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The Crystal and Molecular Structure of μ-Oxo-bis[bis-(*N*-*p*-chlorophenyl-salicylaldiminato)iron(III)]

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The crystal and molecular structure of the title compound has been determined by single-crystal X-ray analysis and refined to an R of 0·092 with diffractometer data. The crystals are orthorhombic, space group $Pna2_1$, with $a=16{\cdot}781$, $b=13{\cdot}794$, $c=19{\cdot}932$ Å, $Z=4$. The Fe–O–Fe bridge is symmetrical within experimental error with an Fe–O (bridge) bond length of 1·76 Å and an Fe–O–Fe angle of 175°.

Introduction

The crystal structures of a number of oxygen-bridged iron(III) complexes have now been determined and are listed in Table 1. These compounds are of particular interest because of their magnetic properties which arise from strong spin exchange *via* the Fe–O–Fe system (Lewis, Mabbs & Richards, 1967). However, the factors governing the geometry of the Fe–O–Fe bridge are not well understood. In three different crystalline environments the $[Fe(salen)]_2O$ molecule has been shown to have virtually the same ligand conformation and almost the same Fe–O–Fe angle (Table 1). This indicates that intermolecular forces do not play an important part in determining the magnitude of the Fe–O–Fe angle, at least in the case of $[Fe(salen)]_2O$. The fact that the Fe–O–Fe angle in $[Fe(salen)]_2O$ is at least 20° smaller than that in any of the other complexes in Table 1 has been attributed primarily to differing intramolecular forces (Davies & Gatehouse, 1973).

Compounds with the general formula $[Fe(sal\text{-}NR)_2]_2O$ were first reported by van den Bergen, Murray, O'Connor, Rehak & West (1968), who prepared them by the reaction of anhydrous $FeCl_3$ with the appropriate Schiff-base in the presence of excess triethylamine and a trace of water. We now report the structure of $[Fe(sal\text{-}N\text{-}p\text{-}chlorophenyl)_2]_2O$ which has been determined to provide further information on this class of compound.

Experimental

Suitable crystals of μ-oxo-bis[bis-(*N*-*p*-chlorophenyl-sal)Fe(III)] were prepared by the method of van den Bergen *et al.* (1968) and were kindly supplied by Dr K. S. Murray of the Chemistry Department, Monash University. The crystals are deep red prisms, elongated along **b**. The crystal morphology is illustrated in Fig. 1.

An interesting feature of the X-ray diffraction patterns obtained from these crystals (and from crystals of the isostructural *p*-bromophenyl derivative) is the existence of marked diffuse scattering. Weissenberg photographs of reciprocal lattice levels *hkl* with *k* odd (Fig. 2) show that diffuse rods extend parallel to **a**. Subsequent solution of the structure of μ-oxo-bis[bis-(*N*-*p*-chlorophenyl-sal)Fe(III)] has shown that the molecular conformation and crystal packing are consistent with this observed diffuse scattering (see later discussion).

Crystal data

$C_{52}Cl_4Fe_2H_{36}N_4O_5$, $M=1050{\cdot}4$, orthorhombic, $a=16{\cdot}781\,(8)$, $b=13{\cdot}794\,(7)$, $c=19{\cdot}932\,(10)$ Å. $U=4614$ Å^3, $D_m=1{\cdot}50$ g cm^{-3} (by flotation), $Z=4$, $D_c=1{\cdot}51$ g cm^{-3}. $F(000)=2144$, $\mu=8{\cdot}71$ cm^{-1} for Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). Space group $Pnma$ (D_{2h}^{16}, No. 62) or $Pna2_1$ (C_{2v}^{9}, No. 33) from systematic absences. Subsequent solution of the structure has proved the space group to be $Pna2_1$. The unit-cell parameters were obtained

Table 1. *Previous structural determinations of compounds containing an* Fe–O–Fe *arrangement*

Compound	Fe–O–Fe(°)	Reference
$[Fe(salen)]_2O\,.\,2py$	139·1	Gerloch, McKenzie & Towl (1969)
$[Fe(salen)]_2O\,.\,CH_2Cl_2$	142·4	(i) Coggon, McPhail, Mabbs & McLachlan (1971). (ii) Atovmyan, D'yachenko & Soboleva (1970)
$[Fe(salen)]_2O$	144·6	Davies & Gatehouse (1973)
$[Fe(HEDTA)]_2O^{2-}$	165·0	Lippard, Schugar & Walling (1967)
$[Fe(TPP)]_2O$	174·5	Hoffman, Collins, Day, Fleischer, Scrivastava & Hoard (1972)
$[Fe(N\text{-n-propyl-sal})_2]_2O$	164	Davies & Gatehouse (1972*b*)
$[(H_2O)BFe\text{-}O\text{-}FeB(H_2O)]_4^-$	180	Fleischer & Hawkinson (1966) (crude data only)

* salen = *N*,*N*′-ethylenebis(salicylaldiminato). HEDTA = *N*-hydroxyethyl-ethylenediaminetriacetato. TPP = α,β,γ,δ-tetraphenylporphinato. sal = salicylaldiminato B = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12,3,1]octadeca-1(18),2,12,14,16-pentaene.

with a Philips PW 1100 computer controlled X-ray diffractometer.

