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Preparation and Characterization of $[Co_2$(bidentate-*N*,*S*$)_3$(triamine)]-Type S-Bridged Dinuclear Complexes

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Synopsis. Three kinds of S-bridged dinuclear complexes, Δ- and Λ-$[Co_2(aet)_3(dien)]^{3+}$ (aet=2-aminoethanethiolate and dien=diethylenetriamine), Δ- and Λ-$[Co_2(aet)_3(dpt)]^{3+}$ (dpt=bis(3-aminopropyl)amine)), and Δ_{LLL}-[Co_2(L-cys-*N*,*S*$)_3$(dien)] (L-cys=L-cysteinate), were prepared by the reactions of $[Co(aet)_3]$ or Δ_{LLL}-[Co(L-cys-*N*,*S*$)_3]^{3-}$ with $[CoCl_3(dien)]$ or $[CoCl_3(dpt)]$. The isomers were characterized from their absorption, CD, and ^{13}C NMR spectra.

The *fac(S)* isomers of [M(aet or L-cys-*N*,*S*$)_3]^{0\text{ or }3-}$ (M=Co(III) or Rh(III), aet=2-aminoethanethiolate ($NH_2CH_2CH_2S^-$), and L-cys=L-cysteinate ($NH_2CH(COO)CH_2S^-$)) function as a terdentate ligand to a variety of transition metal ions, such as Fe(III), Co(III), and Ni(II), using three thiolato donor atoms.[1-10] For example, the S-bridged trinuclear complexes, $[Co^{III}\{Co^{III}$(aet or L-cys-*N*,*S*$)_3\}_2]^{3+\text{ or }3-}$, have been prepared by the reactions of *fac*-[Co(aet or L-cys-*N*,*S*$)_3]^{0\text{ or }3-}$ with Co^{2+} or $[CoCl(NH_3)_5]^{2+}$.[1,2,4-9] These tricobalt(III) complexes contain $Co^{III}S_6$ chromophore besides two $Co^{III}N_3S_3$ ones, and have exhibited unique absorption and CD spectral behavior.[7-9] However, it has not been clarified whether the characteristic spectroscopic properties of the trinuclear complexes depend on the μ-thiolato sulfur atoms or the central $Co^{III}S_6$ chromophore. Therefore, it is worth while investigating S-bridged dinuclear complexes consisting of only the $Co^{III}N_3S_3$ chromophore. This note deals with the preparation and resolution of novel S-bridged dicobalt(III) complexes with the aet or L-cys ligand and dien (diethylenetriamine=$NH_2(CH_2)_2NH(CH_2)_2NH_2$) or dpt (bis(3-aminopropyl)amine=$NH_2(CH_2)_3NH(CH_2)_3NH_2$) ligand (Fig. 1). The obtained isomers were characterized from their absorption, CD, and ^{13}C NMR spectra in comparison with those of *fac*-[Co(aet or L-cys-*N*,*S*$)_3]^{0\text{ or }3-}$ and [Co{Co(aet or L-cys-*N*,*S*$)_3\}_2]^{3+\text{ or }3-}$.

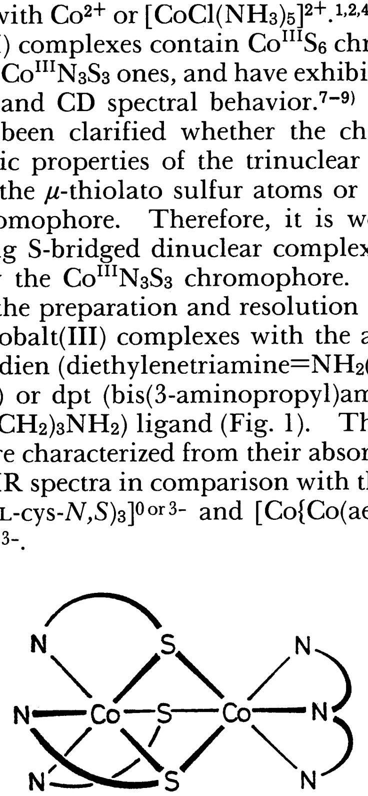

Fig. 1. Structure of the [Co_2(bidentate-*N*,*S*$)_3$(triamine)]-type complexes (Δ-type isomer).

