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SYNTHESIS AND PROPERTIES OF TETRADECACARBONYLHEXACOBALTATE TETRAANION DERIVATIVES

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SUMMARY

The anion $[Co_6(CO)_{14}]^{4-}$ has been obtained by reducing $Co_4(CO)_{12}$ with an alkali metal (Li, Na, K) in tetrahydrofuran, or with cobaltocene as a homogeneous reducing agent. In both cases the initial product was the anion $[Co_6(CO)_{15}]^{2-}$, which was subsequently reduced to $[Co_6(CO)_{14}]^{4-}$.

In toluene, cobaltocene reacted with $Co_2(CO)_8$ to give cobalticinium tetracarbonylcobaltate, while with $Co_4(CO)_{12}$ the brown salt $\{[(\pi\text{-}Cp)_2Co][Co_4(CO)_{11-12}]\}_n$ was precipitated as the first reaction product. This anion is believed to be the first intermediate in the reduction of $Co_4(CO)_{12}$.

The salts $M_4[Co_6(CO)_{14}]$ [M = K, NEt_4 and $(\pi\text{-}Cp)_2Co$] have been characterized by analysis. The solutions containing the anion $[Co_6(CO)_{14}]^{4-}$ reacted with carbon monoxide giving tetracarbonylcobaltate(1–) derivatives. The salt $Na_4[Co_6(CO)_{14}]$ has been obtained in two different isomeric forms; the considerable differences observed in the IR spectra of several salts [Li, Na, K, NEt_4 and $(\pi\text{-}Cp)_2Co$] are in accord with the postulated existence of several isomeric forms of the anion $[Co_6(CO)_{14}]^{4-}$.

INTRODUCTION

In a previous paper we reported the synthesis of some derivatives of the $[Co_6(CO)_{15}]^{2-}$ anion[1]. This anion was obtained by elimination of carbon monoxide from a cobalt(II) tetracarbonylcobaltate *in vacuo*:

$$7\,[CoB_6][Co(CO)_4]_2 \rightleftarrows 3\,[CoB_6][Co_6(CO)_{15}] + 11\,CO \tag{1}$$

B = methanol, ethanol, acetone

This reaction is easily reversed by carbon monoxide, the anion $[Co_6(CO)_{15}]^{2-}$ being stable only in the absence of free ligand. Owing to the major influence of the carbon monoxide in this synthesis we have considered the possibility of using other substrates of low content in carbon monoxide such as dodecacarbonyltetracobalt. Previously this compound has been reduced with sodium in liquid ammonia at −75° to a mixture of sodium tetracarbonylcobaltate and cobalt metal[2].

RESULTS AND DISCUSSION

Reduction of $Co_4(CO)_{12}$ with alkali metals or cobaltocene

When the slightly soluble $Co_4(CO)_{12}$ is allowed to react with alkali metals in tetrahydrofuran (THF) it rapidly dissolves and a mixture of the greenish-yellow $[Co_6(CO)_{15}]^{2-}$ and colourless $[Co(CO)_4]^-$ anions is formed. Further reduction is much slower; when it is complete (about 24 h) the colour of the solution is reddish-brown and the IR spectrum no longer shows absorption bands for $[Co_6(CO)_{15}]^{2-}$. With lithium and sodium this reduction could be carried out at 0–25°, while with potassium it was necessary to raise the temperature to 55°, probably because the potassium salt, being insoluble in THF, separated on the surface of the metal.

The reduction to $[Co_6(CO)_{14}]^{4-}$ can be represented by eqn. (2):

$$5\,Co_4(CO)_{12}+16\,M \rightarrow 2\,M_4[Co_6(CO)_{14}]+8\,M[Co(CO)_4] \qquad (2)$$

This eqn. requires 3.2 g-atoms of sodium for each mole of $Co_4(CO)_{12}$ (found 3.15–4.0) and should yield 1.6 moles of $Na[Co(CO)_4]$ (found ~1.4). Considering the difficulties in separating the reaction products, the agreement is satisfactory.