Intensity measurements

Intensities were collected from a crystal having dimensions 0·10 × 0·25 × 0·40 mm with the diffractometer and Mo $K\alpha$ radiation. A unique data set was collected out to $2\theta(\text{Mo } K\alpha)=47°$ by the θ–2θ scan technique with a symmetric scan range of ± 0·8° in 2θ from the calculated scattering angle. The scan rate was 0·025° sec.^{-1}. The Mo $K\alpha$ radiation was monochromatized with a flat graphite monochromator crystal. No reflexion was sufficiently strong to require the insertion of an attenuation filter. Processing of the data was carried out in the manner previously described (Davies & Gatehouse, 1973) to yield values of F_o^2 and $\sigma(F_o^2)$. A value of 0·04 was used for p in the estimation of $\sigma(F_o^2)$. No corrections were applied for extinction or absorption.

The intensities of 2146 independent reflexions were measured. Of these, 1225 have $F_o^2>2\sigma(F_o^2)$ and 1535 have $F_o^2>\sigma(F_o^2)$. For subsequent calculations it was decided to use all 1535 reflexions having $F_o^2>\sigma(F_o^2)$, for with 67 atoms in the asymmetric unit even this gives a parameter to data ratio of only 1:5. Approximately one fifth of the reflexions used in the refinement of the structure therefore have $F_o^2<2\sigma(F_o^2)$. This is due (at least in part) to the difficulty of accurate measurement of the intensities of those reflexions affected by the presence of diffuse scatter.

Structure solution and refinement

The structure was solved with a set of visually estimated Cu $K\alpha$ intensity data collected by Gardner (1970) for the isostructural *p*-bromophenyl derivative. Initial attempts to solve the structure by vector methods were unsuccessful (Gardner, 1970), primarily because the Patterson function can be solved for the positions of six heavy atoms if the space group is assumed to be *Pnma*. Subsequent solution of the structure has shown that Gardner's heavy-atom solution in space group *Pnma* is substantially correct but that the carbon, nitrogen and oxygen atoms do not conform to *Pnma* symmetry.

The structure was finally solved by direct methods with the program *MULTAN* (Germain, Main & Woolfson, 1970) in the (correct) space group $Pna2_1$. The 253 reflexions for which $|E|>1{\cdot}30$ were used as input. This gave only one set of phases containing 244 phased reflexions. An E map revealed the positions of the six heavy atoms and approximate positions for several of the light atoms. A large number of subsequent structure-factor calculations and difference syntheses with the complete set of visual data (1216 reflexions) finally gave positions for all 67 atoms in the asymmetric unit. An attempt was then made to refine the structure by conventional block-diagonal methods, minimizing the function $\sum w(|F_o|-|F_c|)^2$. Ten cycles of refinement with individual isotropic temperature factors for each atom and with each reflexion assigned unit weight gave $R_1=0{\cdot}151$ and $R_2=0{\cdot}170$ where

$$R_1=\sum||F_o|-|F_c||/\sum|F_o|$$

and

$$R_2=(\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2)^{1/2}\,.$$

Bond lengths and angles within the molecule were reasonable, indicating that the basic structure solution was correct. The high R was attributed to the data,

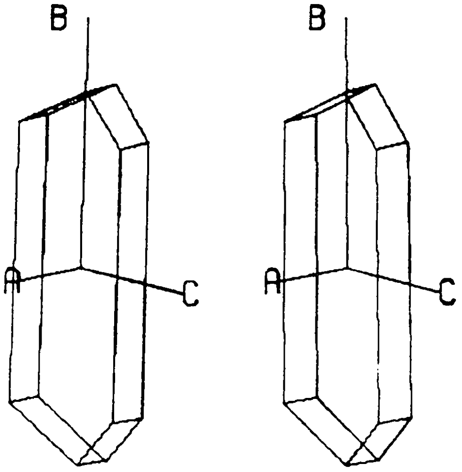

Fig. 1. The crystal morphology of μ-oxo-bis[bis-(*N*-*p*-chlorophenylsalicylaldiminato)Fe(III)].

