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CRYSTAL STRUCTURE OF (S-(2-AMINOETHYL)-L-HOMOCYSTEINATO)(GLYCINATO)COBALT(III) PERCHLORATE

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Four isomers of the title complex, $[Co(L\text{-aehc})(gly)]^+$, were chromatographically isolated. The crystal structure and absolute configuration of the third eluted isomer were determined by X-ray diffraction study. This isomer has Δ configuration. The sulfur donor atom in the coordinated L-aehc has R configuration and the six-membered chelate ring takes a chair conformation.

S-(2-Aminoethyl)-L-homocysteinate (L-aehc) in the title complex cation acts as a quadridentate and forms two five-membered (N-O and N-S) and a six-membered (N-S) chelate rings. When the L-aehc containing an asymmetric carbon atom, S(C), and a bidentate ligand, glycinate, coordinate to cobalt(III) ion, the possible geometrical isomers are regulated to four, Δ-trans(SO), Δ-trans(SN), Λ-trans(SO) and Λ-trans(SN) (Fig. 1).[1)] The sulfur donor atom in each of the Λ isomers takes only S(S) configuration regardless of the conformation of the six-membered chelate ring in the L-aehc. In contrast with the Λ isomers, the two configurations, R(S) and S(S), depending on the conformation are possible for each of the Δ-trans(SO) and Δ-trans(SN) isomers, namely, Δ-trans(SO)-R(S) and Δ-trans(SN)-R(S) for the chair form of the six-membered chelate ring, and Δ-trans(SO)-S(S) and Δ-trans(SN)-S(S) for the skew-boat one. However, it is fairly difficult to distinguish the R(S) and S(S) isomers of Δ-trans(SO) or Δ-trans(SN) by means of their spectrochemical behaviors. So we attempted to determine the crystal structure of

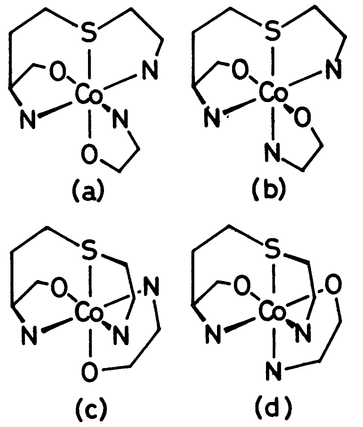

Fig. 1. Geometrical isomers of $[Co(L\text{-aehc})(gly)]^+$; (a) Δ-trans(SO), (b) Δ-trans(SN), (c) Λ-trans(SO), and (d) Λ-trans(SN).

the third eluted isomer of four ones by the X-ray diffraction method, because the absorption and CD spectra of the isomer are useful for the assignment of the remaining three isomers. This letter deals with the preparation and the crystal structure of the third eluted isomer, and also with the absolute configuration determined by X-ray diffraction.

A solution containing 4.0 g of L-Haehc·HBr, which was prepared by a similar procedure to that used for the preparation of S-(carboxymethyl)-L-homocysteinate,$^{2)}$ and 2.0 g of glycine in 40 cm^3 of water was adjusted to pH 7 by addition of a 1 mol dm^{-3} NaOH aqueous solution. To this solution was added a solution containing 2.4 g of $CoCl_2 \cdot 6H_2O$, 0.5 g of activated charcoal, and 4 g of PbO_2 in 20 cm^3 of water. The mixture was stirred at ca. 60°C for 15 min and then filtered. The filtrate was poured onto a column of Dowex 50W-X8 (Na^+ form). After the column sweeping with water, the adsorbed band was eluted with a 0.1 mol dm^{-3} NaCl aqueous solution. Four colored bands were eluted successively. The third eluate was concentrated to a small volume with a rotary evaporator below 25°C and the deposited NaCl was filtered off. By use of the anion exchange column (ClO_4^- form), the chloride salt in the eluate were converted into the perchlorate one. To the eluate was added a small amount of ethanol, and the solution was kept in a refrigerator for several days. The red needle crystals were collected by filtration and recrystallized from warm water. The remaining three isomers were also isolated by similar procedures to that for the third eluted isomer.

The red needle crystals are orthorhombic with space group $P2_12_12_1$; a = 9.633 (1), b = 17.369 (6), c = 9.364 (2) Å, V = 1566.9 (7) Å^3, and Z = 4. The observed density is 1.82 g cm^{-3} and the calculated one 1.81 g cm^{-3}. The crystal structure determination was based on independent 2190 reflections with $|Fo| > 3\sigma(|Fo|)$ collected on a Rigaku-denki four circle diffractometer (AFC-5) by the ω-2θ scan technique up to 60°, employing graphite-monochromated Mo Kα radiation. The structure was solved with the heavy atom method and refined by a full-matrix least-squares refinement of the positional and anisotropic thermal parameters of all the non-hydrogen atoms (program RFINE by L. W. Finger, which was modified by H. Horiuchi (1979), was used). The final residual values were R = 0.054 and Rw = 0.072, respectively.

The absolute configuration was determined by anomalous scattering technique. The atomic scattering factors for all the non-hydrogen atoms were taken from literature.$^{3)}$ When the refinements were carried out by use of a set of the atomic parameters containing the Δ configuration of the complex cation, the residual values converged to R = 0.051 and Rw = 0.070, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Λ configuration) resulted in the residual values of R = 0.060 and Rw = 0.078, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the Δ configuration.

