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Preparation and Characterization of (Iminodiacetato)cobalt(III) Complexes with L-Methioninate and *S*-Methyl-L-cysteinate

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Synopsis. The (iminodiacetato)(L-methioninato or *S*-methyl-L-cysteinato)cobalt(III) complex was prepared and separated into three geometrical isomers by ion-exchange chromatography. The isomers were characterized from the electronic absorption, ^{1}H NMR and CD spectra.

The bis or mixed type cobalt(III) complexes with branched terdentate ligands such as D- or L-aspartate (D- or L-asp), L-methioninate (L-met), and *S*-methyl-L-cysteinate (L-smc), have been investigated in concerning with the spectrochemical and stereochemical properties.[1—5] Regarding the CD spectral analysis of the complexes, however, the branched terdentate ligand such as D- or L-asp was troublesome because of the CD contribution due to *R*(*C*) or *S*(*C*) of the ligand.[3] In this work, we extended the study to the spectrochemical property of the L-met and L-smc cobalt(III) complexes with iminodiacetate (ida) which is a typical linear terdentate ligand. Each complex prepared was chromatographically separated into three possible geometrical isomers and the isomers were characterized from the absorption and ^{1}H NMR spectra.

Experimental

Preparation of Complexes. *1) [Co(ida)(L-met)]:* To a solution containing 0.89 g of iminodiacetic acid and 1.0 g of L-methionine in 30 cm^3 of water (adjusted to pH 8 by NaOH solution) was added a solution containing 1.6 g of $CoCl_2 \cdot 6H_2O$ in 30 cm^3 of water, and then 2 g of PbO_2 and 0.5 g of activated charcoal. The mixture was mechanically stirred at 70 °C for 30 min, cooled to room temperature, and then filtered. The filtrate was passed through a Dowex 1-X8 column (4.5 cm×20 cm) and then a Dowex 50W-X8 one (4.5 cm×20 cm) in order to remove the charged compounds. The eluate concentrated to *ca.* 5 cm^3 was poured onto a Dowex 50W-X8 column (Na^+ form, 200—400 mesh, 3.0 cm×100 cm), and eluted with water. Three colored bands, dark violet (A1), purple (A2), and pink-violet (A3), were eluted in this order. A1, A2, and A3 eluates contained *trans*(N_iN)-, *trans*(N_iS)-, and *trans*(N_iO)-[Co(ida)(L-met)], respectively (A1:A2:A3=*ca.* 55:40:5).[6] A1 and A2 eluates were separately concentrated to dryness. A1 isomer was recrystallized from as little water as possible by adding ethanol. A2 isomer was recrystallized from a little water. A3 eluate was concentrated to a small volume with a rotary evaporator and then kept in a refrigerator overnight. The crystals obtained were filtered and washed with ethanol and ether. Found for A1: C, 28.78; H, 4.99; N, 7.36%. Calcd for [Co(ida)(L-met)]$\cdot 2H_2O = CoC_9H_{15}N_2O_6S \cdot 2H_2O$: C, 28.88; H, 5.12; N, 7.49%. Found for A2: C, 31.21; H, 4.65; N, 7.93%. Calcd for [Co(ida)(L-met)]$\cdot 0.5H_2O$: C, 31.13; H, 4.64; N, 8.07%. Found for A3: C, 30.51; H, 4.77; N, 7.92%. Calcd for [Co(ida)(L-met)]$\cdot H_2O$: C, 30.34; H, 4.81; N, 7.86%.

