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Spectroscopic Studies of Polynuclear Complexes. I. Preparations and Circular Dichroisms of Tetrakis(*l*-propylenediamine)-dicobalt(III) Complexes Containing μ-Amido Group

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New binuclear cobalt(III) complexes, $(-)_D$-$[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{O}_2)\mathrm{Co}(l\text{-pn})_2](\mathrm{NO}_3)_4\cdot 3\mathrm{H_2O}$, $(+)_D$-$[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{O}_2)\mathrm{Co}(l\text{-pn})_2]\mathrm{I}_3\cdot 6\mathrm{H_2O}$, $(+)_D$-$[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{NO}_2)\mathrm{Co}(l\text{-pn})_2]\mathrm{Br}_4\cdot 6\mathrm{H_2O}$, $(+)_D$-$[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{OH})\mathrm{Co}(l\text{-pn})_2](\mathrm{NO}_3)_4\cdot 2\mathrm{H_2O}$ and $(-)_D$-$[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{SO}_4)\mathrm{Co}(l\text{-pn})_2](\mathrm{NO}_3)_3$ were prepared and their absolute configurations determined to be $\Lambda\Lambda$ on the consideration of the stereospecific coordination of *l*-propylenediamine (*l*-pn) to the metal ion. On the basis of these identifications, absolute configurations of the corresponding ethylenediamine-(en) complex ions were assigned. The nature of the d–d bands of these polynuclear complexes seems to be very similar to those of uninuclear cobalt(III) complexes. One of the two central cobalt(III) ions is regarded as a member of an asymmetric chelate ligand to the other cobalt ion, and the CD corresponding to the d–d bands appears to depend mainly on the strength of vicinal effect due to such a chelate ring.

Since the resolution of several binuclear complexes of the type, $[(\mathrm{en})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{a})\mathrm{Co}(\mathrm{en})_2]^{n+}$,[1] and two quadrinuclear hexol complexes, $[\mathrm{Co}\{(\mu\text{-OH,OH})\mathrm{Co}(\mathrm{NH_3})_4\}_3]^{6+}$ and $[\mathrm{Co}\{(\mu\text{-OH,OH})\mathrm{Co}(\mathrm{en})_2\}_3]^{6+}$ [2] by Werner, there has been little work reported[3–6] on the preparation and optical properties of polynuclear cobalt(III) complexes. In 1938, Mathieu[3] measured the circular dichroism (CD) spectra of some of Werner's binuclear complexes, and concluded that the absolute configuration of the polynuclear complexes could not be assigned from their CD behavior.

As a first step of studying the structure and optical properties of such complexes, we have attempted to prepare new binuclear complexes, of which the absolute configuration can be assigned by a consideration of the stereospecific coordination of an optically active ligand to the metal ion. In this paper we report the preparation and the absolute configuration of new optically active binuclear complexes of the type, $[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{a})\mathrm{Co}(l\text{-pn})_2]^{n+}$ [*1] ($\mathrm{a}=\mathrm{O_2}^-, \mathrm{O_2}^{2-}, \mathrm{NO_2}^-, \mathrm{OH}^-$, and "$\mathrm{SO_4}^{2-}$"[*2]) and compare their optical properties with those of corresponding Werner's ethylenediamine complexes.

Experimental

Preparations of the Complexes. *(1) Octaammine-μ-amido-μ-superoxo-dicobalt(III)*[*3] *Nitrate.* $[(\mathrm{NH_3})_4\mathrm{Co}(\mu\text{-NH}_2,\mathrm{O}_2)\mathrm{Co}(\mathrm{NH_3})_4](\mathrm{NO_3})_4$ was prepared and purified by Mori, Weil and Ishiguro's new method[7] with concentrated nitric acid at 20—30°C as oxidizing agent instead of diammonium hexanitratocerate(IV). From 50 g of cobalt nitrate hexahydrate, 10 g of the complex was obtained.

(2) $(+)_D$[*4]*-Tetrakis(ethylenediamine)μ-amido-μ-hydroxo-dicobalt(III) Nitrate.* $(+)_D$-$[(\mathrm{en})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{OH})\mathrm{Co}(\mathrm{en})_2](\mathrm{NO_3})_4$ was prepared by a new method from "$(+)_D$-$[(\mathrm{en})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{SO}_4)\mathrm{Co}(\mathrm{en})_2](\mathrm{NO_3})_3\cdot 2\mathrm{H_2O}$". The starting complex (500 mg) was dissolved in 0.1 N sodium hydroxide (10 m*l*), set aside for 1 day at room tempera-

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[1] A. Werner, *Ber.*, **46**, 3674 (1913); **47**, 1959 (1914).

[2] A. Werner, *ibid.*, **47**, 1977, 3087 (1914).

[3] J. P. Mathieu, *Bull. soc. chim.*, [5], **5**, 103 (1938).

