SYNTHESIS AND PROPERTIES OF PENTADECACARBONYL-HEXACOBALTATE DIANION DERIVATIVES

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SUMMARY

The anion $[Co_6(CO)_{15}]^{2-}$ has been obtained in 80–90% yield by treating $Co_2(CO)_8$ with ethanol in vacuum at 60°. Acetone and methanol give less satisfactory results; isopropanol, dioxane and tetrahydrofuran give $Co_4(CO)_{12}$. Preformed tetracarbonylcobaltates of the type $[Co(ROH)_6][Co(CO)_4]_2$ (R = Me, Et) react with isopropanol in vacuum at 60° to give a mixture of $[Co_6(CO)_{15}]^{2-}$ derivatives and $Co_4(CO)_{12}$ in a one to two ratio. A reaction scheme which explains such a ratio, and involving the intermediate formation of $Co_6(CO)_{16}$ is proposed.

The salts $[Cat]_2[Co_6(CO)_{15}]$ (Cat = K, Cs, NMe_4, NEt_4, NBu_4) have been characterized by analysis and IR spectroscopy. The anion $[Co_6(CO)_{15}]^{2-}$ is diamagnetic. Solutions of $[Co_6(CO)_{15}]^{2-}$ derivatives react easily with carbon monoxide giving tetracarbonylcobaltate monoanion derivatives.

INTRODUCTION

A number of cluster carbonylferrates and carbonylniccolates are known, but only simple tetracarbonylcobaltates have previously been described[1]. Extensive studies of the reaction between $Co_2(CO)_8$ and several reagents as hydroxide ion, Lewis bases and alkali metals have shown only the formation of the $[Co(CO)_4]^-$ anion[1]. Moreover sodium in liquid ammonia[2] and Lewis bases as pyridine[3], ammonia[4] and methanol[5] are known to give the $[Co(CO)_4]^-$ anion via fragmentation of $Co_4(CO)_{12}$. The difficulty of obtaining cluster carbonylcobaltates has been ascribed to the particular stability of the $[Co(CO)_4]^-$ anion[6].

Many reactions catalyzed by cobalt carbonyl systems show a negative kinetic effect with respect to the carbon monoxide partial pressure[7] and are believed to involve species less rich in carbon monoxide; the preparation and characterization of cluster carbonylcobaltates would be of interest in this respect also.

Recently we succeeded in obtaining the cluster carbonylcobaltates $[Co_6(CO)_{15}]^{2-}$ and $[Co_6(CO)_{14}]^{4-}$, which we reported in two preliminary notes. They were obtained by reacting octacarbonyldicobalt with a suitable Lewis base in vacuum[8] or by reducing dodecacarbonyltetracobalt with alkali metals in tetrahydrofuran[9]. In the present work we report the preparation of the pentadecacarbonylhexacobaltate dianion derivatives from $Co_2(CO)_8$ and a Lewis base. The structure determination for $Cs_2[Co_6(CO)_{15}]\cdot 3H_2O$ will be described and discussed in a separate paper[10].

RESULTS

Synthesis of the $[Co_6(CO)_{15}]^{2-}$ *anion*

Octacarbonyldicobalt has been first converted to a tetracarbonylcobaltate by the well known reaction with a Lewis base at 20–60° [3,11–13]:

$$3 Co_2(CO)_8 + 12 B \rightleftarrows 2 [CoB_6][Co(CO)_4]_2 + 8 CO \qquad (1)$$

On further refluxing of the deep red solution of the tetracarbonylcobaltate in vacuum at 60° more carbon monoxide is evolved, and a deep green solution of pentadecacarbonylhexacobaltate of cobalt(II) is obtained:

$$7 [CoB_6][Co(CO)_4]_2 \rightarrow 3 [CoB_6][Co_6(CO)_{15}] + 11 CO \qquad (2)$$

Reaction (2) is very sensitive to the particular base employed; the best yields, (about 80–90%) of $[Co_6(CO)_{15}]^{2-}$, were obtained using anhydrous ethanol. With methanol the reaction is slow, while acetone gives poor yields and much metallic cobalt separates.

