The Structure of Mixed-ligand Complex *NN'*-Ethylene-bis(salicylaldehydeiminato)acetylacetonatecobalt(III) Monohydrate

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Summary In (Co salen acac,H_2O) the salen ligand is shown to have an unusual conformation which is probably determined by the chelating action of the acac group.

THE structures of some cobalt complexes of bis(salicylaldehyde)ethylenedi-imine (salenH_2) and bis(acetylacetone)-ethylenedi-imine (baeH_2) have been determined in this laboratory in order to provide insight into the ability of these ligands to stabilize the metal–carbon bond[1] and to absorb molecular oxygen.[2] The four donor atoms of the salen ligand are always almost coplanar.

Poddar and Biswas[3] have described some monomeric cobalt mixed-ligand chelates containing salen and β-diketones. The *NN'*-ethylenebis(salicylaldehydeiminato)-acetylacetonatecobalt(III) (Co salen acac) was prepared by mixing Co salen and acacH or $Co(acac)_2$ and salenH_2. They suggested for this complex an octahedral co-ordination around the cobalt atom with two *cis*-co-ordination positions occupied by the acac group and the others by the salen ligand in a nonplanar conformation. This unusual conformation of the salen ligand prompted us to undertake the crystal structure analysis of Co salen acac.

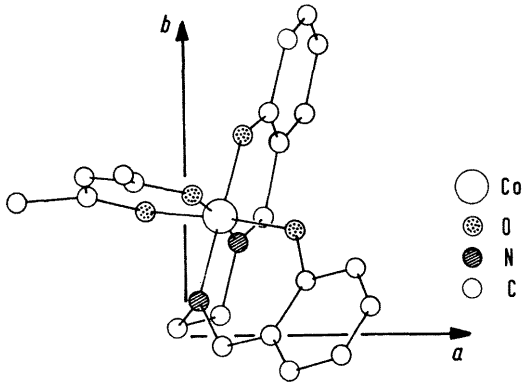

FIGURE. *The complex as viewed along the* c *axis.*

The green crystals of $C_{21}H_{21}O_4N_2Co,H_2O$ belong to the orthorhombic system, space group $P2_12_12_1$ with $a = 17{\cdot}58 \pm 0{\cdot}03$, $b = 13{\cdot}47 \pm 0{\cdot}02$, $c = 8{\cdot}29 \pm 0{\cdot}01$ Å, $Z = 4$, $U = 1963$.

The structure analysis was based on 1054 independent reflexions, collected with the equi-inclination Weissenberg method, using Co-K_α radiation. The intensities of the reflexions were estimated visually. The structure was solved by Patterson and Fourier methods and refined by the isotropic block-diagonal least-squares method to the present *R*-value of 0·14.

The crystal consists of discrete Co salen acac units. The acac group acts as a chelate ligand. The distorted octahedral polyhedron is completed by the quadridentate ligand, as shown in Figure. The Co–O bond lengths range from 1·89 to $1{\cdot}94 \pm 0{\cdot}02$ Å. The mean Co–N value is $1{\cdot}89 \pm 0{\cdot}03$ Å. The angles around the cobalt atom range from 83 to $97 \pm 1°$. The water molecule forms hydrogen bonds with the oxygen atoms of the salen ligand. The structure of this complex is the first example of such an unusual conformation of the salen ligand so far elucidated by *X*-ray analysis.

The mechanism of the reaction between Co salen and acacH can be tentatively explained assuming that, after the oxidation of the cobalt atom, the chelating action of the acac group determines the rearrangement of the Schiff base.

The structure found corresponds to displacement of one oxygen atom from the equatorial plane. The other stereochemical possibility, with the oxygens *trans*, would involve both being displaced from the Co–N–N plane.

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