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The Crystal and Molecular Structure of *trans*(*O*)·*mer*(*N*)-(*S*-(2-Aminoethyl)-L-homocysteinato)(glycinato)cobalt(III) Perchlorate

Ken-ichi Okamoto,* Masutaro Suzuki, Hisahiko Einaga,† and Jinsai Hidaka

Department of Chemistry, University of Tsukuba, Sakura, Ibaraki 305
† *Institute of Materials Science, University of Tsukuba, Sakura, Ibaraki 305*

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Synopsis. The crystal and molecular structure of the title complex, *trans(O)·mer(N)*-[Co(L-aehc)(gly)]$^+$, has been determined by the X-ray analysis. This isomer has Δ configuration. The sulfur donor atom of the coordinated L-aehc has *R* configuration and the six-membered N–S chelate ring takes a chair conformation.

When a quadridentate ligand, *S*-(2-aminoethyl)-L-homocysteinate (L-aehc), and a glycinate coordinate to a cobalt(III) ion, the possible geometrical isomers are four: *Δ-trans(O)·mer(N)*, *Δ-cis(O)·mer(N)*, *Λ-cis(O)·mer(N)*, and *Λ-cis(O)·fac(N)*.[1] In the Δ isomers, two conformations, chair and skew boat, are possible for the six-membered N–S chelate ring of the L-aehc. The *R*(*S*) coordination of the sulfur atom takes a chair-formed N–S chelate ring and the *S*(*S*) coordination takes a skew boat one. We reported that the sulfur donor atom in the *Δ-cis(O)·mer(N)* isomer takes the *R*(*S*) configuration and the six-membered N–S chelate ring takes a chair form.[2] The present work was attempted to investigate whether the six-membered N–S chelate ring of the L-aehc preferably takes a chair form (simultaneously *R*(*S*) configuration) in the *Δ-trans(O)·mer(N)* isomer or not. The first eluted isomer employed in this work can be assigned confidently as the *Δ-trans(O)·mer(N)* isomer from the explicit splitting of the first absorption band.[2–4] In this note, we wish to report the results of the determination of the crystal and molecular structure of the title compound. The absolute configuration of the sulfur donor atom and the conformation of the six-membered N–S chelate ring were determined.

Experimental

[Co(L-aehc)(gly)]Cl was prepared by the method in the literature[2] and chromatographed on the Dowex 50W-X8 (Na$^+$ form, 3 cm × 40 cm) by eluting with 0.1 mol dm^{-3} NaCl aqueous solution. Four colored bands were eluted successively. The absorption and CD spectral measurements showed that the first eluate contained the *Δ-trans(O)·mer(N)* isomer. Then the first eluate was concentrated to a small volume with a rotary evaporator and the deposited NaCl was filtered off. By use of the anion exchange column (ClO_4^- form), the chloride salt in the eluate was converted into the perchlorate salt. Dark violet needle crystals were grown from an aqueous solution by adding ethanol. The cell dimensions and intensity data were measured on a Rigaku-denki four circle diffractometer (AFC-5) using Mo *Kα* (0.710730 Å) radiation. The crystal data are as follows; $CoC_8H_{17}N_3O_8SCl$, $a=7.683$ (2), $b=16.304$ (3), $c=5.855$ (1) Å, $\beta=105.40$ (2)°, $V=707.1$ (2) Å^3, monoclinic, space group $P2_1$, $Z=2$. The intensity data were collected by the ω-2θ scan technique up to $2\theta=60°$. A total of 2283 independent reflections with $|F_o|>3\sigma(|F_o|)$ were observed and employed in solving and refining the structure. No absorption correction was applied.

Structure Determination and Refinement

The structure was solved by the heavy atom method and refined by a full-matrix least-squares method using all the non-hydrogen atoms (program RFINE by L. W. Finger was used). The final residual values were $R=0.055$ and $R_w=0.084$, respectively. The absolute configuration was determined by an anomalous scattering technique. The atomic scattering factors for all the non-hydrogen atoms were taken from the literature.[5] 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 $R=0.053$ and $R_w=0.083$, respectively. On the contrary, the refinements in the enantiomeric atomic parameters (the Λ configuration) resulted in the residual values of $R=0.058$ and $R_w=0.088$, respectively. These facts indicate that the former is probably the correct choice, namely, the complex cation has the Δ configuration. This absolute configuration is supported from the result that the

Table 1. Positional and thermal parameters (×10^4)

Atom	*x*	*y*	*z*	B_{eq}/Å^2 [a]
Co	1329(1)		2939(1)	1.47
S	1097(2)	−1311(1)	4002(3)	1.90
N1	−858(7)	−187(4)	353(10)	2.08
N2	3709(6)	46(4)	5211(8)	1.78
N3	1307(8)	1178(4)	2312(11)	2.18
O1	2652(6)	−198(3)	694(8)	1.72
O2	5372(6)	−552(4)	333(10)	2.44
O3	−19(7)	275(3)	5118(9)	2.32
O4	−535(8)	1309(4)	7363(10)	3.13
C1	4333(8)	−392(4)	1537(11)	1.85
C2	4934(8)	−487(4)	4216(11)	1.92
C3	4775(9)	−1396(4)	4812(13)	2.28
C4	3019(8)	−1809(4)	3378(13)	2.04
C5	−719(9)	−1639(5)	1466(15)	2.73
C6	−882(10)	−1038(5)	−553(14)	2.78
C7	77(9)	1035(5)	5740(11)	2.10
C8	1035(12)	1611(4)	4404(14)	2.60
CL	5686(2)	1778(1)	919(3)	2.59
O11	7098(15)	2346(8)	1559(20)	7.33 [b]
O12	4224(26)	2205(13)	33(32)	12.98 [b]
O13	5217(14)	1415(7)	2939(18)	7.06 [b]
O14	6133(39)	1173(20)	−998(44)	21.03 [b]

a) B_{eq} is the equivalent isotropic temperature factors defined by Hamilton.[14] b) Isotropic temperature factor.