2) [Co(ida)(L-smc)]. This noncharged complex was prepared and separated by the same procedure as described in *1)*, using *S*-methyl-L-cysteine (0.91 g) instead of L-methionine, except for adjusting the solution to pH 6. Three colored eluates, dark violet (B1), purple (B2), and pink-violet (B3), contained *trans*(N_iN)-, *trans*(N_iS)-, and *trans*(N_iO)-[Co(ida)(L-smc)], respectively. B2 and B3 isomers were obtained by a procedure similar to that used for A3 in *1)*. For B1 isomer being unstable, after the fractions containing only the *trans*(N_iN) isomer were concentrated, a large amount of ethanol was immediately added to it. Gray-violet powder was filtered and washed with ethanol and ether. Found for B1: C, 26.38; H, 4.86; N, 7.70%. Found for B3: C, 26.72; H, 4.71; N, 7.89%. Calcd for [Co(ida)(L-smc)]$\cdot 2H_2O = CoC_8H_{13}N_2O_6S \cdot 2H_2O$: C, 26.67; H, 4.76; N, 7.78%. Found for B2: C, 27.91; H, 4.55; N, 7.94%. Calcd for [Co(ida)(L-smc)]$\cdot H_2O$: C, 28.08; H, 4.42; N, 8.19%.

Measurements. The electronic absorption spectra were recorded with JASCO UVIDEC-1 and -610 spectrophotometers and the CD spectra with a JASCO J-20 spectropolarimeter. The ^{1}H NMR spectra were recorded on a JEOL JNM-FX-100 NMR spectrometer in D_2O. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate was used as an internal reference.

Results and Discussion

Three geometrical isomers were isolated for each of [Co(ida)(L-met)] and [Co(ida)(L-smc)] (Fig. 1), and their absorption and CD spectra are shown in Fig. 2. Their absorption spectral behaviors are quite similar to those of the corresponding isomers of [Co(D -or L-asp)(L-met or L-smc)] over the whole region.[2] Considering the splittings of the first d-d absorption bands estimated semiempirically,[2,7] it is assigned that A1 and B1 are *trans*(N_iN), A2 and B2 *trans*(N_iS), and A3 and B3 *trans*(N_iO) (Fig. 1).[6]

The *S*-methyl proton signals of A1 (δ 1.89), B1 (δ 1.79 and 2.02 (*ca.* 4:1 in intensity)), A3 (δ 1.89), and B3 (δ 1.96) appear in the higher field than those of A2 (δ 2.30) and B2 (δ 2.33 and 2.40 (*ca.* 7:2)).[8] These suggest that the *S*-methyl group occupies the trans position to the nitrogen atom of ida for A2 and B2, and to its oxygen atom for A1, A3, B1, and B3, because the resonance lines due to the *S*-methyl group in the trans position to the oxygen atom can be expected to shift to higher field than that to the nitrogen one, as in the case of the cobalt(III) complexes with D- or L-aspartate, L-histidinate, and L-methioninate.[2,4] Therefore, the

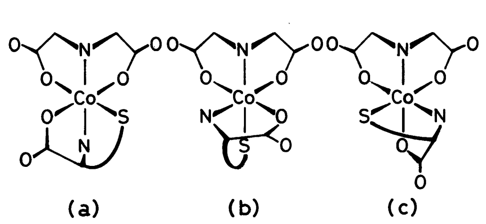

Fig. 1. Three possible isomers of [Co(ida)(L-met or L-smc)]; (a) *trans*(N_iN), (b) *trans*(N_iS), and (c) *trans*(N_iO). The N-S ring is a six-membered ring for L-met and a five-membered one for L-smc.