The anion $[Co_6(CO)_{14}]^{4-}$ may also be obtained by reduction of preformed $K_2[Co_6(CO)_{15}]$ with lithium in THF, but preparation from $Co_4(CO)_{12}$ is more convenient. Conversely $[Co_6(CO)_{15}]^{2-}$ can be easily prepared from $Co_4(CO)_{12}$ by stopping the reduction at the greenish-yellow stage.

Unfortunately because of the heterogeneous nature of the reaction, the mechanism of the synthesis is not easy to investigate. To obtain some insight on the reaction mechanism we replaced the alkali metal by cobaltocene, which has a strong tendency to form the cobalticinium cation and can be considered to be a pseudo-alkali metal. Moreover with cobaltocene it is possible to carry out the reduction in toluene, an inert solvent in which intermediate products sensitive to Lewis bases are stable.

Firstly pure cobaltocene was slowly added to $Co_4(CO)_{12}$ in THF, and the course of the reaction was followed by recording the IR spectrum during the addition. At first there was formation of the $[Co_6(CO)_{15}]^{2-}$ and $[Co(CO)_4]^-$ anions, and a dark green solution was obtained with complete disappearance of the $Co_4(CO)_{12}$ at a $(\pi\text{-}Cp)_2Co/Co_4(CO)_{12}$ ratio of about 2.2:

$$9\,Co_4(CO)_{12}+20\,(\pi\text{-}Cp)_2Co \rightarrow 4\,[(\pi\text{-}Cp)_2Co]_2[Co_6(CO)_{15}]+12\,[(\pi\text{-}Cp)_2Co][Co(CO)_4] \qquad (3)$$

Further addition of cobaltocene cuased precipitation of $[(\pi\text{-}Cp)_2Co]_4[Co_6(CO)_{14}]$ which was complete at a ratio of about 3.2. The whole process can be again represented by eqn. (2).

We then treated cobaltocene with octacarbonyldicobalt in toluene and obtained cobalticinium tetracarbonylcobaltate in a smooth quantitative reaction:

$$2\,(\pi\text{-}Cp)_2Co+Co_2(CO)_8 \rightarrow 2\,[(\pi\text{-}Cp)_2Co][Co(CO)_4] \qquad (4)$$

This reaction appears to be analogous to the reduction of $Co_2(CO)_8$ with lithium[3] or sodium[4] in THF.

In view of the similarity between cobaltocene and alkali metals, we studied the reduction of $Co_4(CO)_{12}$ in toluene. A brown salt was initially precipitated, and the first step was complete when one mole of cobaltocene had been added to dodecacarbonyltetracobalt. Further addition of cobaltocene brought about formation of cobalticinium tetracarbonylcobaltate together with unidentified products; this second step is slower and probably complicated by its heterogeneous nature.

In order to exclude the presence of other reduction products the brown salt was prepared using a 0.7 ratio of $(\pi\text{-Cp})_2Co$ to $Co_4(CO)_{12}$ and the excess $Co_4(CO)_{12}$ was washed out with toluene. The analytical data for the brown powder agree with the formula $\{[(\pi\text{-Cp})_2Co][Co_4(CO)_{11-12}]\}_n$. This compound is insoluble in hydrocarbons, and reacts with Lewis basic solvents such as THF and methanol to give a mixture of salts of the anions $[Co_6(CO)_{15}]^{2-}$ and $[Co(CO)_4]^-$. The IR spectrum shows two strong bands in the carbonyl stretching region at about 1990 and 1812 cm^{-1}. The compound is pyrophoric and, owing to the large effect of minor impurities on the magnetism, no reliable magnetic measurements were possible.