Experimental

A) Preparation of Complexes. (1) $(+)^{\mathrm{CD}}_{600}$**-Δ- and** $(-)^{\mathrm{CD}}_{600}$**-Λ-[$Co_2(aet)_3(dien)$]Cl_3.** To a suspension containing 2.0 g (7.5 mmol) of $[CoCl_3(dien)]$[11] in 30 cm^3 of water was added a solution containing 3.7 g (21.8 mmol) of $AgNO_3$ in 10 cm^3 of water. The mixture was stirred at room temperature for 30 min and the deposited AgCl was filtered off. To a violet filtrate was added 2.0 g (7.0 mmol) of *fac*-$[Co(aet)_3]$;[1] the mixture was stirred at room temperature for 15 min, whereupon the suspension became a dark-brown solution. This solution was poured onto a SP-Sephadex C-25 column (Na^+ form, 3.5 cm×90 cm). After sweeping the column with water, the adsorbed band was eluted with a 0.2 mol dm^{-3} aqueous solution of NaCl. Three bands (brown (**A-1**), brown (**A-2**), and brownish green (**A-3**)) were eluted in this order. The **A-2** and **A-3** eluates showed absorption spectra identical with those of *meso-* and *rac-* $[Co\{(Co(aet)_3\}_2]^{3+}$, respectively.[2,9] The **A-1** eluate was concentrated to a small volume with a rotary evaporator below 25 °C. The deposited NaCl was filtered off and the filtrate was passed through a Sephadex G-10 column (3.5 cm×90 cm) by eluting with water. The eluate was concentrated to a small volume followed by the addition of a large amount of ethanol and ether. The resulting brown complex was collected by filtration.

An aqueous solution of the brown complex (**A-1**) was charged on the top of a SP-Sephadex C-25 column (Na^+ form, 3.5 cm×90 cm). Two bands were separated by eluting with a 0.075 mol dm^{-3} aqueous solution of $K_2[Sb_2(d\text{-tart})_2]\cdot H_2O$. After separation into two bands, each adsorbed band was eluted with a 0.5 mol dm^{-3} aqueous solution of NaCl. It was found from the CD spectral measurements that the earlier and later moving bands contained the $(-)^{\mathrm{CD}}_{600}$-Λ and $(+)^{\mathrm{CD}}_{600}$-Δ isomers, respectively. Each isomer was isolated by the same procedure as that used for the isolation of the racemic one. Found for $(-)^{\mathrm{CD}}_{600}$ isomer: C, 20.13; H, 6.07; N, 14.00%. Calcd for $[Co_2(aet)_3(dien)]Cl_3\cdot 2.5H_2O=C_{10}H_{31}N_6S_3Cl_3Co_2\cdot 2.5H_2O$: C, 19.99; H, 6.04; N, 13.99%. Found for $(+)^{\mathrm{CD}}_{600}$ isomer: C, 20.27; H, 5.89; N, 14.03%. Calcd for $[Co_2(aet)_3(dien)]Cl_3\cdot 2H_2O$: C, 20.29; H, 5.96; N, 14.20%. ^{13}C NMR: δ=33.63 and 34.06 (CH_2S of aet), 44.96 and 48.17 (CH_2NH_2 of dien), 49.55, 49.76, and 49.97 (CH_2NH_2 of aet), 54.92 and 57.62 (CH_2NH of dien).

