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PREPARATION OF THE ISOMERS OF BIS(L-METHIONINATO)COBALT(III) BROMIDE

Jinsai HIDAKA, Shoichi YAMADA,* and Yoichi SHIMURA
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560
*Department of Education, Mie University, Tsu 514

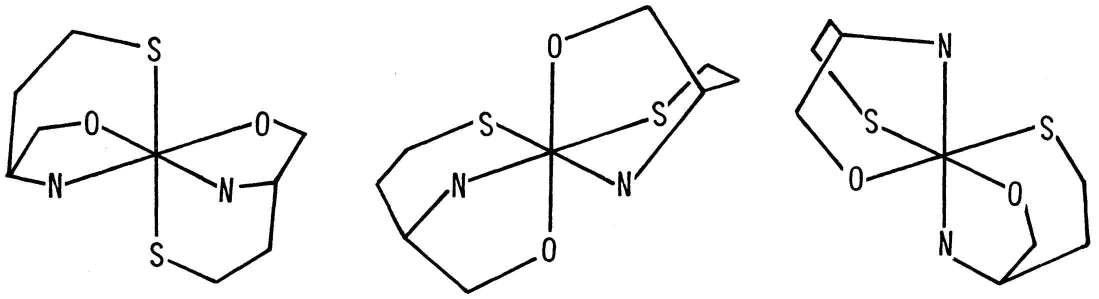
Bis(L-methioninato)cobalt(III) complex was prepared and separated into three isomers, and their absorption and CD curves were presented. The geometrical configurations of three isomers were assigned mainly on the basis of their absorption spectra. The pmr spectra were discussed in relation to another type of isomerism with respect to the configurations of ligand sulfur atoms after coordination.

Metal complexes with sulfur-containing aminocarboxylates have been remarked because of biochemically important functions of the ligands.$^{1)}$ One of them bis(L-methioninato)cobalt(III) complex, $[\mathrm{Co}(N,S,O)_2]^+$, was prepared and separated into three geometrical isomers (Fig.1) as a part of our studies on stereochemistry of cobalt(III) complexes with trifunctional aminocarboxylate chelates.$^{2)}$ The stereochemistry of the present isomers is quite similar in frame-work to those of bis(L-aspartato)-$^{2a)}$ and the related$^{2c,3)}$ complexes but distinct from them in the respect that the sulfur atoms take chiral R or S configuration after coordination. This letter is concerned with the isolations of the three geometrical isomers, *trans(S)*-, *trans(N)*- and *trans(O)*-$[\mathrm{Co(L\text{-}methioninato)_2}]\mathrm{Br}$, and their absorption, CD and pmr spectra.

To a hot solution (ca,70°C) of 3g of $\mathrm{CoCl_2 \cdot 6H_2O}$ and 3g of L-methionine in 200 ml of water was added 0.5g of activated charcoal. Seven grams of $\mathrm{PbO_2}$ was gradually added to the mixed solution on a water bath over about 20 min, whereupon the solution became violet. In order to complete the reaction 5 more grams of $\mathrm{PbO_2}$ was added to the mixture. During these operations, the mixture was stirred constantly at about

70°C. The reaction mixture was filtered to remove the excess of PbO_2 and the charcoal after cooling to room temperature. To the filtrate was added a saturated aqueous solution of 1.5g of Na_2SO_4 and the resultant solution was kept in a refrigerator overnight to separate the precipitate, $PbSO_4$. The precipitate was filtered off and the filtrate was poured into an ion-exchange column (ø 3 x 30 cm) containing Dowex 50W x 8 resin (200-400 mesh, H form). After sweeping the column with water, the adsorbed band was eluted with a 0.3M aqueous solution of NH_4Br. Dark red violet (F1), brown red (F2) and red violet (F3) eluates were obtained in this order. These were separately concentrated in a vacuum evaporator below 30°C and then the deposit, NH_4Br, was filtered off. To each of the filtrates was added a large amount of ethanol. The complexes thus obtained were recrystallized from as little water as possible by adding ethanol. The pure complexes were washed with ethanol (80%) and then ether and dried in a vacuum desiccator over H_2SO_4.

