X-Ray Crystal and Molecular Structure, Absolute Configuration, and Stereoselectivity of (−)$_{435}$-L-Isoleucinato-*NN′*-ethylenebis(α-methylsalicylideneaminato)cobalt(III)

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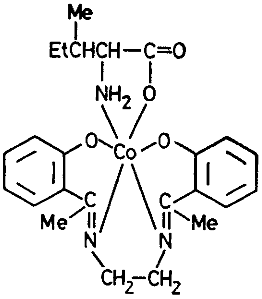
Summary The novel ΛL-*cis*-β_2(*mer*) type structure of the new, mixed-ligand cobalt(III)–Schiff-base complex (−)$_{435}$-L-isoleucinato-*NN′*-ethylenebis-(α-methylsalicylideneaminato)cobalt(III)·1·5H_2O has been determined by *X*-ray analysis; the origin of the thermodynamic stereoselectivity in this complex could be elucidated.

RECENTLY, the preparation of new mixed ligand cobalt(III)–Schiff-base complexes with the general formulae [Co(salen)(aa)], [Co(msalen)(aa)], and [Co(salch)(aa)]† was studied, and the highly stereoselective co-ordination of the optically active amino-acidato ligands found in these complexes was proposed to have a thermodynamic origin.[1,2] In order to clarify the reason for this thermodynamic stereoselectivity, the crystal structure of the title compound (**1**) has been studied by X-ray analysis.



(**1**)

Compound (**1**) afforded dark-green orthorhombic crystals from warm methanol solution. *Crystal data:* $a = 21{\cdot}56(1)$, $b = 11{\cdot}86(1)$, $c = 9{\cdot}80(1)$ Å, space group $P2_12_12_1$, $D_m = 1{\cdot}38$ (chloroform–benzene), $Z = 4$, $D_c = 1{\cdot}38$ g cm^{-3}. A total of 1985 independent reflections was obtained by visual estimation of equi-inclination Weissenberg photographs ($hk0$–$hk5$, and $h0l$–$h2l$) with Ni-K_α ($\lambda = 1{\cdot}6591$ Å) radiation.

The position of the cobalt atom was determined from a sharpened Patterson map, and the structure was solved by Fourier techniques. Refinement by block-diagonal least-squares, using isotropic thermal parameters (anisotropic for Co) led to a current R-value of 0·116.‡

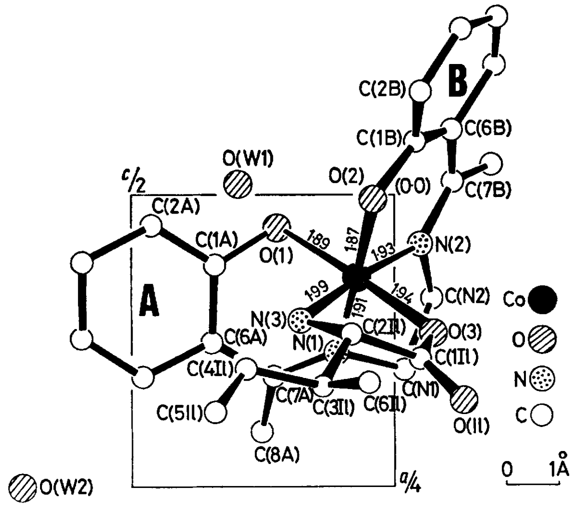


FIGURE. Molecular structure of the title complex (**1**) viewed down the b-axis, with selected bond lengths in Å. Standard deviations, 0·015 Å for bonds to cobalt and 0·03 Å for the remaining bonds. O(W1) and O(W2) are oxygen atoms of water molecules of crystallization.

The structure (Figure) is of the new ΛL-*cis*-β_2(*mer*) type,§ in contrast to the expected ΛL-*cis*-β_1(*fac*) type which had been proposed by one of us.[3]

If the co-ordinated L-amino-acidato ligand in the present structure is replaced by a D-amino-acidato ligand, the equatorial orientation of the alkyl group on the α-carbon atom changes into the more sterically hindered axial orientation [C(2I1) - - - O(2) 2·94 Å]. Thus, based on this structure, the thermodynamic stereoselectivity in these systems can be attributed to the steric repulsion between the co-ordinated oxygen atom of the salicylaldehyde unit B [O(2) in the Figure] and the alkyl group on the α-carbon atom of the co-ordinated amino-acidato ligand.

(*Received, 5th December* 1977; *Com.* 1235.)

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† H_2msalen = *o*-$HOC_6H_4CMe{=}N{-}CH_2CH_2{-}N{=}CMeC_6H_4OH$-*o*; H_2salen = *o*-$HOC_6H_4CH{=}N{-}CH_2CH_2{-}N{=}CHC_6H_4OH$-*o*; Haa = L-amino acid; H_2salch = (1S,2S)-NN'-(1,2-cyclohexylene)bis-salicylideneamine.

‡ All computations were carried out using a HITAC-8700 computer at Hiroshima University, using the UNICS programs of The Crystallographic Society of Japan (1965) with slight modification. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The absolute configuration of the complex was determined to be ΛL by comparison with the known absolute configuration of the L-isoleucinato ligand.

[1] Y. Fujii, T. Isago, M. Sano, N. Yanagibashi, S. Hirasawa, and S. Takahashi, *Bull. Chem. Soc. Japan*, 1976, **49**, 3509

[2] Y. Fujii, M. Sano, and Y. Nakano, *Bull. Chem. Soc. Japan*, 1977, **50**, 2609

[3] See ref. 1 for explanation of the notation 'ΛL-*cis*-β_2(*mer*)' and 'ΛL-cis-β_1(*fac*).