Circular Dichroism of the Paramagnetic μ-Amido-μ-peroxo-tetrakis-(*l*-propylenediamine)-dicobalt Ion

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(Received June 5, 1967)

Little work has been done concerning the preparation and circular dichroism (CD) of polynuclear complexes,[1,2] probably because of difficulties in preparing their optical isomers. Owing to the stereospecificity of *l*-propylenediamine in complex formation, however, we obtained a new optically active binuclear complex, μ-amido-μ peroxo - tetrakis - (*l* - propylenediamine) - dicobalt nitrate trihydrate $(-)_D-[(l\text{-pn})_2\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{smallmatrix}\rangle\mathrm{Co}(l\text{-pn})_2](\mathrm{NO_3})_4\cdot 3\mathrm{H_2O}$; a mixture of $[(\mathrm{NH_3})_4\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{smallmatrix}\rangle\mathrm{Co}(\mathrm{NH_3})_4](\mathrm{NO_3})_4$ (20g) and 4% aqueous *l*-propylenediamine solution (300 g) was warmed on a water bath at 60°C for 5 hr. The resulting brown solution was made acid with concentrated nitric acid, and a large amount of ethanol added. The green precipitate was recrystallized three times from 0.1 N nitric acid (yield 10 g). Found: C, 18.80; H, 6.28; N, 23.64%. Calcd for $\mathrm{C_{12}H_{48}O_{17}N_{13}Co_2}$: C, 18.85; H, 6.33; N, 23.82%.

The absorption band at 14400 cm^{-1} which is characteristic of the complexes involving $-(\mathrm{Co{-}O_2{-}Co})-$ (oxidation number 5) does not show a distinct CD. Linhard and Weigel[3] assigned such a band in a similar complex, $[(\mathrm{NH_3})_5\mathrm{Co{-}O_2{-}Co}(\mathrm{NH_3})_5]^{5+}$ to a split component of the first band (Ia). However, this band would be more appropriately assigned to a spin-forbidden *d-d* transition or to a charge transfer between the peroxo group and the metal ion, since split components of the magnetically allowed first band should be optically active. The band at 21300 cm^{-1} may correspond to the first band of uninuclear Co(III) complexes, and the corresponding CD spectrum shows a strong negative peak at 20300 cm^{-1}. This fact suggests that the absolute configuration around the metal ions might be Λ(L)-type, in coincidence with the expectation from the stereospecific coordination of *l*-propylenediamine to cobalt.[4] Characteristics of CD curve of the corresponding ethylenediamine complex, $(-)_D[(\mathrm{en})_2\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O_2}\end{smallmatrix}\rangle\mathrm{Co}(\mathrm{en})_2]^{4+}$ measured by Mathieu[1] (450 to 650 mμ) are very similar to those of ours. Thus, we would conclude that his complex has a Λ-configuration, too. Garbett and Gillard[5] obtained the uninuclear complexes of known absolute configuration Λ by decomposing Mathieu's complex. A fairly strong CD peak is seen at 32500 cm^{-1} corresponding to the so-called "binuclear band" at 30300 cm^{-1}. On the other hand, the complexes $[(l\text{-pn})_2\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{X}\end{smallmatrix}\rangle\mathrm{Co}(l\text{-pn})_2]^{4+}$ ($\mathrm{X{=}OH^-}$, $\mathrm{NO_2}^-$, *etc.*) fail to exhibit clear CD bands in this region.[6] The bridging chelate ring $\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{O{-}O}\end{smallmatrix}\rangle\mathrm{Co}$ could have an asymmetric non-planar conformation while the four-membered ring $\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{NO_2}\end{smallmatrix}\rangle\mathrm{Co}$ or $\mathrm{Co}\langle\begin{smallmatrix}\mathrm{NH_2}\\ \mathrm{OH}\end{smallmatrix}\rangle\mathrm{Co}$ takes such an assymmetric form with difficulty. A strong positive CD band at 40000 cm^{-1} may correspond to the charge transfer between the metal ion and the *l*-propylenediamine ligand in a λ-gauche form.[7]

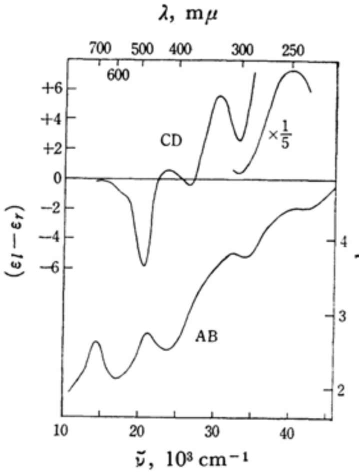

Fig. 1. Absorption (AB) and CD curves in 0.01N nitric acid.

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3) M. Linhard and M. Weigel, *Z. anorg. Chem.*, **308**, 254 (1961).

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7) A. J. McCaffery, S. F. Mason and B. J. Norman, *Chem. Commun.*, **1965**, 49.