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Molecular Structure (X-Ray Analysis) of a Dinuclear Iron(III) Compound Formed with the $[N_4O_3]$ Ligand 'Sal$_3$trien'

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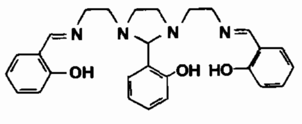
In our studies of metal compounds with multidentate ligands of non-classical shapes we have examined the reactions of the ligand I (abbreviated as sal$_3$trienH$_3$ [1]) with $FeCl_3$ in various solvents.



I

Whilst there is some evidence for a mononuclear complex [Fe(sal$_3$trien)], this is unstable, especially towards hydrolysis. In the presence of traces of water, crystals of various solvates of [Fe_2Cl_2(OH)-(sal$_3$trien)] are obtained as the major product. X-ray analyses of two such solvates have been performed, and the molecular structure observed is shown in the Figure.

Crystal Data

A. (Crystals from a sample separating first from methanol and then from 1,2-dichloroethane solution) [Fe_2Cl_2(OH)(sal$_3$trien)]·CH_3OH·$C_2H_4Cl_2$: $C_{30}H_{36}N_4O_5Cl_4Fe_2$, M = 786.1, tetragonal, a = 19.435(9), c = 18.598(8) Å, D_m = 1.52, D_c = 1.553 g cm^{-3}, Z = 8, Space Group *I4cm*.

B. (Crystals from tetrahydrofuran) [Fe_2Cl_2(OH)-(sal$_3$trien)]·C_4H_8O: $C_{31}H_{36}N_4O_5Cl_2Fe_2$, M = 727.3, orthorhombic, a = 15.375(7), b = 21.533(11), c = 19.346(10) Å, D_m = 1.50, D_c = 1.508 g cm^{-3}, Z = 8, Space Group *Pbca*.

X-ray data for **A** were collected on a Stoe Stadi-2 diffractometer using graphite monochromatised MoK$_\alpha$ radiation. A total of 1595 independent reflections with $I \geqslant \sigma(I)$, not corrected for absorption, were used for the analysis. The structure was solved by conventional Patterson and Fourier techniques and refined by block-diagonal least-squares procedures to a final R of 0.081. All non-hydrogen atoms were allowed anisotropic thermal parameters and hydrogen atoms were included at fixed calculated positions.

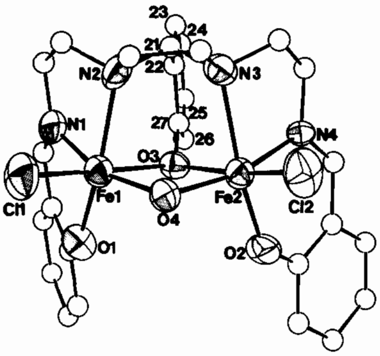


Figure. The structure of the dinuclear molecule in A and B.

The analysis revealed the dinuclear molecules as shown in the Figure, with a crystallographically imposed mirror plane {containing the atoms O(3), O(4) and C(21) to C(27)}. Due to considerable disorder of the solvent molecules satisfactory refinement was difficult; an analysis of the second crystalline modification, **B**, was therefore undertaken.

For **B** 1797 data with $I \geqslant 3\sigma(I)$ were obtained on a Philips PW1100 4-circle diffractometer. The iron and co-ordinated atoms were allowed to refine with anisotropic thermal parameters and the benzene rings were included as rigid bodies (C–C = 1.395 Å), giving a conventional R value of 0.076.

Again the analysis revealed the dinculear molecular species (Figure), this time without imposed mirror symmetry. The tetrahydrofuran molecules are hydrogen-bonded to the bridging OH groups. The molecular dimensions obtained from both analysis agree closely: details of the bond-lengths in the co-ordination polyhedra are given in the Table.

TABLE. Bond Lengths/Å in the Co-ordination Polyhedra of the Iron Atoms.

	Structure B		Structure A
Co-ordinating Atom	Fe(1)	Fe(2)	
O(1)/O(2)	1.87(1)	1.89(1)	1.90(1)
O(3)	2.08(1)	2.06(2)	2.08(1)
O(4)	1.98(1)	1.95(1)	1.98(2)
N(1)/N(4)	2.13(2)	2.10(1)	2.10(1)
N(2)/N(3)	2.28(2)	2.32(2)	2.28(1)
Cl(1)/Cl(2)	2.31(1)	2.30(1)	2.31(1)

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One feature of the observed structures is the remarkable correspondence of the Fe–N(2)/N(3) and the Fe–Cl bond lengths. Very few other observations of a tertiary amine N–Fe^{III} bond length have been published [2–5], but these do show values approaching 2.3 Å. Similarly, the Fe–Cl bond lengths agree closely with other observations of six-co-ordinate species [6, 7].

The formation of the di-iron compound in preference to the mononuclear [Fe(sal_3trien)] seems to be a result of the steric constraints of the ligand. Whilst molecular models indicate that the ligand could be *quinque*dentate, not using the two central tertiary-amine nitrogen atoms, the 'hole' is apparently too big for it to be a *septa*dentate to a single iron atom. Even for larger metal ions, such as La^{III}, mono-nuclear complexes do not appear to be formed [8]. The 1:1 La^{III} compound is a dimer [8], [La_2(sal_3trien)$_2$], and we can now postulate that it has a structure with the two ligands spanning two lanthanum atoms, much as in ref. 8, but with both central phenolates bridging both metals in the mode observed for the present iron compound.

Acknowledgments

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