Anal. Calcd for $[Co(L\text{-methioninato})_2]Br = C_{10}H_{20}N_2O_4S_2BrCo$; C, 27.60; H, 4.67; N, 6.43%. Found: C, 27.53; H, 4.76; N, 6.44% for F1 isomer; C, 27.60; H, 4.64; N, 6.43% for F2 isomer; C, 27.33; H, 4.66; N, 6.35% for F3 isomer. F2 and F3 isomers gradually isomerize to F1 isomer in aqueous solution.



trans(S) *trans(O)* *trans(N)*

Fig. 1 Three isomers of $[Co(L\text{-methioninato})_2]^+$.

The configurations of isomers can be assigned favorably from their characteristic absorption spectral behaviors which are amplified by the coordinated sulfur atoms. As shown in Fig.2, the thioether charge transfer band for F1 isomer (28.5kK, $\log\varepsilon$= 3.92) shifts to lower energy than those for the other two (32.6kK, $\log\varepsilon$=4.04 for F2 isomer and 32.7kK, $\log\varepsilon$=4.04 for F3 isomer) which correspond well with that of *s-cis*-carbonato(1,8-diamino-3,6-dithiaoctane)cobalt(III) cation.4) Since a charge transfer band due to the ligands coordinated in *trans* positions generally locates at lower energy than that due to the ligands coordinated in *cis* positions,5) F1 isomer is assigned to *trans(S)* form and the other two *cis(S)*. The first absorption band for each of the isomers shows the splitting pattern just expected from the semi-empirical rule.$^{6)}$ Namely, F1 isomer assigned to *trans(S)* form shows apparently a sharp band (18.7kK, logε=2.24). F2 isomer shows a band with an explicit shoulder at lower energy of the major peak (20.2kK, logε=2.13), while F3 isomer shows a broad band with a shoulder at higher energy of the major peak (18.5kK, logε=2.17). These splitting patterns affirm that F1 is *trans(S)*, F2 *trans(N)* and F3 *trans(O)*.

