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# The Anion of Mercury Cobalt Carbonyl

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*Mercury cobalt carbonyl is reduced in tetrahydrofuran by 1 equivalent of sodium amalgam to the anion* $\{[Co(CO)_4]_2Hg\}^-$ *which can be precipitated by* $[Fe(C_{12}H_8N_2)_3]^{2+}$*. Reduction by excess sodium amalgam leads to the tetracarbonyl cobaltate anion.*

## Introduction

A great number of metal carbonyl derivatives containing main group metals and metal-metal bonds have been described in recent years, and some of their reactions have been studied. With the exception of mercury cobalt carbonyl, however, no results have been published about the reduction of these complexes. According to Dighe, Orchin,[1] $[Co(CO)_4]_2Hg$ is reduced by sodium amalgam to $[Co(CO)_4]^-$.

We have now found that the reduction of a tetrahydrofuran solution of $[Co(CO)_4]_2Hg$ by sodium amalgam can be stopped at an intermediate step by using one gatom sodium for one mole of mercury cobalt carbonyl. Under such conditions, the initially paint yellow colour of the THF solution turns deep orange and the infrared spectrum shows strong bands at 2035 and 1969 cm$^{-1}$. The relative intensites and positions of these bands are rather similar to the two strong bands of mercury cobalt carbonyl[2] but are shifted by 37-38 cm$^{-1}$ towards lower wave numbers.

Using an excess of sodium amalgam, the characteristic orange colour and the above mentioned infrared bands can be observed for some time too, but in this case the reduction proceeds further, the solution becomes colourless, and the infrared spectrum of the final solution shows the strong band of $[Co(CO)_4]^-$ appearing around 1890 cm$^{-1}$. This is in accordance with the findings of Dighe, Orchin.[1]

These observations suggest the following sequence of reactions:

$$[Co(CO)_4]_2Hg \xrightarrow{Na/Hg} \{[Co(CO)_4]_2Hg\}^- \xrightarrow{Na/Hg}$$

$$2[Co(CO)_4]^- + Hg$$

The formation of the single-charged anion of mercury cobalt carbonyl was proved by precipitating it in the form of its tri-*o*-phenanthroline iron(II) (« ferroin ») salt as a red powder. This solid product shows broad and strong infrared bands at 2035 and 1960 cm$^{-1}$ (in KBr pellet).

The same anion is formed from $[Co(CO)_4]_2Hg$ and $[Co(CO)_4]^-$ in THF, and the oxidation of $\{[Co(CO)_4]_2Hg\}^-$ (*e.g.* by air) yields $[Co(CO)_4]_2Hg$. Both observations point to the reversibility of the reduction steps.

The similar infrared spectra of mercury cobalt carbonyl and its anion suggest similar structures for both complexes, *i.e.* the linear arrangement of the three metal atoms and a $D_{3d}$ symmetry.[2,4] Comparing the magnitude of the C-O frequency shift by going from $[Co(CO)_4]_2Hg$ to $\{[Co(CO)_4]_2Hg\}^-$ (37-38 cm$^{-1}$) with the shifts for example between $Ni(CO)_4$[4] and $[Co(CO)_4]^-$[6] (163 cm$^{-1}$) or $Co_4(CO)_{12}$[4] and $[FeCo_3(CO)_{12}]^-$[7] (37-54 cm$^{-1}$) it can be concluded, that the mercury atom must play a significant role in the distribution of the negative charge.

Results obtained with cadmium cobalt carbonyl make a similar sequence of reduction steps probable, but because of the decreased stability of the cadmium containing analogs and their tendency for metal exchange reactions with the amalgam, no pure products could be obtained.

## Experimental Section

*Preparation of* $[Co(CO)_4]_2Hg$. Instead of the method described for the preparation of $[Co(CO)_4]_2Hg$ in the literature,[5] the procedure described below — and regarded as more convenient — has been used.

6.0 g (17.6 mmole) $Co_2(CO)_8$ are dissolved in 150 ml methanol saturated with $N_2$, and the disproportionation reaction allowed to proced until the solution turnes pink. This solution (containing 24 mmole $[Co(CO)_4]^-$) is filtered into a solution of 3.3 g (12 mmole) $HgCl_2$ in 150 ml water. $[Co(CO)_4]_2Hg$ precipitates in the form of orange fine crystals. The product is filtered and washed with water. Yield 6.0 g (11 mmole), 92%, based on $[Co(CO)_4]^-$.

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*Preparation and precipitation of* $[Co(CO)_4]_2Hg^-$. 2.0 g (3.7 mmole) $[Co(CO)_4]_2Hg$ were dissolved in 50 ml THF, 6 g sodium amalgam (1,5% sodium, 3.9 mg atom) added and the reaction mixture shaken for 1 hr. In the case, that the dark orange solution thus obtained contained $[Co(CO)_4]^-$ besides $\{[Co(CO)_4]_2Hg\}^-$ (as evidenced by its infrared spectrum) a short exposure to the air eliminated this contaminating anion. The solution showing only the infrared bands of $\{[Co(CO)_4]_2Hg\}^-$ was filtered into 70 ml of a 0.025 molar aqueous $[Fe(C_{12}H_8N_2)_3]Cl_2$ solution. The mixture was shaken for 15 min, and the ferroin salt of mercury cobalt carbonyl anion was precipitated in the form of a deep red oil by the addition of 80 ml water. This oil was separated, dissolved in 20 ml ethanol and the ferroin salt was precipitated in the form of a dark red powder by adding 100 ml water. The precipitate was filtered, washed with hexane and dried. Yield 1.14 g (18%) (Found: Co, 14.2; Fe, 3.4; Hg, 22.8. $C_{52}H_{24}Co_4FeHg_2N_6O_{16}$ calcd.: Co, 14.02; Fe, 3.33; Hg, 23.82%).

*Reduction of* $[Co(CO)_4]_2]Hg$ *by* $[Co(CO)_4]^-$. A solution of 0.37 mmole of $NaCo(CO)_4$ in 5 ml THF[8] was added to 0.37 mmole of $[Co(CO)_4]_2Hg$, dissolved in 10 ml THF. The mixture was shaken for 1 hr, during which its colour turned dark orange. The infrared spectrum of the solution showed only the bands characteristic for $\{[Co(CO)_4]_2Hg\}^-$.