Acta Cryst. (1978). B**34**, 3582–3585

The Crystal and Molecular Structure of Lithium [(*S*,*S*)-*N*,*N*′-Ethylenediaminedisuccinato]cobaltate(III) Trihydrate

By František Pavelčík and Jaroslav Majer

Department of Analytical Chemistry, Pharmaceutical Faculty, Comenius University, 88034 *Bratislava, Czechoslovakia*

(*Received* 10 *October* 1977; *accepted* 17 *July* 1978)

Crystals of $Li\{Co[(S,S)\text{-EDDS}]\}.3H_2O$ (H_4EDDS is *N*,*N*′-ethylenediaminedisuccinic acid) are orthorhombic, space group $P2_12_12_1$, $a = 9{\cdot}655$ (10), $b = 10{\cdot}577$ (8), $c = 15{\cdot}506$ (10) Å, $Z = 4$. The pseudosymmetric structure has been solved by phase refinement by the method of modification and Fourier transformation of the approximate electron density. It was refined by least-squares methods with anisotropic temperature factors to give an R value of 0·049 on the basis of 1194 observed reflections collected by diffractometry. The structure consists of complex anions, Li^+ cations and water molecules. The octahedral complex anion has the absolute configuration (OC-6-13-A) with six-membered β-alanine chelate rings disposed equatorially, and five-membered glycine rings in axial positions. The complex anions are held together by LiO_4 tetrahedra and $N—H\cdots O$ hydrogen bonds.

Introduction

There are two possible geometric isomers of the [(*S*,*S*)-*N*,*N*′-ethylenediaminedisuccinato]cobaltate(III) ion, if the ligand [(*S*,*S*)-EDDS] is sexidentate. Schematic drawings and the absolute configurations of the geometric isomers are given in Fig. 1. The absolute configurations are expressed with the most exact CA nomenclature (Brown, Cook & Sloan, 1975). It is shown that the absolute configuration of the chiral centre can be used for classifying the configurational and conformational types of the EDDS moiety of the complexes. The designations *trans*-(O_5) and *trans*-(O_6), respectively, are analogous to the designations used for $Co(Asp)_2^-$ isomers (Oonishi, Shibata, Marumo & Saito, 1973).

Complexes of $\{Co[(S,S)\text{-EDDS}]\}^-$ were prepared by Neal & Rose (1968, 1972) and their optical, NMR, IR and CD spectra, together with a discussion of their absolute configurations, were reported. The authors unambiguously concluded that the complex has one of the possible structures in solution and that the sample was not a mixture of two complexes.

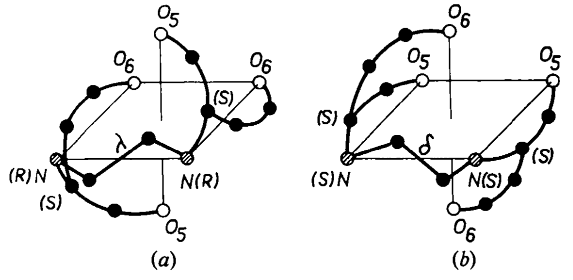

Fig. 1. Schematic drawings and absolute configurations of two geometrical isomers of $Co[(S,S)\text{-EDDS}]^-$ (see text). (*a*) *trans*-(O_5)-Co[(*S*,*S*)-EDDS] (OC-6-13-A). (*b*) *trans*-(O_6)-Co[(*S*,*S*)-EDDS] (OC-6-33-C).

Recently Pavelčik & Majer (1978) studied the energetic aspects for both configurations by molecular-mechanical calculations and showed that the isomer with six-membered rings equatorially disposed has less strain energy. Except for a minor detail (Neal & Rose, 1972) there is no structural information concerning the complex anion. In the present paper, the crystal structure of the Li salt is described.

