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Circular Dichroism Spectra of (Aminocarboxylato)ammine[1,1,1-tris(aminomethyl)ethane]cobalt(III)(2+) Complexes

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Synopsis. Five triple mixed Co(III) complexes with one 1,1,1-tris(aminomethyl)ethane and one aminocarboxylato and one ammine ligand were prepared. The glycinato complex was optically resolved and three L-aminocarboxylato complexes were chromatographically separated into their diastereomers. The circular dichroism spectra of the complexes were discussed.

1,1,1-Tris(aminomethyl)ethane (tame) is a typical tripod ligand and coordinates facially to a Co(III) ion; then three coordination sites remain to be occupied by other ligands. A new type of chirality due to the arrangement of three different groups is expected for such tame complexes, for example, $[Co(gly)NH_3(tame)]^{2+}$ (Fig. 1). This paper deals with the preparation, optical resolution and diastereomer separation of the tame complexes, $[Co(am)NH_3(tame)]^{2+}$, where am =glycinate (gly), L-alaninate (L-ala), L-serinate (L-ser), L-valinate (L-val) and L-isoleucinate (L-ileu). The absorption and circular dichroism (CD) spectra of the complexes are reported and discussed.

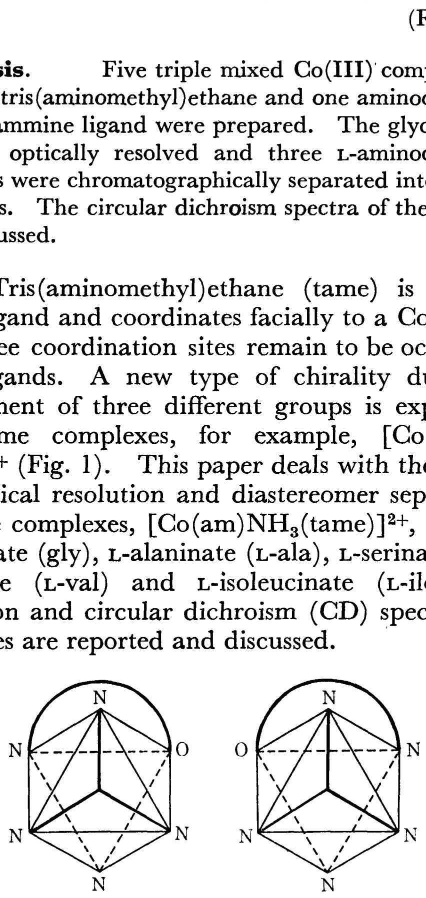

Fig. 1. Optical isomers of $[Co(gly)NH_3(tame)]^{2+}$.

Experimental

1,1,1-Tris(aminomethyl)ethane was prepared by the method of Fleischer *et al.*[1]

$(-)_{589}$-$[Co(gly)NH_3(tame)]Cl_2\cdot 3H_2O$. The mixture of *cis*-$K[Co(CO_3)_2(NH_3)_2]\cdot H_2O$[2] (10 g), tame·3HCl (8.5 g) and sodium hydroxide (4.5 g) in 100 ml of water was stirred at 70 °C for about 2 hr. The product was poured into a column containing cation exchange resin (Dowex 50W×8, Na^+ form) and eluted with 1.0 M NaCl solution. The red eluate was condensed and a crystalline complex was isolated after repeated removal of NaCl deposited out. Anal. Found: C, 22.47; H, 6.67; N, 18.01%. Calcd for $[Co(CO_3)NH_3(tame)]Cl\cdot 1.5H_2O = C_6H_{21}N_4O_{4.5}ClCo$: C, 22.83; H, 6.71; N, 17.75%. To a solution of $[Co(CO_3)NH_3(tame)]Cl\cdot 1.5H_2O$ (2 g) in 20 ml of water about 1.0 g of glycine was added and the mixture was heated at 70 °C for about 2 hr. The solution was poured into a cation exchange column of SP-Sephadex C-25 (Na^+ form) and eluted with 0.15 M NaCl solution. The orange colored eluate was concentrated in a vacuum evaporator. The crude product thus obtained, $[Co(gly)NH_3(tame)]Cl_2$, was recrystallized from as little hot water as possible.

