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RADIOCHEMICAL STUDIES  
of  
COBALT CARBONYL HYDRIDE DERIVATIVES.

by

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of the requirements for the degree  
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ABSTRACT.

1. The compound  $[\text{Co}(\text{CO})_4]_2 [\text{Co}(\text{phth})_3]$  was prepared by a previously described method (15). It was found to be unstable in the dry state and in solution in various organic solvents.
2. The solubility of the compound in various organic compounds was determined.
3. Conductance measurements in benzaldehyde and acetophenone were made. The molar conductances obtained indicate that the compound is a true salt.
4. Transference measurements were made in an acetone solution. The concentrations were determined by making one or other of the cobalt atoms active. The results obtained are probably invalid because of exchange between the two cobalt atoms.
5. Exchange between the two cobalt atoms in  $[\text{Co}(\text{CO})_4]_2 [\text{Co}(\text{phth})_3]$  was studied, and no exchange was found under the conditions of the experiment.
6. The exchange between active, cobalt (II) ions and the cobalt phenanthroline complex ion was studied. The exchange was found to be very rapid, reaching an equilibrium in a few minutes.
7. The exchange between active, cobalt metal and dicobalt octacarbonyl was studied, no exchange being found.

ACKNOWLEDGEMENT.

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## I. HISTORICAL INTRODUCTION

Carbonyl chemistry began in 1890 with the discovery by Ludwig Mond of nickel carbonyl,  $\text{Ni}(\text{CO})_4$ . Since this time many metallic carbonyls and allied compounds have been discovered, and their physical and chemical properties extensively studied.

The covalent metallic carbonyls so far known are restricted to the elements of the transition groups VIa, VIIa, VIIIa, b, c, and Ib of the periodic table. Some of these elements also form carbonyl hydrides, containing one or more atoms of hydrogen, and carbonyl nitrosyls in which one or more of the CO molecules are replaced by NO.

The carbonyls, carbonyl hydrides, and nitrosyl carbonyls so far known are shown in Table I.

The metal carbonyls differ in their physical properties from all other compounds formed by the transition elements. All of the monomeric carbonyls are extremely volatile, and most of the polymeric carbonyls can be sublimed. This volatility connotes lack of cohesion between the molecules, caused by lack of external field. A closed electronic structure is indicated by the fact that all of the simple carbonyls and their substitution products are diamagnetic. The carbonyls and carbonyl hydrides are soluble in non polar organic solvents, and insoluble in polar solvents.

The carbonyl hydrides are extremely volatile substances, existing normally only at temperatures well

below room temperature. Above this temperature they spontaneously decompose into the carbonyl, with the evolution of hydrogen. They are weakly acidic in nature and will form salts with the alkali metals and bulky amine cations.

The present work entailed the preparation and a study of some of the properties of cobalt carbonyl hydride,  $\text{Co}(\text{CO})_4\text{H}$ , dicobalt octacarbonyl,  $[\text{Co}(\text{CO})_4]_2$ , and a salt of cobalt carbonyl hydride,  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  where phth=o-phenanthroline, using radioactive  $\text{Co}^{60}$  as a tracer.

## Group

Carbonyls

Carbonyl

Hydrides

Nitrosyl

Carbonyls.

VIIa	VIIa	VIIIa	VIIIb	VIIIc	Ib
$M(CO)_6$					
Cr, Mo, W.	$[M(CO)_5]_2$	$M(CO)_5$			
	Re	Fe, Ru, Os.			
		$M_2(CO)_9$			
		Fe, Ru, Os.			
		$[M(CO)_4]_3$	$[M(CO)_4]_2$	$M(CO)_4$	
		Fe, Ru.	Co, Rh, Ir.	Ni.	
		$[M(CO)_3]_x$	$[M(CO)_3]_4$		$[M(CO)_3]_2$
		Fe.	Co, Rh, Ir.		Cu.
			$M_4(CO)_{11}$		
			Rh.		
	$M(CO)_5H$	$M(CO)_4H_2$	$M(CO)_4H$		
	Re?	Fe, Ru?, Os.	Co, Rh?, Ir?.		
		$M(CO)_2(NO)_2$	$M(CO)_3NO$		
		Fe	Co		

TABLE I

(3)

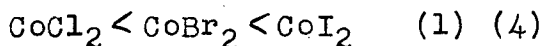
Methods of Preparation of  $[\text{Co}(\text{CO})_4]_2$  and  $\text{Co}(\text{CO})_4\text{H}$ .

(1). High Pressure Synthesis.

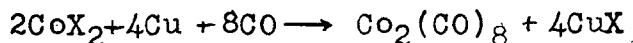
The original and usually the simplest method of formation of the carbonyls is by the direct interaction of the metal with carbon monoxide. The metal must be in a finely divided state, and the reaction is usually carried out under high pressure and temperature. The techniques of this method have been greatly improved by Heiber and his co-workers (1), who used a rotating autoclave capable of withstanding pressures up to 350 At.

Dicobalt octacarbonyl was first prepared in this manner by Mond and Hirtz (2), by passing carbon monoxide over pure cobalt at 30-250 At. and  $150-220^\circ\text{C}$ . This method is somewhat inconvenient however, as the metal must be in a carefully reduced, finely divided state.

In 1939 it was found by Schulten (3) that dicobalt octacarbonyl could conveniently be produced from anhydrous cobalt halides in Heiber's autoclave.  $\text{CoF}_2$  is without reaction, whereas the other halides increase in reactivity in the order



The reaction proceeds according to the equation

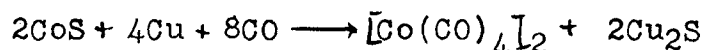


the Cu coming from the autoclave lining. During the reaction no carbonylhalide  $(\text{COX})_2$  was formed, so the reaction did not seem to occur through the reduction of the halide



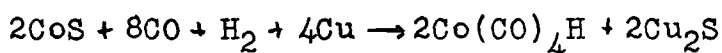
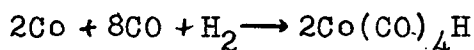
to the metal by carbon monoxide. On the other hand, cobalt iodide was shown to react with carbon monoxide even at room temperature giving an addition compound,  $\text{CoI}_2\text{CO}$  which is appreciably volatile. This is believed to react at the copper or silver walls of the vessel to form  $[\text{Co}(\text{CO})_4]_2$  and the copper halide. The presence of copper or silver to act as halogen acceptor is essential to the process, and it has been found that the admixture of the finely divided metals to the cobalt halide increased the yield.

Cobalt sulphide (1) when treated with carbon monoxide at 200 At. and  $200^\circ\text{C}$ . will also produce the carbonyl according to the equation



In general it has been found that carbonyls can be formed by the compounds of iron, cobalt and nickel with highly polarizable non-metals, i.e. from solids in which the lattice forces are not of purely ionic type.

Cobalt carbonyl hydride has been shown to be formed (1) in the high pressure synthesis whenever the reactants contain traces of moisture. Partial conversion into the hydride also occurs when metallic cobalt or cobalt sulphide is heated in hydrogen (50 At.) and carbon monoxide.



(2) Preparation in Solution.

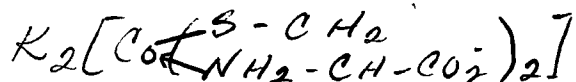
Carbonyls can be prepared by a number of reactions in solution in which the reduction of the metal is brought about by sulphides, cyanides, or even carbon monoxide itself in strongly alkaline solution.

In 1926 Job and his co-workers (5) observed that the reaction between carbon monoxide and the Grignard reagent was accelerated by the presence of salts of the transition metals, and from the reaction mixture they separated an ether soluble compound of chromium which was proven to be chromium hexacarbonyl.

The mechanism of the reaction appears to be the partial reduction of the metal salt, and the combination of carbon monoxide with one of the reduction products, which upon acid decomposition yields, among other products, the metal carbonyl. The product by this method is very pure, and it has proved to be the best method for preparing chromium hexacarbonyl.

Alkaline solutions of cobalt and nickel salts absorb carbon monoxide in the presence of cysteine, a sulphide, cyanide, tartrate, or amino acid, which on acidification give  $\text{Ni}(\text{CO})_4$  and  $\text{Co}(\text{CO})_4\text{H}$  respectively.

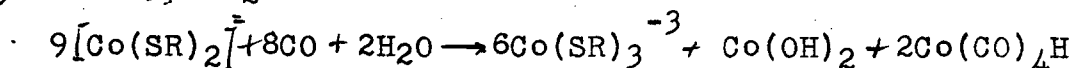
Cysteine,  $\text{SH}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{H}=(\text{H}_2\text{SR})$ , forms with bivalent cobalt a complex salt of the type



which in alkaline solution is sensitive to oxygen and also

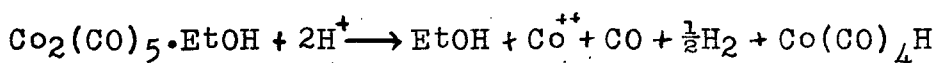
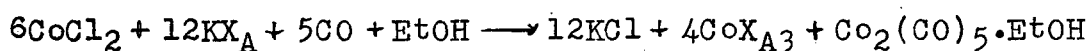
absorbs one molecule of carbon monoxide per atom of cobalt (6). The complex undergoes disproportionation, The cysteine being recovered in the form of a cobalt(III) complex,

$K_3[Co(SR)_3] \cdot 3H_2O$ , and cobalt carbonyl hydride being formed.

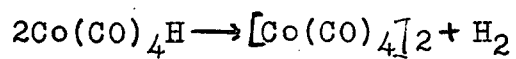
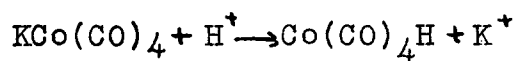
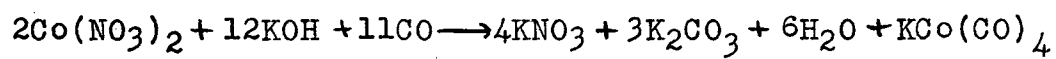
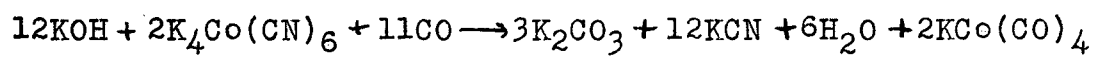
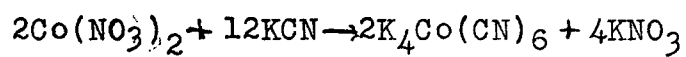


The cysteine is thus regenerated so that a small amount suffices to bring about nearly complete conversion of the cobalt salt (7).