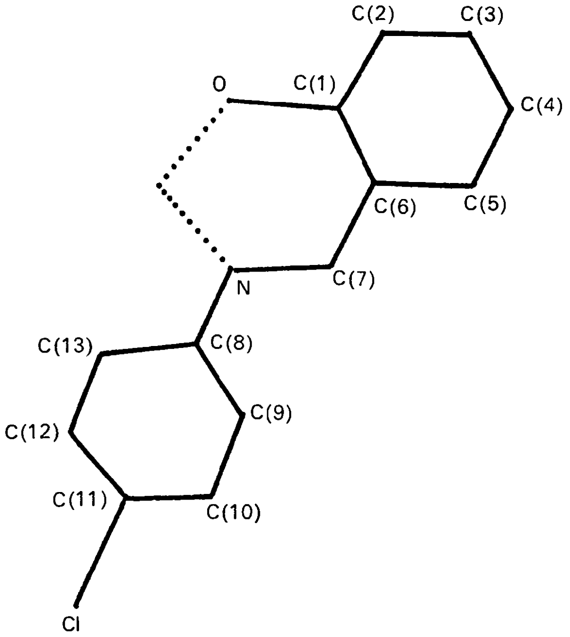

Fig. 3. Labelling scheme for the atoms in one salicylaldimine ligand. The four distinct ligands in the molecule are distinguished in Table 2 by an *A*, *B*, *C* or *D* suffix. Ligands *A* and *B* are attached to Fe(1), *C* and *D* to Fe(2).

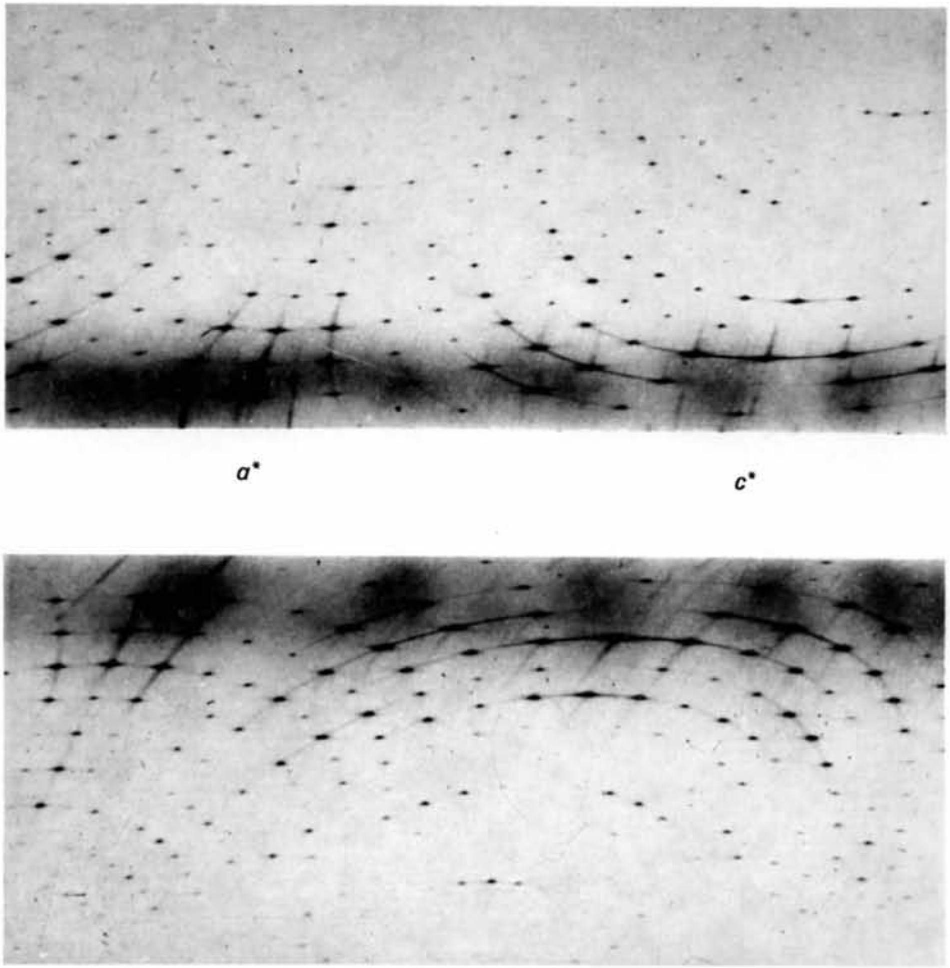

Fig. 2. Equi-inclination Weissenberg photograph of μ-oxo-bis-[bis-(N-p-chlorophenylsalicylaldiminato)Fe(III)], giving the section $h1l$ of reciprocal space. (Co $K\alpha$ radiation.)

which were of poor quality for the following reasons. The data were collected with Cu $K\alpha$ radiation which has a wavelength close to the K absorption edge of iron. This had the effect of markedly increasing the background against which the reflexions were measured and therefore decreasing the total number of observed reflexions. Accurate estimation of the intensities was made even more difficult by the presence of diffuse scattering (Fig. 2). Finally, the lack of sufficiently accurate data, the necessity of using a block-diagonal refinement method (because of computer store limitations) and the presence of four bromine and two iron atoms forming an approximate mirror plane in the asymmetric unit, made the successful refinement of the carbon, nitrogen and oxygen atoms difficult.