By treating octacarbonyldicobalt with other Lewis bases we observed, in the place of the sequence of reactions (1) and (2), the formation of $Co_4(CO)_{12}$ without any separation of metallic cobalt. This was the case with isopropanol in vacuum at 60° and with dioxane at 40–45°; with boiling tetrahydrofuran both $Co_4(CO)_{12}$ and minor quantities of tetracarbonylcobaltates were obtained.

In order to study the synthesis of the $[Co_6(CO)_{15}]^{2-}$ anion in these solvents, the hexaethanol- and hexamethanolcobalt(II) tetracarbonylcobaltates were first prepared using the corresponding anhydrous alcohols and, after removal of the excess alcohol, they were treated with anhydrous isopropanol in vacuum at 60°. This reaction gave a mixture of $Co_4(CO)_{12}$ and cobalt(II) pentadecacarbonylhexacobaltate. After evaporation of the excess isopropanol we separated the $Co_4(CO)_{12}$ by extraction with hexane and isolated the $[Co_6(CO)_{15}]^{2-}$ anion as potassium salt. We found that the two substances were present in ratio of two to one, corresponding to eqn. (3).

$$5 [CoB_6][Co(CO)_4]_2 + 6 B'$$
$$\rightarrow [CoB_6'][Co_6(CO)_{15}] + 2 Co_4(CO)_{12} + CO + 30 B \qquad (3)$$
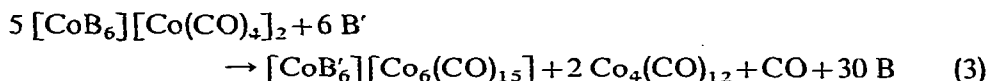
The GLC analysis of the base bound to the cobalt cation showed that a nearly complete exchange between ethanol and isopropanol had taken place. The relevant experimental data are reported in Table 1.

TABLE 1

SYNTHESIS OF THE $[Co_6(CO)_{15}]^{2-}$ ANION IN ISOPROPANOL [eqn. (3)]

B	B'	$Co_4(CO)_{12}(g)$		$K_2[Co_6(CO)_{15}](g)$		iso-PrOH in Co^{II}
		Calcd.	Found	Calcd.	Found	(% of the calcd.)
MeOH	iso-PrOH	4.71	4.7	3.54	3.4	
EtOH	iso-PrOH	1.98	1.9	1.49	1.3	73[a]

[a] In mixture with 7% ethanol, the discrepancy from 100 probably being due to the presence of some water.

Finally, in order to clarify the course of the $[Co_6(CO)_{15}]^{2-}$ synthesis in ethanol, we studied the reaction between $Co_4(CO)_{12}$ and ethanol. We measured the amount of carbon monoxide evolved and we found it to obey eqn. (4).

$$3\,Co_4(CO)_{12} + 24\,B \longrightarrow 4\,[CoB_6][Co(CO)_4]_2 + 4\,CO \qquad\qquad (4)$$
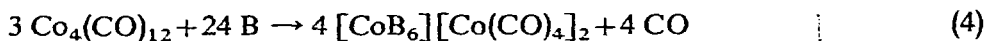
Characterization of the $[Co_6(CO)_{15}]^{2-}$ derivatives

The anion $[Co_6(CO)_{15}]^{2-}$ was separated by precipitation from water solution saturated with potassium bromide or iodide, in which the potassium tetracarbonyl-cobaltate, $K[Co(CO)_4]$, is soluble. The salt $K_2[Co_6(CO)_{15}]$ is soluble in pure water, but it can be washed with saturated solutions of potassium bromide, in which the solubility is very low. The solid product, while containing some potassium bromide, is a satisfactory starting material for the synthesis of other derivatives, it can be purified by dissolution in tetrahydrofuran.