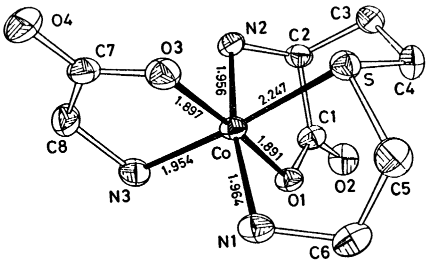

Fig. 1. A perspective drawing of *Δ-trans(O)·mer(N)-R(S)*-[Co(L-aehc)(gly)]$^+$ with the numbering scheme of the atoms.

asymmetric carbon atom of the L-aehc in the Δ configuration is in line with the known *S*(*C*) configuration.$^{6)}$ The final positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table 1. Tables of structure factors, anisotropic temperature factors, bond lengths and angles, and the projected figure of the crystal structure are kept at the Chemical Society of Japan (Document No. 8344).

Results and Discussion

The perspective drawing of the present complex cation is shown in Fig. 1 (ORTEP program$^{7)}$). Each cobalt atom is surrounded by a sulfur, two trans oxygen and three meridional nitrogen atoms, as expected from the splitting pattern of the first absorption band of this complex cation (18.52 (ε=85.1) and 21.14 (ε=91.2)$\times 10^3$ cm^{-1}).$^{2-4)}$ The complex cation is determined to be in the Δ configuration by anomalous scattering technique. The L-aehc coordinates to cobalt atom as a quadridentate and the asymmetric sulfur donor atom takes only *R* configuration. Therefore, the present complex cation is the *Δ-trans(O)·mer(N)-R*(*S*) isomer. The bond lengths and angles of the complex cation are similar to those for the cobalt(III) complexes with other sulfur-containing ligands and amino carboxylates.$^{2,3,8-12)}$ The average Co–N distance for the nitrogen atoms is 1.958 Å and the Co–N3 distance bonded trans to the sulfur atom is 1.954 Å. This fact indicates that the trans effect due to the coordinated sulfur atom can not be recognized in the *Δ-trans(O)·mer(N)* isomer, as in the case of the cobalt (III) complexes with the thioether type ligands such as L-aehc in the *Δ-cis(O)·mer(N)* isomer,$^{2)}$ *N,N'*-ethylenebis(*S*-methyl-L-cysteinate),$^{3)}$ and 2-(methylthio)ethylamine.$^{13)}$

In order to investigate the conformation of the chelate rings, we calculated the displacements of relevant atoms from the chelate ring plane, which is defined by the central cobalt atom and two coordinated atoms in the chelate ring (Table 2). The six-membered N–S chelate ring of the L-aehc (N2–C2–C3–C4–S) takes a chair form, which consists of two almost parallel planes; dihedral angle for the two planes, N2–Co–S and C2–C3–C4, is 3.03°. Similar conformations have been also observed for *Δ-cis(O)·mer(N)-R*(*S*)-[Co(L-aehc)(gly)]$^{+\,1,2)}$ and [Co(*S,S*-ebm)]$^{+,11,12)}$ where *S,S*-ebm denotes *N,N'*-ethylenebis(L-methioninate) whose six-membered chelate rings have the same framework as that of the L-aehc. The five-membered N–S chelate ring takes an envelope form with the λ conformation. The glycinate moiety of the L-aehc takes an envelope form with the λ conformation and the displacement of relevant atoms from the plane N2–Co–O1 does not differ much from that of the glycinate with the δ conformation in the present complex cation.

Table 2. Displacements of atoms from the least-squares plane (d/Å)

Six-membered N-S chelate ring:
$0.6342X-0.3016Y-0.7120Z+0.8235=0$

Co	0.0000	S	0.0000	N2	0.0000	C2	1.3572
C3	1.4283	C4	1.4928				

Five-membered N-S chelate ring:
$0.7495X-0.2876Y-0.5962Z+0.5664=0$

Co	0.0000	S	0.0000	N1	0.0000	C5	0.2564
C6	0.7960						

Glycinate chelate ring (in L-aehc):
$0.0864X+0.9837Y-0.1575Z+0.2125=0$

Co	0.0000	N2	0.0000	O1	0.0000	O2	−0.3497
C1	−0.2859	C2	−0.6731				

Glycinate chelate ring:
$0.6820X+0.1048Y+0.7238Z-1.5854=0$

Co	0.0000	N2	0.0000	O3	0.0000	O4	−0.5850
C7	−0.3682	C8	−0.5645				

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1) The symbols, Δ and Λ, are tentatively denoted by the ring pairing method (J. I. Legg and J. A. Neal, *Inorg. Chem.*, **12**, 1805 (1973)). In the former paper,$^{2)}$ *trans(SO)* was used instead of *cis(O)·mer(N)*, and *trans(SN)* of *trans(O)·mer(N)* and *cis(O)·fac(N)*.

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