Analogous reactions take place with cobalt (II) salts and other thio compounds that form inner complex salts (8). Absorption of carbon monoxide first forms a substituted cobalt carbonyl derivative (9) which furnishes cobalt carbonyl hydride when decomposed with acid. Thus with potassium xanthate,  $KX_A$  ( $X_A = C_2H_5 \cdot O \cdot CS \cdot S^-$ )



An alkaline suspension of a cobalt salt in the presence of cyanide will absorb carbon monoxide, the cyanide again acting as a carrier. This method has been developed by Blanchard and Gilmont as a means of producing  $[Co(CO)_4]_2$  (10) (11). The potassium salt of cobalt carbonyl hydride is formed, which upon acidification yields the free hydride. This decomposes at room temperature or on gentle warming to give dicobalt octacarbonyl and hydrogen. The reactions involved are as follows:



# Properties of $[\text{Co}(\text{CO})_4]_2$ and $\text{Co}(\text{CO})_4\text{H}$

Dicobalt octacarbonyl usually exists as a dark brown microcrystalline solid, but when pure it is obtained as yellow crystals. If it stands in a vacuum it slowly sublimes, forming a few clear orange crystals on the walls.

Cryoscopic molecular weight determinations in benzene and  $\text{Fe}(\text{CO})_5$  (9) indicate the dimeric formula. It has a vapour pressure of 0.07mm. at  $15^\circ\text{C}$ . and melts at  $51^\circ\text{C}$ ., decomposing at slightly above this temperature into tetracobalt dodecacarbonyl  $[\text{Co}(\text{CO})_3]_4$ , and carbon monoxide. Further heating produces the free metal.

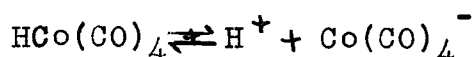
$[\text{Co}(\text{CO})_4]_2$  is insoluble in water, soluble in  $\text{CS}_2$ , ether, naphtha, alcohol and  $\text{Ni}(\text{CO})_4$  (2). If these solutions are kept for some time or warmed decomposition ensues.

The pure carbonyl is unstable in air, forming a violet basic carbonate. It is stable however in an atmosphere of CO or  $\text{H}_2$ .

Cobalt carbonyl hydride is a yellow gas which is extremely poisonous and has a very bad odor. If cooled to below  $-33^\circ\text{C}$  it forms a pale yellow solid, which on warming melts to a light yellow liquid, which darkens rapidly due to decomposition into  $[\text{Co}(\text{CO})_4]_2$  and  $\text{H}_2$ . This reaction has been shown to be reversible,  $[\text{Co}(\text{CO})_4]_2$  being partly converted into the hydride when heated in  $\text{H}_2$  (120 At.) and CO, at  $165^\circ\text{C}$ . (1).

The hydride is relatively stable in CO, and can be distilled in a stream of CO with practically no decomposition.

It dissolves out of such a stream, in water at 0°C., and although the solution decomposes in a few minutes, it persists long enough for a rough estimate of its acid strength to be made. Coleman (12) carried out an experiment of this type by passing CO carrying hydride vapours through a rotary absorption tower containing 200c.c. distilled water and some methyl orange. The methyl orange quickly turned red. Postulating the acid nature:



and making rough estimates of the amount of acid and its neutral salt indicate an ionization constant between that of acetic acid  $1.8 \times 10^{-5}$ , and that of formic acid,  $2 \times 10^{-4}$ .

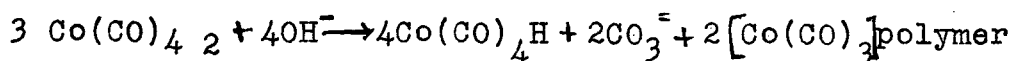
More recently (13) the ionization constant of the similar iron carbonyl hydride,  $\text{Fe(CO)}_4\text{H}_2$ , has been determined with a fair degree of accuracy. Using a potentiometric method, and excluding all air from the apparatus, the values  $K_1 = 4 \times 10^{-5}$  and  $K_2 = 4 \times 10^{-14}$  were obtained for the primary and secondary ionization constants.

#### Reactions of $[\text{Co(CO)}_4]_2$ and $\text{Co(CO)}_4\text{H}$

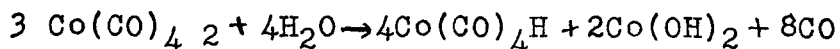
As a class the carbonyls are reactive compounds, undergoing a wide variety of substitution and addition reactions. A good many of the reactions that have been studied for cobalt carbonyl involve the formation of the hydride, or the  $\text{Co(CO)}_4^-$  ion as a primary step in the reaction.

$[\text{Co(CO)}_4]_2$  is hydrolyzed in either strong or weak bases, with the formation of the hydride (14) (15). With

strong bases such as  $\text{Ba(OH)}_2$  or  $\text{KOH}$  the reaction is:



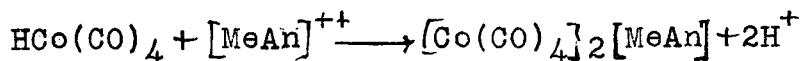
At lower hydroxyl ion concentrations ( $\text{NH}_3$ ) the reaction is given by:



The dilute solutions obtained by hydrolysis reduce methylene blue, and are very easily oxidized by air or mild oxidants, giving cobalt tetracarbonyl.

Cobalt carbonyl hydride acts as a weak monobasic acid, forming true salts with the alkali metals and with bulky ammine cations. It also forms compounds with the heavier metals, but these compounds do not have the properties of true salts, but have conductivities corresponding to weak salts.

From the reaction of an ammonia solution of  $\text{Co(CO)}_4\text{H}$ , obtained by hydrolysis of the carbonyl, with solutions of heavy metal salts, Hieber and Schulten (14) obtained compounds of the following type:

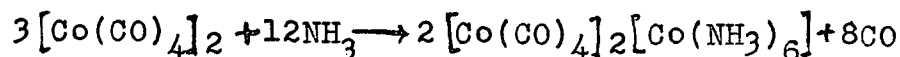


An =  $\text{NH}_3$ , amine.

Me = valence 2 metal.

With hexamine cations of valence 2 metals it was found that no reaction was obtained with Zn, Cd or Cu salt solutions. With hexamine  $\text{CoCl}_2$  solutions  $[\text{Co(CO)}_4]_2[\text{Co(NH}_3)_6]$  was obtained. With  $\text{NiCl}_2$  a similar compound  $[\text{Co(CO)}_4]_2[\text{Ni(NH}_3)_6]$  was formed. Gaseous ammonia will also react directly with

cobalt carbonyl:



Both the cobalt and nickel compound are extremely soluble in water, and therefore difficult to isolate. They are characterized by ease of spontaneous decomposition and ammonia loss.

With trisphenanthroline cations salts of the type  $[\text{Co}(\text{CO})_4]_2[\text{M}(\text{phth})_3]$  are formed, where  $\text{M} = \text{Co}, \text{Ni}$ . These compounds are very insoluble in water and can be used as a method of analysis for  $\text{Co}(\text{CO})_4\text{H}$ . They are reasonably stable in the dry state.

With  $\text{HgCl}_2$  and ammoniacal  $\text{Co}(\text{CO})_4\text{H}$  the compound  $\text{Co}(\text{CO})_4\text{Hg}$  is precipitated. This compound is insoluble in water, soluble in organic solvents. Its formation can be used to detect the presence of  $\text{Co}(\text{CO})_4\text{H}$ . It is unstable, and decomposes in a short time to a grey powder.

With ammoniacal  $\text{AgNO}_3$  the compound  $\text{Co}(\text{CO})_4 \text{Ag}\frac{1}{2}\text{CO}\frac{1}{2}\text{H}_2\text{O}$  can be isolated. This compound is also insoluble in water and soluble in organic solvents.

In order to determine whether or not they could be considered as true salts of the hydride, Hieber (16) made studies of the conductivities of these compounds and the similar compounds of iron carbonyl hydride. He found that in solutions of methanol and of acetone, the salts formed with the hexammine and with the trisphenanthroline cations had molar conductivities corresponding to solutions of strong electrolytes. These compounds may therefore be considered



as true salts of the carbonyl hydrides. The conductivities decreased with time, indicating decomposition of the compounds in solution. With the mercury salts however, the molar conductivity was very low (0.4 for  $\text{Co}(\text{CO})_4\text{HgCl}$  in acetone) and it can be inferred that these compounds are not true salts.

Hieber expresses the view that structures such as  $\text{Co}(\text{CO})_4^-$  are not stable, and can only be stabilized by the formation of salts with complex cations. He also states that alkaline solutions of the hydride contain aquo salts rather than normal salts not yet prepared, and that the formation of metal derivatives of the hydrides is by far not as general as it is supposed to be in an ordinary formation of salts. The preparation of the anhydrous salts  $\text{Fe}(\text{CO})_4\text{K}_2$  and  $\text{Fe}(\text{CO})_4\text{KH}$  (13) and measurement of the ionization constant of  $\text{Fe}(\text{CO})_4\text{H}_2$  as a weak acid, seem to disprove this view.

The reaction of cobalt carbonyl with complex forming amines has also been studied by Hieber and his coworkers (17). They find that in general the amines displace a part of the carbonyl group with the formation of mixed complexes. When cobalt tetracarbonyl or cobalt tricarbonyl are placed in pyridene, effervescence due to escaping CO ensues, and the compound  $\text{Co}_2(\text{CO})_5(\text{C}_5\text{H}_5\text{N})_4$  crystallizes out. In a similar fashion the complex  $\text{Co}(\text{CO})_3(\text{phth})_2$  is formed with a phenanthroline. With alcohols the compounds  $\text{Co}_2(\text{CO})_5\cdot\text{CH}_3\text{OH}$  and  $\text{Co}_2(\text{CO})_5\cdot 1.5\text{C}_2\text{H}_5\text{OH}$  are obtained, and with thioalcohols  $\text{Co}(\text{CO})_3\cdot\text{SC}_2\text{H}_5$  (18). All of these compounds liberate  $\text{Co}(\text{CO})_4\text{H}$  when treated with acid.

