A New Cobalt(III) Complex: $K[Co(CN)_2dg_2] \cdot 3/2\ H_2O$

By Nobufumi Maki

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The dicyano-bis(dimethylglyoximato)cobaltate(III) complex, $K[Co^{III}(CN)_2dg_2] \cdot 3/2\ H_2O$,[1] has been prepared, and its absorption spectrum compared with those of the related dicyano-cobalt(III) complexes.

A solution (200 ml.) containing 13.7 g. of potassium cyanide was mixed with a solution of 50 g. of bis(dimethylglyoximato)diammine-cobalt(III) chloride, $[Co\ dg_2(NH_3)_2]Cl \cdot 5H_2O$,[2] under continuous stirring, and then heated on a water bath until the reaction mixture was evaporated to one-third of its former volume. From the smell of the ammonia evolved, it could be discerned that the following mild reaction was in progress:

$$[Co\ dg_2(NH_3)_2]Cl \cdot 5\ H_2O\ +\ 2\ KCN \rightarrow$$
$$K[Co(CN)_2dg_2] \cdot 3/2\ H_2O\ +\ 2\ NH_3\ +\ KCl$$

During the course of the reaction, an insoluble yellow matter was deposited. These crystalline deposits were eliminated from the solution quickly while it was in a hot state. These insoluble orange yellow crystals are probably tris(dimethylglyoximato)cobalt(III), $[Co(dgH)_3]$,[3] formed from the rupture of the hydrogen bonding due to the alkalinity of the cyanide solution.

After cooling, the lusterous silky yellow crystals which had been deposited were filtered and washed with cold 85% ethanol and ether.

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[1] N. Maki, *Nature*, **188**, 227 (1960).

[2] L. Tschugaeff, *Z. anorg. u. allgem. Chem.*, **46**, 160 (1905).

[3] J. Fujita, A. Nakahara and R. Tsuchida, *J. Chem. Phys.*, **23**, 1541 (1955).

When the mother liquor was concentrated on a water bath, more crystals were obtained and recrystallized from hot water. Large needle-shaped crystals were thus obtained.

Found: Co, 15.49; C, 31.60; N, 21.99; K, 10.22. Calcd. for $K[Co(C_8H_{14}O_4N_4)(CN)_2]$: Co, 15.50; C, 31.58; N, 22.10; K, 10.28%.

The anhydrous salt (dried at 110°C for 3 hr.) was hygroscopic.

cis-Dicyano-bis(ethylenediamine)cobalt(III) chloride⁴⁾ and dicyano-bis(propylenediamine)-cobalt(III) thiosulfate were prepared by the method of Rây and Sarma⁵⁾ or that of Gupta⁶⁾.

The visible and ultraviolet absorption spectra measurements were made manually by a Beckmann DU spectrophotometer in an aqueous solution.

Results and Discussion

The absorption spectra of dicyano-cobalt(III) complexes are shown in Fig. 1. It can be seen that the first band in the visible region shifts towards the shorter wavelength in the following order of ligands:

tn en pn dg.

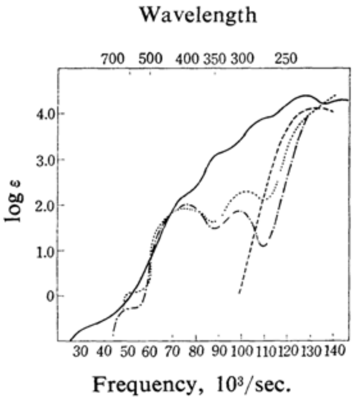

Fig. 1. The absorption spectra of dicyano-cobalt(III) complexes obtained in aqueous solution.

——— $K[Co(CN)_2dg_2]\cdot 3/2\,H_2O$
········· $[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$
—·—· $[Co(CN)_2en_2]Cl$
——— Dimethylglyoxime in ethanol

Table I shows the absorption maxima for dicyano-cobalt(III) complexes. These data were reported recently by Ohkawa, Fujita and Shimura⁷⁾ except for that of a dimethylglyoxime complex.