To minimize most of these difficulties, a complete set of Mo $K\alpha$ intensity data was collected from a crystal of the isostructural *p*-chlorophenyl derivative. The atom coordinates from the last refinement of the *p*-bromophenyl structure were used as a starting point for the new calculations. After eight block-diagonal least-squares cycles with anisotropic temperature factors for the iron and chlorine atoms, the refinement converged with $R_1=0{\cdot}092$ and $R_2=0{\cdot}072$. The success of the weighting scheme [which is very important in this case as one fifth of the data has $F_o^2<2\sigma(F_o^2)$] is demonstrated by the fact that R_2 is some 2% smaller than R_1. A final difference synthesis showed random fluctuations no greater than 0·6 eÅ^{-3}, and the refinement was considered to be complete.

The labelling used for the molecule is defined in Fig. 3 and final values for the positional and vibrational parameters are listed in Table 2, with their estimated standard deviations derived from the inverse least-squares matrix. Table 3 lists the observed and calculated structure factors.

Table 2. *Final positional and thermal parameters*

Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant digits. The B values are the parameters in the isotropic temperature factor expression $\exp[-B(\sin\theta)^2/\lambda^2]$. The U_{ij} are $\times 10^2$ and the atomic scattering factors for the iron and chlorine atoms are expressed as $f=f_0\exp[-2\pi^2(U_{11}a^{*2}h^2+\cdots+2U_{23}b^*c^*kl+\cdots)]$.

(*a*) Positional parameters and isotropic temperature factors.

	x/a	y/b	z/c	$B(\text{Å}^2)$
oxo	0·2881 (7)	0·6301 (8)	0·2785 (13)	3·0 (3)
O*A*	0·4447 (7)	0·7388 (9)	0·2311 (7)	3·1 (4)
C(1)*A*	0·4419 (11)	0·7636 (13)	0·1679 (13)	2·6 (5)
C(2)*A*	0·4600 (11)	0·8622 (15)	0·1566 (13)	3·0 (5)
C(3)*A*	0·4548 (12)	0·8893 (14)	0·0904 (13)	3·1 (5)
C(4)*A*	0·4268 (13)	0·8302 (16)	0·0325 (14)	4·1 (6)
C(5)*A*	0·4139 (11)	0·7358 (15)	0·0483 (13)	2·9 (5)
C(6)*A*	0·4214 (11)	0·7018 (13)	0·1181 (13)	2·2 (5)
C(7)*A*	0·4090 (11)	0·5928 (15)	0·1251 (23)	3·5 (6)
N*A*	0·4070 (9)	0·5558 (12)	0·1860 (10)	3·0 (4)
C(8)*A*	0·4107 (10)	0·4483 (14)	0·1836 (12)	2·0 (5)
C(9)*A*	0·4715 (12)	0·4009 (14)	0·1486 (14)	3·4 (6)
C(10)*A*	0·4737 (12)	0·3009 (14)	0·1507 (14)	3·5 (6)
C(11)*A*	0·4165 (12)	0·2547 (16)	0·1883 (13)	4·1 (6)
C(12)*A*	0·3575 (12)	0·2958 (14)	0·2263 (13)	2·9 (5)
C(13)*A*	0·3541 (12)	0·4004 (14)	0·2222 (13)	3·0 (5)
O*B*	0·4471 (8)	0·5331 (9)	0·3226 (8)	3·5 (4)
C(1)*B*	0·4326 (11)	0·5054 (13)	0·3830 (13)	2·3 (5)
C(2)*B*	0·4435 (12)	0·4026 (14)	0·4021 (14)	3·2 (5)
C(3)*B*	0·4324 (12)	0·3671 (16)	0·4653 (14)	3·8 (6)
C(4)*B*	0·4082 (13)	0·4269 (16)	0·5183 (14)	4·0 (6)
C(5)*B*	0·4021 (12)	0·5311 (14)	0·5004 (13)	3·1 (6)
C(6)*B*	0·4107 (11)	0·5675 (13)	0·4349 (13)	2·3 (5)
C(7)*B*	0·4023 (11)	0·6668 (14)	0·4262 (12)	2·9 (6)
N*B*	0·4017 (9)	0·7134 (11)	0·3687 (10)	2·9 (4)
C(8)*B*	0·3985 (12)	0·8187 (14)	0·3685 (12)	3·0 (5)
C(9)*B*	0·4607 (11)	0·8637 (14)	0·4083 (12)	3·1 (5)
C(10)*B*	0·4595 (12)	0·9665 (14)	0·4072 (13)	3·0 (5)
C(11)*B*	0·4064 (11)	1·0134 (14)	0·3659 (13)	3·0 (5)
C(12)*B*	0·3449 (13)	0·9677 (16)	0·3308 (14)	4·1 (6)
C(13)*B*	0·3487 (12)	0·8662 (15)	0·3305 (13)	3·1 (5)