The Structure of Metal Carbonyls.

A theory for the structure of the monomeric carbonyls has been worked out, which fits in with their peculiar properties, such as volatility, and agrees with the experimental facts. Although a number of structural theories have been proposed for the polymeric carbonyls, none of these has as yet been completely satisfactory, and their structure is still somewhat in doubt.

The use of effective atomic number (E.A.N.) in classifying the volatile monomeric carbonyls has been found extremely helpful and the properties of the carbonyls show a marked uniformity according to this classification. The E.A.N. is defined as the total number of electrons held within the sphere of the atom, and includes those furnished by the atom itself, those added by electron transfer, and those added through establishment of covalent and coordinate bonds. Whenever the E.A.N. of the central metal atom of the compound is equal to that of an inert gas it is possible for the compound to be volatile.

In the volatile carbonyls it can be shown that the CO groups exist as such in the molecule and retain on the whole the bond nature of the CO atom, i.e.  $:C:::O:$ . The CO metal link could thus be represented by  $M:C:::O:$ . It can be seen that each CO molecule thus donates one pair of electrons to the central metal atom. Therefore the criterion for volatility is the attainment by the metal of the E.A.N. of an

inert gas, then for example nickel with an atomic number of 28, which is eight less than the atomic number of krypton, should take up four molecules of CO, forming  $\text{Ni}(\text{CO})_4$ . It has been found that all of the monomeric carbonyls follow this rule, having central metal atoms with the E.A.N. of rare gases. This accounts for their volatility and also the diamagnetism of the molecules.

Elements of odd atomic number cannot attain the E.A.N. of rare gas by the simple coordination of electron pairs, and do not form monomeric carbonyls. In their highest carbonyls the elements of group VIIIb., to which cobalt belongs, coordinate such a number of CO groups as would be expected to give them as E.A.N. of one less than the rare gas structure, and then combine to form dimeric molecules. The lower carbonyls formed by many of the elements are also polymeric, suggesting that the atoms are stabilized in some way by polymerization. The polymeric carbonyls are not volatile, but in most cases can be sublimed.

To explain the case of dicobalt octacarbonyl Sidgwick and Bailey (19) suggested a general principle for formulating polynuclear carbonyls and nitrosyls. Their theory was based on the hypothesis that all the metal atoms should acquire the E.A.N. of a rare gas, and that the CO group can form two collinear coordinate links.



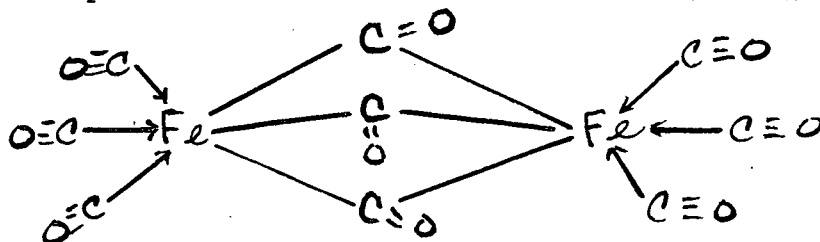
They suggested that in  $[\text{Co}(\text{CO})_4]_2$  one CO molecule forms a second coordinate link through the oxygen as donor, leading

to the structure:

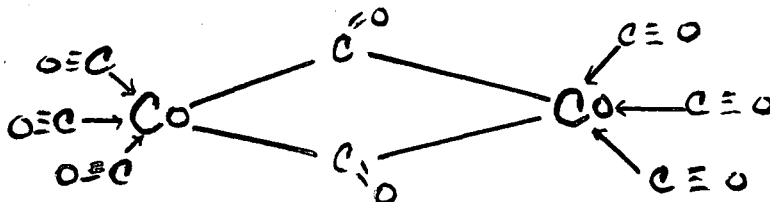


This gives one cobalt atom an E.A.N. of 37 and the other 35, the extra electron on the former being passed along to the latter to give each the krypton structure.

A good deal of doubt has been cast on the structures proposed by Sidgwick and Bailey, mainly through X-ray crystallographic studies on the eneacarbonyl of iron,  $\text{Fe}_2(\text{CO})_9$  (20). This compound has been shown to have the structure:

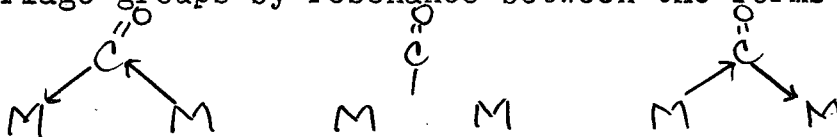


A similar structure for  $\text{Co}(\text{CO})_4$  would be:



These structures however leave each atom with one unpaired electronic spin, and the molecules should be paramagnetic. Their diamagnetism can only be explained by the hypothesis that the two metal atoms are so close together that the electron spins are paired, even though no bond is formed.

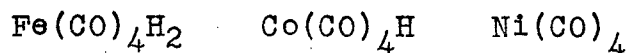
K.A. Jensen (21) has more recently suggested linking of the bridge groups by resonance between the forms



This fits the observed bond lengths of  $\text{Fe}_2(\text{CO})_9$ , and accounts

for the diamagnetism of the molecule.

The structural principle underlying the composition of the series

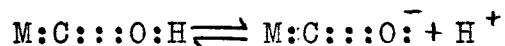


seems to be the attainment of the closed electronic configuration of  $\text{Ni(CO)}_4$ .

In the carbonyl hydrides it is possible for atoms of odd atomic number to attain the effective atomic number of a rare gas, since it can be assumed that the hydrogen atom donates one electron to the central metal atom. This may explain why, in many reactions, cobalt carbonyl hydride is formed in preference to the octacarbonyl. The carbonyl hydrides have been shown by electron diffraction measurements (22) to be isoelectronic with  $\text{Ni(CO)}_4$ . The mode of linkage of the hydrogen is however not definitely established by the electron diffraction data. Hieber (23), (24) holds the view that the hydrogen atoms are incorporated in some way as protons within the core of the cobalt and iron atoms. This structure however does not conform with the observed acid nature of the hydrides.

Evans and Lister (25) have suggested that the hydrogen is situated at the end of the chain  $\text{M-C-O-H}$ . This structure agrees with electron diffraction measurements and also is in agreement with the properties of the hydrides. Oxygen rarely assumes a covalency of four, and it is therefore not surprising that the hydrogen is easily lost. Liberation of a hydrogen atom accounts for the reducing power

and instability of these compounds, which decompose at a temperature well below room temperature. They may also dissociate as an ion:



allowing the hydride to form salts such as for example  $\text{Co(CO)}_4\text{K}$  and  $[\text{Co(CO)}_4]_2[\text{Co(phth)}_3]$ . While the chemical properties of the hydrides seem to agree with this structure, there has as yet been no evidence advanced to show that there are two types of M-C and C-O bond dimensions within the molecule, as would be expected for a structure of this type.

## II. Introduction.

The object of this work was to prepare the compound  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  (phth = o-phenanthroline), and by transference measurements to determine if possible the relation which it bears to the  $\text{Co}(\text{CO})_4^-$  ion. Either the  $\text{Co}(\text{CO})_4^-$  ion or the  $\text{Co}(\text{phth})_3^{++}$  ion could be traced by the use of radioactive cobalt. It was assumed that there was no exchange between the two cobalt atoms in the compound, but this was later proved not to be the case. Difficulties were encountered because of the extreme instability of the compound, and only very rough measurements were obtained. Approximate measurements of the molal conductivity in benzaldehyde and acetophenone were also made, and these compared favorably with measurements made on similar compounds (16), indicating that the compound is a strong electrolyte.

The solubility of the compound and its stability in various organic solvents were determined.

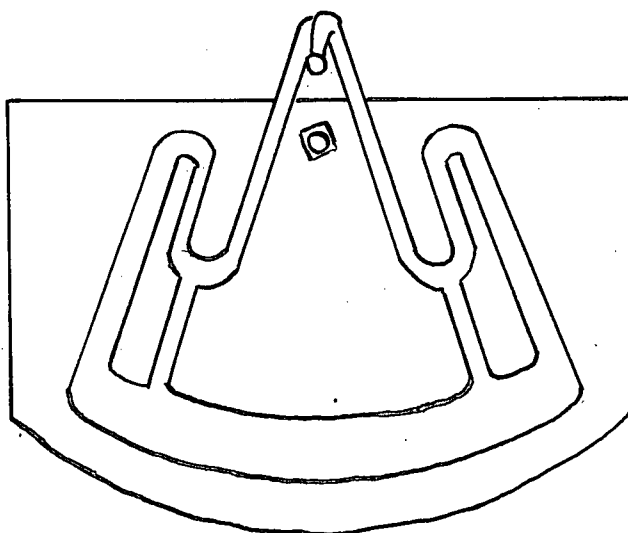
Because of the results obtained in the transference measurements, the exchange between cobalt (II) ions and the  $\text{Co}(\text{phth})_3^{++}$  ion was studied.

### III. Experimental.

The radioactive  $\text{Co}^{60}$  used was prepared in the pile at Chalk River by irradiating  $\text{Co}_2\text{O}_3$ . The oxide was dissolved in concentrated hydrochloric acid and the solution neutralized with ammonium hydroxide. For the experiments an exchange  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was added to the solution of active cobalt to give the desired specific activity, and the amount of cobalt in a given volume was determined using the  $\alpha$ -nitroso $\beta$ -naphthol method (26). Portions of the solution were then counted to obtain the number of counts per gram of cobalt.

The counting circuit consisted of an argon methonal filled Geiger tube attached to a scaling circuit. The tube had a plateau of about 300 volts with about a 1% rise. The background remained constant over the period of operation. The samples were counted on small watch glasses, held in position on an aluminum tray, and were thin enough that internal absorption could be neglected. The standard and samples were counted under identical conditions of geometry. The half life of five years for  $\text{Co}^{60}$  is long enough so that decay of the active cobalt, over the period of measurement, could be neglected.





CO from  
 $\text{H}_2\text{SO}_4$   
 formic acid  
 generator.

