

NOTIZEN

**The Preparation and Structure of Lithium
(R,S)-Ethylenediamine-N,N'-disuccinato-
cobaltate(III) Trihydrate**

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X-ray, Crystal Structure, Cobalt(III) Complex,
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Crystals of $\text{LiCo}[(\text{R,S})\text{-EDDS}] \cdot 3 \text{H}_2\text{O}$ have been synthesized and its structure was determined by X-ray analysis. Monoclinic, $a = 9.624$, $b = 12.788$, $c = 12.049$ Å, $\beta = 94.85^\circ$, space group $\text{P}2_1/\text{c}$. The crystal consists of binuclear units $\text{Co}_2[(\text{R,S})\text{-EDDS}]_2^{2-}$. The central ethylenediamine chelate ring has an envelope conformation.

Ethylenediamine-N,N'-disuccinic acid (EDDS), an isomer of EDTA, can be found in three stereo isomers which provide thus a wide range of possible arrangements in co-ordination compounds. An unusual structure of the cobalt(III) complex of the EDDS meso-form was suggested by the NMR spectrum¹.

Experimental

By condensation of equimolar amounts of ethylenediamine with sodium salt of maleic acid in aqueous solution (48 h, 100°C) followed by acidification with HCl to pH 3, a mixture of EDDS isomers was obtained, which was then separated by fractional crystallization into meso and racemic forms. The individual isomers were purified by crystallization of copper(II) complexes with the molar ratio being $\text{Cu:EDDS} = 2:1$. The cobalt(III) complex was prepared by dissolving equimolar amounts of (R,S)-EDDS, $\text{Co}(\text{OH})_2$ and Li_2CO_3 in water, followed by oxidation of the formed solution by H_2O_2 in the presence of active carbon. The compound which crystallized from the solution had a composition $\text{LiCo}[(\text{R,S})\text{-EDDS}] \cdot 3 \text{H}_2\text{O}$.

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$\text{C}_{10}\text{H}_{18}\text{CoLiN}_2$

Calcd	C 29.43	N 6.68	Co 14.44,
Found	C 29.19	N 6.63	Co 14.20.

The crystallographic data were determined from Weissenberg photographs, the lattice constants were refined from diffractometric data (Mo $K\alpha$): $a = 9.624(10)$, $b = 12.788(6)$, $c = 12.049(6)$ Å, $\beta = 94.85(6)^\circ$, $V = 1477.6$ Å³, $D_{\text{exp}} = 1.80$, $D_{\text{calcd}} = 1.83$ g · cm⁻³, $\text{MW} = 408.18$, $Z = 4$, space group $\text{P}2_1/\text{c}$. Intensities were measured on a SYNTeX $\text{P}2_1$ diffractometer with graphite-monochromatized Mo $K\alpha$ radiation and Θ - 2Θ scan technique. The 3785 reflections were collected of which 1787 were observed with $I > 1.96 \sigma(I)$. The position of the cobalt atom was deduced from the Patterson synthesis. The following Fourier syntheses showed the positions of all non hydrogen atoms. The structure was refined by least-squares methods with anisotropic temperature factors to give an R value of 0.08 on the basis of the observed reflections.

Discussion

The crystal structure consists of binuclear units $\text{Co}_2[(\text{R,S})\text{-EDDS}]_2^{2-}$, LiO_4 tetrahedra, and a molecule of crystal water. Two molecules of water are bonded to the Li^+ cation together with two oxygens of carboxyl groups of different binuclear units, forming thus infinite layers which are interconnected through hydrogen bonds. Two nitrogen atoms of imino groups and four oxygenatoms of carboxyl groups are octahedrally coordinated to a cobalt atom. The bond distances in the co-ordination sphere are shorter than commonly found for the cobalt(III) complexes, Co-N 1.90 and 1.87 Å, Co-O 1.86–1.91 Å. These bonds are even shorter than those in the analogous $\text{Co}(\text{Asp})_2^-$ complex². The co-ordination polyhedra are slightly deformed. Valence angles are within the range 86.5 – 95.4° . The six-donor ligand is bonded to two centrosymmetrically related atoms of cobalt. To each central atom five donors are bonded from one (R,S)-EDDS: one whole aspartic unit, an ethylenediamine residue, and a glycine ring of the second aspartic unit, while the β -alanine branch is not closed to form a six-membered ring, but this part of the molecule is instead bonded to the adjacent atom of cobalt. Thus, two bridging branches form a twelve-membered ring, as shown in Fig. 1. The conformations of the glycine and β -alanine chelate rings are analogous to those of the chelate rings occurring in other complex compounds of amino acids. The ethylenediamine ring is in an energetically unfavourable

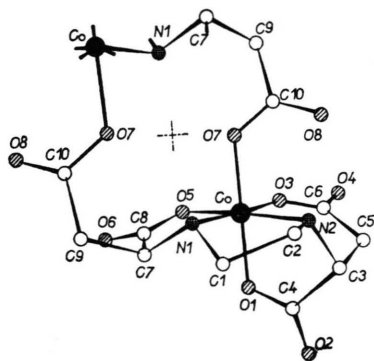


Fig. 1. A perspective drawing of one half of the dimeric complex $\text{Co}[(R,S)\text{-EDDS}]_2^{2-}$, showing the twelve-membered ring and the numbering scheme of the atoms.

¹ P. BALGAVÝ, P. NOVOMESKÝ, and J. MAJER, to be published.

vourable envelope conformation. The distance of carbon C1 from the plane-N1-Co-N2 is 0.63 Å, while carbon atom C2 is situated in this plane (the deviation being 0.01 Å). The valence angles in the ethylenediamine ring are: N1-Co-N2 88.3°, Co-N1-C1 109.5°, Co-N2-C2 109.3°, N1-C1-C2 103.7°, N2-C2-C1 111.4°. The dihedral angle N1-C1-C2-N2 is 43.9°. The greatest angular deformations in the complex are those of the angles between the rings C1-N1-C7 115.0 and C2-N2-C3 116.8°.

The occurrence of a dimer which is disadvantageous from the aspects of thermodynamics, because of considerable losses of translation entropy in the solution, can be explained by a stabilization through strong intramolecular hydrogen bonds between the imino groups and the oxygen atoms of carboxyl groups of the twelve-membered ring. The distance N2...O8 is 2.76 Å, and N1...O7 2.64 Å.

² I. OONISHI, M. SIHATA, F. MARUMO, and Y. SAITO, *Acta Crystallogr. B* **29**, 2448 [1973].