From $K_2[Co_6(CO)_{15}]$ we obtained other derivatives by metathetical reactions; the cesium and the tetrabutylammonium salt were obtained as well formed crystals, and other tetraalkylammonium salt (NMe_4, NEt_4 and NMe_3Bz) as green powders. Addition of Tl^I, Ba^{II}, Zn^{II} and Cd^{II} ions to a water solution of $K_2[Co_6(CO)_{15}]$ do not give any precipitate; Hg^{II} and Fe^{III} ions oxidize the anion to $Co_6(CO)_{16}$ (ref. 9).

The potassium and cesium salts contain some water of crystallization, their composition being dependent on the drying conditions; *e.g.* the cesium salt $[Cs-(H_2O)_n]_2[Co_6(CO)_{15}]$ has been obtained with $n=4$, 2.5 and 0. The anhydrous salt shows the same habit as the hydrated salts, but the crystals give an X-ray powder diagram which shows that a rearrangement of the crystal structure has taken place.

On heating these salts begin to decompose at $135°-185°$. They are fairly soluble in tetrahydrofuran, acetone, and methanol, and give solutions with a typical green-yellow colour. These solutions are immediately oxidized in air, but some of the solid compounds are more stable. For instance, the tetraethylammonium salt is reasonably stable in air, but the potassium salt is pyrophoric. The salt like character of these compounds, which is consistent with the water solubility of the potassium and cesium salt, was proved by the structure determination of the cesium salt[10] and by their conductivity in water/acetone, $\dfrac{\varLambda o - \varLambda e}{\sqrt{c}} = 425$ [14].

Solutions containing the $[Co_6(CO)_{15}]^{2-}$ anion react with carbon monoxide at atmospheric pressure; the ease of this absorption explains why it is necessary to carry out the synthesis in vacuum. The amount of carbon monoxide absorbed in pyridine solution was 95.3% of the calculated according to eqn. (5).

$$3\,[NEt_4]_2[Co_6(CO)_{15}] + 11\,CO + 24\,Py \longrightarrow$$
$$6\,[NEt_4][Co(CO)_4] + 4\,[CoPy_6][Co(CO)_4]_2 \qquad (5)$$
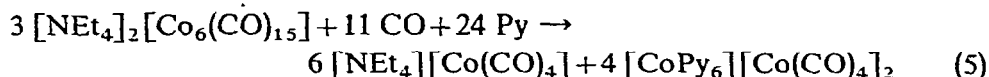
In tetrahydrofuran IR spectral studies show the intermediate formation of a mixture of $Co_2(CO)_8$ and $[Co(CO)_4]^-$ derivatives. This observation strongly supports a primary reaction with no change in the amount of negative charges on the cobalt atoms:

$$[NEt_4]_2[Co_6(CO)_{15}] + 9\,CO \longrightarrow 2\,[NEt]_4[Co(CO)_4] + 2\,Co_2(CO)_8 \qquad (6)$$

The tetraethylammonium salt was found to be diamagnetic. In the CO stretching region the IR spectra of these salts are very similar: 2042 m, 1982 s, 1959 (sh), 1778 s, 1737 s, 1685 m for $Cs_2[Co_6(CO)_{15}]$ in tetrahydrofuran; a shoulder at 1890 cm^{-1} being probably due to impurity of $[Co(CO)_4]^-$ anion. For C_{3v} symmetry[10] we expect 6 IR active bands for the terminal carbon monoxide groups ($3A_1 + 3E$) and four bands for the bridging groups ($2A_1 + 2E$).
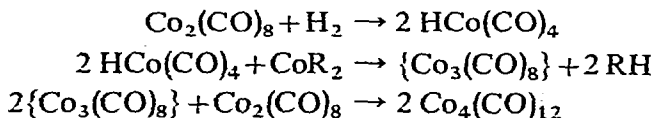
DISCUSSION .

