The Structure of the 1:2 Adduct of Oxygen with *NN'*-Ethylene-bis(salicylaldehydeiminato)cobalt(II) Containing Dimethylformamide

By M. CALLIGARIS, G. NARDIN, and L. RANDACCIO*
(*Istituto di Chimica, Università di Trieste, Italy*)

THE importance of synthetic molecular oxygen carriers has been realised for many years, but only recently have *X*-ray structural studies of some reversible and irreversible adducts of oxygen with co-ordination compounds been undertaken.[1] *NN'*-Ethylene-bis(salicylaldehydeiminato)cobalt(II), Co salen, and its oxygenated derivatives have been extensively studied, but no direct information on the oxygen bonding and the uptake mechanism in the solid state is available at present.

The crystal structure of the form of Co salen inactive to oxygenation has been already determined[2] as a part of a research programme on the structure of oxygen carriers. We report the results of a three-dimensional *X*-ray analysis of the adduct $(\text{Co salen})_2\cdot O_2\cdot(\text{dimethylformamide})_2$, $[(\text{Co salen})_2(O_2)(\text{DMF})_2]$.

Small but well developed, prismatic crystals were obtained according to the method of Calderazzo *et al.*[3] The unit cell parameters determined from precession photographs, taken with Co-K_α radiation, are: $a = 28{\cdot}85 \pm 0{\cdot}04$, $b = 12{\cdot}94 \pm 0{\cdot}02$, $c = 11{\cdot}32 \pm 0{\cdot}02$ Å, $\beta = 118{\cdot}7 \pm 0{\cdot}3°$; $Z = 8$ Co salen (O) DMF units.

The possible space groups are $C2/c$ and Cc; the former was chosen on the basis of the vector distribution of the Patterson map and was confirmed by the successful refinement.

1105 independent reflections were collected by the equi-inclination Weissenberg method using Co-K_α radiation and their intensities were estimated visually.

The structure was solved by three-dimensional Patterson and Fourier syntheses and refined by the isotropic block-diagonal least-squares method to the present *R*-value of 0·11. The structure consists of dimeric units, $[(\text{Co salen})_2(O_2)(\text{DMF})_2]$, in which the cobalt atoms are σ-bonded to the bridging oxygen atoms, as shown in the Figure. The

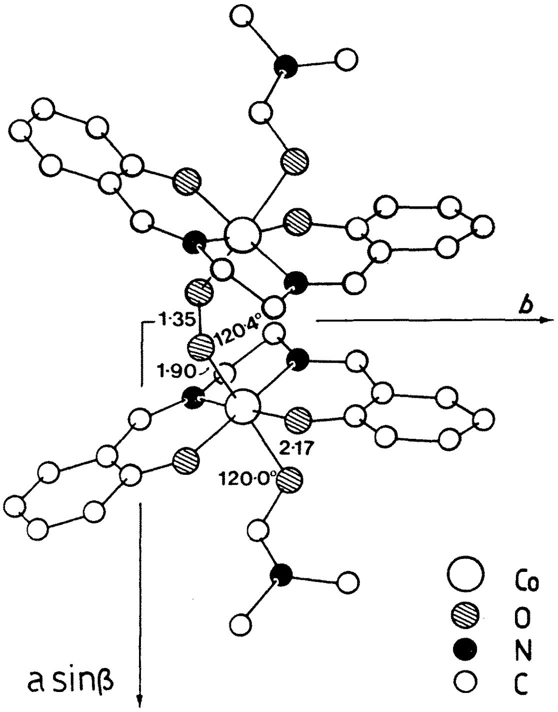

FIGURE. *A sketch of the dimer as viewed along the* c *axis.*

two halves of the dimer are related by a crystallographic two-fold axis. The co-ordinating ligands about the cobalt atoms form distorted octahedra. The equatorial positions are occupied by the tetradentate "salen" ligand with average Co–O and Co–N distances of 1·91 ± 0·01 Å and 1·90 ± 0·01 Å, respectively. The dimethylformamide molecule, planar within 0·02 Å, is bonded in an axial position through its oxygen atom, the Co–O distance being 2·17 ± 0·01 Å. The other axial position is occupied by an oxygen atom of the O_2 bridge with the Co–O distance of 1·90 ± 0·01 Å. The O–O bond length is 1·35 ± 0·01 Å and the Co–O–O bond angle is 120·4 ± 0·3°. The torsional angle around the O–O bond of the Co–O–O–Co group is 108·7°.

The non-planarity of this group suggests a peroxide type of bonding. However, the value of the O–O bond length, smaller than that expected for a peroxo bridge (1·48 Å), may be indicative of a partial transfer of electrons from cobalt to oxygen. This appears to be related to the reversibility of the oxygenation.

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