn(SO₃F)_6]^- + HSO₃F & \xrightarrow{K_1} H_2SO₃F^+ + [Sn(SO₃F)_6]^2^- \quad (A.5) \\
2HSO₃F & \xrightarrow{K_2} H_2SO₃F^+ + SO₃F^- \quad (A.6)
\end{align*}
\]

\[
K_1 = \frac{(x+y)(x+z)}{(m-x-z)} \quad (A.7)
\]

\[
K_2 = (x+y)(y) \quad \text{and} \quad (A.8)
\]

\[
\kappa = \lambda^*H(x+y) + \lambda^*Sx(y) + \lambda^*HSn(x)(m-x-z) + \lambda^*Snx(x+z) \quad (A.9)
\]

where, most of the terms have similar definitions as in Appendix (A.1)

and \( y \) = dissociation of HSO₃F

\[
\lambda^*S = \lambda^*(SO₃F^-)
\]

\[
\lambda^*HSn = \lambda^*(H[Sn(SO₃F)_6]^-)
\]

\[
\lambda^*Sn = \lambda^*([Sn(SO₃F)_6]^2-)
\]

\[
r = KSO₃F/KSn(SO₃F)_5
\]

a) For each set of \( \lambda^*K \) and \( \lambda^*HSn \),

\( K_1 \) is found at \( r=0 \) and \( r=1 \), using \( \kappa \) at \( r=0 \) and \( \kappa \) at \( r=1 \), respectively, and a test value for \( \lambda^*Sn \). Using the Secant method, the two \( K_1 \) values (which should be identical), are
made to converge by solving for:

$$K_1 |_{r=0} + K_1 |_{r=1} - 1 = 0$$  \hspace{1cm} (A.10)

As $I$ is unknown at the beginning of this procedure, it is found by successive approximation by resubstitution similar to procedure b) in Appendix (A.1), $\lambda^*Sn$ and $K_1$ are obtained.

b) In equation (A.7), $x$ is substituted by $y$ using equation (A.8). A polynomial of 3rd order in $y$, for which the roots can be found, is obtained. The titration is calculated for increasing values of $r$, therefore $x$ should become progressively smaller. The value of $x$ which is closest to, but less than, the last $x$ is chosen.

c) $I$ can then be obtained, and subsequently, $\kappa$.

d) For the conductivity of $KSn(SO_3F)_5$ solutions at the above set of $\lambda^*$ values, for increasing concentrations, using procedures b) and c), the results of $x, I$ and $\kappa$ are calculated by letting $z=0$.

e) Similarly, procedures b) and c) can be used to calculate the conductivity of $K_2[Sn(SO_3F)_6]$ solutions by letting $z=m$. Because of the choose-x procedure in b), the calculation begins at the highest concentration.
A.3 HSO$_3$F-Pt(SO$_3$F)$_4$

This system is a combination of the two previous ones, and the titration consists of both a strong and a weak acid with a strong base. Two assumptions are made: the conductivity at r=0 is essentially that of the strong acid, and at r=0, the conductivity is due solely to the dissociations of [Pt(SO$_3$F)$_6$]$^{2-}$ and HSO$_3$F. Again, no polymerization is taken into account. The titration can be represented by the following three equilibria and equations.

\[ \text{H}_2\text{[Pt(SO}_3\text{F)}_6] + \text{HSO}_3\text{F} \xleftrightarrow{K_1} \text{H}[\text{Pt(SO}_3\text{F)}_6]^- + \text{H}_2\text{SO}_3\text{F}^+ \quad (A.11) \]

\[ \text{m-w} \quad \text{w-x} \quad \text{w+x+y-z} \]

\[ \text{H}[\text{Pt(SO}_3\text{F)}_6]^- + \text{HSO}_3\text{F} \xleftrightarrow{K_2} [\text{Pt(SO}_3\text{F)}_6]^{2-} + \text{H}_2\text{SO}_3\text{F}^+ \quad (A.12) \]

\[ \text{w-x} \quad \text{x} \quad \text{w+x+y-z} \]

\[ \text{HSO}_3\text{F} \xleftrightarrow{K_3} \text{H}_2\text{SO}_3\text{F}^+ + \text{SO}_3\text{F}^- \quad (A.13) \]

\[ \text{w+x+y-z} \quad \text{y} \]

\[ K_1 = \frac{(w-x) \times (w+x+y-z)}{(m-w)} \quad (A.14) \]