The reaction of the $[Co(ROH)_6][Co(CO)_4]_2$ derivatives (R = Me, Et) with isopropanol give a mixture of $[Co(iso\text{-}PrOH)_6][Co_6(CO)_{15}]$ and $Co_4(CO)_{12}$ in ratio one to two, but in the same conditions octacarbonyldicobalt gives only Co_4-$(CO)_{12}$. These two different results might be interpreted by assuming that in the reaction between $Co_2(CO)_8$ and isopropanol the $[Co(ROH)_6][Co(CO)_4]_2$ derivatives are not formed. However a more fruitful hypothesis, which accounts for many of the facts, is that such derivatives are indeed formed, but that, in the presence of unreacted $Co_2(CO)_8$, they transformed to $Co_4(CO)_{12}$:

$$2\,[CoB_6][Co(CO)_4]_2 + Co_2(CO)_8 \rightarrow 2\,Co_4(CO)_{12} + 12\,B \qquad (7)$$
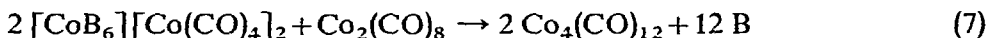
Reaction (7) agrees with the different behaviour of the homologous alcohols: methanol[11,12] and ethanol[11,12] give stable tetracarbonylcobaltate derivatives, but isopropanol and tert-butanol[11], for which there is much more steric crowding on the cobalt(II) cation, give $Co_4(CO)_{12}$.
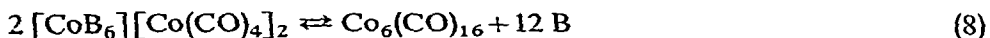
It has been previously claimed that in some reactions between $Co_2(CO)_8$ and weak oxygen-containing Lewis bases (as dioxane, benzophenone and acetophenone) it is possible to isolate tetracarbonylcobaltate derivatives in which the cobalt(II) cation apparently has a low coordination number, e.g.[13] $[Co(dioxane)_4]$-$[Co(CO)_4]_2$. However we think that the nature of these compounds should be examined by a more extensive use of IR spectroscopy; because where compounds of this type have been studied by this technique only $Co_4(CO)_{12}$ has been found to be present[15].

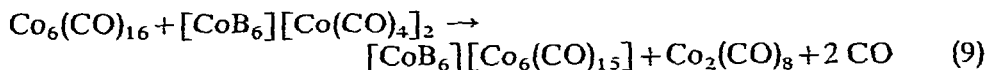Reaction (7) explains also the quantitative formation of $Co_4(CO)_{12}$ in the reaction of hydrogen, $Co_2(CO)_8$ and a suitable cobalt salt[16]:

$$Co_2(CO)_8 + H_2 \rightarrow 2\,HCo(CO)_4$$

$$2\,HCo(CO)_4 + CoR_2 \rightarrow \{Co_3(CO)_8\} + 2\,RH$$

$$2\{Co_3(CO)_8\} + Co_2(CO)_8 \rightarrow 2\,Co_4(CO)_{12}$$

A related reaction is the synthesis of the $[FeCo_3(CO)_{12}]^-$ anion[17] and we have recently obtained this anion by insertion of $Fe(CO)_5$ in preformed $[Co(Et\text{-}OH)_6][Co(CO)_4]_2$ (ref. 18).

The present work gives some further evidence in support of the hypothesis that $[CoB_6][Co(CO)_4]_2$ derivatives can behave as a coordinatively unsaturated species. In the absence of other reactive species, the hypothetical $Co_3(CO)_8$ intermediate is expected to condense to $Co_6(CO)_{16}$ and we can explain the formation of the $[Co_6(CO)_{15}]^{2-}$ anion by the following reactions:

$$2\,[CoB_6][Co(CO)_4]_2 \rightleftharpoons Co_6(CO)_{16} + 12\,B \qquad (8)$$

$$Co_6(CO)_{16} + [CoB_6][Co(CO)_4]_2 \rightarrow$$
$$[CoB_6][Co_6(CO)_{15}] + Co_2(CO)_8 + 2\ CO \qquad (9)$$

Reaction (8) is reversible as it is proved by the istantaneous formation of tetracarbonylcobaltates by reaction of $Co_6(CO)_{16}$ with Lewis bases[9].

