A Novel Bis(dimethylglyoximato)cobalt(III) Complex with a *cis*-Configuration

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Numerous cobalt(III) complexes of the *trans*-$[CoX_2(dgH)_2]$ type[1] have been reported, but the corresponding *cis*-isomers have not yet been synthesized. The steric condition arising from the extremely stable square-planar structure of the $[Co(dgH)_2]$ type with a pair of hydrogen bonds is the reason why the formation of *cis*-isomers is so difficult. Nakahara,[2] however, has prepared the $[Co(dgH)_3]\cdot 5/2\ H_2O$ complex in a strongly basic solution for the rupture of the hydrogen bonds. The present communication will describe one of our attempts to prepare three new compounds of a cis-type involving an ethylenediamine, $[Co(dgH)(dgH_2)en]Cl_2\cdot 2H_2O$, $[Co(dgH)(dgH_2)en]Br_2\cdot 2H_2O$, and $[Co(dgH)_2en]ClO_4\cdot 1/3\ H_2O$.

Thirty grams of the $[Co\ en_3]Cl_3\cdot 3H_2O$ complex[3] were completely dissolved in 850 m*l* of water at 80°C. To this solution we then added 45.7 g of $Na_2dg\cdot 8H_2O$. The solution was directly heated to the boil (100°C) for 3 hr, and finally it was concentrated to 130 m*l*. On heating, the orange-yellow color of the solution soon turned dark brown, but no deposition of metallic cobalt was observed during the reaction. After the solution had been cooled in ice, sodium chloride precipitates formed and were filtered off. To the filtrate (130 m*l*), 36 m*l* of 35% HCl were added under ice-cooling. Then, brown crystals were deposited from the solution; these crystals were separated by filtration and washed with a small amount of cold water, ethanol, and ether. The yield was 34% of the theory. The purifications were carried out as follows: the crude complex (14 g) was dissolved in a requisite small amount of a 0.5 M NaOH solution (110 m*l*). After the filtration of the solution, the complex was precipitated again by stirring in 36 m*l* of HCl (25%), drop by drop, at 0°C. This procedure was repeated three times. The complex was then dried on $CaCl_2$ under 1 atmosphere. Found: Co, 18.72; C, 26.58; N, 18.83; H, 6.31; Cl, 15.74%. Calcd for $[Co(dgH)(dgH_2)en]Cl_2\cdot 2H_2O$: Co, 18.89; C, 26.27; N, 18.38; H, 5.95; Cl, 15.51%.

The bromide and perchlorate of the complex were likewise precipitated by adding the corresponding acid (30—35%) instead of hydrochloric acid to the basic filtrate. The purification procedure was quite the same as above. Found: Co, 10.65; C, 21.53; N, 15.78; H, 5.11; Br, 29.15%. Calcd for $[Co(dgH)(dgH_2)en]Br_2\cdot 2H_2O$: Co, 10.79; C, 21.99; N, 15.39; H, 4.98; Br, 29.26%. Found: Co, 12.78; C, 26.05; N, 18.71; H, 4.89; Cl, 8.03%. Calcd for $[Co(dgH)_2en]ClO_4\cdot 1/3\ H_2O$: Co, 12.96; C, 26.42; N, 18.48; H, 5.03; Cl, 7.80%.

The molar ratio of the halide ion to the complex cation was also examined by volumetric analyses; the results established an approximately 2 : 1 ratio for both the halide ions. The aqueous solutions of these compounds are strongly acidic with pH-values ranging from 0 to 1.2. Therefore, the DC polarograms of these compounds were almost in accord with the hydrogen waves in aqueous solutions. On the other hand, the results of examining them in DMSO revealed this complex to take a *cis*-configuration.[4]

Figure 1 shows the absorption spectra of *cis*-bis(dimethylglyoximato)ethylenediaminecobalt(III) and its related complexes in the visible and ultraviolet regions. Although its first *d–d* band is partly overlapped with the charge-transfer band due to the oxime ligands, it seems likely that the first band shifts to a shorter wavelength in the following sequence of complexes: $[Co\ en_3]^{3+}$, $[Co(dgH)_2en]^{+}$, $[Co(dgH)_3]$.

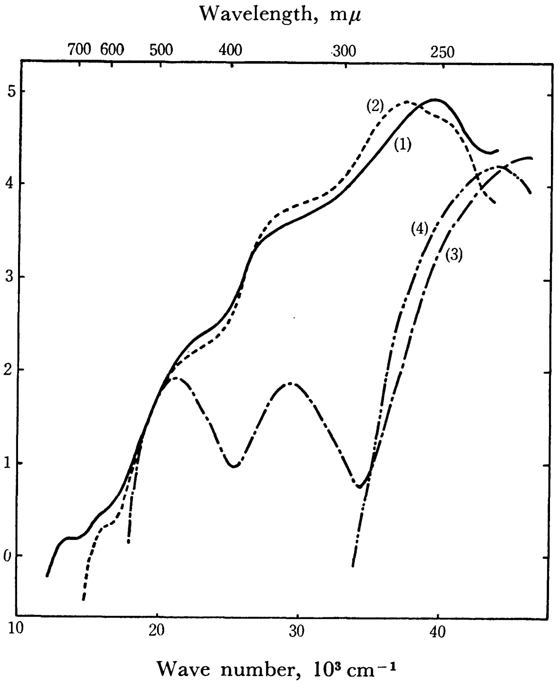

Fig. 1. Absorption spectra of *cis*-bis(dimethylglyoximato)-cobalt(III) and its related complexs: (1) —— *cis*-$[Co(dgH)_2en]ClO_4\cdot 1/3\ H_2O$ in 0.1 N NaOH; (2) ---- *dl*-$[Co(dgH)_3]\cdot 5/2\ H_2O$ in 0.1 N NaOH; (3) —·—·— *dl*-$[Co\ en_3]Cl_3$ in H_2O; (4) -·-·-·-·- $Na_2dg\cdot 8H_2O$ in H_2O.

Since the pmr spectrum of the *cis*-$[Co(dgH)(dgH_2)en]Cl_2\cdot 2H_2O$ complex in 99.7% D_2O shows that the broad band at 2.9 ppm downfield from DSS is in the same position as the single broad CH_2 band in the spectrum of $[Co\ en_3]^{3+}$, this band adjacent to the peak of CH_3-group may be assigned to the CH_2-group; this suggests the presence of an ethylenediamine bound to the cobalt.

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[1] Abbreviation used: $dg=CH_3C(NO)\cdot C(NO)CH_3$.

[2] A. Nakahara, This Bulletin, **27**, 560 (1954).

[3] "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., New York, N. Y. (1946), p. 221.

[4] N. Maki, This Bulletin, **44**, 1446 (1971).