We assume that this product is dimeric, because if monomer it would represent the first example of a paramagnetic carbonylmetallate. It seems therefore that the first reaction step is condensation of two Co_4 units to give a Co_8 cluster, and that this is followed by the reaction with the Lewis basic solvent giving further splitting into a Co_6 cluster and Co_1 units. This mechanism also agrees with some recent studies on the formation of the Rh_6 clusters, where a similar stepwise condensation of Rh_4 units to give a Rh_{12} derivative is followed by final breaking in two Rh_6 clusters[4].

The mechanism of formation of the Co_6 cluster by reduction of $Co_4(CO)_{12}$ is therefore very different from that of formation of the Co_6 cluster by the process of eqn. (1). In the latter case the synthesis of $[Co_6(CO)_{15}]^{2-}$ involves the formation of $Co_6(CO)_{16}$ by dimerization of a cobalt(II) tetracarbonylcobaltate[1]. Such a mechanism has been recently confirmed by the synthesis of the $[Ni_2Co_4(CO)_{14}]^{2-}$ anion starting from a nickel(II) tetracarbonylcobaltate[5].

Isolation and characterization of derivatives of the $[Co_6(CO)_{14}]^{4-}$ anion

Reaction (2) gives a mixture of the alkali salts of tetradecacarbonylhexacobaltate(4–) and tetracarbonylcobaltate(1–) and they have been separated in two different ways. Firstly the reaction mixture was evaporated to dryness and after redissolution in water, the tetradecacarbonylhexacobaltate(4–) was separated as potassium salt by saturating with solid potassium bromide or iodide. In the second method the dried mixture was extracted with diethyl ether, in which only tetracarbonylcobaltate(1–) salts are soluble; the lithium and sodium tetradecacarbonylhexacobaltates could not be isolated in pure state and a further redissolution in THF or in methanol, followed by filtration, was necessary.

The tetraethylammonium derivatives $[NEt_4]_4[Co_6(CO)_{14}]$, were prepared by metathetical reactions in methanol using both the lithium and the sodium salts and tetraethylammonium bromide or iodide. No precipitation was obtained with tetramethylammonium chloride or tetrabutylammonium iodide.

The sodium salt has been obtained in two isomeric forms which differ in their solubility in THF. When a THF solution of the soluble form is left standing the insoluble form slowly separates. Both forms undergo exchange with potassium bromide in water to give the same potassium derivative, and in methanol exchange with tetraethylammonium iodide gives the same tetraethylammonium derivative.

The IR spectra of the two forms of the sodium salt are reported in Table 1 and show considerable differencies. Generally each salt of the $[Co_6(CO)_{14}]^{4-}$ anion

TABLE 1

IR SPECTRA OF THE SALTS $[\text{CATION}]_4[Co_6(CO)_{14}]$

Cation	Solvent	CO stretching frequencies (cm^{-1})					
K	Methanol	1990 w	1940 s	1910 s			1660 s
Na (sol.)	THF	2000 w	1950 w	1925 w,	1885 s, 1855 w	1730 s	1670 s
Li	THF	1980 w	1927 s		1885 w	1758 s	1644 s
Na (insol.)	Nujol mull	2040 w			1890 s		1680 s
NEt_4	Nujol mull	1970 w			1892 s	1730 s	
$(\pi\text{-}Cp)_2Co$	Nujol mull				1905 s, 1865 s	1708 s	1677 s

presents a unique IR spectrum in the carbonyl stretching region; four main ranges of absorption at about 1940–1927, 1910–1885, 1758–1730 and 1680–1644 cm^{-1}, have beeen observed as is shown in Table 1.

In some cases the isomerisation of the $[Co_6(CO)_{14}]^{4-}$ anion can be followed by IR spectroscopy. For example the potassium salt and the insoluble form of the sodium salt can be dissolved in THF by addition of lithium chloride. In both cases there is a slow change in the IR spectrum: after about 24 h the strongest band, at 1898 cm^{-1}, has moved to 1927 cm^{-1}, while the intensity of the band at 1640 cm^{-1} has been reduced and a new band has appeared at 1758 cm^{-1}. The original potassium salt is recovered on addition of water and potassium iodide, showing that the isomerisation can be easily reversed.

