The Crystal and Molecular Structure of a Binuclear Cobalt(III) Complex with Bis-(3-methoxysalicylaldehyde)ethylenedi-imine. Evidence for the Bridging Ability of Some Quadridentate Schiff Bases

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Summary Cobalt(III) complexes of general formula $Co_2(chel)_3$ [chel = *NN'*-ethylenebis(salicylidene- and 3-methoxysalicylidene-iminato)] have been isolated, in which the Schiff base acts both as quadridentate ligand, in a non-planar conformation, and as chelate ligand bridging the two cobalt atoms.

THE cobalt(II) complexes with quadridentate Schiff bases such as bis(acetylacetone)ethylenedi-imine (bae-H_2) or bis(salicylaldehyde)ethylenedi-imine (salen-H_2) are able to absorb molecular oxygen reversibly in aprotic co-ordinating solvents.[1–3] These ligands, in fact, are able to adjust the redox potential of the metal atom in such a way that only a partial transfer of electrons can occur from the cobalt atom to the bound oxygen molecule, thus preventing irreversible oxidation.[4] However, oxidation products can be obtained from solutions of the oxygen adducts in the presence of protic ligands.[5]

In an attempt to grow single crystals of the addition compound of molecular oxygen with *NN'*-ethylenebis-(3-methoxysalicylideneiminato)cobalt(II) and dimethyl sulphoxide, [Co(3-MeOsalen)$_2$(O_2)(Me_2SO)],[2] by very slow evaporation, in the air, of a dimethyl sulphoxide solution of the oxygenated compound, small black crystals separated out which were found, by an *X*-ray analysis, to be the oxidation product [Co_2(3-MeOsalen)$_3$, $2H_2O$, $2Me_2SO$], $C_{58}H_{70}Co_2N_6O_{16}S_2$, the contents of water and dimethyl sulphoxide being, however, not exactly stoicheiometric.

The crystals are triclinic. The cell parameters, determined from precession photographs taken with Co-K_α radiation, are: $a = 15{\cdot}14(2)$, $b = 11{\cdot}00(2)$, $c = 12{\cdot}41(2)$ Å, $\alpha = 101{\cdot}8(3)°$, $\beta = 129{\cdot}8(3)°$, $\gamma = 76{\cdot}4(3)°$, $U = 1547{\cdot}7$ Å^3, $Z = 1$ (from structure analysis).

The structure, based on 1851 independent reflexions collected on equi-inclination Weissenberg photographs with Co-K_α radiation, was solved by the heavy-atom method assuming the centrosymmetric space group.

The crystals consist of discrete Co_2(3-MeOsalen)$_3$ molecules and contain about two molecules of H_2O and of Me_2SO per unit cell as suggested by the electron density maps. The dimethyl sulphoxide molecules seem to be affected by a severe occupancy disorder.

An isotropic block-diagonal least-squares refinement led to the present *R*-value of 0·20, the atomic parameters of the solvent molecules being kept constant. No improvement of the structure refinement was obtained with the *P*1 space group.

The two cobalt atoms are bridged by a "3-MeOsalen" ligand which acts as a bis-bidentate ligand occupying two *cis*-co-ordination positions of each Co^{III} atom. The octahedral co-ordination polyhedron of each metal atom is completed by a quadridentate "3-MeOsalen" ligand in a non-planar conformation (Figure).

At this stage of refinement the Co–O bond lengths range from 1·90(2) to 1·94(2) Å, whereas the mean value of the Co–N bond distance is 1·93(2) Å. The angles around the cobalt atoms range from 82·5(8) to 94·9(8)°.

The mechanism of the formation of the complex has not been investigated. However, the main features of such a reaction may tentatively be indicated as: oxidation of the metal atom, elimination of a cobalt ion as any simple cobalt compound, chelating action of the "3-MeOsalen" group, and rearrangement of the quadridentate equatorial ligand. No attempt was made to identify the cobalt by-product.

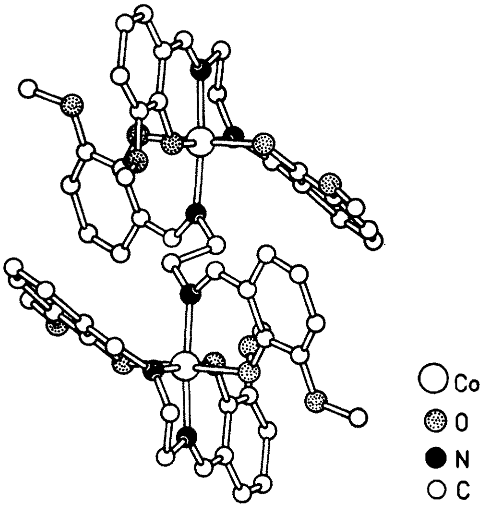

FIGURE. *A perspective drawing of the binuclear cobalt*(III) *complex* Co_2(3-MeOsalen)$_3$. *The two halves of the molecule are related by asymmetry centre set between the carbon atoms of the ethylenedi-imine bridge.*

The structure of this compound resembles that of the Co^{III} complex [Co(salen)(acac)] (acac = acetylacetonate) herein the "salen" ligand also adopts a non-planar conformation.[6] The latter compound can be obtained[7] by mixing, in a vessel open to the air, Co(salen) and acac-H whose chelating action probably determines the distortion of the Schiff base from its usual planar conformation. The results suggest that a similar reaction could occur between cobalt(II) complexes with a "salen"-type ligand and the Schiff base itself. In fact, the reaction of Co^{II}(3-MeOsalen) with an excess of the ligand in Me_2SO at *ca.* 50°, in the presence of O_2, gives a product whose *X*-ray powder spectrum is identical with that of compound (I). Similar products can be obtained starting from stoicheiometric amounts of cobalt(II) acetate and ligand. Analogous salen derivatives have also been obtained.

The above reactions show that "salen" and "3-MeOsalen" can readily act as bis-bidentate ligands bridging two cobalt atoms. Such behaviour of these quadridentate ligands has not been observed before; however, it seems likely that other Schiff bases could behave similarly if the steric requirements are satisfied in forming binuclear complexes. Formation of chains is more probable in polymethylenedi-imine derivatives, as suggested for *NN'*-polymethylenebis(salicylideneiminato)nickel(II).[8]

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