	x/a	y/b	z/c	$B(\text{Å}^2)$
O*C*	0·1364 (8)	0·5288 (9)	0·2254 (8)	3·5 (4)
C(1)*C*	0·1529 (12)	0·5061 (14)	0·1598 (14)	3·2 (5)
C(2)*C*	0·1436 (13)	0·4048 (15)	0·1444 (14)	3·7 (6)
C(3)*C*	0·1631 (13)	0·3786 (17)	0·0780 (14)	4·5 (7)
C(4)*C*	0·1792 (13)	0·4477 (16)	0·0258 (15)	4·4 (6)
C(5)*C*	0·1903 (13)	0·5417 (16)	0·0425 (16)	4·3 (6)
C(6)*C*	0·1753 (12)	0·5699 (14)	0·1106 (14)	3·6 (6)
C(7)*C*	0·1801 (13)	0·6784 (15)	0·1227 (14)	3·9 (6)
N*C*	0·1724 (8)	0·7135 (10)	0·1808 (10)	2·2 (4)
C(8)	0·1795 (12)	0·8188 (14)	0·1807 (13)	3·1 (5)
C(9)*C*	0·1221 (11)	0·8723 (14)	0·2160 (13)	3·1 (5)
C(10)*C*	0·1279 (12)	0·9770 (15)	0·2166 (14)	3·5 (6)
C(11)*C*	0·1912 (11)	1·0159 (14)	0·1771 (13)	2·7 (5)
C(12)*C*	0·2494 (13)	0·9659 (15)	0·1443 (15)	4·0 (6)
C(13)*C*	0·2433 (11)	0·8619 (14)	0·1466 (13)	2·9 (5)
O*D*	0·1347 (8)	0·7306 (9)	0·3229 (8)	3·4 (4)
C(1)*D*	0·1453 (12)	0·7532 (15)	0·3836 (13)	3·5 (5)
C(2)*D*	0·1227 (11)	0·8528 (14)	0·4041 (13)	3·0 (5)
C(3)*D*	0·1270 (12)	0·8799 (15)	0·4726 (13)	3·8 (6)
C(4)*D*	0·1502 (13)	0·8098 (16)	0·5219 (14)	4·1 (6)
C(5)*D*	0·1702 (14)	0·7144 (16)	0·5042 (14)	4·5 (6)
C(6)*D*	0·1651 (12)	0·6860 (14)	0·4383 (14)	3·2 (6)
C(7)*D*	0·1735 (11)	0·5858 (12)	0·4251 (12)	2·0 (5)
N*D*	0·1654 (8)	0·5451 (10)	0·3642 (10)	2·2 (4)
C(8)*D*	0·1746 (13)	0·4381 (15)	0·3625 (14)	3·9 (6)
C(9)*D*	0·2352 (11)	0·3948 (14)	0·3996 (13)	3·0 (5)
C(10)*D*	0·2315 (12)	0·2894 (14)	0·4006 (14)	3·5 (6)
C(11)*D*	0·1719 (11)	0·2429 (14)	0·3670 (13)	3·1 (5)
C(12)*D*	0·1120 (13)	0·2838 (16)	0·3326 (14)	4·0 (6)
C(13)*D*	0·1093 (12)	0·3874 (15)	0·3288 (13)	3·2 (5)

(*b*) Positional parameters and anisotropic temperature factors

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe(1)	0·3930 (1)	0·6333 (2)	0·2763 (3)	3·6 (2)	2·7 (1)	2·8 (3)	−0·2 (2)	0·3 (3)	−0·2 (2)
Fe(2)	0·1830 (1)	0·6301 (2)	0·2732 (3)	3·5 (2)	2·7 (1)	3·2 (4)	0·0 (2)	−0·1 (3)	0·1 (2)
Cl*A*	0·4249 (3)	0·1252 (4)	0·1933 (4)	7·2 (4)	2·9 (3)	8·8 (9)	0·3 (3)	−1·4 (5)	−0·5 (4)
Cl*B*	0·4004 (3)	1·1407 (4)	0·3739 (4)	6·5 (4)	2·7 (3)	7·5 (9)	−0·1 (3)	1·5 (5)	−0·7 (4)
Cl*C*	0·1945 (3)	1·1453 (4)	0·1789 (4)	7·4 (5)	3·0 (3)	10·3 (1·0)	−0·6 (3)	−1·3 (5)	0·2 (4)
Cl*D*	0·1719 (3)	0·1150 (4)	0·3773 (4)	6·6 (4)	2·7 (3)	8·8 (9)	−0·2 (3)	0·7 (5)	0·3 (4)

The scattering factors were those tabulated by Ibers (1962) and the major programs used during the refinement were modified versions of the SF block-diagonal least-squares program of Shiono (1968) and the Fourier summation program of White (1965). Diagrams were drawn with the program *ORTEP* (Johnson, 1965) and all calculations were performed on the Monash University CDC 3200 and B5500 computers.