The determination of the structure of the potassium salt $K_4[Co_6(CO)_{14}] \cdot 6\,H_2O$ is reported in a separate paper[6]: each cobalt atom of the octahedral cluster is bonded to a terminal carbon monoxide group and the eight octahedral faces are occupied by the other eight carbon monoxide groups. Two of these "face" bridging carbon monoxide groups are nearly regular, but the other six form asymmetric bridges, their situation being intermediate between those of "edge" and "face", bridging groups.

The IR bands in the range 1758–1730 cm^{-1} agree with the presence of "edge" bridging carbon monoxide groups, and the bands in the range 1680–1644 cm^{-1} support the presence of "face" bridging carbon monoxide groups. It is noteworthy that the last bands are the only ones observed in the potassium salt. It therefore seems probable that the two forms of the sodium salt differ in the presence of only "face" (insoluble form), or of both "face" and "edge" (soluble form), bridging groups.

The transfer of a carbon monoxide group from terminal to "edge", or from "edge" to "face" position, can be represented as an internal nucleophilic attack due to the presence of negative charge on a neighbour metal atom[7], and it seems possible that the structure of $[Co_6(CO)_{14}]^{4-}$ is related to the free negative charge on the anion. A complete dissociation of the tetraanion, with formation of the greatest degree of free charge, is expected to occur in water; this would give an isomer with only "face" bridging groups. On the other hand in methanol or in THF some formation of undissociated ion pairs is expected, corresponding to a minor free charge: this should lead to the presence of "edge" and "face" bridging groups. The fact that in these solvents the results depend on the cation may be due to the different tendency of the cation to give ion pairs.

In the solid state the potassium salt is moderately stable in air, but the tetraethylammonium salt is pyrophoric; on heating both salts decompose at about 210–230°. Solutions containing the $[Co_6(CO)_{14}]^{4-}$ anion are rapidly oxidised by air, and react rapidly with carbon monoxide. At atmospheric pressure and room temperature this reaction gives initially, after about 90 min, a mixture of derivatives of the anions $[Co_6(CO)_{15}]^{2-}$ and $[Co(CO)_4]^-$:

$$2\,[Co_6(CO)_{14}]^{4-} + 11\,CO \rightarrow [Co_6(CO)_{15}]^{2-} + 6\,[Co(CO)_4]^- \quad (5)$$

By further reaction the $[Co_6(CO)_{15}]^{2-}$ is converted into $[Co(CO)_4]^-$ (ref. 1).

This easy fragmentation of the clusters by carbon monoxide contrasts with the stability of the $[Co_6(CO)_{15}]^{2-}$ anion to reduction and oxidation[8], in which not only the type of cluster, but also its electronic configuration is preserved. Such a configuration with 86 electrons corresponds to an excess of two electrons over the noble gas configuration and has been so far found in all the octahedral clusters: $Rh_6(CO)_{16}$ (ref. 9), $[Rh_{12}(CO)_{30}]^{2-}$ (ref. 10), $Ru_6(CO)_{14}$ (arene) (ref. 11) and $[Ni_2Co_4(CO)_{14}]^{2-}$ (ref. 5). A theory which accounts to a first approximation for such electronic configuration was put forward in a previous paper[12].

EXPERIMENTAL

Analysis

For the determination of the cobalticinium ion the compounds were dissolved in methanol in the presence of NaOH and decomposed by slow addition of diluted H_2O_2. (Caution: some decomposition of the cobalticinium ion can occur by heating in highly concentrated solutions of alkali). The acidified solution was buffered with sodium acetate and the cobalticinium ion precipitated at 40–50° by adding a small excess of a 0.1 *M* solution of $NaBPh_4$. The precipitate was warmed at 60° for 6 h and then separated by filtration. After washing with water the $[(\pi\text{-}Cp)_2Co][BPh_4]$ was dried to constant weight at 120°. The other analytical data were obtained as reported in a previous paper[1].