[4] S. F. Mason and J. W. Wood, *Chem. Commun.*, **1967**, 209.

[5] R. D. Kern and R. A. D. Wentworth, *Inorg. Chem.*, **6**, 1018 (1967).

[6] G. R. Bulbaker and B. E. Douglas, *ibid.*, **6**, 1562 (1967).

[*1] In this paper most of the binuclear complexes have double bridging structure: *e.g.* $[(l\text{-pn})_2\mathrm{Co}\langle{}^{\mathrm{NH_2}}_{\mathrm{a}}\rangle\mathrm{Co}(l\text{-pn})_2]^{n+}$. Such a structure is expressed by the formula $[(l\text{-pn})_2\mathrm{Co}(\mu\text{-NH}_2,\mathrm{a})\mathrm{Co}(l\text{-pn})_2]^{n+}$.

[*2] Concerning the structure of the "sulfato bridge," nothing decisive can be stated at the present stage. (see p. 151).

[*3] The name "μ-superoxo" was used for paramagnetic $\mu\text{-O}_2^-$ complexes, according to the proposal of U. Thewalt and R. Marsh. (*J. Am. Chem. Soc.*, **89**, 6364 (1967)).

[7] M. Mori, J. A. Weil and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).

[*4] $(+)_D$ and $(-)_D$ refer to the signs of the optical rotation at sodium D-line (589 mμ).

ture, and cooled in an ice bath. The red crystals were filtered off, dissolved in a little water and a small quantity of barium nitrate was added. The barium sulfate was removed and the filtrate concentrated till the crystals appeared and cooled to 0°C. The orangered crystals were recrystallized from hot water. Yield 200 mg.

Found: C, 15.27; H, 6.03; N, 28.43%. Calcd for $C_8H_{35}N_{13}O_{13}Co_2$: C, 15.03; H, 5.52; N, 28.48%.

(3) (−)$_D$*-Tetrakis(l-propylenediamine)μ-amido-μ-superoxo-dicobalt(III) Nitrate Trihydrate,* $(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2](NO_3)_4\cdot 3H_2O$. $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4](NO_3)_4$ (20 g) in 5% aqueous *l*-propylenediamine (300 m*l*) was warmed at about 55°C on a water bath for about 5 hr, then cooled to room temperature, the brown solution treated with concentrated nitric acid until the color changed to green, and then with a large volume of ethanol. Green hygroscopic precipitate was filtered. When the filtrate was green, ethanol was added to obtain further aliquot. The product was recrystallized from 0.1 N nitric acid. The circular dichroism curve of the green fine needles remained unchanged on further recrystallization. Yield 5–7 g. The product seems to consist of only one of the optical isomers.

Found: C, 18.80; H, 6.28; N, 23.64%. Calcd for $C_{12}H_{48}N_{13}O_{17}Co_2$: C, 18.85; H, 6.33; N, 23.83%.

(4) (+)$_D$*-Tetrakis(l-propylenediamine)μ-amido-μ-peroxo-dicobalt(III) Iodide Hexahydrate,* $(+)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2]I_3\cdot 6H_2O$. $(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2](NO_3)_4\cdot 3H_2O$ (500 mg) was dissolved in 28% aqueous ammonia (3 m*l*). To this solution an excess of ammonium iodide was added. The brown precipitate was recrystallized from 15% aqueous ammonia by adding excessive ammonium iodide. Brown powder, yield 100 mg.

Found: C, 15.07; H, 5.40; N, 13.16%. Calcd for $C_{12}H_{54}N_9O_8I_3Co_2$: C, 15.15; H, 5.72; N, 13.25%.

(5) (+)$_D$*-Tetrakis(l-propylenediamine)μ-amido-μ-nitrito-dicobalt(III) Bromide Hexahydrate,* $(+)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,NO_2)Co(l\text{-pn})_2]Br_4\cdot 6H_2O$. $(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2](NO_3)_4\cdot 3H_2O$ (1 g) was dissolved in 5 m*l* of water, and treated with sodium nitrate (1 g). The color of the solution gradually changed from green to dark brown. The solution was kept at room temperature for 1 hr, then cooled in an ice bath and treated with concentrated hydrobromic acid (3 m*l*) slowly and carefully with stirring. The reddish orange crystals were filtered off and recrystallized from water. Yield 300 mg.

Found: C, 15.89; H, 5.49; N, 15.39%. Calcd for $C_{12}H_{54}N_{10}O_8Br_4Co_2$: C, 15.94; H, 5.80; N, 15.49%.

(6) (−)$_D$*-Tetrakis(l-propylendiamine)μ-amido-μ-"sulfato"-dicobalt(III) Nitrate,* $(-)_L$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,SO_4)Co(l\text{-pn})_2](NO_3)_3$. $(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2](NO_3)_4\cdot 3H_2O$ (1 g) was suspended in water (2 m*l*) saturated with sulfur dioxide, warmed on a water bath (60—70°C) for a few minutes and kept in an ice bath. The dark red crystals were filtered off, treated with water (2 m*l*) saturated with sulfur dioxide, and finally recrystallized from hot water. Reddish violet crystals, yield 400 mg.