Figure 2 shows the absorption spectra for bis(dimethylglyoximato)cobalt(III) complexes of the $[Co^{III}dg_2X_2]$-type.⁸⁾ The order of the spectrochemical series of ligands is as follows:

CN^- NO_2^- NH_3 dgH^- Cl^-

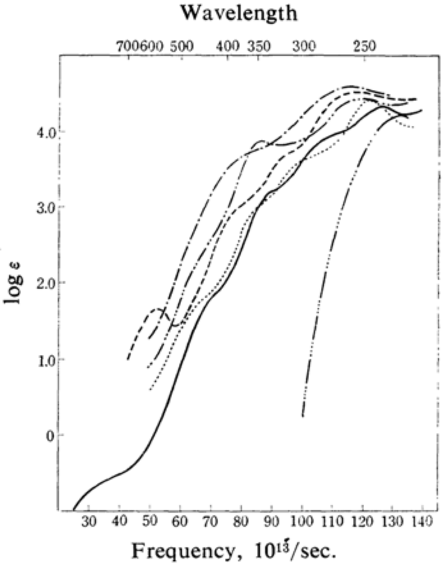

Fig. 2. The absorption spectra for dimethylglyoximato-cobalt(III) complexes.

—·—· $[Co(dgH)_3]$ in H_2O
—··—·· $NH_4[Co(NO_2)_2dg_2]\cdot H_2O$ in H_2O
—···— Dimethylglyoxime in ethanol
——— $H[CoCl_2dg_2]$ in 3 M HCl
········· $[Co(NH_3)_2dg_2]Cl\cdot 5\,H_2O$ in H_2O
——— $K[Co(CN)_2dg_2]\cdot 3/2\,H_2O$ in H_2O

TABLE I. ABSORPTION MAXIMA FOR DICYANO-COBALT(III) COMPLEXES

Compound	Spin-forbidden band		Spin-allowed band		Allowed band	
	A	B	I	II	I	II
$K[Co(CN)_2dg_2]\cdot 3/2\,H_2O$	—	—	ca. 78(2.3)	ca. 92(3.24)?	ca. 110(3.9)?	125.2(4.45)
cis-$[Co(CN)_2en_2]Cl$*	49.7(1.67)	—	74.2(1.91)	97.1(1.93)	142.1(4.32)	
cis-$[Co(CN)_2pn_2]_2S_2O_3\cdot H_2O$*	50.6(1.73)	—	74.5(1.90)	97.4(1.94)	140.8(4.38)	
cis-$[Co(CN)_2tn_2]_2S_2O_3$*	47.2(1.60)	—	73.6(1.89)	95.6(1.97)	137.0(4.38)	

* The absorption maxima data were adopted from Ref. 7.
tn = trimethylenediamine pn = propylenediamine

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4) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, **1963**, 966.

5) P. R. Rây and B. Sarma, *J. Indian Chem. Soc.*, **28**, 59 (1951).

6) N. R. Sen Gupta, *Z. anorg. u. allgem. Chem.*, **326**, 108 (1963).

7) K. Ohkawa, J. Fujita and Y. Shimura, This Bulletin, **38**, 66 (1965).

8) A. Nakahara, ibid., **28**, 207 (1955).

As for the dicyano complex, two dimethylglyoximes co-ordinate with the central cobalt(III) ion in a planary manner as a pair of chelate rings with two hydrogen bonds, and two dicyano ligands co-ordinate with it at position above and below its coplanar structure. Each co-ordinate bond appears to have a strong π-bonding character in its co-ordination sphere. Therefore, this complex has a configuration similar to that of cobalamine (vitamin B_{12}) and shows a quite analogous behavior in solution.[1] This stable complex, in view of this, will be useful for the study of a catalytic reaction.

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Radiation Center of Osaka Prefecture
Shinke-cho, Sakai, Osaka