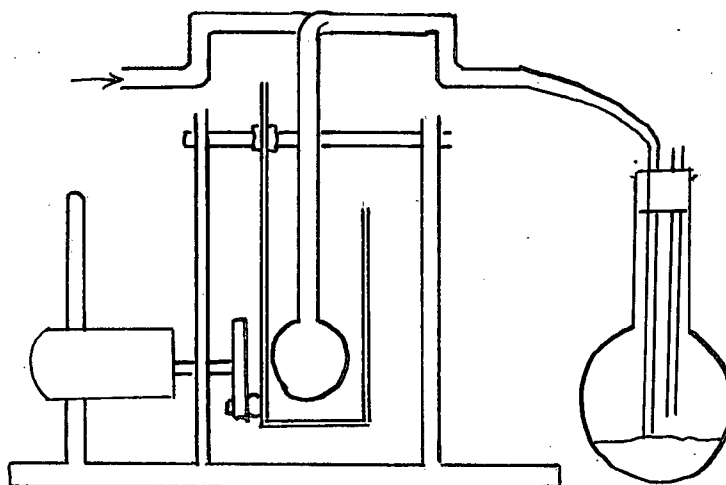


Figure I.

Preparation of Dicobalt Octacarbonyl.

Dicobalt octacarbonyl was prepared by the method outlined by Gilmont and Blanchard (11) using the same amounts of reagents as described by them. In this procedure the alkali salt of cobalt tetracarbonyl hydride is first prepared by shaking an alkaline cobalt(II) cyanide suspension in the presence of carbon monoxide. A shaker of the type shown in fig.1 was used and the carbon monoxide was passed in a slow stream through the apparatus during the shaking process. The  $\text{Co}(\text{CO})_4\text{K}$  formed is very easily oxidized and it was found that any trace of air in the apparatus led to darkening of the suspension, and no  $\text{Co}(\text{CO})_4\text{K}$  was obtained. To prevent air entering the exit sidearm during the shaking a trap was attached consisting of a glass tube just touching the surface of a small amount of water contained in a 500ml. flask. This procedure was found to be effective in preventing the oxidation of the  $\text{Co}(\text{CO})_4\text{K}$ .

Cobalt carbonyl hydride was liberated from the solution of the potassium salt by the addition of 12N hydrochloric acid. The set-up used for collecting the hydride is shown in fig.2. The solution was swept with CO for about ten hours and the hydride collected in a U-shaped tube cooled to  $-79^\circ\text{C}$ . in dry ice-alcohol mixture. When the hydride had been collected the tube containing it was evacuated at  $-79^\circ$  and then allowed to come to room temperature. The  $\text{Co}(\text{CO})_4\text{H}$  melts to a light yellow liquid

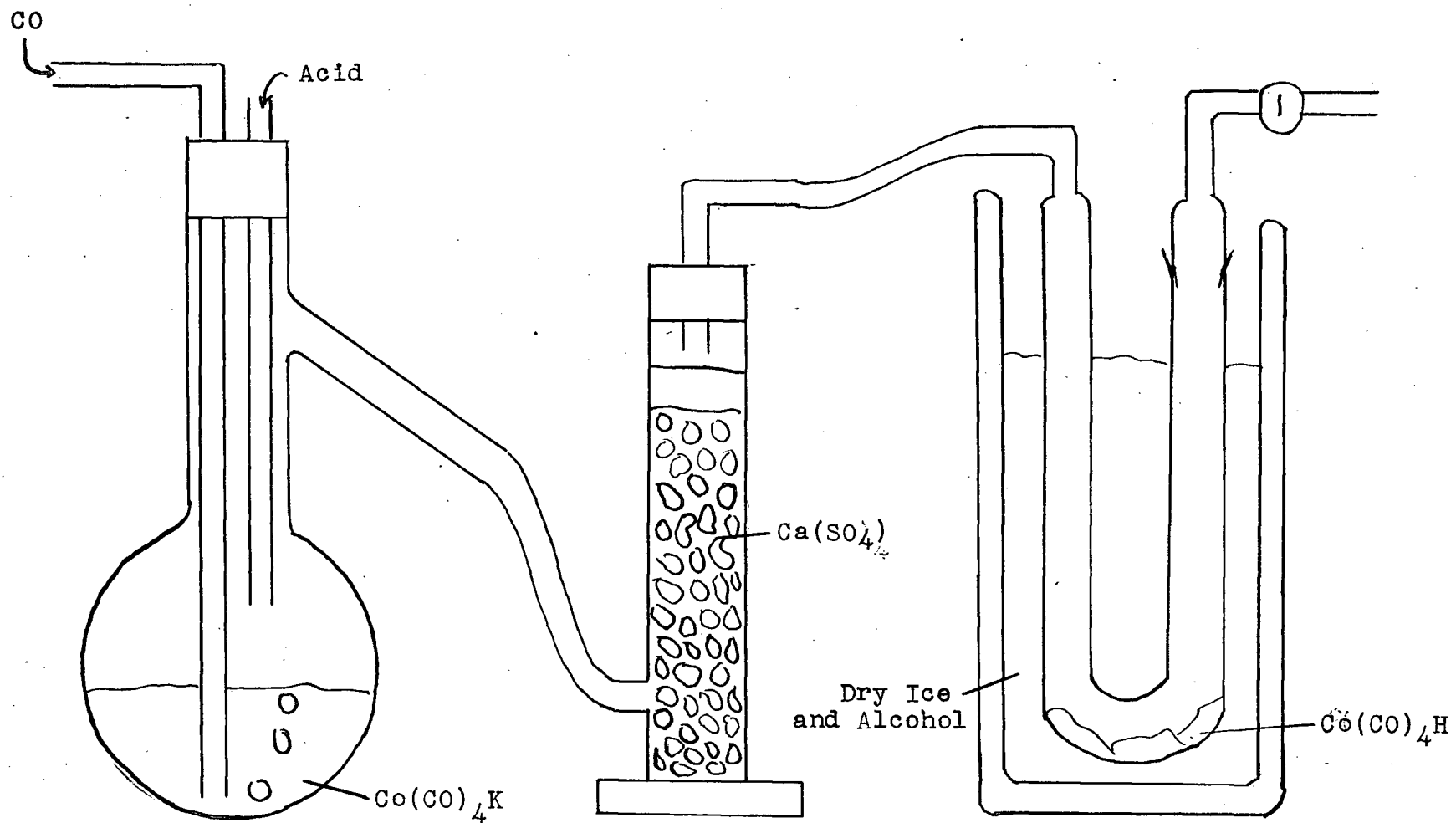


Figure II.

which darkens rapidly due to decomposition into  $[\text{Co}(\text{CO})_4]_2$  and  $\text{H}_2$ .

The dicobalt octacarbonyl formed in this manner is a dark brown microcrystalline solid. It decomposes in the presence of air to give a violet basic carbonate. It is stable in an atmosphere of carbon monoxide or hydrogen, and it was found that it could be kept without decomposition in the tube in which it had been prepared if no air was allowed to enter.

Most of the  $[\text{Co}(\text{CO})_4]_2$  could be removed from the tube for use by gently tapping the sides of the tube. Any that could not be removed in this manner was washed out with the particular solvent to be used, usually concentrated  $\text{NH}_4\text{OH}$ .

Preparation of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ .

$[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  was prepared by shaking for 36 hours  $[\text{Co}(\text{CO})_4]_2$  with concentrated  $\text{NH}_4\text{OH}$ , in the ratio 1.25gms.  $[\text{Co}(\text{CO})_4]_2$  per 150mls.  $\text{NH}_4\text{OH}$ . It was found that air must be excluded from the apparatus during shaking, or a dark red solution is obtained which will not precipitate the phenanthroline complex. To accomplish this a stopcock was attached to the shaking flask so that the system could be evacuated after the carbonyl had been weighed, and the  $\text{NH}_4\text{OH}$  then added. The colorless or faintly pink solution prepared in this way was added to an equal volume of solution containing 0.6gms.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 1.4gms. o-phenanthroline monohydrate per 50mls. water. The heavy flocculent reddish brown precipitate which immediately formed was filtered through a Gooch crucible, washed with water, and dried in a vacuum dessicator under high vacuum. It was found to be unstable, decomposing to a grey brown substance which would not dissolve in any of the solvents which dissolve the original compound. The decomposition of the product depends to a large degree on the rapidity with which it is dried. Washing the precipitate with Water and drying it in a vacuum dessicator was found to generally result in partial decomposition, unless the amount of precipitate was extremely small, allowing rapid drying. If the precipitate was washed with ether or alcohol to remove the water, it was found to decompose very little during drying and

could be kept for several days over  $P_2O_5$ . The precipitate is slightly soluble in these substances, but the rate of solution seems to be slow and the amount of product lost during the washing was amply compensated for by lack of decomposition during drying.

Hieber and Schulten (14) state that the compound is relatively stable in the dry state. It was found however that even when thoroughly dry it could not be kept more than a few days without considerable decomposition taking place. Storage in an atmosphere of carbon monoxide did not seem to alter the rate of decomposition. These workers purified the product by dissolving it in a little acetone, filtering the solution and reprecipitating the compound with water. This procedure however leads to further decomposition during the drying, and no attempt was made in these experiments to purify the compound in this manner. If partial decomposition had set in the compound was dissolved in the particular solvent to be used, and the insoluble residue filtered out.

In transference and exchange measurements one or other of the two cobalt atoms was radioactive. Wherever possible the cobalt in  $Co(phth)_3^{++}$  was made active, since making the carbonyl cobalt atom active involves the handling of the extremely volatile  $Co^*(CO)_4H$ .

In order to make the cobalt atom in the phenanthroline complex active a given volume of standard radioactive solution was added to orthophenanthroline and enough

enough  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  then added to give the necessary weight of  $\text{CoCl}_2 \cdot [\text{Co}(\text{CO})_4]_2 [\text{Co}(\text{phth})_3]$  was then precipitated by the addition of ammoniacal cobalt carbonyl solution.

If it was necessary to make the cobalt carbonyl active, the active cobalt chloride solution was added in the preparation of the carbonyl.

#### Solubility of $[\text{Co}(\text{CO})_4]_2 [\text{Co}(\text{phth})_3]$ .

$[\text{Co}(\text{CO})_4]_2 [\text{Co}(\text{phth})_3]$  dissolves readily in acetone forming an orange-brown solution. Upon standing this solution gradually turns cloudy, and eventually a flocculent dark brown precipitate is formed. If the cobalt atom in the phenanthroline complex is made active, almost all of the activity is removed by filtering off this precipitate. When analysed radiochemically it showed 2.5% active cobalt. It is soluble in water, forming a pale yellow solution.

