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GEOMETRICAL ISOMERISM OF COBALT(III) COMPLEXES WITH MULTIDENTATE THIOLATO LIGANDS

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Two complexes of $[Co(amine)_4(thiolato)_2]$ type were newly prepared and separated into two isomers each by a column chromatography. The geometrical configurations of the isomers were assigned mainly on the basis of their ^{13}C-NMR and ultraviolet absorption spectra. The sulfur-to-metal charge transfer band of trans(S) isomer appears at lower energy than that of cis(S) isomer.

So far several cobalt(III) complexes of thiolato ligands such as cysteine$^{1)}$ and penicillamine$^{2)}$ have been reported with biochemical or structural interest, but no more than one isomer have ever been isolated in all cases. This is caused partly by the strong trans effect of thiolato ligand which prevents the formation of trans(S) isomer and partly by the extra-reactivity of coordinated thiolato donor atom to produce polynuclear complexes.

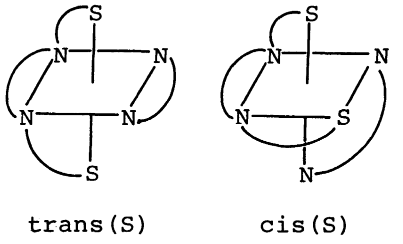

Fig. 1. Two geometrical isomers of $[Co(eddt)(en)]^+$.

With a view to eliminating these difficulties, we chose two new types of multidentate ligands, 3,6-dimethyl-3,6-diazaoctane-1,8-dithiol($HSCH_2CH_2N(CH_3)CH_2CH_2N(CH_3)CH_2CH_2SH$; H_2eddt) and 1,3-diamino-2-propanethiol($NH_2CH_2CH(SH)CH_2NH_2$; Hdpt). The present study deals with the syntheses and first complete separation of the geometrical isomers of $[Co(N)_4(S)_2]$-type complexes, $[Co(eddt)(en)]^+$(Fig. 1) and $[Co(dpt)_2]^+$ (Fig. 2).

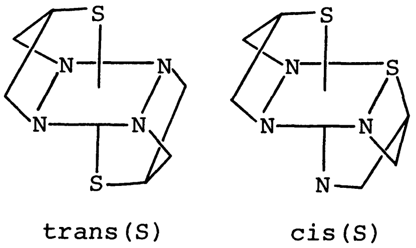

Fig. 2. Two geometrical isomers of $[Co(dpt)_2]^+$.

To a solution of 3.15 g of $[Co(en)_3]Cl_3 \cdot 3H_2O$ in 20 cm^3 of water was added a mixture of 1.74 g of H_2eddt[3] (90% purity) and 0.6 g of NaOH in 20 cm^3 of water. The mixed solution was stirred for 2 hr at room temperature. The resulting dark green solution was poured onto a column of SP-Sephadex C-25(Na^+ form), washed with water, and eluted with a 0.1 mol dm^{-3} $NaClO_4$ solution. Two partly overlapping bands, dark green(A-1) and dark violet(A-2), were eluted in this order. Each eluate was concentrated in a vacuum evaporator to give crystals of the desired perchlorate salt. Found for A-1: C, 28.33; H, 6.20; N, 13.12%. Found for A-2: C, 28.17; H, 6.22; N, 13.17%. Calcd for $[Co(eddt)(en)]ClO_4$ = $C_{10}H_{26}N_4S_2O_4CoCl$: C, 28.27; H, 6.17; N, 13.19%. The perchlorate salt was converted into the corresponding chloride salt using a QAE-Sephadex column(Cl^- form). The highly soluble chloride salt was used for ^{13}C-NMR measurements.

The terdentate ligand Hdpt·2HCl was prepared by the reaction of $NH_2CH_2CH(Cl)$-$CH_2NH_2 \cdot 2HCl$[4] and NaHS, and obtained as powder. To a solution of 1.7 g of $[Co(NH_3)_6]Cl_3$ in 30 cm^3 of water was added a mixture of 3.12 g of Hdpt·2HCl(73% purity) and 1.53 g of NaOH in 20 cm^3 of water. The mixed solution was stirred at 90 °C for *ca*. 80 min, whereupon the solution became dark brown. When the odor of ammonia was no longer present, the solution was filtered, poured onto a column of SP-Sephadex C-25(Na^+ form), and eluted with a 0.3 mol dm^{-3} NaCl solution. Two partly overlapping bands, dark green(B-1) and brown(B-2), were eluted in this order. Each eluate was concentrated in a vacuum evaporator to give crystals of the chloride salt. Found for B-1: C, 23.67; H, 5.93; N, 18.45%. Calcd for $[Co(dpt)_2]Cl$ = $C_6H_{18}N_4S_2CoCl$: C, 23.65; H, 5.95; N, 18.39%. Found for B-2: C, 22.32; H, 6.22; N, 17.39%. Calcd for $[Co(dpt)_2]Cl \cdot H_2O$ = $C_6H_{20}N_4S_2OCoCl$: C, 22.33; H, 6.25; N, 17.36%. Chromatographic optical resolution with a solution of 0.3 mol dm^{-3} $K_2[Sb_2(d\text{-}tart)_2] \cdot 3H_2O$ was successful only for the B-2 isomer.