The perspective drawing of the present complex cation is shown in Fig. 2. The cobalt atom are surrounded by a sulfur, two cis oxygen and three meridional nitrogen atoms, and the L-aehc coordinates to cobalt atom as a quadridentate. The configuration of the asymmetric carbon atom in Δ-[Co(L-aehc)(gly)]$^+$ is consistent with the S configuration as expected.[2)] The asymmetric sulfur atom in the coordinated L-aehc takes the R configuration. Therefore, the present complex cation is the Δ-trans-(SO)-R(S) isomer. The six-membered chelate ring in the L-aehc (N1-C2-C3-C4-S) takes the chair form, which consists of almost parallel two planes; dihedral angle for the two planes, N1-Co-S and C2-C3-C4, is 2.19°. The N-S five-membered chelate ring (S-C5-C6-N2) in the L-aehc takes an asymmetric gauche form with the δ conformation, resembling strikingly the ethylenediamine chelate ring.[4,5)] The glycinate chelate ring has an envelope form with the λ conformation. The glycinate moiety of the L-aehc takes an envelope form with the λ conformation, furthermore, the displacement

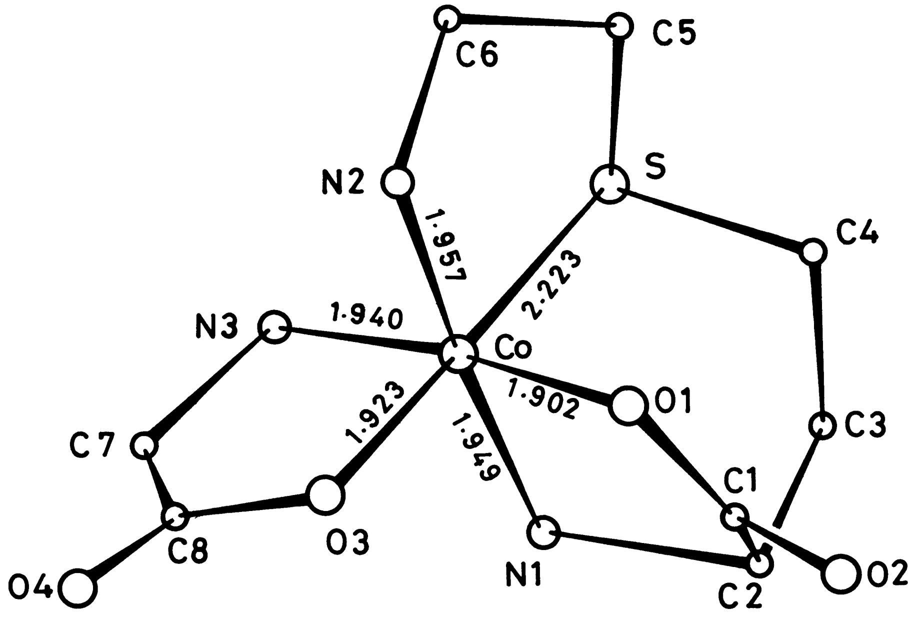

Fig. 2. View of the Δ-trans(SO)-R(S)-[Co(L-aehc)(gly)]$^+$ with distances (Å) around the metal.

of relevant atoms from the plane N1-Co-O1 in this conformation does not differ much from those of the glycinate and other amino carboxylates.[4,5] The cobalt-ligand bond lengths are similar to those for the cobalt(III) complexes with the sulfur-containing ligands and amino carboxylates.[4-7] The Co-O3 distance bonded trans to the sulfur atom is 1.923 (5) Å. This fact indicates that the trans effect due to the coordinated sulfur atom can not be almost recognized as the case of the cobalt(III) complexes with thioether type ligands.[4,5,8)

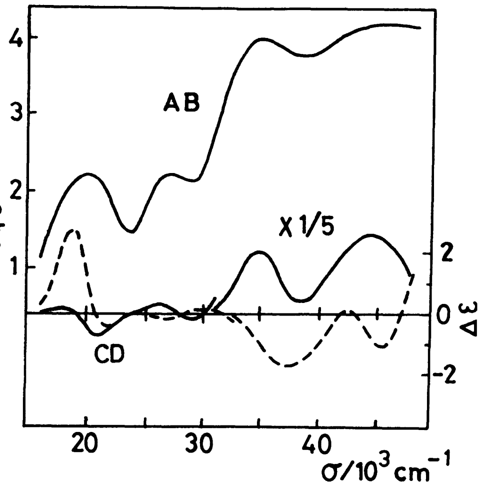

Fig. 3. Absorption and CD spectra of the second eluted (----) and third eluted (——) isomers of [Co(L-aehc)(gly)]$^+$.

The absorption and CD spectra of the Δ-trans(SO)-R(S) isomer are shown in Fig. 3 together with the CD spectrum of the second eluted isomer. The Δ-trans(SO)-R(S) isomer shows the broad first absorption band with a vague shoulder at lower energy side and this absorption spectral pattern coincides well with the first absorption band of the second eluted isomer. This fact suggests that the second eluted isomer is Λ-trans(SO) and simultaneously takes S(S) configuration. The CD contribution due to the configuration of the sulfur donor atom in the L-aehc is remarkable in the first absorption band region (Fig. 3).

References

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