The glycinato complex was resolved by using $K_2[Sb_2(d\text{-tart})_2]\cdot 3H_2O$ as resolving agent. The racemic glycinato complex chloride (0.5 g) was completely dissolved in 5 ml warm water (60 °C) and to the solution 0.5 g of the resolving agent was dissolved. The less soluble diastereomer gradually crystallized when the solution was kept in a refrigerator. Anal. Found: C, 20.43; H, 3.90; N, 7.88%. Calcd for $(-)_{589}$-$[Co(gly)NH_3(tame)][Sb_2(d\text{-tart})_2]\cdot 4H_2O = C_{15}H_{34}N_5O_{18}CoSb_2$: C, 20.59; H, 3.92; N, 8.01%. The diastereomer was converted to optically active chloride by using an anion exchange resin (Dowex 1×8, Cl^- form). Anal. Found: C, 21.69; H, 7.15; N, 17.99%. Calcd for $(-)_{589}$-$[Co(gly)NH_3(tame)]Cl_2\cdot 3H_2O = C_7H_{28}N_5O_5Cl_2Co$: C, 21.44; H, 7.20; N, 17.86%.

The L-aminocarboxylato complexes were prepared by the method similar to that used for the racemic glycinato complex chloride, using L-alanine, L-serine, L-valine or L-isoleucine instead of glycine. Anal. Found: C, 24.56; H, 7.29; N, 18.05%. Calcd for $[Co(\text{L-ala})NH_3(tame)]Cl_2\cdot 2H_2O = C_8H_{28}N_5O_4Cl_2Co$: C, 24.75; H, 7.27; N, 18.04%. Found: C, 29.68; H, 7.48; N, 17.17%. Calcd for $[Co(\text{L-val})NH_3(tame)]Cl_2\cdot 1.5H_2O = C_{10}H_{31}N_5O_{3.5}Cl_2Co$: C, 29.57; H, 7.69; N, 17.24%. Found: C, 31.74; H, 7.68; N, 17.11%. Calcd for $[Co(\text{L-ileu})NH_3(tame)]Cl_2\cdot H_2O = C_{11}H_{32}N_5O_3Cl_2Co$: C, 32.05; H, 7.82; N, 16.99%. Found: C, 25.37; H, 6.68; N, 18.50%. Calcd for $[Co(\text{L-ser})NH_3(tame)]Cl_2\cdot 0.5H_2O = C_8H_{25}N_5O_{3.5}Cl_2Co$: C, 25.28; H, 6.68; N, 18.57%. These analytical values of each the complex are for a mixture of two diastereomers. Each the complex except L-serinato one was separated into the two diastereomers by column chromatography of SP-Sephadex C-25 (3×30 cm, Na^+ form) by using 0.075 M $Na_2[Sb_2(d\text{-tart})_2]\cdot 2H_2O$ solution as eluent. The levels F1 and F2 denote the isomer separated earlier and later, respectively. It was confirmed that the F1 dominates over the F2 in quantity. The separation of L-serinato diastereomers was unsuccessful. The CD spectra of these diastereomers were measured with the eluates, and the concentrations were calculated from the determination of optical densities refering those of the diastereomeric mixtures (It was assumed that the two diastereomers of each the complex have identical molar absorption coefficients).

Results and Discussion

Figure 2 shows typical electronic absorption and CD spectra of the present tame complexes. These complexes can be assigned safely as $[Co^{III}(O)(N)_5]$ type[3] from their first ($\log\varepsilon = 1.92$ at 20600 cm^{-1}) and second ($\log\varepsilon = 2.05$ at 28900 cm^{-1}) absorption bands. The optical isomer of the glycinato complex, $(-)_{589}$-$[Co(gly)NH_3(tame)]^{2+}$, which was obtained from the less soluble diastereomer, shows two CD bands ($\Delta\varepsilon = +0.016$ at 18400 cm^{-1} and $\Delta\varepsilon = -0.44$ at 20500 cm^{-1}) in the first absorption band region and two weak CD bands ($\Delta\varepsilon = -0.037$ at 27500 cm^{-1} and $\Delta\varepsilon = +0.029$ at 30100 cm^{-1}) in the second absorption band region (Fig. 3). The configurational CD contribution arised from the chirality due to the arrangement of glycinate and NH_3 is considerably small

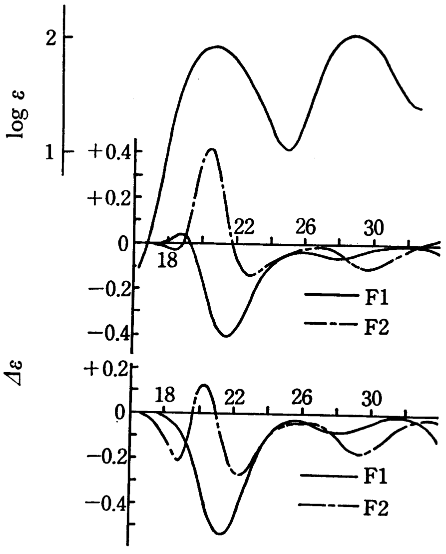

Fig. 2. Upper: Absorption and CD spectra of $[\mathrm{Co(L\text{-}ala)NH_3(tame)}]^{2+}$. Lower: CD spectra of $[\mathrm{Co(L\text{-}val)NH_3(tame)}]^{2+}$.