Reaction (9) is consistent with the different reducing power of the two anions; the higher reducing power of the $[Co(CO)_4]^-$ anion being attributed to the higher negative charge on cobalt atoms. This different reducing power agrees with the formation of $[Co(iso-PrOH)_6][Co_6(CO)_{15}]$ in the reaction of $[Co(EtOH)_6][Co(CO)_4]_2$ with isopropanol: the stability of the system *solvated cobalt(II) cation–carbonylcobaltate anion* being dependent not only on the solvation of the cation, but also on the reducing power of the anion.

A more definite proof for this mechanism is found in the ratio of $[Co_6(CO)_{15}]^{2-}$ to $Co_4(CO)_{12}$ obtained by reacting $[Co(ROH)_6][Co(CO)_4]_2$ derivatives in isopropanol, according to reaction (3). In this case the $Co_2(CO)_8$ formed in reaction (9) would react with the tetracarbonylcobaltate according to reaction (7) giving $Co_4(CO)_{12}$; the expected equation obtained by summing up (7), (8) and (9) is in accord with the experimental results.

Finally the course of the $[Co_6(CO)_{15}]^{2-}$ anion synthesis in ethanol, reaction (2), is explained by postulating that the reaction between ethanol and $Co_4(CO)_{12}$, *i.e.* reaction (4), converts the byproduct $Co_4(CO)_{12}$ back into tetracarbonylcobaltate. The overall effect is that the $[Co_6(CO)_{15}]^{2-}$ anion is formed practically quantitatively.

EXPERIMENTAL

Starting materials
Ethers were distilled over $LiAlH_4$. Methanol and ethanol were dehydrated with magnesium, and isopropanol with aluminum. All the solvents were saturated with nitrogen before use. Commercial tetraalkylammonium halides (Fluka) were used as obtained. Crystalline octacarbonyldicobalt was prepared from cobalt carbonate[19].

Analysis
Analytical data were obtained by the following procedure. A sample of the substance is weighed using a long narrow tube previously swept out with nitrogen, and is then transferred to a flask containing NaOH (about 0.1 g) and water or methanol (10 ml). It is oxidized by addition of H_2O_2 (dil. 1/10) and, after some hours on the water bath the mixture is cautiously acidified with diluted sulfuric acid. This solution is taken to dryness and the residue redissolved in water; cobalt in this solution is determined by titration with EDTA[20], and potassium[21], cesium[21] and tetraalkylammonium[22] by gravimetric analysis.

Carbon monoxide was determined by reaction with iodine and pyridine using a gas volumetric precision burette[16].

Manipulation
All the operations were carried out in a nitrogen atmosphere ($O_2 < 5$ ppm).

Synthesis of $K_2[Co_6(CO)_{15}]$

In a 500 ml two necked flask with magnetic stirrer and condenser, $Co_2(CO)_8$ (21.9 g) and absolute ethanol (100 ml) were gently heated together at 50°. When the colour of the solution was deep red and no more carbon monoxide was evolved at atmospheric pressure, the flask was evacuated at the water pump and the temperature was raised to 60°. The vacuum was renewed about each 15 min (in order to take out the carbon monoxide evolved) and this treatment was continued for about 9 h giving a dark green solution. The ethanol was then evaporated in vacuum and the product was dried at 0.1 mm. In order to eliminate the last quantities of tetracarbonyl-cobaltates, the solid was again suspended in isopropanol (50 ml), the suspension was boiled in vacuum for two h and the solid was then again recovered and dried in vacuum.