It was thought that the decomposition of the compound in acetone might be due to the presence of small amounts of water in the acetone used. The acetone was accordingly redistilled over activated alumina to remove any traces of water. It was found however that the compound was still unstable in this solvent.

The solubility and stability of the compound were measured in various other organic solvents in an effort to find a solvent in which it was more stable. The results obtained are given in table II. The acetone used was

C.P. grade and was dried in the method described. It had a boiling point of 56.5 C. No attempt was made to purify any of the other solvents used, but they were all of C.P. grade. The  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  was purified by dissolving it in acetone, filtering off the insoluble residue, and evaporating the solution to dryness under reduced pressure. The compound prepared in this manner was completely soluble in acetone.

The solubility of equal amounts of compound in equal amounts of solvent were tested at room temperature for the following solvents.

Table II.

<u>Solvent.</u>	<u>Solubility</u>	<u>Stability.</u>
acetone.	+	heavy ppt. overnight
methyl ethyl ketone.	+	slight ppt. 1 hr. heavy overnight
acetophenone.	+	slight ppt. overnight
methyl paratolyl ketone.	sl. sol.	ppt. in few hrs.
formaldehyde	—	
benzaldehyde	+	no. ppt.
salicylaldehyde	+	no ppt.
cinnamaldehyde	+	no ppt.
benzene	—	
ether	sl. sol.	
absolute ethanol	dissolves slowly	
ethyl acetate	+	heavy ppt. in few hrs.



If the stability of the compound in various solvents is judged by the rapidity with which an insoluble precipitate is formed, it would appear that the compound is unstable in ketones, stable in aldehydes. However if the precipitate formed in an acetone solution is filtered off, and its solubility tested in the various aldehydes used, it is found to be soluble. The apparent stability of the compound in aldehydes therefore appears to be due only to the solubility of the products of disintegration in these solvents.

The Conductance of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  in Benzaldehyde and Acetophenone.

As a result of the solubility measurements and the fact that  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  appears to be more stable in benzaldehyde or acetophenone than it is in acetone, the molal conductance of the compound in these solvents was determined to see if they would be suitable as solvents for transference measurements. Since the instability of the compound precludes making accurate measurements of the conductance, only very approximate values were obtained.

The resistance of the solutions was measured in the following manner. The solution was contained in a weighing bottle, and two silver electrodes, approximately 1 cm. square, were inserted into the solution through a rubber stopper. Resistance across the two electrodes was measured with a Simpson resistance meter. The cell was standar-

dized by measuring the resistance of an equal volume of 0.1M KCl solution. The following results were obtained:

Benzaldehyde:

conc. - 0.00084M

resistance of pure benzaldehyde -  $1.2 \times 10^6 \Omega$

Table III.

Time	Resistance	Time	Resistance
0 min.	$8 \times 10^4 \Omega$	45 min.	$6.5 \times 10^4 \Omega$
5	$7.5 \times 10^4$	60	$6.0 \times 10^4$
10	$7.8 \times 10^4$	150	$5.3 \times 10^4$
17	$7.8 \times 10^4$	1110	$6.2 \times 10^4$
26	$7.4 \times 10^4$	1170	$6.2 \times 10^4$

Acetophenone:

conc. - 0.0023M

resistance of pure acetophenone -  $24 \times 10^4 \Omega$

Table IV.

Time	Resistance	Time	Resistance
0 min.	$3 \times 10^4 \Omega$	105 min.	$17.0 \times 10^4 \Omega$
5	$3.6 \times 10^4$	18 hrs.	$13.5 \times 10^4$
10	$4.0 \times 10^4$	19	$13.0 \times 10^4$
15	$4.4 \times 10^4$	20	$12.7 \times 10^4$
25	$5.3 \times 10^4$	22	$11.7 \times 10^4$
40	$8.0 \times 10^4$	23	$11.0 \times 10^4$
75	$16.0 \times 10^4$	24	$10.5 \times 10^4$

For a 0.1M KCl soln:

R=1500

T = 20°C.

From the resistance in the cell of 0.1M KCl, the cell constant J was calculated, using the relation

$$J = LR \quad \text{where } L = \text{the specific conductance}$$

$$R = \text{the measured resistance}$$

At 18°C. the specific conductance of 0.1 demal KCl is  $0.011166 \Omega^{-1}$  (27). The demal solution is defined as a solution containing a gram mol. of salt dissolved in a cubic decimeter of solution at zero degrees. The corrections involved in changing this to molar concentration are outside the accuracy obtained in the above conductance measurements.

Knowing the cell constant, the specific conductance of the  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  solutions were calculated from the measured resistances, the conductance due to the solvent being subtracted from the conductance of the solution. The molar conductance was then calculated using the relation,

$$\Lambda_m = 1000 \frac{L}{C} \quad \text{where } \Lambda_m = \text{molar conductance}$$

C = concentration of solution in moles/liter.

The values given are for the initial readings only, before the solutions had decomposed to any extent.

Table V. Molar Conductivity of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$

Solvent	J	Conc.	$L \Omega^{-1}$	$\Lambda_m \Omega^{-1}$
Benzaldehyde	16.7	$0.84 \cdot 10^{-3}$	$1.95 \cdot 10^{-4}$	232
Acetophenone		$2.3 \cdot 10^{-3}$	$5.57 \cdot 10^{-4}$	212

Hieber (16) has measured the conductivity of compounds similar to this, in methanol and acetone. Some of his results are shown in table VI:

Table VI.

Compound	Solvent	$\Delta_{m. \Omega^{-1}}$
$[\text{FeH}(\text{CO})_4]_2[\text{Ni}(\text{phth})_3]$	$\text{CH}_3\text{OH}$	129.7
$[\text{FeH}(\text{CO})_4]_2[\text{Ni}(\text{phth})_3]$	Acetone	114.0
$[\text{Co}(\text{CO})_4]_2[\text{Ni}(\text{phth})_3]$	Acetone	248.8-280.15
$[\text{FeH}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$	Acetone	168.4

Measurements made in acetone solutions showed that the conductivities decreased with time.

Table VII

Compound	$\Delta_{m. \Omega^{-1}}$
$[\text{FeH}(\text{CO})_4]_2[\text{Ni}(\text{NH}_3)_6]$	114.5    88.4(75')    74.2(4hr.) 44.1(25hrs.)
$[\text{FeH}(\text{CO})_4]_2[\text{Co}(\text{NH}_3)_6]$	133.5    102.4(15')    99.5(25') 95.6(50')

From conductivity measurements of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  in benzaldehyde it can be seen that the resistance decreases with time, indicating an increase in conductivity. This result may be due to the fact that benzaldehyde is easily oxidized to benzoic acid, which would contribute to the conductivity of the solution.

In acetophenone the conductivity decreases at first, then increases slightly. The decrease in activity can be

attributed to decomposition of the solute. The subsequent increase may be due to the fact that in the course of decomposition ions, such as  $\text{Co}^{++}$ , may be formed which are soluble in acetophenone and lead to an increase in the conductivity.

Since the molar conductivity of a solution is equal to the sum of the molar conductivities of the ions present, the molar conductivity of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  can be calculated from the data given by Hieber in table VI. This calculation gives a value of  $303.2 - 334.6 \Omega^{-1}$  for the molar conductivity of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  in acetone. The higher the dielectric constant of the solvent, the higher will be the conductivity in that solvent. The dielectric constants of acetone, acetophenone and benzaldehyde are 20.4, 18.6 and 18 respectively. It can therefore be seen that the values of 232 for the molar conductivity in benzaldehyde, and 212 for the molar conductivity in acetophenone, agree within experimental error with the value obtained by Hieber in acetone.

#### Transference Measurements.

A transference cell of the type designed by Washburn (28) was used in an attempt to measure transference numbers of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  in solutions of acetone and acetophenone. The cell had a volume of approximately 100mls. and a distance between electrodes of 45cms. The electrodes were of platinum and were set in horizontally through

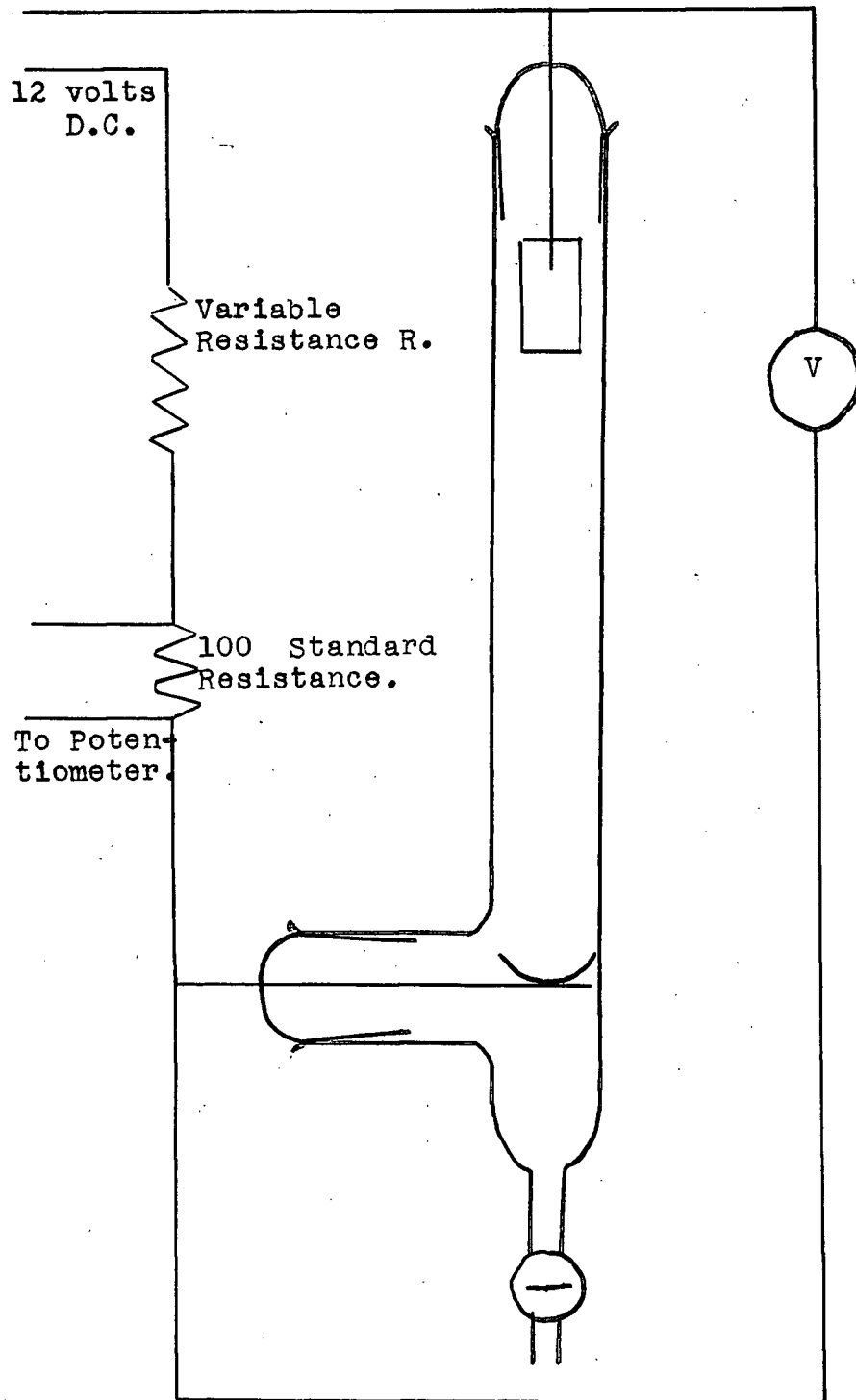


Figure III.

ground glass stoppers so that they could be removed for counting.

