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Preparation and Characterization of (L-Histidinato)(L-methioninato)cobalt(III) Bromide

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Synopsis. The (L-histidinato)(L-methioninato)cobalt(III) complex was prepared and separated into three geometrical isomers by ion-exchange chromatography. The isomers were characterized from their absorption, ^{1}H NMR, and CD spectra.

Some cobalt(III) complexes with terdentate amino carboxylates, such as L-methioninate, L-histidinate, and L-2,4-diaminobutyrate, have been investigated.[1–8] However, the stereochemical property of the thioether type sulfur atom of the L-met has not been clarified yet.[1,7] The coordinated L-met has a flexible conformation for the six-membered N–S chelate ring, while the L-his takes a rigid conformation for the six-membered N–N chelate ring. This rigidity of the L-his chelate ring is favorable for the investigation of the stereochemical property of the coordinated L-met. This note presents the preparation and separation of (L-histidinato)(L-methioninato)cobalt(III). The isomers obtained are characterized from their absorption, ^{1}H NMR and CD spectra and by comparison with those of $[\mathrm{Co(L\text{-}met)_2}]^+$[1] and $[\mathrm{Co(L\text{-}his)_2}]^+$.[2,3]

Experimental

$[\mathrm{Co(L\text{-}his)(L\text{-}met)}]\mathrm{Br}$. A solution of 2.4 g of $\mathrm{CoCl_2 \cdot 6H_2O}$ in 5 cm^3 of water was added to a solution containing 1.5 g of L-Hhis and 1.5 g of L-Hmet in 25 cm^3 of water. To the solution 0.75 g of activated charcoal and 3 g of $\mathrm{PbO_2}$ were gradually added and the mixture was then stirred at 60 °C for 40 min. The reaction mixture was filtered in order to remove the excess of $\mathrm{PbO_2}$ and activated charcoal after cooling to room temperature. The filtrate was poured onto a column of Dowex 50W-X8 ($\mathrm{Na^+}$ form, 4 cm × 70 cm). After the column had been swept with water, the adsorbed band was eluted with 0.1 mol dm^{-3} aqueous solution of ammonium bromide. Nine colored bands, F1—F9, were eluted in succession. The F3 and F4 eluates or the F6 and F7 ones partially overlapped. Their absorption and CD spectral measurements showed that the F1, F6, and F8 eluates contained the isomers of $[\mathrm{Co(L\text{-}his)_2}]^+$[2,3] and the F2, F3, and F5 ones were the isomers of $[\mathrm{Co(L\text{-}met)_2}]^+$.[1] The F4 (violet), F7 (dark violet), and F9 (brown red) eluates, of which the formation ratio was *ca.* F4:F7:F9=2:2:1, were separately concentrated to about 10 cm^3 with a rotary evaporator below 30 °C. The deposited $\mathrm{NH_4Br}$ was filtered off and the filtrate was treated with a gel filtration chromatography (Sephadex G-10 resin). The resulting aqueous solution was concentrated with a rotary evaporator again. The crystals of each isomer were obtained by adding ethanol and then ether to the concentrated solution. Found for F4: C, 30.85; H, 4.30; N, 12.57%. Calcd for $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]\mathrm{Br} = \mathrm{CoC_{11}H_{18}N_4O_4SBr}$: C, 29.94; H, 4.11; N, 12.96%. Found for F7: C, 27.31; H, 4.29; N, 13.41%. Calcd for $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]\mathrm{Br \cdot 0.5NH_4Br}$: C, 26.95; H, 4.11; N, 12.85%. Found for F9: C, 14.28; H, 4.11; N, 13.30%. Calcd for $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]\mathrm{Br \cdot 5NH_4Br}$: C, 14.19; H, 4.11; N, 13.54%.

Measurements. Electronic absorption spectra were recorded with a JASCO UVIDEC-1 spectrophotometer and CD spectra with a JASCO J-20 spectropolarimeter. ^{1}H NMR spectra were recorded on a JEOL JNM-MH-100 NMR spectrometer in $\mathrm{D_2O}$. Sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was used as an internal reference. All the measurements were carried out at room temperature.