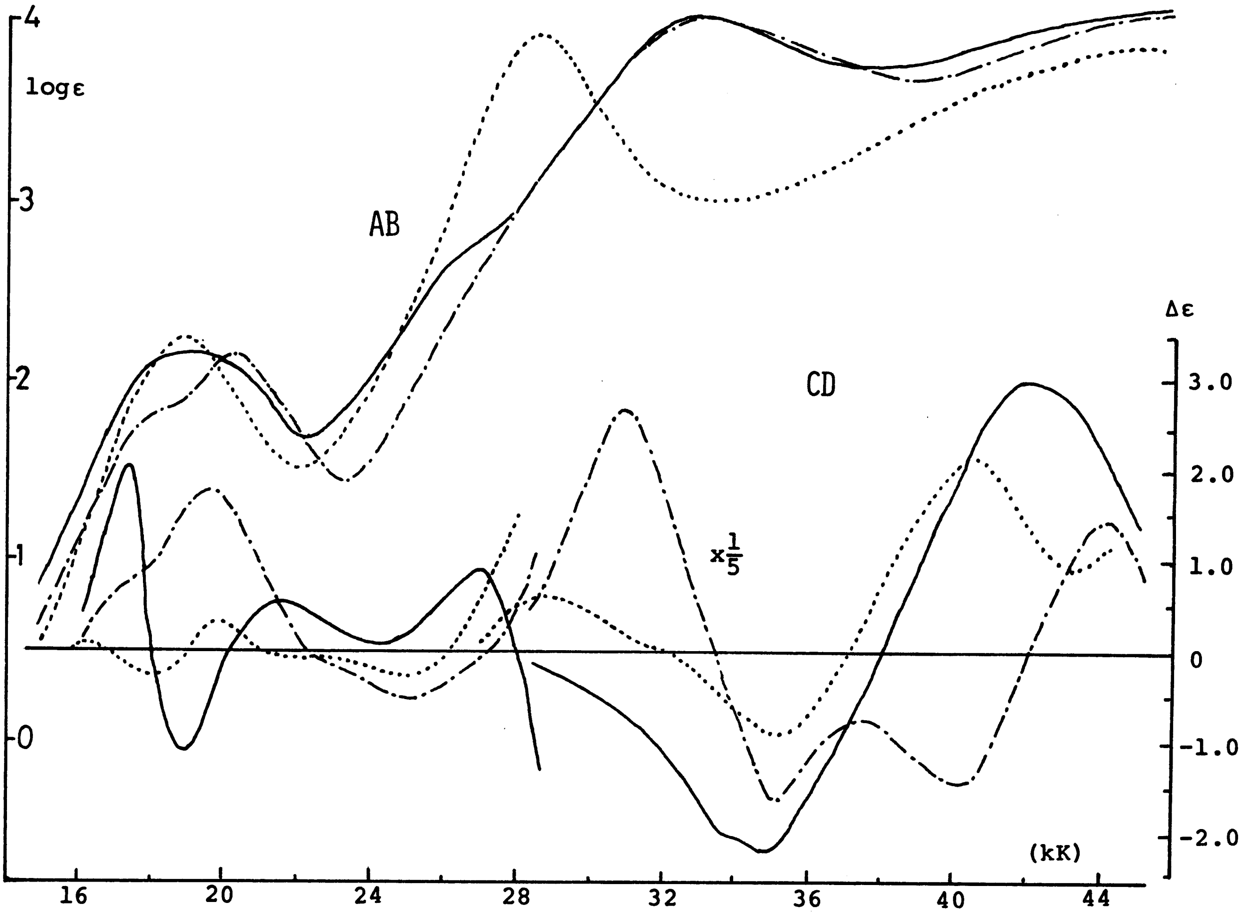


Fig. 2 Absorption and CD spectra of, ... *trans(S)*-, —·—·— *trans(N)*- and ——— *trans(O)*-[Co(L-methioninato)$_2$]Br.

For each of the three geometrical isomers another type of three isomers with respect to the absolute configuration (R or S) of ligand sulfur atom coordinated, RR, RS and SS, are formally expected. The pmr spectrum of *trans(S)* isomer shows one sharp signal (2.025 ppm*) due to the methyl protons of L-methioninate. This suggests that *trans(S)* isomer stereoselectively takes SS or RR configuration which has C_2 symmetry, and model construction reveals that the SS-configuration is most probable for *trans(S)* isomer. Three signals of *trans(N)* isomer (2.250, 2.201 and

2.164 ppm*) suggest that the isomer is a mixture of SS- and SR-configurations. In this case model construction rejects the RR-configuration because of crowding of the two methyl groups of ligands. Similar spectrum is also observed for *trans(O)* isomer (2.336, 2.280 and 2.250 ppm*) and it seems that the isomer is a mixture of RR-, SS- and SR-configurations. Here, it should be noted that the signals of *trans(O)* isomer locate more downfield from those of *trans(N)*. In the RR-configuration, which is most probable for *trans(O)* isomer, the two methyl groups are perfectly deshielded by the C-O bond of the other ligand, while each of the two methyl groups of SS-*trans(N)* isomer, which is most probable *trans(N)* one, is in the shield position from the C-O bond of the other ligand.7) From this reason, it is possible to expect that the methyl signal of the most probable configuration in *trans(O)* is downfield from that of most probable configuration of *trans(N)*. The pmr behaviors agree with the assignments of *trans(N)* and *trans(O)* isomers on the basis of the absorption spectra. Further studies, especially for the CD spectra, will be reported shortly with those for the corresponding isomers of bis(*S*-methyl-L-cysteinato)cobalt(III) complex.

* Values are ppm downfield from DSS (DSS=0).

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