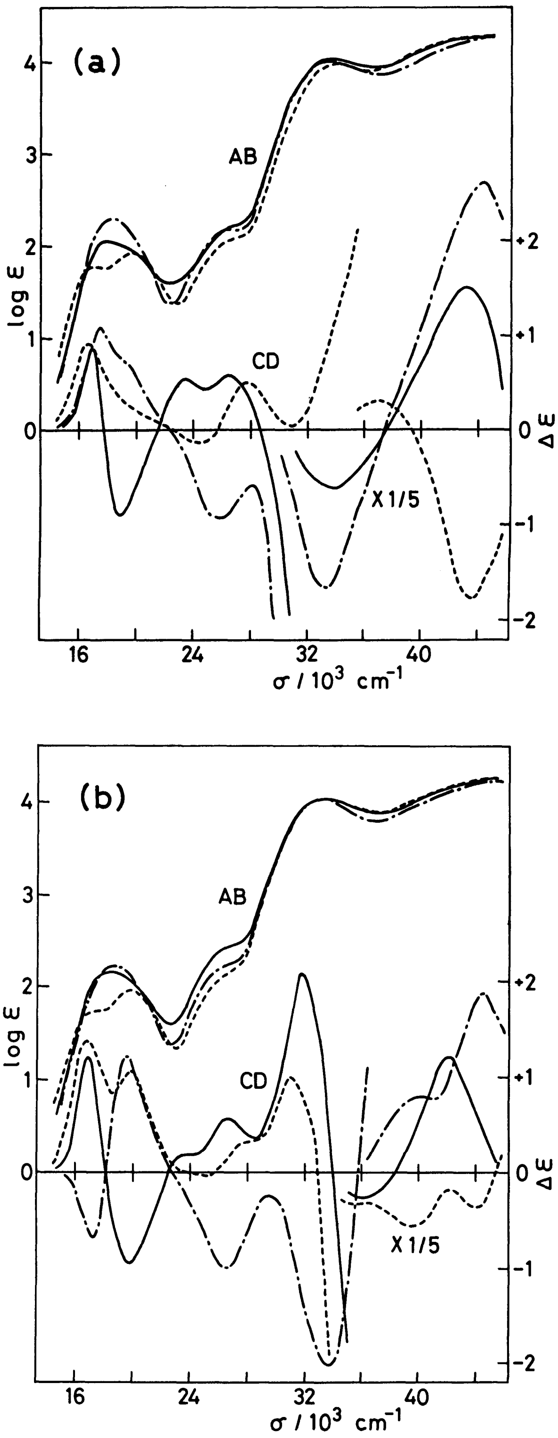

Fig. 2. Absorption and CD spectra of (a) [Co(ida)(L-met)] and (b) [Co(ida)(L-smc)]; *trans*(N_iN) (------), *trans*(N_iS) (——), and *trans*(N_iO) (—·—·—).

results from the ^{1}H NMR spectra of the three isomers for [Co(ida)(L-met or L-smc)] support the assignment on the basis of the absorption spectra.

Trans (N_iO)-[Co(ida)(L-met)] exhibits the CD spectrum almost enantiomeric to the *trans*(N_iS) isomer in the d-d absorption band region (Fig. 2(a)), reflecting that the two geometrical isomers have mutually quasi-enantiomeric configurations (Fig. 1). Here, it should be noted that, in the first d-d absorption band region, the enantiomeric CD spectral relation of the *trans*(N_iO) and *trans*(N_iS) isomers of [Co(ida)(L-met)] is opposite in sign to that of the corresponding isomers of [Co(D- or L-asp)(L-met)].[2] *Trans*(N_iO)- and *trans*(N_iS)-[Co(ida)(L-smc)] also exhibit enantiomeric CD patterns on the whole, but an interesting deviation is observed in the first d-d absorption band region (Fig. 2(b)). Namely, the CD band at *ca.* 17×10^3 cm^{-1} of the *trans*(N_iO) L-smc isomer exhibits the reversed sign of the corresponding CD band of the *trans*(N_iO) L-met one, though the CD pattern of the *trans*(N_iS) L-smc isomer coincides well with that of the *trans*(N_iS) L-met one (Fig. 2). This deviation is probably related to the difference of the configurations around the sulfur donor atoms or the flexibilities of the N-S rings in *trans*(N_iO)-[Co(ida)(L-met)] and -[Co(ida)(L-smc)].

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6) N_i denotes an imino nitrogen atom in the coordinated ida.

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8) The coordinated sulfur atom of each isomer is possible to take two absolute configurations, *R* and *S*.