Results and Discussion

Three geometrical isomers were isolated for $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]^+$ (Fig. 1), and their absorption and CD spectra are shown in Fig. 2. Splitting pattern of the first absorption band is expected to reflect the geometry of each of the three isomers, as in the case of $[\mathrm{Co(L\text{-}met)_2}]^+$[1] and $[\mathrm{Co(L\text{-}his)_2}]^+$.[2,3] Namely, F4, F7, and F9 are assigned to *trans*($N_\mathrm{i}S$), *trans*($N_\mathrm{i}O$), and *trans*($N_\mathrm{i}N$), respectively, where N_i denotes an imidazole nitrogen atom in the L-his, in accordance with the expected

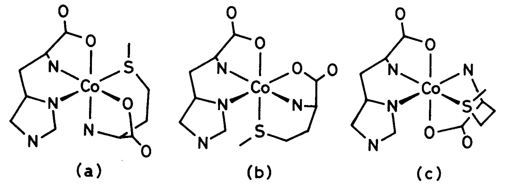

Fig. 1. Three possible isomers of $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]^+$; (a) *trans*($N_\mathrm{i}S$), (b) *trans*($N_\mathrm{i}O$), and (c) *trans*($N_\mathrm{i}N$).

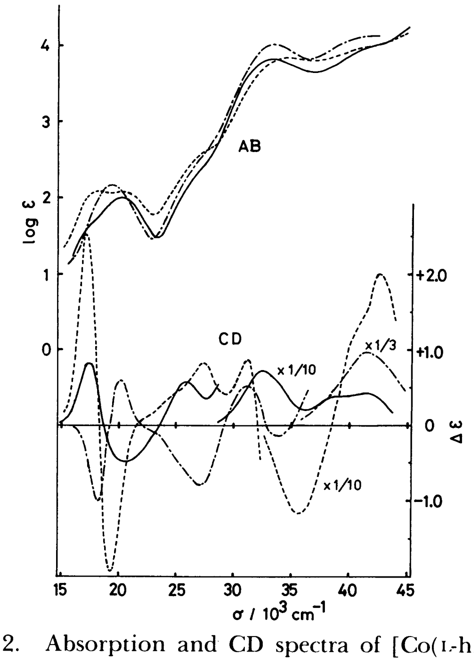

Fig. 2. Absorption and CD spectra of $[\mathrm{Co(L\text{-}his)(L\text{-}met)}]^+$; *trans*($N_\mathrm{i}S$) (-·-·-), *trans*($N_\mathrm{i}O$) (——), and *trans*($N_\mathrm{i}N$) (----).

TABLE 1. ^{1}H NMR SPECTRAL DATA OF [Co(L-his) (L-met)]$^+$

	S-CH$_3$	H(C$_2$)$^{b)}$	H(C$_5$)$^{b)}$
trans ($N_\mathrm{i}S$)	2.03$^{a)}$	7.78	7.24
trans ($N_\mathrm{i}O$)	1.86	7.88	7.18
	2.12	8.22	7.26
trans ($N_\mathrm{i}N$)	2.29	8.40	7.30

a) Ppm from DSS. b) H(C$_2$) and H(C$_5$) denote the 2-proton and 5-proton of imidazole, respectively.

splittigs which were estimated semiempirically.[1—7] As is shown in Table 1, the S-methyl proton signals of the *trans*($N_\mathrm{i}S$) and *trans*($N_\mathrm{i}N$) isomers appear in lower field than those of the *trans*($N_\mathrm{i}O$) one. This is in line with the ^{1}H NMR spectral behavior of the cobalt(III) complexes with D- or L-aspartate and L-methioninate;[7,8] namely, this result suggests that the imidazole and amino nitrogen atoms occupy the trans position to the sulfur atoms of the *trans*($N_\mathrm{i}S$) and *trans*($N_\mathrm{i}N$) isomers and the oxygen atom occupies the trans position to the sulfur atom of the *trans*($N_\mathrm{i}O$) one.[9,10] The information from the ^{1}H NMR spectra of the three isomers supports the assignment based on the absorption spectra. When the sulfur, oxygen or nitrogen atom occupies the trans position to the imidazole nitrogen atom, the resonance line of the C$_2$ proton (near 8 ppm) on the imidazole moiety shifts to the higher field in the order of S, O, and N.