Experimental

Crystal data

$C_{10}H_{12}CoLiN_2O_8.3H_2O$, $M_r = 408{\cdot}2$, orthorhombic, $a = 9{\cdot}655$ (10), $b = 10{\cdot}577$ (8), $c = 15{\cdot}506$ (10) Å, $U = 1583{\cdot}5$ Å^3, $D_m = 1{\cdot}71$ (5), $D_x = 1{\cdot}71$ g cm^{-3}, $Z = 4$, Mo $K\alpha$ ($\lambda = 0{\cdot}7107$ Å), $\mu = 11{\cdot}9$ cm^{-1}, space group $P2_12_12_1$ (No. 19).

Single crystals were prepared by dissolving equimolar amounts of (*S*,*S*)-H_4EDDS, $Co(OH)_2$ and Li_2CO_3 in water. The resulting solution was oxidized with H_2O_2 in the presence of active carbon and slowly evaporated. The elemental analysis gave: C 29·11, N 6·76, Co 14·23%, $C_{10}H_{18}CoLiN_2O_{11}$ requires C 29·43, N 6·86, Co 14·44%. The crystal used for the structure determination was of prismatic form {110}, {001} with approximate dimensions 0·30 × 0·25 × 0·15 mm. The density was measured by the flotation method in a mixture of ethanol and 1,2-dibromoethane. Unit-cell parameters were determined by a least-squares fit of the angular positions of nine independent reflections on the diffractometer.

The structure was solved using photographic data (Nonius integrating Weissenberg camera, Co $K\alpha$ radiation) and refined with diffractometer data. The intensities of 1624 independent reflections (up to $2\theta = 50°$) were collected on a four-circle fully automated Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the θ–2θ scan technique. The background was measured at each end of the scan for one half of the reflection scan time. To check stability, two standard reflections were measured after every 148 reflections. The net counts of these reflections did not change significantly during data collection. 1194 reflections with $I > 1{\cdot}96\sigma(I)$ were considered as observed and reflections with $I < 1{\cdot}96\sigma(I)$ as unobserved. To weak reflexions with $I < 0{\cdot}698\sigma(I)$ a value of $0{\cdot}698\sigma(I)$ was assigned. The intensities were corrected for Lorentz and polarization factors. No corrections for absorption or extinction were made. The intensities were brought to an approximately absolute scale by means of a Wilson (1942) plot. Normalized structure factors were calculated.

Solution and refinement of the structure

The approximate position of the Co atom was determined from a three-dimensional Patterson map. The symmetry of the crystal, based on the position of the heavy atom occupying a position on the twofold screw axis, can be described by the centrosymmetric space group *Pmmn* with a shortening of the *c* axis to one half. The effect of the existence of rationally dependent atoms is that $\langle |E_s|^2 \rangle_s$ differs significantly from unity over subsets of *hkl* (Hauptman & Karle, 1959). In the present work, if l is even then $\langle |E_{hkl}|^2 \rangle_{l=2n} = 1{\cdot}68$; if l is odd, then $\langle |E_{hkl}|^2 \rangle_{l=2n+1} = 0{\cdot}35$. A Fourier synthesis based on the contributions of the heavy atom (reflections with $l = 2n$) showed only six peaks in the coordination sphere of the Co atom. These peaks were situated on pseudo-planes, but at the corners of an approximate octahedron, indicating their positions to be approximately correct. To destroy the pseudosymmetry, a peak in a general position at a chemically reasonable distance from one of the six donors was chosen. The phases of the structure factors calculated from the eight atoms were refined by the method of modification and Fourier transformation of the approximate electron density (Gassmann, 1975) using the weighted maxima approach (Simonov, 1975). The weights were equal to unity if $M_i/M_a > 0{\cdot}7$, otherwise $w_i = M_i/M_a$, M_a being the mean height of the maxima of six atoms, bound to the Co atom. The reflections with $F_c/F_o < 0{\cdot}25$ were excluded from the calculation of the electron density. After four cycles of phase correction, the model could be found among the 25 highest peaks (21 were correct, two were pseudosymmetrically related and two were spurious). The following Fourier synthesis revealed the positions of all O, N and C atoms of the ligand, together with the O atoms of three water molecules. The coordinates of the atoms and the isotropic temperature factors were refined by the least-squares method with a full-matrix program written by P. K. Gantzel, C. J. Sparks and K. N. Trueblood. Scattering factors were taken from *International Tables for X-ray Crystallography* (1968). A difference Fourier synthesis showed the position of the Li atom. Further cycles of least-squares refinement were carried out on the basis of diffractometer data; only observed reflections were used. The positional parameters and anisotropic temperature factors were refined. R decreased to $0{\cdot}07$. A difference synthesis showed all the positions of the H atoms, except those of the water molecules. In the following refinement cycles, 12 H atoms of the anion were included at their calculated positions ($B = 3{\cdot}0$ Å^2); no parameters were varied for these atoms. This calculation converged at $R_1 = 0{\cdot}049$ and $R_2 = 0{\cdot}053$ for the observed reflections. R_1 for all reflections was $0{\cdot}07$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized; a weighting scheme $w = 1{\cdot}0$ if $|F_o| < 60$ and $w = 60/F_o$ if $|F_o| > 60$ was employed. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w^{1/2}(|F_o| - |F_c|)^2 / \sum w^{1/2}|F_o|^2]^{1/2}$. The average values of the minimized functions, obtained after the final cycle of refinement, showed little dependence on $|F_o|$ or $\sin\theta$, which

