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Preparation of Pentacyanotriphenylphosphine- and Tetracyanobis(triphenylphosphine)cobaltate(III)*1

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As far as octahedral cobalt(III) complexes containing the ligand triphenylphosphine are concerned, a few types are known. They are [Co(DH)$_2$P(C$_6$H$_5$)$_3$X] (DH=dimethylglyoxime monoanion, X=halogen, alkyl and phenyl[1]; X=CN[2]), [Co(TSB)P(C$_6$H$_5$)$_3$Br][3] (TSB=tetradendate Schiff base dianion) and [Co(CN)$_2$(acac)(P(C$_6$H$_5$)$_3$)$_2$][4] (acac=acetylacetone anion).

We have attempted to prepare some triphenylphosphine complexes by using the so-called Werner-type complexes as the starting materials; we have now succeeded in obtaining two complexes of the cyanotriphenylphosphine series.

Experimental

Potassium Pentacyanotriphenylphosphinecobaltate(III) Trihydrate, K$_2$ [Co(CN)$_5$P(C$_6$H$_5$)$_3$]·3H$_2$O. Potassium bromopentacyanocobaltate(III)[5] (3.8 g, 0.01

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mol) was dissolved in a minimum amount of water (2 m*l*). On the other hand, triphenylphosphine (5.2 g, 0.02 mol) was dissolved in glacial acetic acid (70 m*l*). The former solution was added to the latter solution, and the mixture was stirred at 75°C for 6 hr. The resulting yellow solution was filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was treated with a large amount of water (100 m*l*). After the filtration of the aqueous solution, the filtrate was again evaporated to dryness under reduced pressure. The residue was treated with methanol (100 m*l*) and the methanolic solution was concentrated to a small volume (30—40 m*l*). This concentrated solution was added to a cellulose column which had previously been washed with methanol. When methanol was passed through the column, a yellow band of the desired complex was eluted. This eluted solution was concentrated to a small volume under reduced pressure. When this solution was cooled a pale-yellow material separated out, this was dried over calcium chloride. Yield, 1 g. The complex was soluble in water and methanol, but not soluble in benzene.

Found: C, 47.45; H, 3.27; N, 12.65%. Calcd for $K_2[Co(CN)_5P(C_6H_5)_3]\cdot 3H_2O$: C, 47.30; H, 3.59; N, 12.00%.

The use of iodopentacyano- or chloropentacyanocobaltate(III) in place of the bromo complex gave the same product, but the yield was extremely poor in the case of the iodo complex.

Potassium Tetracyanobis(triphenylphosphine) cobaltate(III) Dihydrate, $K[Co(CN)_4(P(C_6H_5)_3)_2]\cdot 2H_2O$. To a triphenylphosphine solution in glacial acetic acid (5.2 g in 70 m*l*), was added an aqueous solution (a few m*l*) of potassium iodopentacyanocobaltate (III)[5] (4.3 g, 0.01 mo*l*), after which the mixture was stirred at 75°C for 6 hr. The resulting yellow solution was filtered, and a large quantity of water (500 m*l*) was added to the filtrate; then the whole was kept in a refrigerator until a yellow solid began to appear on the surface of the solution. The solid was collected by filtration and suspended in benzene (200 m*l*) in oder to remove any unreacted triphenylphosphine. Finally, the remaining solid was dried over calcium chloride. Yield, 2.5 g. This complex was soluble in methanol to some extent, but it was insoluble in water and benzene.

Found: C, 63.05; H, 4.76; N, 7.48%. Calcd for $K[Co(CN)_4(P(C_6H_5)_3)_2]\cdot 2H_2O$: C, 62.99; H, 4.46; N, 7.34%.

The use of the other halogenopentacyano complexes for the preparation was also possible, but their reaction times were considerably different; the use of the chloro complex took the longest time, while the use of the iodo complex was the best.

Results and Discussion

The two complexes thus obtained were characterized by their electronic absorption spectra (Fig. 1). Each spectrum shows an absorption band as a shoulder in the longer wavelength region. Although its intensity was quite high, this band may be due to a ligand-field transition.

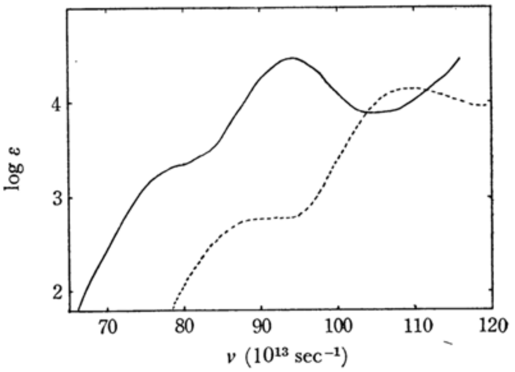

Fig. 1. Absorption spectra in methanol solution.
----- $K_2[Co(CN)_5P(C_6H_5)_3]\cdot 3H_2O$
—— $K[Co(CN)_4(P(C_6H_5)_3)_2]\cdot 2H_2O$

The existence of water of crystallization in the present complexes was established by the thermal analyses and the IR spectra. The presence of complexed CN^- was ascertained from the IR absorption peak in the neighborhood of 2100 cm^{-1} ($\nu_{C\equiv N}$); the pentacyano complex showed a well-split band (2118, 2140 cm^{-1}), and the tetracyano one, a sharp peak with a shoulder (2110, 2150_{sh} cm^{-1}). Concerning the existence of triphenylphosphine, a large number of the characteristic bands were observed for both complexes (1435, 1190, 1090, 1020, 1000 and 750 cm^{-1}). It is not certain which structure, *trans* or *cis*, is to be assigned to the present tetracyano complex.