Manipulations

All the operations were carried out in a nitrogen atmosphere ($O_2 < 5$ ppm), and all the solvents were saturated with nitrogen before use.

Starting materials

Ethers were distilled over $LiAlH_4$. Cobaltocene was prepared according to the literature[13]. Dodecacarbonyltetracobalt was obtained as follows: octacarbonyldicobalt (30 g) was dissolved in toluene (150 ml). The brown solution was filtered, then heated at 85° for 90 min and then at 95° for 2 h. After cooling overnight the black crystals of $Co_4(CO)_{12}$ were filtered off, washed two times with pentane and vacuum dried (21.2 g or 84% yield).

Synthesis of $K_4[Co_6(CO)_{14}]$

Dodecacarbonyltetracobalt (9.91 g), sodium in small pieces (1.57 g) and THF (100 ml) were stirred together at room temperature. After 4 h the solution was yellowish-green and the IR spectrum showed the presence of $[Co_6(CO)_{15}]^{2-}$ (1892, 1778 and 1737 cm^{-1}) and $[Co(CO)_4]^-$ (1890 cm^{-1}) anions. After 48 h the colour was reddish-brown and the $[Co_6(CO)_{15}]^{2-}$ bands had disappeared. The insoluble isomer and the excess sodium were filtered off. The insoluble isomer was dissolved by adding anhydrous LiCl (1 g) and THF (25 ml). After the washing with THF, the sodium was decomposed with methanol and the filter was washed with water. The solution obtained was titrated with 1 *N* HCl (44.75 ml); the reacted sodium corresponded to 3.15 g-atoms/mole $Co_4(CO)_{12}$.

The original THF solution was taken to dryness under vacuum. The residue, R, was dissolved in water (65 ml), filtered and saturated with solid KI (75 g); if there was separation of an oil, due to the presence of THF, this was kept in a vacuum until it crystallized. After 12 h the dark crystals were separated by filtration and washed with a saturated solution of KI, and redissolved in water (80 ml) and, after filtration methanol (20 ml) was added. After 12 h the recrystallized black salt was filtered off, washed with a mixture of water and methanol (5 ml; 1/1) and vacuum dried for a short time [$K_4Co_6(CO)_{14}\cdot 11\ H_2O$, 3.5 g or 46% yield]. (Found: Co, 32.0; K, 14.2. $C_{14}H_{22}Co_6K_4O_{25}$ calcd.: Co, 32.05; K, 14.20%.)

After 48 h high vacuum drying the compound is anhydrous. (Found: CO, 42.3; Co, 38.8; K, 17.2. $C_{14}Co_6K_4O_{14}$ calcd.: CO, 43.47; Co, 39.19; K, 17.33%.)

The hydrated salt is soluble in water and in methanol, but is insoluble in THF. The anhydrous salt is insoluble in methanol.

Synthesis of $[NEt]_4[Co_6(CO)_{14}]$ *by double exchange*

Exchange between a methanol solution of $Na_4[Co_6(CO)_{14}]$ or $Li_4[Co_6(CO)_{14}]$ (both obtained from the residue R after extraction of the alkali tetracarbonylcobaltate with diethyl ether) and a methanol solution of NEt_4Br or NEt_4I gave a fine red-brown precipitate, which was separated by filtration, washed with water and vacuum dried. [Found: CO, 31.6; Co, 27.9; $N(C_2H_5)_4$, 38.2. $C_{46}H_{80}Co_6N_4O_{14}$ calcd.: CO, 30.96; Co, 27.91; $N(C_2H_5)_4$, 41.13%.] This salt is not very soluble in water, and only slightly soluble in methanol and THF.