Table 1. *Final atom parameters and their estimated standard deviations*

The values have been multiplied by 10^4.

	x	*y*	*z*
Co	7594 (1)	4965 (1)	4426 (1)
O(1)	7597 (5)	3173 (4)	4447 (3)
O(2)	6079 (5)	1611 (4)	4527 (4)
O(3)	4495 (5)	4790 (6)	2706 (3)
O(4)	6402 (4)	4998 (6)	3448 (3)
O(5)	7551 (5)	6748 (4)	4441 (3)
O(6)	8958 (5)	8365 (4)	4714 (4)
O(7)	11272 (5)	4918 (7)	3242 (4)
O(8)	9089 (4)	4904 (6)	3623 (3)
N(1)	6095 (5)	4792 (5)	5208 (3)
N(2)	8814 (5)	5187 (5)	5389 (3)
C(1)	6397 (7)	2735 (7)	4603 (5)
C(2)	5303 (7)	3684 (6)	4895 (4)
C(3)	4419 (7)	4028 (7)	4144 (4)
C(4)	5161 (7)	4647 (6)	3377 (5)
C(5)	8662 (7)	7251 (7)	4746 (4)
C(6)	9655 (7)	6315 (6)	5167 (5)
C(7)	10791 (6)	5978 (6)	4524 (5)
C(8)	10364 (7)	5199 (7)	3757 (5)
C(9)	6683 (8)	4578 (8)	6088 (4)
C(10)	7950 (8)	5385 (7)	6183 (4)
W(1)	7906 (5)	163 (6)	3613 (3)
W(2)	7742 (7)	7531 (5)	2580 (4)
W(3)	9326 (7)	2586 (7)	2558 (5)
Li	7385 (12)	9384 (12)	2527 (8)

Table 2. *Interatomic distances* (Å) *and angles* (°) *in the complex anion and* LiO_4 *tetrahedra with their estimated standard deviations in parentheses*

Co—N(1)	1·897 (5)	C(1)—O(1)	1·271 (8)
Co—N(2)	1·917 (5)	C(1)—O(2)	1·234 (9)
Co—O(1)	1·896 (4)	N(2)—C(6)	1·484 (9)
Co—O(4)	1·904 (4)	C(6)—C(7)	1·525 (10)
Co—O(5)	1·887 (4)	C(7)—C(8)	1·504 (10)
Co—O(8)	1·906 (4)	C(8)—O(7)	1·222 (9)
N(1)—C(9)	1·495 (9)	C(8)—O(8)	1·287 (8)
N(2)—C(10)	1·501 (9)	C(5)—C(6)	1·526 (10)
C(9)—C(10)	1·498 (11)	C(5)—O(5)	1·287 (8)
N(1)—C(2)	1·481 (9)	C(5)—O(6)	1·214 (9)
C(2)—C(3)	1·490 (10)	Li—*W*(1)	1·940 (14)
C(3)—C(4)	1·534 (10)	Li—*W*(2)	1·992 (14)
C(4)—O(3)	1·232 (9)	Li—O(3)	1·900 (12)
C(4)—O(4)	1·259 (8)	Li—O(7)	1·850 (13)
C(2)—C(1)	1·526 (10)		

