The Crystal and Molecular Structure of some Derivatives of *NN'*-Ethylenebis(salicylaldehydeiminato)cobalt(III)

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Summary The crystal and molecular structure of the Co(salen) complexes with acetonitrile, pyridine, acetone, and methoxyl as further ligands [cyanomethyleneCo(salen) with methanol, methoxy-Co(salen) with pyridine and methanol, acetonylCo(salen) with methanol] have been determined by *X*-ray structural analysis.

As a part of a research programme on oxygen-carrying compounds we have resolved, by *X*-ray diffraction analysis, the crystal structure of some derivatives of *NN'*-ethylenebis(salicylaldehydeiminato)cobalt(III), Co(salen), $C_{16}H_{14}N_2O_2Co$.

We report the results on the following compounds:

(I) CyanomethyleneCo(salen) with methanol [Co(salen)–CH_2CN/CH_3OH);

(II) MethoxyCo(salen) with pyridine and methanol [Co(salen)–OCH_3/Py/CH_3OH);

(III) AcetonylCo(salen) with methanol [Co(salen)–$CH_2 \cdot CO \cdot CH_3/CH_3OH$).

Crystal data: (I) orthorhombic, $a = 9{\cdot}07 \pm 0{\cdot}02$, $b = 11{\cdot}21 \pm 0{\cdot}03$, $c = 17{\cdot}21 \pm 0{\cdot}04$ Å, space group $P2_12_12_1$, $Z = 4$; (II) monoclinic, $a = 11{\cdot}30 \pm 0{\cdot}02$, $b = 18{\cdot}12 \pm 0{\cdot}04$, $c = 13{\cdot}10 \pm 0{\cdot}02$ Å, $\beta = 120{\cdot}2 \pm 0{\cdot}5°$, space group $P2_1/c$, $Z = 4$; (III) monoclinic, $a = 7{\cdot}68 \pm 0{\cdot}02$, $b = 20{\cdot}01 \pm 0{\cdot}04$, $c = 12{\cdot}61 \pm 0{\cdot}02$ Å, $\beta = 99{\cdot}6 \pm 0{\cdot}5°$, space group $P2_1/c$, $Z = 4$.

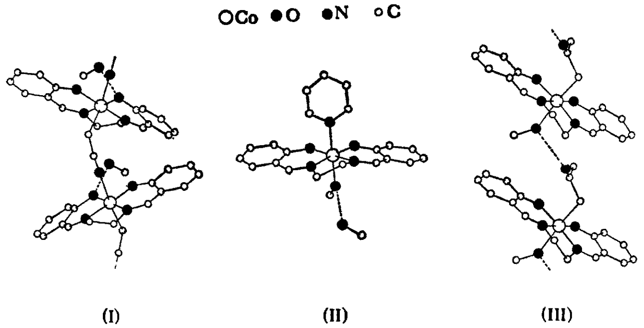

FIGURE 1. *Molecular structures of the three* Co(salen) *derivatives. For* (I) *and* (III), *two molecules are shown to account for the polymeric structure of the former and the intermolecular hydrogen bond in the latter.*

Three-dimensional data were obtained by visual estimation of equi-inclination Weissenberg photographs, using Co-K_α radiation. Resolution of the structures was performed by standard procedures. No correction for absorption was made. Structure refinement was carried out *via* Booth differential synthesis for compound (I) (1076 independent reflections, $R = 0{\cdot}09$) and by the anisotropic block-matrix least-squares method for compounds (II) and (III) (2030 and 1345 independent reflections, $R = 0{\cdot}10$ and $R = 0{\cdot}11$, respectively). The essential features of the molecular structures are given in Figure 1. Common details regarding the tetradentate ligand (salen) may be better discussed by referring to the Figure 2.