(2) $(+)^{\mathrm{CD}}_{600}$**-Δ- and** $(-)^{\mathrm{CD}}_{600}$**-Λ-[$Co_2(aet)_3(dpt)$]Cl_3.** This complex was prepared and chromatographed by a procedure similar to that used for (1), using 2.2 g (7.4 mmol) of $[CoCl_3(dpt)]$[12] instead of $[CoCl_3(dien)]$. Four bands (brown (**B-1**), brown (**B-2**), brownish green (**B-3**), and brown (**B-4**)) were eluted in this order. It was found from the absorption spectral measurements that the **B-1** band contained the desired complex. This complex was optically resolved by the same column chromatographic method as that used for (**1**). It was found from the CD spectral measurements that the earlier and later moving bands contained the $(-)^{\mathrm{CD}}_{600}$-Λ and $(+)^{\mathrm{CD}}_{600}$-Δ isomers respectively. Found for $(-)^{\mathrm{CD}}_{600}$ isomer: C, 22.64; H, 6.46; N, 13.19%. Found for $(+)^{\mathrm{CD}}_{600}$ isomer: C, 22.66; H, 6.36; N, 13.14%. Calcd for $[Co_2(aet)_3(dpt)]Cl_3\cdot 3H_2O=C_{12}H_{35}N_6S_3Cl_3Co_2\cdot 3H_2O$: C, 22.59; H, 6.48; N, 13.17%. ^{13}C NMR: δ=25.76 and 26.37 (CH_2 of dpt), 34.14, 34.26, and 34.90 (CH_2S of aet), 40.94 and 41.08 (CH_2NH_2 of dpt), 49.05, 49.24, and 49.34 (CH_2NH_2 of aet), 50.65 and 52.40 (CH_2NH of dpt).

(3) $(+)^{\mathrm{CD}}_{600}$**-Δ_{LLL}-[Co_2(L-cys-*N*,*S*$)_3$(dien)].** To a suspension containing 0.5 g (1.8 mmol) of $[CoCl_3(dien)]$[11] in 10 cm^3 of water was added a solution containing 0.9 g (5.4 mmol) of $AgNO_3$ in 5 cm^3 of water. The mixture was stirred at room temperature for 30 min and the deposited AgCl was filtered off. To the violet filtrate was added a solution containing 1.25 g (1.7 mmol) of Δ_{LLL}-*fac*-K_3[Co(L-cys-*N*,*S*)$_3$]·9H_2O·0.5KCl;[6] the mixture was stirred at room temperature for 15 min, whereupon the solution became dark brown. The dark-brown solution was poured onto a QAE-Sephadex A-25 column (Cl^- form, 3.5 cm×40 cm), which was eluted with water. The brown eluate was then poured onto a SP-Sephadex C-25 column (Na^+ form, 3.5 cm×40 cm), which was eluted with water. The neutral eluate was concentrated to a small volume, followed by the addition of a large amount of ethanol. The resulting brown complex was collected by filtration. It was found from the CD and ^{13}C NMR spectral measurements that this complex contained only the $(+)^{CD}_{600}$-Δ_{LLL} isomer. Found: C, 23.45; H, 5.82; N, 12.24%. Calcd for [Co_2(L-cys)$_3$(dien)]·5H_2O=$C_{13}H_{28}N_6O_6S_3Co_2$·5$H_2O$: C, 23.36; H, 5.73; N, 12.57%. ^{13}C NMR: δ=36.89 and 37.43 (CH_2S of L-cys), 44.84 and 48.38 (CH_2NH_2 of dien), 54.82 and 57.75 (CH_2NH of dien), 66.20 and 66.42 (CH of L-cys), 177.31 (COO of L-cys).

B) Measurements. The electronic absorption spectra were recorded with a JASCO UVIDEC-610 spectrophotometer and the CD spectra with a JASCO J-20 spectropolarimeter at ambient temperature. The ^{13}C NMR spectra were recorded with a JEOL JNM-FX-90Q NMR spectrometer in D_2O at the probe temperature. Sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) was used as the internal reference.

Results and Discussion

As shown in Fig. 2, the three brown complexes obtained in this work exhibit absorption spectra quite similar to each other, giving two intense d-d bands at ca. 18 and 23×10^3 cm^{-1} and more intense absorption bands at ca. 31 and 38×10^3 cm^{-1}. This absorption spectral behavior agrees well with that of the related S-bridged dicobalt(III) complexes, [Co_2(1,5-diamino-3-pentanethiolato-*N*,*S*,*N*)$_3$]$^{3+}$,[13] which consist of two $Co^{III}N_3S_3$ chromophores. The elemental analytical and ^{13}C NMR spectral data for the brown complexes are in good agreement with the proposed formulas, [Co_2(aet or L-cys-*N*,*S*)$_3$ (dien or dpt)]$^{3+ \text{or} 0}$. These facts suggest that the present brown complexes take the S-bridged dinuclear structure, as depicted in Fig. 1.