N(1)—Co—N(2)	89·0 (2)	O(4)—Co—O(5)	88·7 (2)
N(1)—Co—O(1)	83·9 (2)	O(4)—Co—O(8)	86·5 (2)
N(1) Co O(4)	92·8 (2)	O(5) Co O(8)	93·3 (2)
N(1)—Co—O(5)	94·1 (2)	Co—N(1)—C(2)	105·1 (4)
N(1)—Co—O(8)	172·5 (3)	Co—O(1)—C(1)	111·5 (4)
N(2)—Co—O(1)	96·2 (2)	Co—O(4)—C(4)	129·7 (5)
N(2)—Co—O(4)	171·8 (3)	N(1)—C(2)—C(1)	105·1 (6)
N(2)—Co—O(5)	83·2 (2)	C(2)—C(1)—O(1)	116·6 (6)
N(2)—Co—O(8)	92·7 (2)	C(2)—C(1)—O(2)	119·3 (6)
O(1)—Co—O(4)	91·9 (2)	O(2)—C(1)—O(1)	124·0 (6)
O(1)—Co—O(5)	177·9 (2)	N(1)—C(2)—C(3)	111·0 (5)
O(1)—Co—O(8)	88·7 (2)	C(1)—C(2)—C(3)	109·0 (6)
C(3)—C(4)—O(4)	120·2 (6)	C(2)—C(3)—C(4)	116·3 (6)
C(3)—C(4)—O(3)	117·6 (6)	Co—N(1)—C(9)	107·9 (4)
O(3)—C(4)—O(4)	122·2 (7)	Co—N(2)—C(10)	108·4 (4)
Co—N(2)—C(6)	104·7 (4)	N(1)—C(9)—C(10)	108·3 (6)
Co—O(5)—C(5)	113·5 (4)	N(2)—C(10)—C(9)	107·1 (6)
Co—O(8)—C(8)	127·7 (5)	C(2)—N(1)—C(9)	112·1 (5)
N(2)—C(6)—C(5)	106·1 (5)	C(6)—N(2)—C(10)	112·5 (5)
C(6)—C(5)—O(5)	114·4 (6)	C(6)—C(7)—C(8)	116·6 (6)
C(6)—C(5)—O(6)	119·9 (6)	C(7)—C(8)—O(8)	121·5 (6)
O(5)—C(5)—O(6)	125·6 (6)	C(7)—C(8)—O(7)	116·9 (6)
N(2)—C(6)—C(7)	111·0 (5)	O(7)—C(8)—O(8)	121·5 (6)
C(5)—C(6)—C(7)	108·9 (6)	O(3)—Li—O(7)	118·5 (7)
O(3)—Li—*W*(1)	108·5 (6)	O(3)—Li—*W*(2)	113·3 (7)
O(7)—Li—*W*(1)	104·4 (6)	O(7)—Li—*W*(2)	101·9 (6)
W(1)—Li—*W*(2)	109·7 (6)		

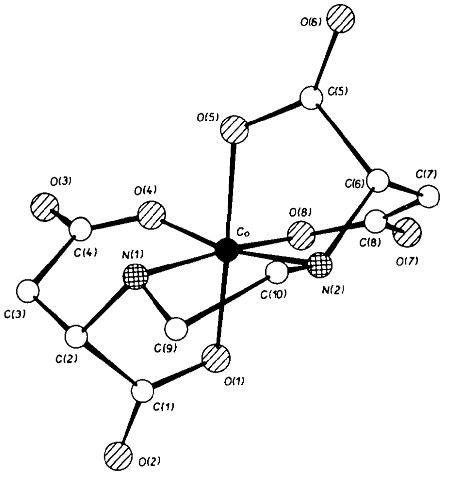

Fig. 2. A perspective drawing of *trans*-(O_5)-Co[(*S*,*S*)-EDDS]$^-$ and the numbering scheme of the atoms.

indicates that the relative weighting scheme is reasonable. The atomic positions are in Table 1 together with their standard deviations.*

Description and discussion of the structure

The crystal is built up of *trans*-(O_5)-Co[(*S*,*S*)-EDDS]$^-$ anions held together by Li^+ cations and water molecules. A perspective drawing of the complex anion with the correct absolute configuration (see Fig. 1 for nomenclature) and the numbering scheme are given in Fig. 2. The absolute configuration of the complex was determined on the basis of the known absolute configuration of (*S*)-aspartic acid. The bond lengths and angles within the complex anion and LiO_4 tetrahedra are listed in Table 2.