The residual solid was dissolved in a 10% KBr solution (40 ml), filtered and washed with water (20 ml). To the dark green aqueous solution was added solid KBr (36 g). which caused immediate precipitation of crystalline $[K(H_2O)_x]_2$-$[Co_6(CO)_{15}]$. After 24 h the crystals were filtered and washed with saturated solution of KBr. The solid was dried in vacuum over P_2O_5 giving $K_2[Co_6(CO)_{15}]$ containing some KBr(13.9 g). This solid was dissolved in THF (100 ml) and filtered giving, after evaporation of the solvent in vacuum, the pure compound (12.5 g or 80.5% yield). (Found: Co, 40.9; CO, 45.2; K, 9.5. $K_2Co_6(CO)_{15}$ calcd.: Co, 41.50; CO, 49.32; K, 9.18%.) This salt decomposes at about 165°–175°.

Synthesis of $Co_4(CO)_{12}$ by reaction of $Co_2(CO)_8$ with Lewis bases

(a) *Dioxane*. Dioxane (50 ml) and $Co_2(CO)_8$ (2 g) were boiled in vacuum at 40°–45° for six h. Crystals of $Co_4(CO)_{12}$ separated and were identified by IR spectroscopy, the IR spectrum of the solution showed also that no $[Co(CO)_4]^-$ anion was present.

(b) *Isopropanol*. Isopropanol (25 ml) and $Co_2(CO)_8$ (4.85 g) were boiled in vacuum at 50° for 10 h and then the suspension was taken to dryness. The IR spectra of the original solution and of the dry solid showed only the presence of $Co_4(CO)_{12}$. The solid product was completely soluble in methanol, proving the absence of metallic cobalt.

(c) *Tetrahydrofuran*. THF (100 ml) and $Co_2(CO)_8$ (7.0 g) were boiled in vacuum at room temperature for 68 h. The carbon monoxide was pumped out intermittently. Black crystals of $Co_4(CO)_{12}$ separated, and the IR spectrum of the solution showed the presence of a mixture of $Co_4(CO)_{12}$ and $[Co(CO)_4]^-$ derivatives. The same result was obtained by boiling at 64°.

Reaction between $[Co(ROH)_6][Co(CO)_4]_2$ and isopropanol

(a) *Using methanol as ROH*. Absolute methanol (50 ml) and $Co_2(CO)_8$ (10.6 g) were warmed together at 50° until no more carbon monoxide was evolved at atmospheric pressure. The methanol was evaporated at 0° in high vacuum; the IR spectrum of the black solid showed only the band at 1890 cm^{-1} typical of $[Co(CO)_4]^-$ derivatives. Isopropanol (25 ml) was added and the mixture was boiled at 60° in vacuum for 3 h. The isopropanol was evaporated off, fresh isopropanol (25 ml) was added, and the treatment was repeated. The solid product was extracted with hexane giving

$Co_4(CO)_{12}$ (4.74 g). The residue was dissolved in water (40 ml), and the solution was filtered and then treated with solid KBr (25 g) to give, after THF purification, $K_2[Co_6-(CO)_{15}]$ (3.42 g).

(b) *Using ethanol as ROH*. Absolute ethanol (50 ml) and $Co_2(CO)_8$ (9.1 g) were warmed at 60° until no more carbon monoxide was evolved. The ethanol was evaporated in high vacuum and the residue was treated twice with isopropanol as in (a). The solid product was dissolved in water (20 ml) and the solvents were distilled in high vacuum in traps at −80° to give two fractions of about 8 ml each. By GLC analysis (column 3 m long and 3 mm ∅, 30% Carbowax and 70% 2-ethylsebacate on Columpack, 65°) we found isopropanol (1.8 g) and ethanol (0.16 g). Calcd. isopropanol 2.46 g.

Double exchange reactions of $K_2[Co_6(CO)_{15}]$

(a) *With tetramethylammonium bromide*. Impure $K_2[Co_6(CO)_{15}]$ (1.35 g) was dissolved in water (30 ml) and, after filtration, a solution of NMe_4Br (1 g) in water (10 ml) was added. The fine precipitate was washed with water and then dried over P_2O_5 in high vacuum. (Found: C, 30.34; H, 2.85; Co, 39.2; N, 3.20; $N(CH_3)_4$, 16.9. $C_{23}H_{24}Co_6N_2O_{15}$ calcd.: C, 29.96; H, 2.61; Co, 38.36; N, 3.04; $N(CH_3)_4$, 16.08%.) This salt is slightly soluble in water; by heating it decomposes at about 140°–150°.