Table 3. *Observed and calculated structure factors*

$|F_o|$ and $|F_c|$ are × 10. Those reflexions for which $F_o^2 < \sigma(F_o^2)$ are indicated by an asterisk.

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Table 3 (*cont.*)

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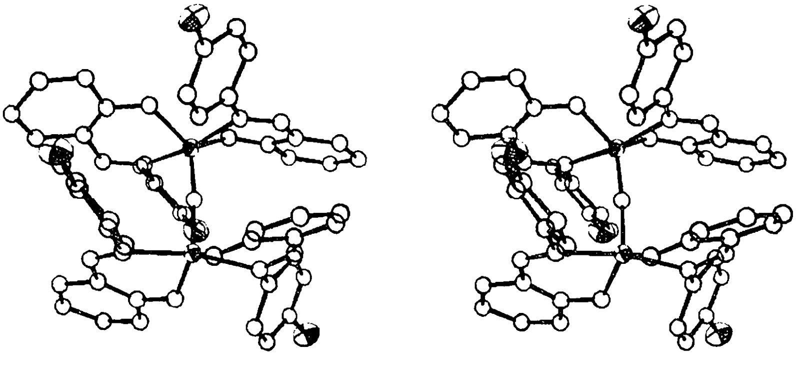

Fig. 4. The molecular structure of μ-oxo-bis[bis-(N-p-chlorophenylsalicylaldiminato)Fe(III)].

Discussion of the structure

The molecular conformation is illustrated in Fig. 4. Both iron atoms are five-coordinate with a stereochemistry very similar to that observed in the monomer chlorobis-(*N*-n-propyl-sal)iron(III) (Davies & Gatehouse, 1972*a*) and the dimer μ-oxo-bis[bis-(*N*-n-propyl-sal)iron(III)] (Davies & Gatehouse, 1972*b*). This stereochemistry can perhaps best be described as intermediate between trigonal bipyramidal (with the two nitrogen atoms apical) and square pyramidal (with the oxygen bridge atom apical).

With the two nitrogen atoms in one (*p*-chlorophenyl-sal)$_2$Fe moiety *trans* to each other (a *cis* configuration would involve very large steric interactions), there are two possible arrangements for the four salicylaldimine groups in the molecule (Fig. 5). The arrangement adopted in both μ-oxo-bis[bis-(*N*-*p*-chlorophenyl-sal)-Fe(III)] and μ-oxo-bis[bis-(*N*-*n*-propyl-sal)Fe(III)] (Davies & Gatehouse, 1972) is that depicted in Fig. 5(*b*). It is interesting to note that the four *p*-chlorophenyl groups in the former molecule are arranged approximately parallel to each other, and so are the four n-propyl groups in the latter (Fig. 7). This particular arrangement appears to minimize intramolecular interactions.

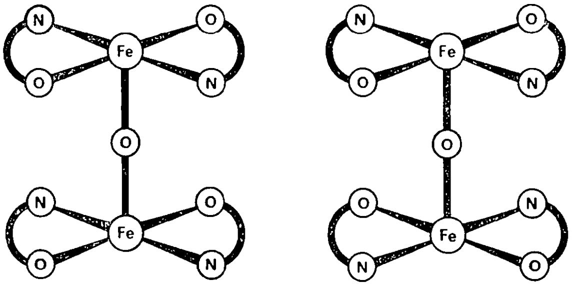

Fig. 5. The two possible arrangements of the four salicylaldimine groups within the molecule (assuming *trans* oxygen and nitrogen atoms).

The packing is illustrated in Figs. 6 and 7. There are no unusual intermolecular contacts and (excluding the hydrogen atoms) the shortest intermolecular contact is 3·31 Å between atoms C(10)*A* and C(4)*D* ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $-\frac{1}{2}+z$).* The molecules pack such that all iron and chlorine atoms in the structure are related by approximate mirror planes at $z=\frac{1}{4},\frac{3}{4}$ (Fig. 6) and this confused early attempts to solve the structure (Gardner, 1970). Chlorine atoms related by these 'mirror planes' belong to separate molecules, however, and the space group is not *Pnma* as Gardner originally believed.