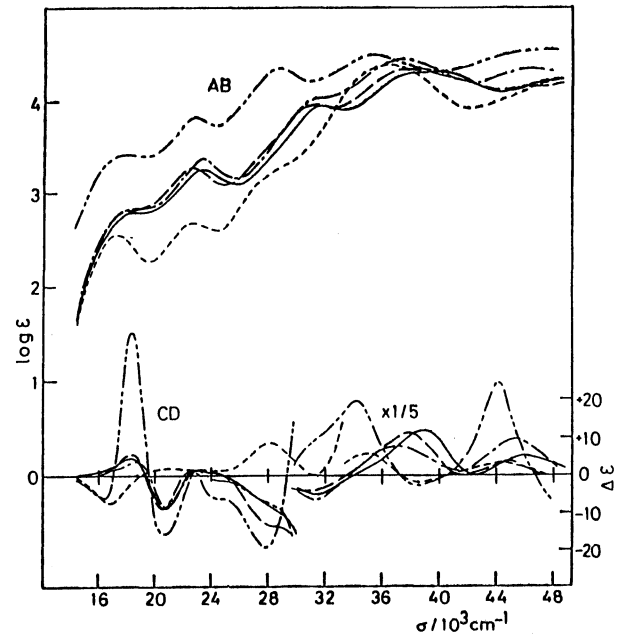

Fig. 2. Absorption and CD spectra of Δ-[Co_2(aet)$_3$-(dien)]$^{3+}$ (——), Δ-[Co_2(aet)$_3$(dpt)]$^{3+}$ (----), Δ_{LLL}-[Co_2(L-cys-*N*,*S*)$_3$(dien)] (—·—), Δ_{LLL}-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ (------), and $\Delta_{LLL}\Delta_{LLL}$-[Co{L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$ (—··—), ε values are given in unit of mol^{-1} dm^3 cm^{-1}.

Two isomers, Δ_{LLL} and Λ_{LLL}, are possible for [Co_2(L-cys-*N*,*S*)$_3$(dien)] (C_1 symmetry), considering the absolute configuration of the *fac*-[Co(L-cys-*N*,*S*)$_3$] moiety. The L-cys dinuclear complex gives five ^{13}C NMR signals due to nine carbon atoms of the three L-cys ligands and four signals due to four carbon atoms of the dien ligand. The ^{13}C NMR spectral behavior points out that the L-cys dinuclear complex takes either of the Δ_{LLL} or Λ_{LLL} isomer. In the ^{13}C NMR spectra of the S-bridged trinuclear complexes, [Co{Co(aet)$_3$}{Co(L-cys-*N*,*S*)$_3$}] and [Co{Co(L-cys-*N*,*S*)$_3$}$_2$]$^{3-}$, [5-7] the signals due to the methine carbon atoms for the Δ_{LLL}-[Co(L-cys-*N*,*S*)$_3$] moiety have commonly appeared at δ=66—67, while those for the Λ_{LLL} moiety appeared at δ=63—64. The present $(+)^{CD}_{600}$ L-cys isomer shows ^{13}C NMR signals due to the methine carbon atoms at δ=66.20 and 66.42. Accordingly, it is probable to assign that the $(+)^{CD}_{600}$ L-cys isomer is Δ_{LLL}-[Co_2(L-cys-*N*,*S*)$_3$(dien)], retaining the absolute configuration of the starting Δ_{LLL}-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$ in the reaction with [CoCl_3(dien)].

For [Co_2(aet)$_3$(dien)]$^{3+}$ and [Co_2(aet)$_3$(dpt)]$^{3+}$, two isomers, Δ and Λ, are also possible. The two $(+)^{CD}_{600}$ aet isomers show CD spectra quite similar to that of $(+)^{CD}_{600}$-Δ_{LLL}-[Co_2(L-cys-*N*,*S*)$_3$(dien)] over the whole region (Fig. 2), and moreover, the CD spectra of the $(-)^{CD}_{600}$ isomers are enantiomeric to those of the corresponding $(+)^{CD}_{600}$ ones. These facts suggest that the $(+)^{CD}_{600}$ aet isomers are Δ-[Co_2(aet)$_3$(dien or dpt)]$^{3+}$ and that the $(-)^{CD}_{600}$ aet isomers are Λ.