Found: C, 20.57; H, 6.01; N, 23.60%. Calcd for $C_{12}H_{42}N_{12}O_{13}S_1Co_2$: C, 20.23; H, 5.94; N, 23.59%. The structure will be discussed in the following section.

(7) (+)$_D$*-Tetrakis(l-propylenediamine)μ-amido-μ-hydoxo-dicobalt(III) Nitrate Dihydrate.* $(+)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,OH)Co(l\text{-pn}_2](NO_3)_4\cdot 2H_2O$ was prepared from "$(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,SO_4)Co(l\text{-pn})_2](NO_3)_3$" by a similar method to that for $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,OH)Co(en)_2](NO_3)_4$. From 500 mg of the starting material, 200 mg of the complex was obtained. Found: C, 19.58; H, 6.86; N, 24.79%. Calcd for $C_{12}H_{47}N_{13}O_{15}Co_2$: C, 19.71; H, 6.48; N, 24.89%.

Resolution of Tetrakis(ethylenediamine)-μ-amido-μ-superoxo-dicobalt(III) Ion. This was resolved by Werner's method[1)] with silver *d*-bromcamphorsulfonate. Yield, 2 g of nitrate of $(-)_D$ form and 3 g of $(+)_D$ form from 35 g of $[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]Br_4$.

Measurements. Absorption and circular dichroism spectra were measured with Hitachi 124 Spectrophotometer and JASCO Model ORD/UV-5 recorder with CD attachment respectively in water at room temperature. All the complexes were stable in water.

Results and Discussion

Stereospecificity of *l*-Propylenediamine for Binuclear Complexes. It is known that the stable conformation of the chelated *l*-(D)-propylenediamine will be a λ-form with equatorial methyl group.[8)] In tris complexes of *l*-propylenediamine, the two diastereoisomers, Δ and Λ[*5] have the "ob" and the "lel" structure, respectively. The lel isomer is estimated to be more stable than the ob isomer.[8)] In fact, the products obtained on the reaction between cobalt and *l*-propylenediamine always consist mostly of Λ-$[Co(l\text{-pn})_3]^{3+}$ with the lel structure.[9)]

The energy difference between the ob and the lel isomer is said to be small for *cis*-bis-(*l*-propylenediamine) complexes. As stated before, however, the reaction of $[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]^{4+}$ and *l*-propylenediamine in an aqueous solution seemed to yield only one of the three possible optical isomers of $[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2]^{4+}$. We ignore the geometrical isomers depending on the position of the methyl groups, since they would have structurally similar stabilization energies with one another, and could not be separated by usual chemical methods. The pure crystalline isomer exhibits a strong CD, indicating that it is one of the two diastereoisomers ΔΔ and ΛΛ, and not ΔΛ (so-called "meso" form). The isomer, $(-)_D$-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-pn})_2]^{4+}$, could be assigned reasonably to the ΛΛ configuration, when the stereospecific coordination of *l*-propylenediamine mentioned above is considered.

No indication of the formation of the other isomers was observed from the CD measurements of many samples obtained at different stages of recrystallization. Studies with molecular models

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8) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

[*5] The symbols Δ and Λ designate the absolute configuration around the central metal ion, suggested by the Commission on the Nomenclature of Inorganic Compounds of IUPAC (1966).

9) E. P. Dwyer and F. L. Garvan, *J. Am. Chem. Soc.*, **81**, 2955 (1959).

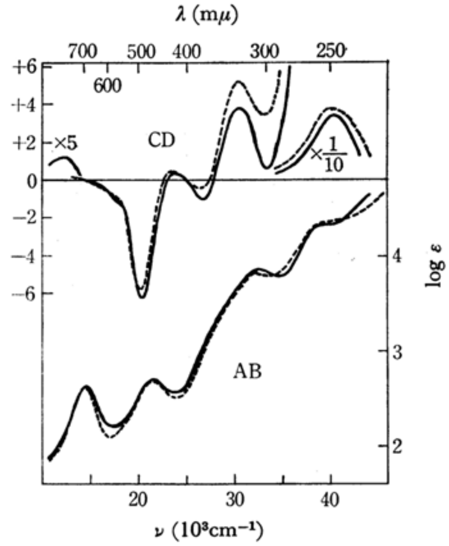

Fig. 1. The absorption (AB) and CD spectra of $(-)_D$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2](NO_3)_4$ (——) and $(-)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-}pn)_2](NO_3)_4$ (------) in water.