\[ K_2 = \frac{(x) \times (w+x+y-z)}{(w-x)} \quad (A.15) \]

\[ K_3 = (w+x+y-z) \times (y) \quad (A.16) \]

and

\[ = \lambda^*\text{H}(w+x+y-z) + \lambda^*\text{S}(y) + \lambda^*\text{K}(z) + \lambda^*\text{H}_{\text{Pt}}(w-x) + \lambda^*\text{Pt}(x) \quad (A.17) \]

where \( w = \text{dissociation of H}_2\text{[Pt(SO}_3\text{F)}_6] \)
\( x = \text{dissociation of H}[\text{Pt(SO}_3\text{F)}_6] \)
\( y = \text{dissociation of HSO}_3\text{F} \)
z = amount of KSO₃F, z = r x m

r = K/Pt

$\lambda^*H_{Pt} = \lambda^*(H[Pt(SO_3F)_{6}]^-)$

$\lambda^*Pt = \lambda^*([Pt(SO_3F)_{6}]^{2-})$

a) For each value of r, m, and z are calculated.

b) For each set of $\lambda^*K$, $\lambda^*H_{Pt}$ and $\lambda^*Pt$,

$K_1$ is obtained from $\kappa$ at $r=0$ and by letting $x=y=z=0$,

$K_2$ is obtained from $\kappa$ at $r=2$ and by letting $w=m$.

A check at the end of the calculation shows that both approximations are valid.

c) Equations (A.14) and (A.15) are combined into one containing only $x$ and $w$ as the variables.

$$K_1(m-w) \times (w-x) - K_2 x \times (w-x) = 0 \quad \text{(A.18)}$$

$w$ can be calculated given $x$.

d) By solving equation (A.16), $y$ can be calculated given $x$ and $w$.

e) By solving equation (A.14), $K_1$ can be calculated given $x$, $w$, and $y$.

f) For each value of $r$, $x$ is found by applying the Secant Method to solve for:

$$K_1^* \div K_1 - 1 = 0 \quad \text{(A.19)}$$

where $K_1^*$ is the value of $K_1$ calculated for each test value of $x$ using procedures c), d), and e). Although $K_1$ can be substituted by $K_2$ in equation (A.19), a higher degree of accuracy is obtained in calculating $K_1$ because $K_1 > K_2$. When
K_2 was used, the function described by equation (A.19) also became quite ill-conditioned and was found not to converge in certain cases.

g) After finding the value of \( x \) (therefore \( w \) and \( y \)) that satisfies equation (A.18). \( \kappa \) can be calculated.

h) For all the calculations involving \( \lambda^* \) and an unknown quantity of I, the latter is found by the successive approximation method similar to that described in procedure b) in Appendix (A.1).

i) The conductivity of pure HSO_3F-Pt(SO_3)\(_6\) is found by using equation (A.14), letting \( x=y=z=0 \).
APPENDIX B GOLD-TRIFLUOROMETHYL SULFATE

B.1 INTRODUCTION

The gold-trifluoromethylsulfate system was investigated as a possible ansolvo-acid in the HSO$_3$CF$_3$ solvent system. While the acidity of HSO$_3$CF$_3$ is only slightly lower than that of HSO$_3$F$^{47}$, the former has the advantage of being stable in the presence of water. If Au(SO$_3$CF$_3$)$_3$ is found to be a strong acid in HSO$_3$CF$_3$ and if it is also compatible with the aqueous system, then the scope of application of this superacid system could conceivably be wider than that of the corresponding fluorosulfate system. Ag(SO$_3$CF$_3$)$_2$ was also studied in this laboratory$^{209}$, and the results of both investigations have been published in reference 212; the gold-SO$_3$CF$_3$ system will be discussed briefly here as it is related to a degree to the topic of this thesis. For a more detailed discussion, the reader is asked to refer to reference 212.