It was found to be impossible to obtain results with a cell of this type, because of the following difficulties:

In an acetone solution the compound showed signs of decomposition by the formation of a precipitate, before the current had been passed long enough to secure accurate results. With decomposition the current through the cell dropped rapidly, resulting in practically no current at the end of about an hour.

In acetophenone the compound was more stable, but also less soluble, so that only very dilute solutions could be prepared. The resistance of these solutions was so high that very little current flowed through the cell, even before decomposition had set in.

To overcome these difficulties a cell of the Hittorf type was designed, having a volume of approximately 25ml. and a distance between electrodes of 8cm. With a cell of these dimensions the resistance of the solution is much reduced, and measurements can be made in a shorter time before the solution has time to decompose appreciably.

The cell that was used is shown in fig. 3. The electrodes were of platinum and were set in through ground glass joints, with the cathode at the bottom. This helps to prevent mixing, since the  $[\text{Co}(\text{phth})_3]^{++}$  which presumably migrates to the cathode, is heavier than the  $[\text{Co}(\text{CO})_4]^-$  ion.

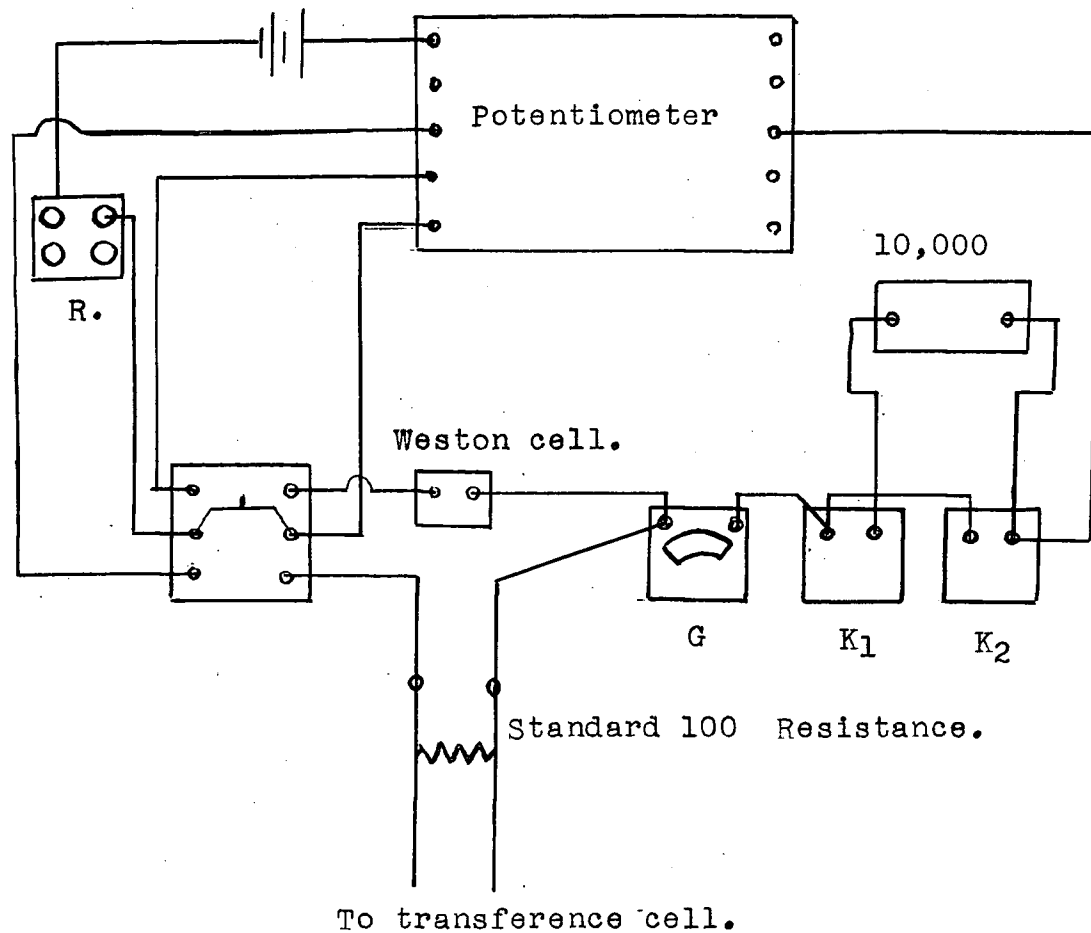


Figure IV.



The cathode was set in through the side of the cell, so that it could be removed easily to count any precipitate formed on it, and was cup shaped so that it would hold the precipitate more easily.

The stopcock at the bottom was for the purpose of removing the solution from the cell, but it was found that if the solution was removed in this way mixing resulted from some of the cathode portion remaining in the side arm and running out with the anode portion. The anode and middle portions were therefore removed with a suction pipette from the top of the cell, and the cathode portion then run out from the bottom. To test whether or not mixing resulted when the solution was removed in this manner a few crystals of potassium permanganate were placed in the cathode portion and the cell filled with water, giving a colored solution around the cathode. No mixing of the solution could be observed when it was removed in the manner described.

The circuit used is shown in the diagram. It was found that for the small number of coulombs passed during a measurement a silver coulometer would not give sufficiently accurate results. A potentiometer was used to measure the voltage drop across a standard hundred ohm resistance connected in series with the transference cell. The circuit used is shown in fig.4. The potentiometer was standardized against a standard Weston cell before the

run and several times during measurements. The voltage drop across the standard resistance was measured every few minutes during a run, and from the calculated current a graph was plotted of current vs. time. The area under the curve represented the number of coulombs passed.

Procedure:

Transference measurements were made in solutions of acetone. The acetone was C.P. grade and was redistilled several times over activated alumina to remove any water. The  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  was dissolved in the acetone, and any insoluble residue that remained due to decomposition was filtered off. The cathode and anode were weighed accurately and after the solution had been introduced into the cell, were sealed in with paraffin. After the current had been passed for the desired length of time the anode was carefully removed, and the solution drawn out as described into weighed glass stoppered bottles, and the three portions weighed. The solutions were kept tightly stoppered to prevent evaporation of acetone.

The solution was drawn out in three portions, the anode portion extending to about two cm. below the anode, the middle portion to about two cm. above the cathode, the remaining solution being run out as the cathode portion.

During electrolysis a heavy dark brown precipitate was formed on the cathode. This was removed, washed with acetone, and weighed. The anode was also weighed after each run, but no weight difference was found. A gas

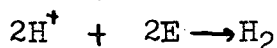
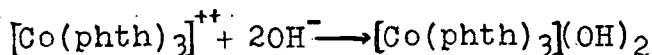
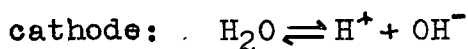
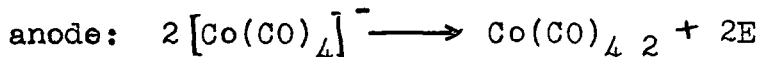
appeared to be formed at both the anode and cathode, but was not collected in sufficient quantities to be identified .

The concentration of the original solution was obtained by evaporating known volumes to dryness, obtaining the weight of the  $[\text{Co}(\text{CO})_4]_2$   $[\text{Co}(\text{phth})_3]$  in this volume, and then counting the samples. The concentration of the three portions after electrolysis could then be obtained by evaporating known volumes to dryness and counting them under the same conditions.

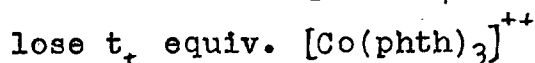
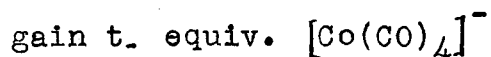
The precipitate on the cathode was also counted, and from its weight the percent active cobalt calculated. From the weight of the precipitate on the cathode and the number of coulombs passed it should be possible to calculate the equivalent weight of the precipitate. No consistent results could be obtained however, probably due to the fact that the precipitate did not adhere to the cathode very well, and was probably not all removed for weighing.

#### Results and Calculations:

Transference numbers were calculated, assuming the following reactions to take place:



at anode:



at cathode:

lose  $t_-$  equiv.  $[\text{Co}(\text{CO})_4]^-$

gain  $t_+$  equiv.  $[\text{Co}(\text{phth})_3]^{++}$

deposit 1 equiv.  $[\text{Co}(\text{phth})_3](\text{OH})_2$

net result:

lose  $(1 - t_+)$  equiv. =  $t_-$  equiv.  $[\text{Co}(\text{phth})_3]^{++}$

The cobalt atom in  $[\text{Co}(\text{phth})_3]^{++}$  was made active. At the end of the run the middle portion had changed concentration. Since its final concentration was the same as that of the cathode portion, the two were taken together.

Table VIII.

	cts./min.* 10.2ml.	conc. equiv./l.	volume in mls.	equiv. transferred
original	2398 $\pm$ 28	0.0117		
cathode	2291 $\pm$ 30	0.0113	10.005	$3.8 \times 10^{-6}$
middle	2288 $\pm$ 38	0.0113	2.02	$0.81 \times 10^{-6}$
anode	2151 $\pm$ 38	0.0106	2.05	$2.20 \times 10^{-6}$

coulombs passed = 0.83

$= 8.6 \times 10^{-6}$  faradays

\* Background subtracted.