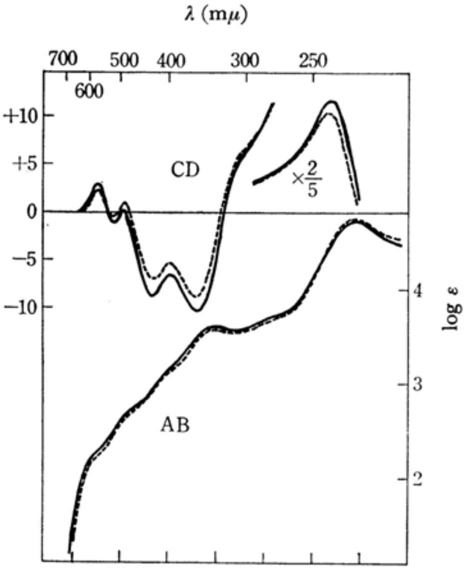

Fig. 2. The absorption (AB) and CD spectra of $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2, O_2) Co(en)_2]I_3$ (——) and $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-}pn)_2]I_3$ (------) in water.

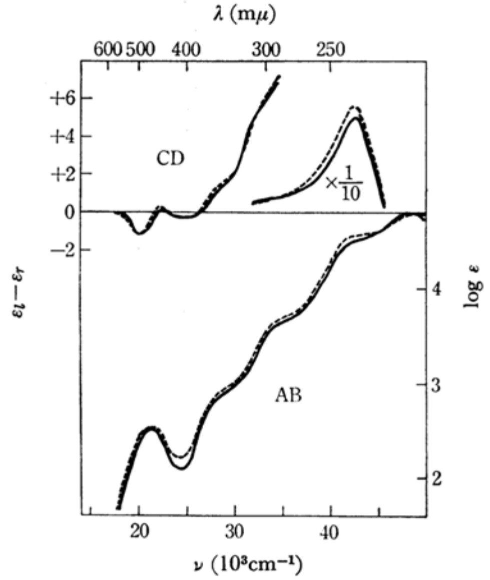

Fig. 3. The absorption (AB) and CD spectra of $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,NO_2)Co(en)_2](NO_3)_4$(——) and $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,NO_2)Co(l\text{-}pn)_2]Br_4$ (------) in water.

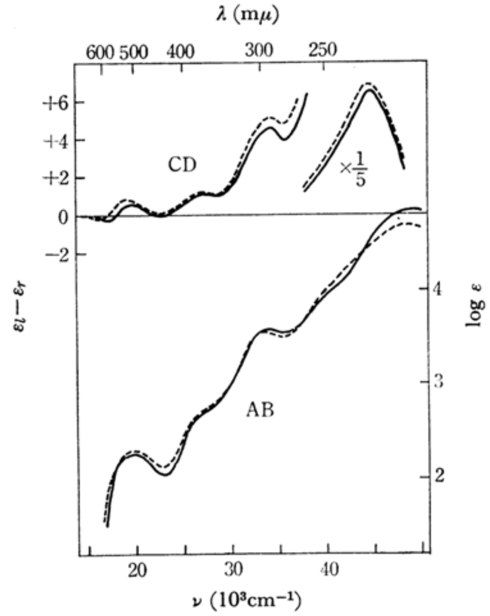

Fig. 4. The absorption (AB) and CD spectra of $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,OH)Co(en)_2](NO_3)_4$ (——) and $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,OH)Co(l\text{-}pn)_2]$-$(NO_3)_4$ (------) in water.

of the isomers show that the repulsion between the amino groups of *l*-propylenediamines around the bridging region seems to be less in the $\Delta\Delta$ and the $\Lambda\Lambda$ form than in the $\Delta\Lambda$ form.

Four complexes, $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-}pn)_2]^{3+}$, $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,NO_2)Co(l\text{-}pn)_2]^{4+}$, $(-)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,SO_4)Co(l\text{-}pn)_2]^{3+}$ and $(+)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,OH)Co(l\text{-}pn)_2]^{4+}$, which were derived from the $\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)$-$Co(l\text{-}pn)_2]^{4+}$, would be concluded to have the same $\Lambda\Lambda$ configuration too, from their CD measurement, as discussed later. Complete inversion to the $\Delta\Delta$ form during their syntheses from the $\Lambda\Lambda$ isomers seems to be very improbable for these binuclear complexes.

With these *l*-propylenediamine complexes as standard, the absolute configurations of the corresponding ethylenediamine complexes could be assigned safely from their CD spectra. As Fig. 1 shows, the CD spectra of the two $(-)_D$-μ-amido-μ-superoxo-dicobalt complexes of ethylenediamine and *l*-propylenediamine are very similar to each other. Therefore, we conclude that the isomer, $(-)_D$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$ has the $\Lambda\Lambda$ configuration. The following complex ions prepared from this isomer would be assigned to the $\Lambda\Lambda$ configuration; $(-)_D$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{3+}$, $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,NO_2)Co(en)_2]^{4+}$, $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,SO_4)Co(en)_2]^{3+}$ and $(+)_D$-$[(en)_2Co(\mu\text{-}NH_2,OH)Co(en)_2]^{4+}$.