(b) *With tetraethylammonium iodide*. The tetraethylammonium salt was similarly obtained. (Found: Co, 34.9; CO, 40.4; $N(C_2H_5)_4$, 25.8. $C_{31}H_{40}Co_6N_2O_{15}$ calcd.: Co, 34.20; CO, 40.63; $N(C_2H_5)_4$, 25.19%.) This salt was obtained as a green diamagnetic powder ($\chi_g = -0.21\cdot10^{-6}$ c.g.s. units at 25°) that begins to decompose at about 135°–150°. It is very slightly soluble in water.

(c) *With tetrabutylammonium chloride*. The tetrabutylammonium salt was similarly obtained and it was crystallized from acetone by addition of isopropanol. (Found: Co, 28.5; CO, 32.5; $N(C_4H_9)_4$, 38.5. $C_{47}H_{72}Co_6N_2O_{15}$ calcd.: Co, 28.10; CO, 33.35; $N(C_4H_9)_4$, 38.55%.) Green black crystals that begin to decompose at about 170°–185°. In acetone containing 2% water we obtained the following values of the conductibility (Λ in $\Omega\cdot cm^{-1}$): 39.5; 42.8; 45.6; 47.2; 49.4. Concn. in mEq: 2.91; 1.94; 1.45; 1.16; 0.97.

(d) *With cesium chloride*. The cesium salt was similarly obtained. It contains different amounts of water depending on the drying conditions, as is shown by the analytical data reported in Table 2.

TABLE 2
ANALYTICAL DATA OF $[Cs(H_2O)_n]_2[Co_6(CO)_{15}]$

Drying conditions	n	Cs(%)		Co(%)		CO(%)	
		Calcd.	Found	Calcd.	Found	Calcd.	Found
Half h in vacuum	4	22.46	22.6	29.87	29.5	33.49	34.5
24 h in vacuum	2.5	23.55	23.5	31.30	31.2		
P_2O_5 in vacuum	0	25.57	26.2	34.01	35.05	40.42	38.8

Reaction between $[Co_6(CO)_{15}]^{2-}$ derivatives and carbon monoxide

(a) *In tetrahydrofuran*. The cesium salt ($n=4$; 0.27 g) was dissolved in THF (20 ml) and this solution was exposed to carbon monoxide at atmospheric pressure.

After one h the IR spectrum showed little $[Co_6(CO)_{15}]^{2-}$ (1982 cm^{-1}) and strong bands of $[Co(CO)_4]^-$ (1890 cm^{-1}) and $Co_2(CO)_8$ (2070, 2045 and 2025 cm^{-1}). After 3 days the band of $[Co_6(CO)_{15}]^{2-}$ and of $Co_2(CO)_8$ have disappeared.

(b) *In pyridine.* A gas volumetric apparatus was charged with pyridine (25 ml) and carbon monoxide and then $[NEt_4]_2[Co_6(CO)_{15}]$ (0.4707 g) was added. At 17° the reaction was slow, and so the mixture was warmed at 45°–55° for three h. In this time, 35.6 Nml of carbon monoxide was absorbed, *i.e.* 95.3% of that calculated according to eqn. (5). The IR spectrum of the pink solution showed only the presence of the $[Co(CO)_4]^-$ anion.

Reaction between $Co_4(CO)_{12}$ and ethanol

Absolute ethanol (10 ml) and $Co_4(CO)_{12}$ (0.1581 g) were warmed together at 40° in vacuum for one h, the evolved gas was pumped out using a Töpler pump and its volume was measured: Found 8.1 Nml; calcd. 8.28. The IR spectrum of the pink solution showed only the band of the $[Co(CO)_4]^-$ anion at 1890 cm^{-1}.

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