Novel Dicyano Complexes of Cobalt(III)

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Mixed cyano complexes of cobalt(III) have been synthesized by the use of particular methods,1) and it has been recognized that the reactions of familiar complexes of cobalt(III), such as those of the luteo or praseo type, with cyanides in an aqueous solution are usually unsuccessful when used for the synthesis of such mixed cyano complexes.

We have found a new method of preparing several mixed cyano complexes in which suitable complexes of cobalt(III) are treated with a suitable cyanide near 0°C in cold solvents containing activated charcoal. Here we wish to report the synthesis of $K[Co(CN)_2(acac)_2]$ (I) from tris(acetylacetonato)cobalt(III) in methanol by this new method, and also the synthesis of $[Co(CN)_2(acac)(P\phi_3)_2]$ (II) from (I) and $P\phi_3$. We have also studied the preparation of cobalt(III) complexes of cyanoammine or cyanodiamine series in an aqueous solution2) by this method.

The treatment of a slurry of $Co(acac)_3$ in methanol with the calculated amount of powdered KCN in the presence of activated charcoal at −5—0°C for 4 hr gave a dark red solution. After the filtration and concentration of the reaction mixture at about 5°C, the concentrate was chromatographed on an alumina column in order to separate the (I) from the other substances. By the use of a methanol-ethanol mixture (2 : 1) as the eluant, several fractions were obtained.[*1] From the third fraction, red crystals of (I) were obtained in a 20% yield; they were recrystallized from a solution of potassium acetylacetonate in a mixture of methanol and ethanol (3 : 1). Elemental analysis was undertaken after the substance had been dried for several hours in a vacuum at room temperature. Found: C, 41.09; H, 4.22; N, 7.76%. Calcd for $C_{12}H_{14}O_4N_2KCo$: C, 41.38; H, 4.05; N, 8.04%.

The complex I reacted readily with an excess of triphenylphosphine in boiling ethanol for one hour. After the evaporation of the solvent, the residue was extracted with small portions of boiling benzene and separated on an alumina column, using a mixture of benzene and acetone (5 : 1) as the eluant. From the second fraction[*2] orange crystals of II were obtained. Found: C, 69.86; H, 5.45; N, 3.75%. Calcd for $C_{43}H_{37}O_2N_2P_2Co$: C, 70.30; H, 5.08; N, 3.81%.

The complexes I and II, having $Co(C)_2(O)_4$ and $Co(C)_2(O)_2(P)_2$ configurations respectively, are the first examples of compounds with such configurations. The IR spectra of I and II show sharp peaks at 2130 and 2100 cm^{-1} respectively, and strong peaks in the 1500—1600 cm^{-1} region, indicating the presences of the CN^- and the acetylacetonate groups. The PMR spectrum of (I) in CD_3OD shows that methyl protons of acetylacetone ions are not equivalent, exhibiting two sharp peaks (at 7.79 and 8.06 ppm) with the same intensity. This suggests the *cis*-configuration of the bisacetylacetonato complex.3) The UV spectrum of (I) shows two absorption components at 57×10^{13} sec^{-1} ($\log\varepsilon$: 1.97) and *ca.* 70×10^{13} sec^{-1} ($\log\varepsilon$: *ca.* 2.45), while no component appears to be spin allowed in the longer-wavelength region. These features will be discussed in detail later. The PMR spectrum of II in $CDCl_3$ shows only one sharp peak of the CH_3 group, at 8.94 ppm. This suggests that the complex has the *trans*(C) or the *trans*(P) configuration. The UV spectrum of II in dichloromethane shows a large absorption band with a distinct maximum in the visible region (at 63×10^{13} sec^{-1}, $\log\varepsilon$ 3.58, half width: 12×10^{13} sec^{-1}). No known triphenylphosphine complexes of cobalt(III) belonging to the Werner type have ever shown such a distinct maximum but only vague shoulders in the region of the ligand-field bands. The absorption data on II may be also useful for the determination of the position of the $P\phi_3$ molecule in the spectrochemical series. The complex I reacts readily with other phosphine derivatives; the detailed results will be reported elsewhere.

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1) a) P. Ray and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951). b) M. Shibata, M. Mori and E. Kyuno, *Inorg. Chem.*, **3**, 1573 (1964). c) H. Siebert, *Z. anorg. Chem.*, **327**, 63 (1964). d) K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965). e) H. Yoneda, T. Baba and M. Muto, *ibid.*, **40**, 1736 (1967).

2) Some results from the initial stage of the work of this series are in press. *Inorg. Chem.* (1968).

[*1] The first fraction is green, while the second one is faintly violet.

[*2] The first fraction, faintly grey, mainly contained $P\phi_3$.

3) R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, **4**, 1583 (1965).