The Co atom is bonded octahedrally to two N atoms and one O atom from each of the four carboxylate arms of the complexing species. (*S*,*S*)-EDDS acts as a sexidentate ligand. Five-, six- and seven-membered rings are formed. In the complex, two O atoms of the

Table 3. *Least-squares planes for* Li{Co[(*S*,*S*)-EDDS]}.3H_2O

The planes are described by $Ax + By + Cz = D$, in which x, y and z are Cartesian coordinates, and D is the distance of the plane from the origin (Å).

	A	*B*	*C*	*D*
Plane *G*1: Co, C(6), C(7), C(8), O(8)	−0·2589	0·8374	−0·4815	−0·7374
Plane *G*2: Co, C(2), C(3), C(4), O(4)	0·3431	−0·8660	−0·3638	−4·4653
Plane *R*1: Co, C(1), C(2), O(1)	−0·3034	0·0227	−0·9526	−8·6653
Plane *R*2: Co, C(5), C(6), O(5)	0·4902	−0·0165	−0·8715	−2·4953

Deviations (Å) from least-squares planes

	*G*1	*G*2	*R*1	*R*2
Co	−0·068	−0·063	0·023	0·022
C(1)			0·059	
C(2)		0·086	−0·030	
C(3)		−0·098		
C(4)		0·013		
C(5)				0·055
C(6)	0·059			−0·028
C(7)	−0·042			
C(8)	−0·054			
O(1)			−0·052	
O(4)		0·063		
O(5)				−0·050
O(8)	0·014			
N(1)		−0·843	−0·697	
N(2)	−0·895			−0·707

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33818 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

five-membered chelate rings are in *trans* positions and those of the six-membered rings are *cis*. The Co—N distances are 1·917 and 1·897 Å respectively; these are shorter than the distances observed in other Co^{III} complexes. The Co—O distances range from 1·887 to 1·908 Å. As can be seen from Table 2, they are longer for the oxygens in *cis* positions than for those in *trans* positions, as in the $Co(Asp)_2^-$ complexes (Oonishi, Shibata, Marumo & Saito, 1973). Deviations from 90° of N—Co—O and O—Co—O angles in the coordination sphere range from +6·2 to −6·8°. The coordination octahedron is slightly distorted. These distortions seem to be due to the formation of the strained chelate rings. The conformations of the chelate rings in the aspartic moieties are close to those of the chelate rings in the *trans*-(O_5)-$Co(Asp)_2^-$ complex. The equatorial *β*-alanine six-membered chelate rings have half-chair conformations, as can be seen from Table 3, which lists the deviations from the least-squares planes. The five atoms of the chelate ring lie approximately in the plane, the N atoms being displaced below it by 0·895 and 0·843 Å respectively. The five-membered glycine rings have an envelope form, where the N atoms are bent from the plane of the remaining four atoms of the chelate ring by 0·697 and 0·707 Å respectively. These axial rings show significant deviations from planarity, in contrast to the almost planar *R* rings in the complex $Co(EDTA)^-$ (Weakliem & Hoard, 1959). Also the angles O_G—Co—O_G [here O(4)—Co—O(8)] differ, being 103° in $Co(EDTA)^-$ and 86·5° in $Co[(S,S)\text{-EDDS}]^-$, indicating the 6-5-6 combination of chelate rings in the equatorial plane to be more favourable than the 5-5-5. The central ethylenediamine ring has a *λ gauche* conformation. The crystal structure analysis supported the thermodynamic preference of the *trans*-(O_5) configuration in the Co[(*S*,*S*)-EDDS] complex.