In all the three structures the cobalt atom lies in the plane of the oxygen and nitrogen atoms [O(1), O(2), N(1), N(2)] of the salen ligand within a maximum deviation of 0·05 Å. In (I) a net distortion of the salen is observed; it is possible to establish, within a maximum deviation of 0·05 Å, two mean planes, one containing the O(1), C(1, · · · 7), and C(8) atoms, the other one containing the remaining part of the ligand in addition to the O(1) atom, which is common to the two planes. The angle between the planes is 22°. A relation between such a distortion and the hydrogen bond on the O(1) atom, due to the methanol molecule, is evident; a similar situation has recently been observed in a related structure.[1] A quite similar deviation from planarity occurs in (II), the angle between the two planes being 17°. In (III) the previous scheme does not hold. The situation for this last compound may be described as follows: the plane containing the C(10, · · · , 16) and O(2) atoms, *i.e.* the part of the salen which is situated below the acetone group, is bent down by 11° with respect to the plane containing the Co, N(1), N(2), O(1), and O(2) atoms; the opposite part, *i.e.* the O(1), C(1, · · · , 7) plane, is bent up by 4° with respect to the same central plane. The internal rotation angle around the carbon–carbon bridge of ethylenediamine is 34·6°, 43·0°, and 37·0° for (I), (II), and (III), respectively.

These various distortions of the salen ligand are in agreement with the general observation drawn by Randaccio and his co-workers[1] in studying the structures of some pyramidal and octahedral derivatives of *NN'*-ethylenebis(acetylacetoneiminato)cobalt-(II) and (III), Co(bae): *i.e.* that the steric effects of σ-bonded apical groups disturb the condition for the most efficient π-back bonding, which is best satisfied in planar tetraco-ordinate complexes. In fact, Co(bae) adopts an exactly planar geometry, in spite of the more stable *gauche* conformation of the ethylenediamine bridge. More evidence for this point of view has been given very recently by the bis(salicylaldehyde)ethylene-di-imine-cobalt(II) monochloroformate structure,[3] where the salen ligand is essentially planar and the rotation angle at the ethylenediamine bridge is only 10·7°.

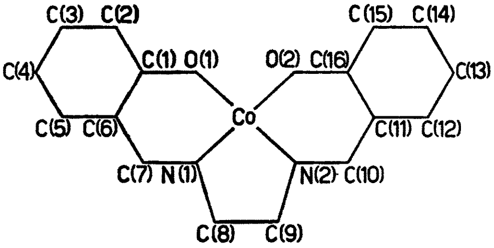

FIGURE 2. *Numbering scheme for the atoms of the* Cosalen *molecule.*

The values of the interatomic distances in the salen ligand agree well with those observed in related structures.[1–3] The mean Co–O and Co–N bond lengths (1·90 ± 0·01 and 1·89 ± 0·01 Å, respectively) are slightly, but significantly, larger than those reported for cobalt chelate.[3]

The compound (I) shows a polymeric structure, on account of the acetonitrile (Co–C = 1·99 ± 0·02, Co–N = 2·09 ± 0·02 Å), while in the compound (III) the molecules are bonded through an OH · · · O hydrogen bridge between the apical methanol group (Co–O = 2·20 ± 0·02 Å) and the carbonyl group of the acetonyl ligand is bonded to another molecule (Co–C = 2·02 ± 0·02 Å). In (II) the two *trans*-positions are occupied by a pyridine (Co–N = 2·03 ± 0·01 Å) and a methoxy-ligand (Co–O = 1·89 ± 0·01 Å) which is hydrogen-bonded to a methanol molecule.

There is a correlation between the hydrogen-bond distances and the related C–O bond lengths in the three structures, the former being longer when the last are shorter: in (I), OH · · · O = 2·86 and C–O = 1·33 ± 0·02 Å in the methanol molecule; in (III), OH · · · O = 2·70 and C–O = 1·42 ± 0·02 in the methanol, and C–O = 1·21 ± 0·01 Å in the carbonyl group; finally in (II), OH · · · O = 2·60 and C–O = 1·39 ± 0·01 in the methanol and C–O = 1·45 ± 0·02 Å in the methoxy-ligand.

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