B.2 DISCUSSION

The number of known synthetic routes to trifluoromethylsulfates is very limited, mainly due to the instabilities of oxidizing agents such as (CF$_3$SO$_3$)$_2$$^{213}$ and CF$_3$SO$_3$Cl$^{214}$, the analogues of S$_2$O$_5$F$_2$ and ClSO$_3$F in the fluorosulfate system. Most
known syntheses involve the solvolysis of salts of other acids in HSO$_3$CF$_3$. Au(SO$_3$CF$_3$)$_3$ and Cs[Au(SO$_3$CF$_3$)$_4$] are prepared by the following reactions:

\[
\text{Au(SO}_3\text{F)}_3 + \text{HSO}_3\text{CF}_3 \rightarrow \text{Au(SO}_3\text{CF}_3)_3 + \text{HSO}_3\text{F} \quad (B.1)
\]

\[
\text{Cs[Au(SO}_3\text{F)}_4] + \text{HSO}_3\text{CF}_3 \rightarrow \text{Cs[Au(SO}_3\text{CF}_3)_4] + \text{HSO}_3\text{F} \quad (B.2)
\]

the HSO$_3$F formed presumably decomposed by reactions with HSO$_3$CF$_3$. These are most likely mass-action type reactions, since the reversal of both reactions was found to occur when HSO$_3$F was added to the trifluoromethylsulfates.

Neither compounds were found to be very soluble in HSO$_3$CF$_3$, thus limiting the possibility of Au(SO$_3$CF$_3$)$_3$ being a useful ansolvo-acid in the solvent system. The formation of Cs[Au(SO$_3$CF$_3$)$_4$], however, does indicate that Au(SO$_3$CF$_3$)$_3$ may act as a trifluoromethylsulfate ion acceptor.

The vibrational spectra of these two diamagnetic compounds suggest structural similarities to the fluorosulfates—square planar coordination for Au(III), the presence of monodentate SO$_3$CF$_3$ groups in Cs[Au(SO$_3$CF$_3$)$_4$] and the presence of both monodentate and bidentate SO$_3$CF$_3$ groups in Au(SO$_3$CF$_3$)$_3$.

**B.3 CONCLUSION**

Au(SO$_3$CF$_3$)$_3$ was found to exhibit a lower sensitivity to moisture than Au(SO$_3$F)$_3$, but it is still very hygroscopic.
Furthermore, the former's low solubility in the parent acid limited its use as an ansolvo-acid in the system. Lewis acidity towards \( \text{SO}_3\text{CF}_3^- \), however, was established for the compound by the synthesis of the complex \( \text{Cs}[\text{Au(SO}_3\text{CF}_3)_4] \). The solvolysis of a fluorosulfate in \( \text{HSO}_3\text{CF}_3 \) should find use as a synthetic route to trifluoromethylsulfates containing transition metals in relatively high oxidation states.
APPENDIX C LIST OF ABBREVIATIONS

Magnetoochemistry and Electronic Spectroscopy

B \quad \text{interelectronic repulsion parameter, unit=cm}^{-1}
B^o \quad B \text{ of free ion}
B \quad B/B^o
D_Q \quad \text{ligand field splitting parameter, unit=cm}^{-1}
\Delta_o \quad \text{octahedral ligand field splitting energy, } \Delta_o=10 \text{ } D_Q
k \quad \text{electronic delocalization factor}
\Sigma X_{\text{dia}} \quad \text{sum of all diamagnetic susceptibilities in c.g.s. units}
\chi_m \quad \text{molar magnetic susceptibility}
\chi_C \quad \chi_m \text{ corrected for } \Sigma X_{\text{dia}}
\theta \quad \text{Weiss constant}
TIP \quad \text{Temperature Independent Paramagnetism}
\mu_B \quad \text{Bohr Magneton}
\mu_{\text{eff}} \quad \text{effective magnetic moment, unit=}\mu_B
\mu_{\text{eff}}^T \quad \mu_{\text{eff}} \text{ corrected for TIP}
\lambda \quad \text{spin orbital coupling constant, unit=cm}^{-1}

Vibrational Spectroscopy

s \quad \text{strong} \quad \nu_s \quad \text{symmetric stretch}
m \quad \text{medium} \quad \nu_{as} \quad \text{asymmetric stretch}
w \quad \text{weak} \quad \rho \quad \text{bending mode}
v \quad \text{very} \quad \delta \quad \text{deformation mode}
b \quad \text{broad}

Conductometry

H_o \quad \text{Hammett acidity function}
K_{\text{ap}} \quad \text{autoprotoalysis equilibrium constant}
mmol \quad 10^{-3} \text{ mole}
\kappa \quad \text{specific conductance, unit=}\Omega^{-1}\text{cm}^{-1}
R \quad \text{base/acid ratio in a titration}
\Lambda^+ \quad \text{molar conductivity of the cation}
\Lambda^- \quad \text{molar conductivity of the anion}