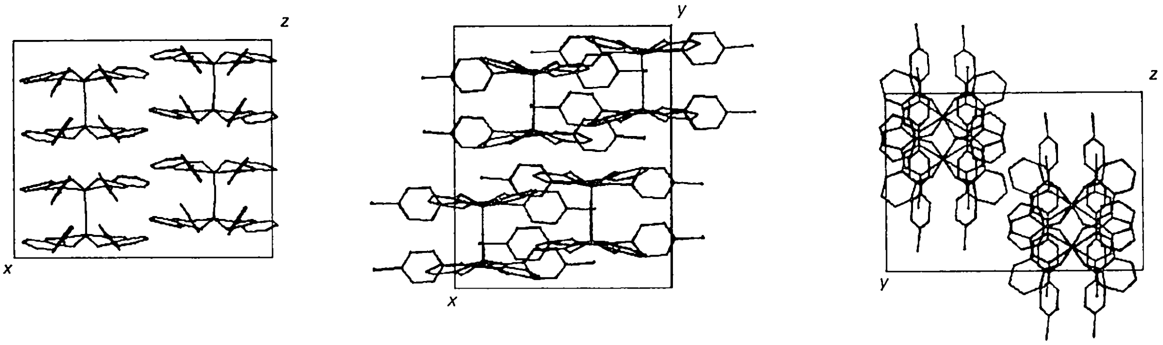

Fig. 6. Projection diagrams of the structure looking down each crystal axis in turn.

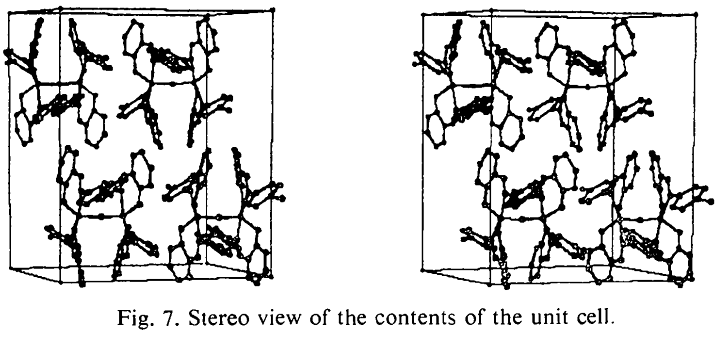

Fig. 7. Stereo view of the contents of the unit cell.

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* The symmetry transformation in parentheses is that to be applied to coordinates listed in Table 1.

The two salicylaldimine groups in each (*N*-*p*-chlorophenyl-sal)$_2$Fe moiety are approximately planar and all such moieties in the structure are orientated parallel to one another (Fig. 6). This arrangement can be correlated with the observed diffuse scattering (Fig. 2). The characteristic feature of diffuse patterns from structures containing flat molecules which are orientated parallel to each other is the presence of diffuse rods in reciprocal space extending in a direction normal to the plane of the molecules (Wooster, 1962). This is exactly what is observed in the present structure. The diffuse rods extend parallel to **a** and therefore normal to the salicylaldimine planes. The diffuse clouds far removed from reciprocal lattice points are probably due to molecular vibrations and librations and it is likely that the scattering near to reciprocal lattice points is related to the elastic constants as simple inorganic compounds (Wooster, 1962).

Table 4. *Selected intramolecular distances and angles*

(*a*) Distances (Å)

	A	*B*	*C*	*D*
Fe——N	2·11 (2)	2·15 (2)	2·18 (2)	2·18 (2)
Fe——O	1·92 (1)	1·89 (2)	1·86 (2)	1·89 (2)
O——C(1)	1·31 (3)	1·29 (3)	1·37 (3)	1·26 (3)
C(1)—C(2)	1·41 (3)	1·48 (3)	1·44 (3)	1·48 (3)
C(1)—C(6)	1·35 (3)	1·39 (3)	1·37 (4)	1·47 (4)
C(2)—C(3)	1·37 (4)	1·36 (4)	1·41 (4)	1·42 (4)
C(3)—C(4)	1·49 (4)	1·40 (4)	1·44 (4)	1·43 (4)
C(4)—C(5)	1·36 (3)	1·49 (3)	1·35 (3)	1·40 (3)
C(5)—C(6)	1·47 (4)	1·41 (4)	1·43 (4)	1·37 (4)
C(6)—C(7)	1·52 (3)	1·39 (3)	1·52 (3)	1·41 (3)
C(7)—N	1·32 (5)	1·31 (3)	1·26 (3)	1·34 (3)
N——C(8)	1·49 (3)	1·45 (3)	1·46 (3)	1·48 (3)
C(8)—C(9)	1·40 (3)	1·45 (3)	1·40 (3)	1·39 (3)
C(9)—C(10)	1·38 (3)	1·42 (3)	1·45 (3)	1·46 (3)
C(10)–C(11)	1·38 (3)	1·37 (3)	1·43 (3)	1·36 (3)
C(11)–C(12)	1·37 (3)	1·40 (3)	1·36 (3)	1·34 (3)
C(12)–C(13)	1·45 (3)	1·40 (3)	1·44 (3)	1·43 (3)
C(13)–C(8)	1·39 (3)	1·30 (3)	1·40 (3)	1·46 (3)
C(11)–Cl	1·80 (2)	1·77 (2)	1·79 (2)	1·78 (2)