The $R(S)$ or $S(S)$ configuration is expected for the coordinated sulfur atom of each isomer. The *trans*($N_\mathrm{i}O$) isomer shows two signals due to the S-methyl protons and two sets of signals for each of the C$_2$ and C$_5$ protons of the imidazole moiety of the L-his (Table 1).[3,5,6] These facts indicate that the *trans*($N_\mathrm{i}O$) isomer is a mixture of $R(S)$ and $S(S)$ configurations. On the other hand, only one signal of the S-methyl protons and one set of signals due to the imidazole moiety are observed for the *trans*($N_\mathrm{i}S$) and *trans*($N_\mathrm{i}N$) isomers (Table 1). These suggest that the *trans*($N_\mathrm{i}S$) and *trans*($N_\mathrm{i}N$) isomers selectively take the $R(S)$ or $S(S)$ configuration. Model construction reveals that the $S(S)$ configuration is more probable for the *trans*($N_\mathrm{i}S$) isomer. The *trans*($N_\mathrm{i}N$) isomer has the $R(S)$ configuration because the $S(S)$ configuration is rejected by the striking repulsion between the S-methyl group and imidazole ring. The chromatographic separation was repeated for the F7 eluate which contained the *trans*($N_\mathrm{i}O$) isomer, but all of its fractionated eluates showed quite similar CD spectra.

The *trans*($N_\mathrm{i}S$)- and *trans*($N_\mathrm{i}N$)-[Co(L-his)(L-met)]$^+$ isomers are quasi-antipodal in framework and show almost enantiomeric CD spectra in the first and second absorption band region (Fig. 2). In the region of (30—45)$\times10^3$ cm^{-1}, however, the *trans*($N_\mathrm{i}S$) and *trans*($N_\mathrm{i}N$) isomers show similar CD patterns. The CD spectral behavior in the region of (30—45)$\times10^3$ cm^{-1} depends mainly on the absolute configuration of the coordinated L-met and/or L-his, as in the case of the cobalt(III) complexes with S-methyl-L-cysteinate and S-methyl-L-penicillaminate.[11,12] In the first absorption band region, the *trans*($N_\mathrm{i}N$)-[Co(L-his)(L-met)]$^+$ isomer whose coordinated sulfur atom is regulated to the $R(S)$ configuration shows a similar CD pattern and a similar intensity to those of the *trans*(O)-[Co(L-met)$_2$]$^+$[1] and *trans*(O)-[Co(L-his)$_2$]$^+$[2,3] whose frameworks are similar to that of the mixed complex. Some differences are observed for the other isomers of [Co(L-his)(L-met)]$^+$, [Co(L-met)$_2$]$^+$, and [Co(L-his)$_2$]$^+$.[1—3] In the first absorption band region, the *trans*($N_\mathrm{i}O$)-[Co(L-his)(L-met)]$^+$ isomer shows two CD bands weaker than those of the *trans*(N)-[Co(L-met)$_2$]$^+$ and *trans*(N)-[Co(L-his)$_2$]$^+$ isomers, though the CD components in the higher energy side of the three isomers align at *ca.* 20$\times10^3$ cm^{-1}.[1—3] A similar trend is observed for the *trans*($N_\mathrm{i}S$)-[Co(L-his)(L-met)]$^+$, *trans*(S)-[Co(L-met)$_2$]$^+$, and *trans*(N_i)-[Co(L-his)$_2$]$^+$, namely, the negative CD bands at *ca.* 18$\times10^3$ cm^{-1} weaken gradually and shift to the lower energy in the order of the *trans*(N_i), *trans*($N_\mathrm{i}S$) and *trans*(S) isomers.[1—3] These results suggest that the CD bands in the first absorption band region are contributed from the flexibility of the conformation of the six-membered N–S chelate ring in the L-methioninate.

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