The assignment for the ethylenediamine complexes coincides with that by Garbett and Gillard.[10] They obtained the uninuclear complexes of the known absolute configuration Λ by decomposing $(+)_D$-$[(en)_2NH_3Co(\mu\text{-}NH_2)CoNH_3(en)_2]^{5+}$, derived from $(-)_D$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]^{4+}$, which was assigned to have $\Lambda\Lambda$ configuration as stated above.

Absorption and Circular Dichroism Spectra. Absorption spectra of the present binuclear complexes exhibit a similar pattern in essential to that of uninuclear complexes, indicating that no strong metal-metal interaction will exist in them. Fairly strong absorptions at *ca.* 30000 to 35000 cm^{-1} known as "the polynuclear band" seem probably to owe to charge transfer transitions between the metal ions and the bridging ligand groups, although the origin is still uncertain.[11]

Medium intensity bands in the visible region seem to be the so called "first" band, corresponding approximately to the d–d transitions $(^1A_1\text{–}^1T_1)$, of uninuclear complexes. Table 1 shows that the shifts of these bands can be interpreted by the spectrochemical series,[12] although the field strength of a ligand seems to increase somewhat upon bridging coordination. A similar observation was made by Brubaker and Douglas[6] in their new trinuclear complexes.

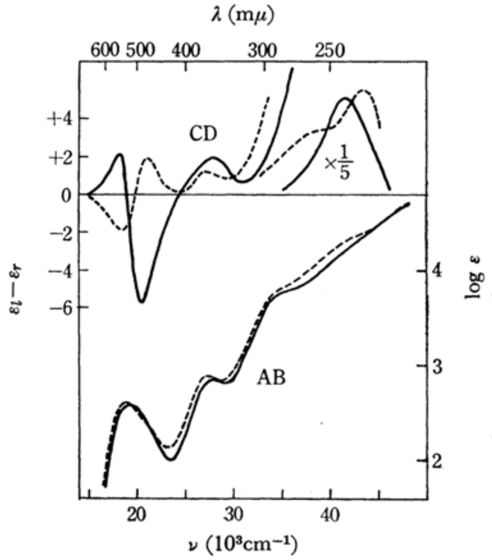

Fig. 5. The absorption (AB) and CD spectra of "$(+)_D$-$[(en)_2(\mu\text{-}NH_2,SO_4)Co(en)_2](NO_3)_3$" (——) and "$(-)_D$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,SO_4)Co(l\text{-}pn)_2]$-$(NO_3)_3$" (------) in water.

Ammine complexes with the superoxo bridge have a characteristic absorption band at *ca.* 14500 cm^{-1} with a medium intensity. Linhard and Weigel[13] assigned such a band in the complex, $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ to a split component

TABLE 1. NUMERICAL DATA OF ABSORPTION IN WATER

	ν_{max}*(logε)	ν_{max}*(logε)	ν_{max}*(logε)	ν_{max}*(logε)	ν_{max}*(logε)
$[(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5]Cl_5$	14.9(2.92)	20.8(2.43)		33.6(4.35)	
$[(NH_3)_4Co(\mu\text{-}NH_2,O_2)Co(NH_3)_4]Cl_4$	14.3(2.45)	20.8(2.50)		33.0(3.61)	41.3(4.21)
$\Lambda\Lambda$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2](NO_3)_4$	14.6(2.64)	21.4(2.72)		32.5(3.87)	39.5(4.3)**
$\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-}pn)_2](NO_3)_4$	14.4(2.61)	21.3(2.72)		32.4(3.82)	39.5(4.3)**
$\Lambda\Lambda$-$[(en)_2Co(\mu\text{-}NH_2,O_2)Co(en)_2]I_3$	17 (2.2)**	20 (2.6)**	24 (3.0)**	29.8(3.59)	44.5(4.74)
$\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,O_2)Co(l\text{-}pn)_2]I_3$	17 (2.2)**	20 (2.6)**	24 (3.0)**	29.7(3.52)	44.3(4.74)
$\Lambda\Lambda$-$[(en)_2Co(\mu\text{-}NH_2,NO_2)Co(en)_2](NO_3)_4$		21.1(2.51)	29 (2.9)**	35 (3.7)**	48.5(4.76)
$\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,NO_2)Co(l\text{-}pn)_2]Br_4$		21.1(2.54)	29 (2.9)**	35 (3.7)**	46.5(4.63)
$\Lambda\Lambda$-$[(en)_2Co(\mu\text{-}NH_2,OH)Co(en)_2](NO_3)_4$		19.7(2.27)	27 (2.7)**	33.9(3.59)	48.5(4.8)**
$\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,OH)Co(l\text{-}pn)_2](NO_3)_4$		20.0(2.28)	27 (2.7)**	33.9(3.53)	48.3(4.63)
$\Lambda\Lambda$-$[(en)_2Co(\mu\text{-}NH_2,SO_4)Co(en)_2](NO_3)_3$		19.1(2.57)	27.8(2.84)	35 (3.8)**	48.5(4.69)
$\Lambda\Lambda$-$[(l\text{-}pn)_2Co(\mu\text{-}NH_2,SO_4)Co(l\text{-}pn)_2](NO_3)_3$		18.9(2.60)	27.6(2.90)	35 (3.8)**	48 (4.7)**