As shown in Fig. 2, each absorption component of [Co_2(aet or L-cys-*N*,*S*)$_3$(dien or dpt)]$^{3+ \text{or} 0}$ which contains three μ-thiolato atoms commonly shifts to higher energy than that of *fac*-[Co(L-cys-*N*,*S*)$_3$]$^{3-}$. Furthermore, in the lower-energy region (16—32×10^3 cm^{-1}), the absorption intensities of the former complexes are stronger than those of the latter complex, which suggests the formation of an S-bridged structure. In contrast to these absorption bands, little difference is observed for the charge transfer bands at ca. 36×10^3 cm^{-1}. A similar relationship is also observed between the absorption spectra of the S-bridged trinuclear complexes, [Co{Co(aet or L-cys-*N*,*S*)$_3$}$_2$]$^{3+ \text{or} 3-}$,[5-9] and the dinuclear ones (Fig. 2). Namely, the absorption bands in the region of 16—32×10^3 cm^{-1} of the trinuclear complexes are drastically intensified, compared with those of the dinuclear complexes. This absorption spectral difference can be attributed to the CoS_6 chromophore in addition to the two CoN_3S_3 ones for the S-bridged trinuclear complexes.

The CD spectral behavior of the Δ-type isomers of [Co_2(aet or L-cys-*N*,*S*)$_3$(dien or dpt)]$^{3+ \text{or} 0}$ differ significantly from that of Δ_{LLL}-[Co(L-cys-N,S)$_3$]$^{3-}$ in the lower-energy region (16—32×10^3 cm^{-3}), as in the case of the absorption spectral behavior (Fig. 2). That is, the CD spectra of the Δ-type dinuclear isomers are almost enantiomeric to that of Δ_{LLL}-[Co(L-cys-N,S)$_3$]$^{3-}$, taking the absorption spectral shift into consideration. Further, the CD spectral pattern of the Δ-type dinuclear isomers in this region is roughly similar to that of the $\Delta\Delta$-type isomers of [Co{Co(aet or L-cys-N,S)$_3$}$_2$]$^{3+ \text{ or } 3-}$, although the CD intensities of the latter isomers are much stronger than those of the former isomers. These facts suggest that the asymmetric μ-thiolato sulfur atoms, which take the *S* configuration in the Δ-type dinuclear isomer, contribute significantly to the CD spectra in this region.

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References

1) D. H. Bush and D. C. Jicha, *Inorg. Chem.*, **1**, 884 (1962).

2) G. R. Brubaker and B. E. Douglas, *Inorg. Chem.*, **6**, 1562 (1967).

3) P. R. Bulter and E. L. Blinn, *Inorg. Chem.*, **17**, 2037 (1978).

4) M. J. Heeg, E. L. Blinn, and E. Deutsch, *Inorg. Chem.*, **24**, 1118 (1985).

5) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Chem. Lett.*, **1985**, 1017.

6) K. Okamoto, S. Aizawa, T. Konno, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **59**, 3859 (1986).

7) S. Aizawa, K. Okamoto, H. Einaga, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 1601 (1988).

8) S. Miyanowaki, T. Konno, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **61**, 2987 (1988).

9) T. Konno, S. Aizawa, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **62**, 585 (1989).

10) T. Konno, S. Aizawa, K. Okamoto, and J. Hidaka, *Bull. Chem. Soc. Jpn.*, **63**, 792 (1990).

11) P. H. Crayton, *Inorg. Synth.*, **7**, 211 (1963).

12) This complex was prepared by a procedure similar to that used for [CoCl$_3$(dien)], using dpt instead of dien. Anal. Found: C, 24.23; H, 5.86; N, 14.53%. Calcd for [CoCl$_3$(dpt)]=C$_6$H$_{17}$N$_3$Cl$_3$Co: C, 24.30; H, 5.78; N, 14.17%.

13) I. Murase, S. Ueno, and S. Kida, *Bull. Chem. Soc. Jpn.*, **56**, 2748 (1983).