As shown in Fig. 1, two geometrical isomers, trans(S) and cis(S), are possible for $[Co(eddt)(en)]^+$. The trans(S) and cis(S) isomers have C_2 and C_1 symmetries, respectively, and are assignable on the basis of ^{13}C-NMR spectra. The A-1 isomer shows five signals (Fig. 3(a)) and therefore is assigned to the trans(S) geometry. The A-2 isomer shows fifteen signals (Fig. 3(b)). However, the five peaks with relatively higher intensities coincide completely with those of the A-1 isomer. The accelerated isomerization A-2→A-1 is attributable to the effect of 1,4-dioxane as an internal standard because such remarkable change was not observed in a solution without 1,4-dioxane. The remaining ten signals of the A-2 isomer is consistent with the cis(S) geometry. The absorption spectra of the trans(S)(A-1) and cis(S)(A-2) isomers are shown in Fig. 4. The first d-d absorption band of each isomer is composed of two components(16900 and 21500(sh) cm^{-1} for A-1; 16400(sh) and 18600 cm^{-1} for A-2) and the lower energy component is characteristic of thiol coordination in general.5) The sulfur-to-metal charge transfer band of the trans(S) isomer appears at 29700 cm^{-1}($\log\varepsilon$ = 4.39), but that of the cis(S) isomer at 33600 cm^{-1}($\log\varepsilon$ = 4.17). Such a difference has been observed between geometrical isomers having two thioether6) or sulfito7) donor atoms; the charge transfer band of trans(S) isomer locates at lower energy than that of cis(S) one. Thus the relative positions of the charge transfer bands confirm the above assignments.

The bis(1,3-diamino-2-propanethiolato)-cobalt(III) chloride $[Co(dpt)_2]Cl$ provides two geometrical isomers, trans(S) and cis(S), as in Fig. 2. The absorption spectra of B-1 and B-2 isomers in Fig. 5 are very similar to those of A-1 and A-2 isomers, respectively, in the whole region. The charge transfer band of B-1 isomer(30900 cm^{-1}, $\log\varepsilon$ = 4.41) appears at lower energy than that of B-2 isomer(35500 cm^{-1}, $\log\varepsilon$ = 4.24). The results indicate that the B-1 and B-2 isomers are assignable to the trans(S) and cis(S) structures, respectively. This assignment is supported by the optical resolution of B-2 isomer(Fig. 5).

The ^{13}C-NMR spectra of B-1 and B-2 isomers showed three signals(60.9, 48.5, and 30.1 ppm for B-1; 59.3, 49.4, and 31.7 ppm for B-2). If the trans(S) isomer has a plane of symmetry, only two signals are expected for the B-1 isomer. Therefore, some distortion seems to exist in the B-1 isomer. Further information

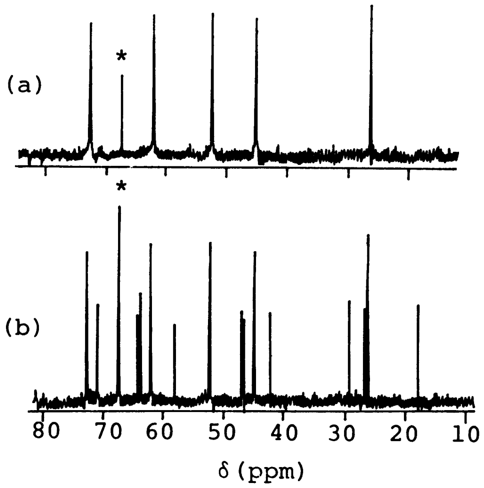

Fig. 3. The ^{13}C-NMR spectra of $[Co(eddt)(en)]^+$: (a) A-1 and (b) A-2 isomers; * 1,4-dioxane.

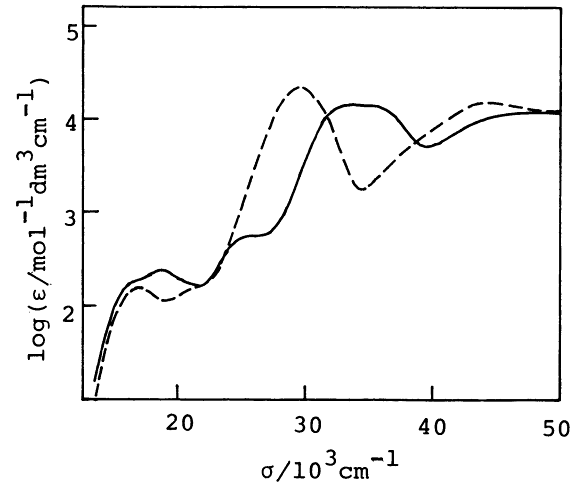

Fig. 4. Absorption spectra of $[Co(eddt)(en)]ClO_4$: trans(S) (-----) and cis(S)(———).

of the structure was derived from the X-ray photoelectron spectral data of B-1 and B-2 isomers.[8)] The S-$2p_{3/2}$ binding energies of both isomers are within the thiolato energy region and exclude the possibility of μ-thiolato polynuclear complex.

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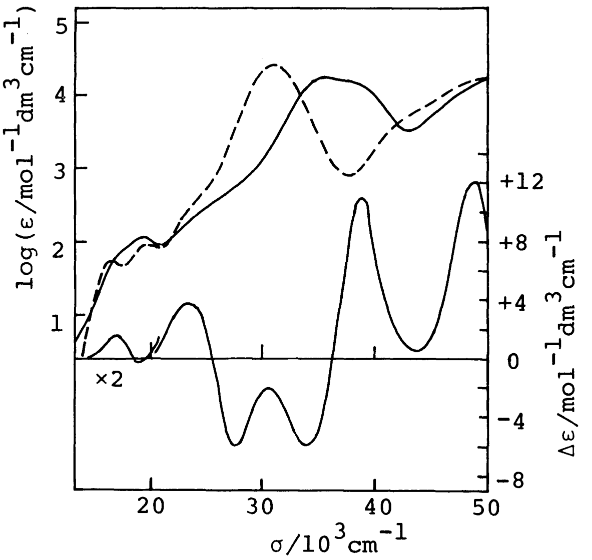

Fig. 5. Absorption and CD spectra of [Co(dpt)$_2$]Cl: trans(S)(-----) and cis(S)(———).

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