* The frequencies are given in 10^{3}cm^{-1}. ** shoulder

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[10] K. Garbett and R. D. Gillard, *Chem. Commun.*, **1966**, 99.

[11] Y. Inamura and Y. Kondo, *Nippon Kagaku Zassi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **74**, 627 (1953); A. W. Chester and C. H. Brubaker, Jr., *J. Inorg. Nucl. Chem.*, **30**, 213 (1968).

[12] Y. Shimura and R. Tsuchida., This Bulletin, **29**, 311 (1956).

[13] M. Linhard and M. Weigel., *Z. anorg. Chem.*, **308**, 254 (1961).

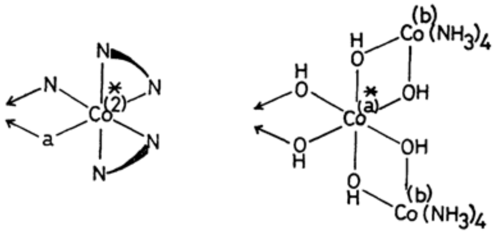
TABLE 2. NUMERICAL DATA OF CIRCULAR DICHROISMS IN WATER

	ν_{max}*($\Delta\varepsilon$)	ν_{max}*($\Delta\varepsilon$)	ν_{max}*($\Delta\varepsilon$)	ν_{max}*($\Delta\varepsilon$)
$\Lambda\Lambda$-[(en)$_2$Co(μ-NH$_2$,O$_2$)(Co(en)$_2$](NO$_3$)$_4$	20.4(−6.20) 23.8(+0.48)	26.7(−1.05)	30.3(+ 3.82)	*ca.* 40(ca.+34)
$\Lambda\Lambda$-[(*l*-pn)$_2$Co(μ-NH$_2$,O$_2$)Co(*l*-pn)$_2$](NO$_3$)$_4$	20.2(−5.90) 23.3(+0.50)	26.5(−0.45)	30.3(+ 5.52)	*ca.* 40(*ca.*+35)
$\Lambda\Lambda$-[(en)$_2$Co(μ-NH$_2$,O$_2$)Co(en)$_2$]I$_3$	17.5(+3.06) 19.4(−1.16) 20.4(+0.33)	23.3(−8.76)	27.8(−10.33)	*ca.* 42(*ca.*+30)
$\Lambda\Lambda$-[(*l*-pn)$_2$Co(μ-NH$_2$,O$_2$)Co(*l*-pn)$_2$]I$_3$	17.3(+2.49) 19.3(−0.77) 20.5(+0.71)	23.4(−7.07)	27.8(− 8.61)	*ca.* 42(*ca.*+25)
$\Lambda\Lambda$-[(en)$_2$Co(μ-NH$_2$,NO$_2$)Co(en)$_2$](NO$_3$)$_4$	20.3(−1.28) 22.3(+0.09)	*ca.*25.5(−0.30)**		*ca.* 42(*ca.*+50)
$\Lambda\Lambda$-[(*l*-pn)$_2$Co(μ-NH$_2$,NO$_2$)Co(*l*-pn)$_2$]Br$_4$	20.2(−1.16) 22.1(+0.25)	*ca.*25.0(−0.25)**		*ca.* 42(*ca.*+50)
$\Lambda\Lambda$-[(en)$_2$Co(μ-NH$_2$,OH)Co(en)$_2$](NO$_3$)$_4$	17.2(−0.35) 19.9(+0.57) 22.7(−0.07)	26.9(+1.05)	34.0(+ 4.6)	*ca.* 44(*ca.*+30)
$\Lambda\Lambda$-[(*l*-pn)$_2$Co(μ-NH$_2$,OH)Co(*l*-pn)$_2$](NO$_3$)$_4$	16.7(−0.23) 18.9(+0.78)	26.7(+1.05)	34.0(+ 4.5)	*ca.* 44(*ca.*+30)
$\Lambda\Lambda$-[(en)$_2$Co(μ-NH$_2$,SO$_4$)Co(en)$_2$](NO$_3$)$_3$	17.7(+2.24) 20.4(−5.66)	27.8(+2.04)		*ca.* 42(*ca.*+25)
$\Lambda\Lambda$-[(*l*-pn)$_2$Co(μ-NH$_2$,SO$_4$)Co(*l*-pn)$_2$](NO$_3$)$_3$	18.5(−2.55) 21.0(+1.91)	27.4(+1.28)		*ca.* 42(*ca.*+25)