Transference numbers calculated:

(1) from change in conc. of anode portion:

$$t_+ = 0.256$$

$$t_- = 0.744$$

(2) from change in conc. of cathode portion:

$$t_+ = 0.465$$

$$t_- = 0.535$$

The precipitate on the cathode was dark brown in colour, with a small amount of lighter brown material on the surface. It was soluble in water, forming a yellow solution. Calculation of its equivalent weight, from the weight of precipitate deposited and the number of coulombs passed, gave the following results, including values obtained in previous runs:

Table IX.

Wt. of ppt.	Coulombs.	Equiv. Wt. (Gms)
0.0036 gms.	0.83	420
0.0176	5.18	293
0.0176	5.45	312
0.0026	1.167	216

A radiochemical analysis of the precipitate gave the following results:

Table X.

Wt. ppt.	Counts/min.	Gms. Co	% Co
0.0067gms.	4533 $\pm$ 33	0.00025	3.76
0.0118	7241 $\pm$ 41	0.00040	3.41
0.0103	6549 $\pm$ 39	0.00036	3.53

Ave. - 3.57%

If the precipitate is  $[\text{Co}(\text{phth})_3](\text{OH})_2$  the following values should be obtained:

Molecular weight - 616.2

Equivalent weight - 308.1

Percent active cobalt - 9.58%  
(assuming no exchange)

Measurements were also made with the cobalt in the  $[\text{Co}(\text{CO})_4]^-$  ion active. The results obtained were too inaccurate to calculate transference numbers, as the difference in concentration between the cathode portion and the original solution was too small to be significant. The anode portion showed a definite increase in activity, which agrees with the equations postulated. The precipitate on the cathode however was found to be active. If this precipitate is  $[\text{Co}(\text{phth})_3](\text{OH})_2$  as has been postulated, it should not have been active in this case, unless exchange had occurred between the two cobalt atoms. Analysis of the precipitate showed that it contained 6.7% active cobalt, a much larger percentage than was found when the cobalt in the phenanthroline complex was active.

An attempt was made to analyse the precipitate for total cobalt content using the  $\alpha$  - nitroso- $\beta$  naphthol method. However it was found that only a very small amount of the cobalt could be precipitated in this manner, since the ortho-phenanthroline complex prevents the precipitation of cobalt in the usual manner.

Study of Exchange between the Two Cobalt Atoms in  
 $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$

Because of the results obtained in the transference measurements, which seem to indicate exchange of some type, an experiment was carried out to determine whether or not exchange occurs between the two cobalt atoms in  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ .

Because of the weak acid nature of  $\text{Co}(\text{CO})_4\text{H}$ , it should be possible to liberate  $\text{Co}(\text{CO})_4\text{H}$  from  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  by the addition of a strong acid such as  $\text{HCl}$ , and this was found to be the case. The activity of this will be a measure of the exchange if only the phenanthroline Co was active initially.

$[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  was prepared as previously, with the cobalt atom in the phenanthroline complex active. The precipitate was washed well with water, but no attempt was made to dry it. A small distilling flask was connected through the side arm to a drying train, and a trap cooled to  $-79^\circ\text{C}$ . The precipitate was washed into the drying flask with a small amount of distilled water, the system was attached to the carbon monoxide generator and concentrated hydrochloric acid added until the precipitate completely dissolved, giving a bright blue solution. About an hour elapsed between the time the compound was made, and the time that it was acidified. A slow stream of carbon monoxide was allowed to pass for about ten hours

at the end of which time a small amount of  $\text{Co}(\text{CO})_4\text{H}$  had collected in the trap. The trap was evacuated at  $-79^\circ\text{C}$ . and allowed to come to room temperature, giving dicobalt octacarbonyl. This was dissolved in benzene, evaporated to dryness, and counted.

background -  $61 \pm 3$

$\text{Co}(\text{CO})_4$  2 -  $60 \pm 3$

This indicates that there was no exchange between the two cobalt atoms, under the conditions of the experiment.

### Study of the Exchange Between $\text{Co}^{++}$ and $[\text{Co}(\text{phth})_3]^{++}$ .

Since it appears that there is no exchange between the two cobalt atoms in  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ , some other explanation must be sought to account for the results obtained in transference measurements. If the  $[\text{Co}(\text{CO})_4]^-$  ion were to decompose in acetone solution, giving cobalt ions, it might be possible for these cobalt ions to exchange with the cobalt in  $[\text{Co}(\text{phth})_3]^{++}$ . Such an exchange has been observed between  $\text{Fe}^{++}$  ions and  $[\text{Fe}(\text{phth})_3]^{++}$  (29).

A standard radioactive cobalt solution was prepared in the following manner. Approximately 0.2gms.  $\text{Co}_2^*\text{O}_3$  were dissolved in  $\text{HCl}$  and a little  $\text{HNO}_3$ . The solution was made up to approximately 100ml. and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  added to obtain the desired specific activity. Three 2.0ml. samples were measured out, evaporated nearly to dryness to get rid of the  $\text{HNO}_3$ , diluted to 10ml., and analysed for cobalt using  $\alpha$ -nitroso $\beta$ -naphthol.



Table XI.

	Wt. of $\text{Co}(\text{C}_{10}\text{H}_6\text{O}_2\text{N})_3 \cdot 2\text{H}_2\text{O}$ .	Wt. Co.
1.	0.1252 gms.	0.0121 gms.
2.	0.1170	0.0118
3.	0.1299	0.0120

Ave.- 0.0120 gms. Co/ 2 mls. Solution.

0.0060 gms. Co/ 1 ml. Solution.

1 portions of the solution were evaporated to dryness and counted:  $2400 \pm 57$  counts/min.

1 gm. cobalt =  $4 \times 10^8$  counts/min.

In order to study the exchange between  $\text{Co}^{++}$  and  $[\text{Co}(\text{phth})_3]^{++}$ , a solution was prepared by adding to a known weight of ortho-phenanthroline sufficient  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  to complex the ortho-phenanthroline and provide a  $\text{Co}^{++}$  ion concentration of approximately 0.02M. To this was added 5mls. of standard  $\text{Co}^{++}\text{Cl}_2$  solution, and the solution was diluted to 50mls. At the end of the desired length of time 5 mls. of solution were withdrawn and the  $[\text{Co}(\text{phth})_3]^{++}$  precipitated with an ammoniacal solution of  $\text{Co}(\text{CO})_4\text{H}$ , as  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ . The time was taken as the time at which the precipitate formed. The precipitate was filtered through a Gooch crucible, washed well with water and a little alcohol, and dried in a vacuum. When dry the precipitate was weighed in the crucible, and then dissolved in acetone, usually leaving a small amount of insoluble residue. After drying in a vacuum the crucible was

reweighed, giving the weight of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  in solution. The solution was diluted to 50mls. and 0.4 ml. samples counted. From the weight of precipitate in the acetone solution and its activity, the activity of the  $[\text{Co}(\text{phth})_3]^{++}$  was calculated, and hence the percent exchange, the percent exchange being taken as the percent of cobalt which had been transferred from the cobalt ion to the phenanthroline complex. From the concentrations of  $\text{Co}^{++}$ ,  $\text{Co}^{*++}$ , and  $[\text{Co}(\text{phth})_3]^{++}$  in the original solution, the theoretical percent exchange at equilibrium was calculated, using the fact that at equilibrium the ratio of active to inactive cobalt atoms will be the same for  $\text{Co}^{++}$  and for  $[\text{Co}(\text{phth})_3]^{++}$ .

The following results were obtained:

1. Wt. o-phth. $\cdot\text{H}_2\text{O}$  - 0.5940 gms.
2. Wt.  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  - 0.3000 gms.
- 5 mls.  $\text{Co}^* \text{Cl}_2$  soln. - 0.0300 gms.  $\text{Co} = 1.2 \cdot 10^7$  c/m.
- Wt. of cobalt as  $\text{Co}^{*++}$  - 0.0454 gms.
- Wt. Co in Complex - 0.0589 gms.

Table XII.

<u>Time.</u>	<u>%Exchange.</u>
1 hr.	44.4 %
2 hrs.	43.2 %
4 hrs.	44.9 %

Theoretical percent exchange at equilibrium - 56.5%

2.	Wt. o-phth.H <sub>2</sub> O	-	0.5943 gms.
	Wt. CoCl <sub>2</sub> .6H <sub>2</sub> O	-	0.3459 gms.
	5 mls. Co <sup>*</sup> Cl <sub>2</sub> soln. =		0.0300 gms. Co
			1.2 10 <sup>7</sup> c/m.
	Wt. cobalt as Co <sup>++</sup>		0.0568 gms.
	Wt. cobalt in complex		0.0589 gms.

Table XIII.

<u>Time.</u>	<u>% Exchange.</u>
2.5 min.	31.5
10	30.9
20	36.9
30	34.5
40	35.4

Theoretical percent exchange at equilibrium

- 50.95%

From these results it can be seen that the cobalt seems to exchange very rapidly reaching an equilibrium value in a few minutes. This equilibrium value is however, considerably lower than the theoretical value which is expected. The method used has the disadvantage that the precipitate of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  might carry down with it a certain amount of adsorbed  $\text{Co Cl}_2$ . Then if the rate of exchange is slow, the adsorbed  $\text{Co}^*\text{Cl}_2$ , which would be expected to be a constant, would cover up any change in the percentage exchange, and make it appear as though an equilibrium had been attained. The slight upward trend in the figures in the second set of measurements make it appear

as though this may be the case.

In order to ascertain whether the observed results are due to a very rapid exchange between cobalt ions and the cobalt in  $[\text{Co}(\text{phth})_3]^{++}$ , or whether the activity is merely the result of adsorption of active cobalt chloride by the precipitate, a different method of separating the  $\text{Co}^{++}$  and  $[\text{Co}(\text{phth})_3]^{++}$  ions was devised.

