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, EDTA Isomer, Chelate Ring Conformation

Crystals of LiCo[(R,S)-EDDS] • 3 H2O have been synthetized and its structure was determined by X-ray analysis. Monoclinic, a = 9.624, b = 12.788, c = 12.049 Å, β = 94.85°, space group P21/c. The crystal consists of binuclear units Co2[(R,S)-EDDS]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 spectrum 1.

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 Cu : EDDS = 2 :1. The cobalt(III) complex was prepared by dissolving equimolar amounts of (R,S)-EDDS, Co(OH)2 and Li2CO3 in water, followed by oxidation of the formed solution by H2O2 in the presence of active carbon. The compound which crystallized from the solution had a composition LiCo[(R,S)-EDDS] • 3 H2O.

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C10H18CoLiN2

Calcd C 29.43 N 6.68 Co 14.44,


Discussion

The crystal structure consists of binuclear units Co2[(R,S)-EDDS]2+, LiO4 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-0 1.86-1.91 Å. These bonds are even shorter than those in the analogous Co(Asp)2+ complex 2. 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 unfa-
Fig. 1. A perspective drawing of one half of the dimeric complex Co[(R,S)-EDDS]^{2-}, showing the twelve-membered ring and the numbering scheme of the atoms.

1 P. Balgavý, P. Novomeský, and J. Major, to be published.