* The frequencies are given in 10^3 cm^{-1} ** shoulder.

of the first band (I$_a$). However, this band would be more appropriately assinged to a spin-forbidden d–d transition or to a charge transfer between the superoxo group and the metal ion, since the present μ-amido-μ-superoxo complexes do not show distinct CD in this band region. Split components of the magnetically allowed first band should be optically active. Ohkawa *et al.*[14] detected no CD band in the region of the strong spin-forbidden band of the $(-)_{546}$-*cis*-[Co(I)(CN)(en)$_2$]$^+$ ion.

The CD spectra corresponding to the d–d transitions (^{1}A$_1$–^{1}T$_1$) of the $\Lambda\Lambda$-[(diamine)$_2$Co(μ-NH$_2$,a)Co(diamine)$_2$]$^{n+}$ exhibit various appearances depending on the kinds of substituent a, as pointed out by Mathieu.[3] Such a variety could be interpreted by considering "a kind of vicinal effect" of the chelate ring involving an optically active cobalt ion. For example, when we designate the cobalt(III) ions in the binuclear complex as Co$^{(1)}$ and Co$^{(2)}$, the Co$^{(1)}$ is considered to be coordinated with two diamines and a chelate ligand involving an asymmetric Co$^{(2)}$ ion (Fig. 6a). Such an optically active chelate ligand might give a significant vicinal effect more or less to the bands due to Co$^{(1)}$ ion.



(a) (b)

Fig. 6. Bidentate ligands involving asymmetric cobalt ion(s).

The CD of the $(-)_D$-[Co$^{(a)}$\{(μ-OH,OH)Co$^{(b)}$-(NH$_3$)$_4$\}$_3$]$^{6+}$ in the d–d transition (^{1}A$_1$–^{1}T$_1$) region[4] would be interpreted by considering this vicinal effect (Fig. 7). The two absorption peaks at *ca.* 16000 and 20000 cm^{-1} of this complex may correspond approximately to the ^{1}A$_1$–^{1}T$_1$ transition of the Co$^{(a)}$ and the Co$^{(b)}$ ion, respectively. The higher energy band exhibits a distinct CD, although the terminal Co$^{(b)}$ ions have no asymmetry around themselves. The optical activity of this band will be considered to be introduced by the vicinal effect of the chelate ring involving the optically active Co$^{(a)}$ ion (Fig. 6b). Mason and Wood[4] assigned the $(-)_D$-isomer of this complex to the Δ configuration, since the main CD component corresponding to the band at *ca.* 16000 cm^{-1} (d–d transition of Co$^{(a)}$) has a plus sign. These results suggest that in polynuclear complexes, the vicinal effect of asymmetric cobalt ion with a Δ configura-

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[14] K. Ohkawa, J. Hidaka and Y. Shimura, This Bulletin, **40**, 2830 (1967).

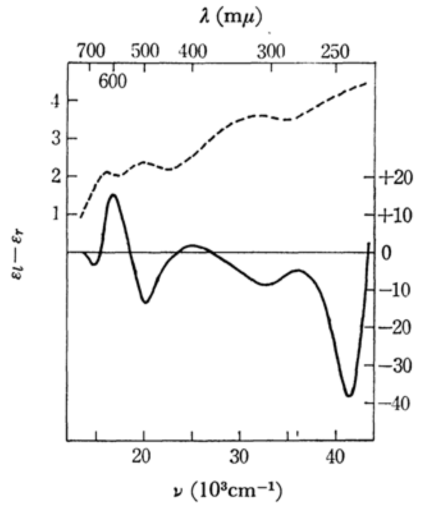

Fig. 7. The absorption (------) and CD spectra (——) of (−)-$[Co\{(\mu\text{-}OH,OH)Co(NH_3)_4\}_3]^{6+}$ ion in water. (Ref. 4)

tion gives a negative CD sign for the d–d band ($^1A_1$–$^1T_1$) of the other cobalt ions.

The present binuclear complexes, ΛΛ-$[(\text{diamine})_2Co(\mu\text{-}NH_2,a)Co(\text{diamine})_2]^{n+}$, should show strong negative CD bands in their first band region, if such a vicinal effect were very weak. This will be the case for the μ-superoxo complexes, as is seen in Fig. 1. The other μ-NO_2 and μ-hydroxo complexes, on the other hand, exhibit very weak CD bands in this region. Strong negative CD components corresponding to each Λ-cobalt ion would be compensated by the positive CD bands resulting from the vicinal effect of each of other asymmetric cobalt ion with the same configuration.