Synthesis of $[(\pi\text{-}Cp)_2Co]_4[Co_6(CO)_{14}]$

A tetrahydrofuran solution (40 ml) of cobaltocene (1.515 g, 8 mmoles) was dropped from a burette into a stirred THF suspension (40 ml) of $Co_4(CO)_{12}$ (1.145 g, 2 mmoles) at 0°. IR spectra were recorded after addition of 5, 10, 15, 20, 22.5, 25, 32, and 35 ml of the cobaltocene solution. During the addition of the first 22.5 ml, there was an increasing formation of the $[Co(CO)_4]^-$ (band at 1890 s cm^{-1}) and $[Co_6(CO)_{15}]^{2-}$ [bands at 2042 m, 1982 vs, 1959 (sh), 1778 s and 1737 s cm^{-1}] anions, while the $Co_4(CO)_{12}$ disappeared (bands 2072 s, 2060 s and 1860 s cm^{-1}). Further addition of cobaltocene caused formation of a precipitate, and at 32 ml the $[Co_6(CO)_{15}]^{2-}$ anion disappeared. The precipitate of $[(\pi\text{-}Cp)_2]_4[Co_6(CO)_{14}]$ was separated by filtration, washed with THF and vacuum dried. [Found: $(\pi\text{-}Cp)_2Co$, 50.0; Co (anionic), 23.8. $[(\pi\text{-}Cp)_2Co]_4[Co_6(CO)_{14}]$ calcd.: $(\pi\text{-}Cp)_2Co$, 50.36; Co (anionic), 23.54%.] The compound is insoluble in methanol, acetone, THF and water.

Synthesis of $[(\pi\text{-}Cp)_2Co][Co(CO)_4]$

Crystalline octacarbonyldicobalt (1.9575 g) was dissolved in toluene (20 ml) and a solution of cobaltocene (2.419 g) in toluene (50 ml) slowly added with stirring.

The red precipitate was separated by filtration and recrystallized from benzene/methanol (4.0 g or 90% yield). [Found: (π-Cp)$_2$Co, 52.5; Co (anionic), 16.35. [(π-Cp)$_2$Co][Co(CO)$_4$] calcd.: (π-Cp)$_2$Co, 52.20; Co (anionic), 14.92%.] The compound is insoluble in benzene, but very soluble in methanol, acetone, and THF. In an evacuated capillary tube it melts at 185–188°. In the carbonyl stretching region of the IR spectrum there are bands at 1998 w, 1865 vs, and 1845 (sh) cm^{-1} (nujol mull).

Synthesis of $\{[(\pi\text{-}Cp)_2Co][Co_4(CO)_{11-12}]\}_n$

Dodecacarbonyltetracobalt (3.960 g) was partially dissolved in toluene (80 ml) and a solution of cobaltocene (0.920 g) in toluene (46 ml) was slowly added during 90 min with stirring. The brown precipitate was separated by filtration and washed with toluene (80 ml) until no more $Co_4(CO)_{12}$ was dissolved, the residue weighted 3.5 g. [Found: (π-Cp)$_2$Co, 26.25; Co (anionic) 31.0; CO, 42.6. [(π-Cp)$_2$Co][Co$_4$(CO)$_{11}$] calcd.: (π-Cp)$_2$Co, 25.80; Co (anionic) 32.16, CO, 42.035%.] In the carbonyl stretching region of the IR spectrum there are bands at 2065 w, 1990 vs, 1945 (sh), 1848 w, 1812 s and 1790 (sh) cm^{-1} (nujol mull).

A series of similar experiments was carried out using ratios of 0.3, 0.7, 1.0, 1.5, 2.0 and 3.0 between cobaltocene and $Co_4(CO)_{12}$. The IR spectra of the reaction products showed the following facts:

(*a*). Dodecacarbonyltetracobalt disappears at ratio 1.0.

(*b*). The intensity of the bands of the $[Co_4(CO)_{11-12}]^-$ anion is maximum at ratio 1.0.

(*c*). The band of [(π-Cp)$_2$Co][Co(CO)$_4$] at 1865 cm^{-1} appears only at ratios higher than 1.0.

(*d*). Some unreacted cobaltocene is present at ratio 3.0.

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