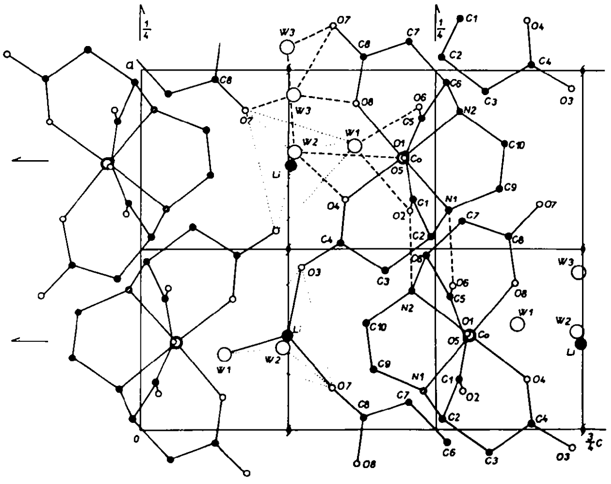

Fig. 3. The projection of the structure in the direction of the *b* axis. Intermolecular hydrogen bonds are represented by dashed lines.

Table 4. *Intermolecular contacts less than* 3·3 Å

O(2)···*W*(1)	2·732 (7)	O(6)···*W*′(1)	2·750 (8)
W(2)···*W*′(3^{i})	2·839 (10)	N(1)···O(6^{ii})	2·841 (7)
O(2)···N′(2^{ii})	2·901 (7)	O(8)···*W*(3)	2·966 (9)
O(5)···*W*(2)	3·007 (7)	O(7)···*W*′(3^{i})	3·136 (10)
O(4)···*W*(2)	3·265 (8)	O(7)···*W*(3)	3·277 (10)
C(8)^{n}···*W*′(3^{i})	3·259 (11)	O(2)^{n}···C′(7^{ii})	3·122 (9)
C(9)^{n}···*W*(2^{iii})	3·262 (10)		

The equivalent positions are: (i) $-x, y+\frac{1}{2}, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, 1-z$; (iii) $\frac{3}{2}-x, 1-y, z+\frac{1}{2}$. The atoms marked by a prime are from neighbouring unit cells. The superscript *n* represents a non-hydrogen contact.

The structure projected along the *b* axis is shown in Fig. 3. It can be seen that pseudosymmetry is caused not only by the special position of the heavy atom, but also by the position and orientation of the whole complex anion. The pseudosymmetric twofold axis of the complex anion, passing through the Co atom and through the middle of the C—C bond in the ethylenediamine ring, is almost identical with the twofold screw axis of the crystal.

The complex anions are held together by the Li^+ cations (LiO_4 tetrahedra are formed), giving infinite chains parallel to the *a* axis. The chains are held together by a system of hydrogen bonds (which is clear from Fig. 3) and by van der Waals forces. Important intermolecular contacts are given in Table 4.

Calculations were performed on a Siemens 4004/150 computer at the Research Computing Centre of the Comenius University in Bratislava and on a Syntex XTL module.

References

BROWN, M. F., COOK, B. R. & SLOAN, T. E. (1975). *Inorg. Chem.* **14**, 1273–1277.
GASSMANN, J. (1975). International Summer School on Crystallographic Computing, Prague.
HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 846–850.
International Tables for X-ray Crystallography (1968). Vol. III. Birmingham: Kynoch Press.
NEAL, J. & ROSE, N. J. (1968). *Inorg. Chem.* **7**, 2405–2412.
NEAL, J. & ROSE, N. J. (1972). *Inorg. Chem.* **12**, 1226–1232.
OONISHI, I., SHIBATA, M., MARUMO, F. & SAITO, Y. (1973). *Acta Cryst.* B**29**, 2448–2455.
PAVELČÍK, F. & MAJER, J. (1978). *Collect. Czech. Chem. Commun.* **43**, 239–249.
SIMONOV, V. I. (1975). International Summer School on Crystallographic Computing, Prague.
WEAKLIEM, H. A. & HOARD, J. L. (1959). *J. Am. Chem. Soc.* **81**, 549–555.
WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.