Such an interpretation would be supported by examining the vicinal effect curve of *l*-propylenediamine. In general, the vicinal effect curve of *l*-propylenediamine in cobalt(III) complexes shows one medium strong positive and one small negative peak from longer to shorter wavelength in the region of the first band.[15] The vicinal effect curve of the *l*-propylenediamine for the binuclear complexes could be obtained by subtracting the CD curve of the ethylenediamine complex from that of the corresponding *l*-propylenediamine complex. Both contributions from the configurational and the vicinal effect of the asymmetric cobalt ions would be eliminated from these curves so far as these effects are additive. As Fig. 8 shows, the curves thus obtained show similar appearances to those of uninuclear complexes of *l*-propylenediamine. These results seem to indicate the following conclusions; the nature of the d–d bands of polynuclear cobalt(III) complexes are very similar to those of uninuclear cobalt(III) complexes, and therefore, the CD behavior corresponding to these bands depends mainly on the strength of the vicinal effect of asymmetric cobalt(III) ion.

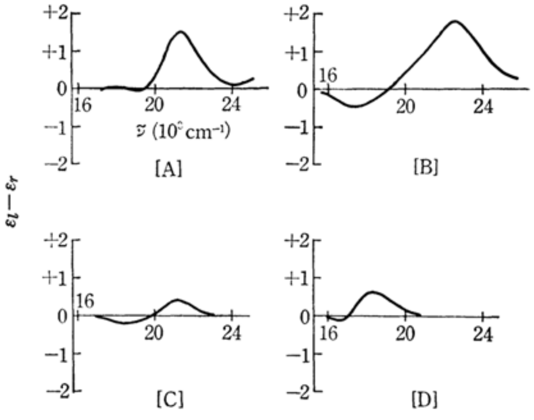

Fig. 8. The vicinal effect curves of four chelated *l*-propylenediamine in the complexes, $[(l\text{-pn})_2Co(\mu\text{-}NH_2,a)Co(l\text{-pn})_2]^{n+}$.
(A) $a=O_2^-$ (B) $a=O_2^{2-}$ (C) $a=NO_2^-$ (D) $a=OH^-$ (obtained by subtracting the CD of ΛΛ-$[(en)_2Co(\mu\text{-}NH_2,a)Co(en)_2]^{n+}$ from that of ΛΛ-$[(l\text{-pn})_2Co(\mu\text{-}NH_2,a)Co(l\text{-pn})_2]^{n+}$.)

Weak CD bands were observed in the region of the other d–d band ($^1A_1$–$^1T_2$), but their behavior has not been made clear.

Corresponding to the so-called polynuclear band at *ca.* 30000 to 35000 cm⁻¹ region, the ΛΛ complexes exhibit fairly strong CD bands with a positive sign. Although the origin of these bands is uncertain, the fact that the CD sign is always positive as that of the CD for strong charge transfer bands at *ca.* 40000 cm⁻¹ indicates that these bands would have also a charge transfer character.

Concerning the CD of charge transfer bands in tris-diamine[16] and tris-aminoalcohol[17] cobalt(III) complexes, it has been suggested that their sign depends mainly on the absolute configuration around the metal ion, and that it will be positive for a Λ-type complex and negative for a Δ-type complex. Although a positive CD component due to the vicinal effect of the chelated diamines with λ-form[16] may be involved in these CD bands, their positive sign seems to support the previous conclusion that all the complexes have the ΛΛ configuration.

"μ-Sulfato" Complexes. All the *l*-propylenediamine complexes except for the "μ-amido-μ-sulfato" complex give very similar absorption and CD curves to those of the corresponding ethyl-

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[15] C. J. Hawkins, E. Larsen and I. Olsen, *Acta Chem. Scand.*, **19**, 1915 (1965).

[16] K. Ogino, K. Murano and J. Fujita, *J. Inorg. Nucl. Chem. Letters*, **4**, 351 (1968).

[17] K. Ohashi, J. Fujita, B. Shimoyama and K. Saito, This Bulletin, **41**, 2422 (1968).

enediamine complexes. However, the CD curves of the two "μ-sulfato" complexes appear almost enantiomeric with each other in the d–d transition band region. Such a difference might be originated in a difference between the bonding structure of the bridging sulfato ligands in these two complexes, since both the complexes would have the same $\Lambda\Lambda$ configuration. The aqueous solutions of these complexes decompose gradually to give the $\Lambda\Lambda$-μ-amido-μ-hydroxo complexes.[3,18] Furthermore, addition of barium ions to these solutions results in only a slow precipitation of barium sulfate upon warming, to indicate that the sulfate ions coordinate to the metal ions, and are not the outer sphere ions. Detailed studies about these problems are now in progress, and will be published later.

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[18] A. G. Sykes and R. D. Mast, *J. Chem. Soc.*, (*A*), **1967**, 784.