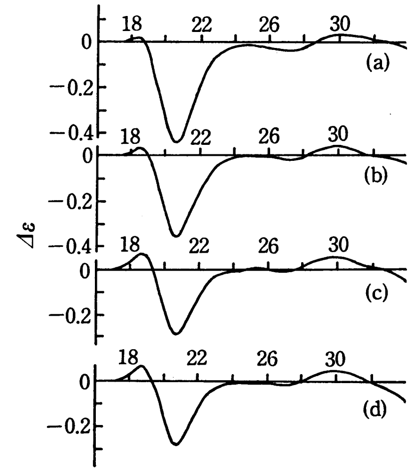

Fig. 3. CD curve of $(-)_{589}$-$[\mathrm{Co(gly)NH_3(tame)}]\mathrm{Cl_2 \cdot 3H_2O}$ (a), and calculated configurational effect curves, $1/2 \times \{\Delta\varepsilon(\mathrm{F1}) - \Delta\varepsilon(\mathrm{F2})\}$; (b) $[\mathrm{Co(L\text{-}ala)NH_3(tame)}]^{2+}$, (c) $[\mathrm{Co(L\text{-}val)NH_3(tame)}]^{2+}$, and (d) $[\mathrm{Co(L\text{-}ileu)NH_3(tame)}]^{2+}$.

in comparison with those of the complexes of bis or tris chelate type.[4] The CD curves of L-alaninato, L-valinato and L-isoleucinato diastereomers deviate considerably from that of the $(-)_{589}$-glycinato isomer. However, applying the additivity rule of the configurational and vicinal contributions[5] to the CD curves of each the diastereomeric pair, a configurational CD curve similar to that of $(-)_{589}$-glycinato isomer is produced by subtracting the CD of F2 from that of F1 (Fig. 3). On the other hand, the calculated vicinal CD curves are similar to those of the corresponding $[\mathrm{Co(L\text{-}am)(NH_3)_4}]^{2+}$ complexes[6] (Fig. 4). This fact points out that all three F1 isomers have the same absolute configuration and this is also the same as that of $(-)_{589}$-glycinato isomer.

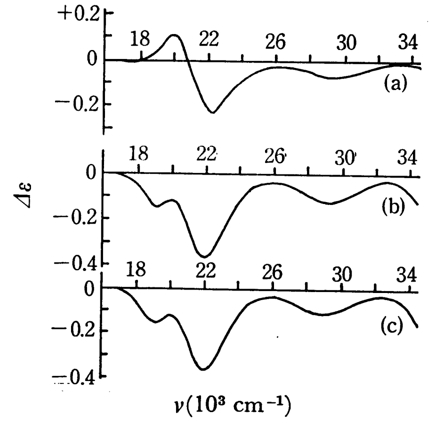

Fig. 4. Calculated vicinal effect curves: $1/2 \times \{\Delta\varepsilon(\mathrm{F1}) + \Delta\varepsilon(\mathrm{F2})\}$; (a) $[\mathrm{Co(L\text{-}ala)NH_3(tame)}]^{2+}$, (b) $[\mathrm{Co(L\text{-}val)NH_3(tame)}]^{2+}$, and (c) $[\mathrm{Co(L\text{-}ileu)NH_3(tame)}]^{2+}$.

References

1) E. B. Fleischer, A. E. Gebala, A. Lever, and P. A. Tasker, *J. Org. Chem.*, **36**, 3042 (1971).

2) M. Mori, M. Shibata, E. Kyuno, and K. Hoshiyama, This Bulletin, **31**, 291 (1958).

3) J. Fujita, T. Yasui, and Y. Shimura, *ibid.*, **38**, 654 (1965); N. Matsuoka, J. Hidaka, and Y. Shimura, *ibid.*, **40**, 1868 (1967).

4) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, **1965**, 2883; A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, **1965**, 5094.

5) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964); N. Matsuoka, J. Hidaka, and Y. Shimura, *ibid.*, **9**, 719 (1970).

6) T. Yasui, J. Hidaka, and Y. Shimura, This Bulletin, **39**, 2417 (1966); C. J. Hawkins and P. J. Lawson, *Aust. J. Chem.*, **23**, 1735 (1970).