Cobalt forms two insoluble hydroxides, cobaltous hydroxide,  $\text{Co}(\text{OH})_2$ , and cobaltic hydroxide,  $\text{Co}(\text{OH})_3$ . Since cobalt normally has the valence of two,  $\text{Co}(\text{OH})_2$  is generally formed on the addition of a base such as sodium hydroxide. If however the cobalt is first oxidized to a valence of three with an oxidizing agent such as hydrogen peroxide, cobaltic hydroxide can be precipitated, and is much more insoluble than cobaltous hydroxide, having a solubility in water of 0.00032 gms./100 mls.

It should thus be possible to separate  $\text{Co}^{++}$  from  $[\text{Co}(\text{phth})_3]^{++}$  by the precipitation of the cobalt ions as cobaltic hydroxide, provided that this method does not also precipitate some of the cobalt from the phenanthroline complex. After filtering off the precipitate of  $\text{Co}(\text{OH})_3$ , determination of the activity of the solution gives the amount of exchange. By running a blank containing cobalt ions only, the activity due to cobalt ions unprecipitated by the hydroxide can be determined and subtracted from the activity of the solution.

To determine whether or not the cobalt in  $[\text{Co}(\text{phth})_3]^{++}$  can be precipitated as cobaltic hydroxide, a solution was made up containing enough  $\text{CoCl}_2$  and  $\% \text{ o-phenanthroline}$  to form the cobalt phenanthroline complex and provide a very slight excess of o-phenanthroline. A few drops of 30% hydrogen peroxide were then added, and the solution made basic with 6N NaOH to a P.H. of about 10. Under these conditions no precipitate of cobaltic hydroxide could be observed.

A solution was prepared containing  $[\text{Co}(\text{phth})_3]^{++}$  ions and active cobalt (II) chloride. To separate the two ions after the desired length of time had elapsed, 5 ml. portions of the solution were withdrawn, 3 drops of 30%  $\text{H}_2\text{O}_2$  were added, and 10 drops 6NaOH to bring the P.H. to about 10. The precipitate of  $\text{Co}(\text{OH})_3$  was coagulated by bringing the solution to the boiling point, and was filtered off through a double thickness of filter paper. The precipitate was washed with about 45 ml. distilled water to bring the volume of the filtrate to 50 mls. 0.3 ml. portions were evaporated to dryness and counted. A blank was prepared containing the same amount of active cobalt (II) chloride, but no cobalt phenanthroline complex.  $\text{Co}(\text{OH})_3$  was precipitated under the same conditions as described above and the activity found in the filtrate subtracted from the activity obtained in the exchange measurements.

The following results were obtained:

Wt. of o-phth. $\text{H}_2\text{O}$  - 0.5897 gms.  
 Wt. of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  - 0.3457 gms.  
 5 mls. active  $\text{CoCl}_2$  soln. containing  
     0.0211gms. Co =  $8.425 \times 10^6$  cts/min.  
 Solution diluted to 50 mls.  
 Wt. of cobalt in complex - 0.0586 gms.  
 Wt. of cobalt as  $\text{Co}^{++}$  - 0.0480 gms.  
 Blank -  $16 \pm 5$  cts./min./0.3mls.

Table XIV.

Time	cts./min./0.3 mls. of filtrate	% Exchange
5 min.	$3659 \pm 51$	72.2%
1 day	$3788 \pm 46$	74.6
2 days	$3681 \pm 26$	72.5
3 days	$3830 \pm 34$	75.4
8 days	$3693 \pm 60$	72.6

Theoretical percent exchange at equilibrium

- 55.04 %.

These figures confirm the result found previously, that  $\text{Co}^{++}$  ions exchange very rapidly with  $[\text{Co}(\text{phth})_3]^{++}$ , reaching an equilibrium value in a few minutes.

The equilibrium value found experimentally however, is much higher than the value calculated from the concentrations of the various ions. This is probably due to the fact that  $\text{Co}(\text{OH})_3$ , in the presence of  $[\text{Co}(\text{phth})_3]^{++}$ , tends to form a colloidal solution, which is hard to filter.

$\text{Co(OH)}_3$  left in the filtrate in this manner would increase the activity of the filtrate, making the experimental exchange value too high.

Study of the Exchange Between Cobalt Metal and Dicobalt Octacarbonyl.

The exchange between active cobalt metal and cobalt octacarbonyl in a solution of benzene, was studied at room temperature. The active cobalt was prepared in the following manner: 0.0508 gms. of  $\text{Co}_2\text{O}_3$  were dissolved in  $\text{H}_2\text{SO}_4$ , 10 gms. of  $(\text{NH}_4)_2\text{SO}_4$  and 40 mls. conc.  $\text{NH}_4\text{OH}$  added, and the solution diluted to 150 mls. The solution was electrolysed between platinum electrodes using 1 amp. at 5 volts. The deposit of cobalt was washed well with water, dried and weighed.

Wt. of Co deposit = 0.0191 gms.

This would contain  $1.1 \times 10^8$  c/m. 0.0445 gms.  $[\text{Co}(\text{CO})_4]_2$  were dissolved in benzene, giving a 0.00325M solution. The radioactive cobalt was added, the system evacuated, and allowed to stand for 18 hrs. at room temperature. At the end of this time a good deal of the carbonyl had decomposed, forming a pinkish precipitate. The active cobalt metal was removed from the solution, the precipitate filtered off, the solution evaporated to dryness, and both precipitate and solution counted.

Background -  $50 \pm 1$  cts./min.

Solution -  $50 \pm 1$

Precipitate -  $62 \pm 2$

This indicates no exchange between cobalt metal and  $[\text{Co}(\text{CO})_4]_2$ .



#### IV. Discussion of Results.

The compound  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  was prepared and found to be unstable both in the dry state and in solution in various organic solvents. Conductivity measurements in acetophenone and benzaldehyde indicate that the compound has a molar conductivity corresponding to that of a strong electrolyte, indicating that it is a true salt of cobalt carbonyl hydride. The results obtained agree with those quoted by previous workers.

Transference measurements indicate that the transference number of the  $[\text{Co}(\text{CO})_4]^-$  ion is greater than that of the  $[\text{Co}(\text{phth})_3]^{++}$  ion. This is to be expected, since the latter ion is probably the larger, and hence would have a lower ionic mobility.

The precipitate formed on the cathode during the electrolysis of an acetone solution of  $[\text{Co}(\text{CO})_4]_2[\text{Co}^*(\text{phth})_3]$  was found to contain 3.5% active cobalt, whereas with the cobalt atom in  $[\text{Co}(\text{CO})_4]^-$  active the precipitate contained 6.7% active cobalt. If the reactions postulated are correct the precipitate should be  $[\text{Co}(\text{phth})_3](\text{OH})_2$ , which would contain 9.58% active cobalt in the first case and should be inactive in the second case. It is possible that the precipitate could be a compound containing both  $[\text{Co}(\text{phth})_3]^{++}$  and  $[\text{Co}(\text{CO})_4]^-$  in some manner. This does not seem probable however because of the highly ionized form of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ . It seems likely, there-

fore that the precipitate contains only the  $[\text{Co}(\text{phth})_3]^{++}$  ion, and the results can only be explained by exchange of some sort between the two cobalt atoms. It has been shown that the two cobalt atoms in  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  do not exchange at room temperature in an acid solution over a period of a few hours. This does not preclude their exchange in an acetone solution, but it is hardly to be expected that if such an exchange did occur it would be rapid enough to give the results obtained.

Exchange has been observed however between cobalt (II) ions and  $[\text{Co}(\text{phth})_3]^{++}$  ions in solution. This exchange is very rapid and reaches an equilibrium value almost instantaneously. If, therefore,  $\text{Co}^{++}$  ions were present in the acetone solution, due to decomposition of  $[\text{Co}(\text{CO})_4]^-$ , they would exchange with the  $[\text{Co}(\text{phth})_3]^{++}$  ions, giving the results obtained. Assuming this to be the case, and that the precipitate on the cathode is  $[\text{Co}(\text{phth})_3](\text{OH})_2$  the amount of cobalt exchanged at equilibrium, and hence the percent active cobalt in the precipitate can be calculated.

For  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$ :

In one mole of the compound,

118 gms. Co in  $[\text{Co}(\text{CO})_4]_2$

59 gms. Co in  $[\text{Co}(\text{phth})_3]$

Then at equilibrium, the ratio of active to inactive atoms will be the same in both cases so that:

$$\frac{x}{118} = \frac{59 - x}{59} \quad \text{where } x = \text{wt. of active cobalt transferred from } \text{Co(phth)}_3 \text{ to } \text{Co(CO)}_4$$

$$x = 39 \text{ gms.}$$

The  $[\text{Co(phth)}_3]$  therefore now contains

$59 - x = 20$  gms. active cobalt. The percent

active cobalt in  $[\text{Co(phth)}_3](\text{OH})_2$  is therefore,

$$\frac{20}{616.2} \times 100\% = 3.25\%$$

Similar calculations for  $[\text{Co(CO)}_4]_2[\text{Co(phth)}_3]$  give for the weight of active cobalt in  $[\text{Co(phth)}_3]$  at equilibrium a value of 39 gms. , and a percent active cobalt of 6.5%. These calculations assume that all the cobalt is in a form in which it can exchange. It can be seen that these values agree very closely with those obtained experimentally.

Percent Active Cobalt in  $[\text{Co(phth)}_3](\text{OH})_2$ :

	<u>Experimental.</u>	<u>Calculated.</u>
$[\text{Co(CO)}_4]_2[\text{Co}^*(\text{phth})_3]$	3.57%	3.25%
$[\text{Co}^*(\text{CO})_4]_2[\text{Co(phth)}_3]$	6.7%	6.5%

In the presence of an exchange such as this it is of course impossible to obtain the correct transference numbers by the method described.

### V. Suggestions for Further Work.

An analysis of the precipitate formed on the cathode during the electrolysis of  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  should be made, to determine whether or not its formula agrees with that postulated. Because the presence of o-phenanthroline eliminates the normal ionic reactions of valence two cobalt, this can not be done by any of the usual analytical methods. Hieber (15) however has devised a suitable method for analysing the cobalt in  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  by heating the substance in a platinum crucible, decomposing the residue with  $\text{KHSO}_4$ , dissolving it in water, and precipitating the cobalt as the anthranilate.

The possibility of exchange between the cobalt atoms in  $[\text{Co}(\text{CO})_4]_2[\text{Co}(\text{phth})_3]$  should be studied further, especially in solutions of acetone. Exchange may be present, but may not have been sufficient to detect in the short time that the compound was in existence.

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