(*b*) Angles (°)	*A*	*B*	*C*	*D*
oxo—Fe——N	96·9 (7)	93·4 (7)	97·6 (7)	94·9 (7)
oxo—Fe——O	118·9 (7)	116·7 (7)	116·7 (7)	113·4 (7)
O——Fe——N	86·2 (7)	85·7 (7)	86·0 (7)	86·0 (7)
O——Fe——N′	89·0 (7)	89·6 (7)	88·0 (7)	91·2 (7)
O——Fe——O′	124·4 (7)		129·7 (7)	
N——Fe——N′	169·7 (7)		167·5 (7)	
Fe——O——C(1)	129 (1)	126 (1)	125 (1)	129 (1)
O——C(1)—C(2)	114 (2)	120 (2)	114 (2)	117 (2)
C(2)—C(1)—C(6)	123 (2)	116 (2)	120 (2)	116 (2)
O——C(1)—C(6)	124 (2)	124 (2)	126 (2)	126 (2)
C(2)—C(1)—C(6)	123 (2)	116 (2)	120 (2)	116 (2)
C(2)—C(3)—C(4)	128 (2)	122 (2)	124 (2)	120 (2)
C(3)—C(4)—C(5)	113 (2)	114 (2)	119 (2)	122 (2)
C(4)—C(5)—C(6)	121 (2)	124 (2)	118 (2)	120 (2)
C(5)—C(6)—C(1)	121 (2)	119 (2)	124 (2)	123 (2)
C(5)—C(6)—C(7)	113 (2)	117 (2)	114 (2)	117 (2)
C(1)—C(6)—C(7)	126 (2)	123 (2)	122 (2)	120 (2)
C(6)—C(7)—N	118 (2)	126 (2)	121 (2)	125 (2)
C(7)—N——Fe	126 (2)	120 (1)	124 (2)	121 (1)
C(7)—N——C(8)	111 (2)	120 (2)	112 (2)	115 (2)
C(8)—N——Fe	123 (1)	121 (1)	121 (1)	120 (1)
C(8)—C(9)—C(10)	118 (2)	114 (2)	119 (2)	114 (2)
C(9)—C(10)–C(11)	118 (2)	119 (2)	115 (2)	120 (2)
C(10)–C(11)–C(12)	128 (2)	125 (2)	127 (2)	127 (2)
C(11)–C(12)–C(13)	114 (2)	115 (2)	116 (2)	118 (2)
C(12)–C(13)–C(8)	119 (2)	122 (2)	120 (2)	115 (2)
C(13)–C(8)—C(9)	124 (2)	124 (2)	123 (2)	126 (2)
C(10)–C(11)–Cl	116 (2)	117 (2)	113 (2)	114 (2)
C(12)–C(11)–Cl	116 (2)	117 (2)	120 (2)	119 (2)

(*c*) Fe–O–Fe geometry

Fe(1)–oxo	1·76 (1) Å	Fe(1)–oxo–Fe(2)	175 (1)°
Fe(2)–oxo	1·77 (1)		

Intramolecular distances and angles are listed in Table 4. Equations defining pertinent least-squares planes (Blow, 1960) are quoted in Table 5 with the deviations of individual atoms from the planes. Bond lengths within the salicylaldimine groups are consistent with average values reported by Lingafelter & Brown (1966) and are in good agreement with values reported for the analogous n-propyl derivative (Davies & Gatehouse, 1972*b*). In the *p*-chlorophenyl groups, the average carbon–carbon distance is 1·40 Å and the average angle between any three adjacent carbon atoms is 120°. While these averages are in good agreement with the values observed in *p*-chloroaniline (Trotter, Whitlow & Zobel, 1966), individual distances and angles show deviations of up to 0·6 Å and 8° respectively (Table 4). The present authors believe that these deviations from the average values are not chemically

Table 5. *Weighted least-squares planes**

(*a*) Deviations from the planes (Å)

	Plane *A*1	*B*1	*C*1	*D*1
O	−0·06 (1)	−0·04 (1)	0·02 (1)	0·03 (2)
C(1)	0·00 (2)	0·01 (2)	−0·01 (2)	0·10 (2)
C(2)	0·04 (2)	0·00 (2)	0·03 (2)	−0·04 (2)
C(3)	0·06 (2)	0·01 (2)	−0·05 (2)	−0·08 (2)
C(4)	−0·06 (2)	0·04 (2)	0·05 (2)	−0·04 (2)
C(5)	−0·04 (2)	−0·04 (2)	−0·03 (2)	0·07 (2)
C(6)	−0·01 (2)	0·01 (2)	−0·03 (2)	0·09 (2)
C(7)	0·08 (2)	−0·06 (2)	0·04 (2)	−0·02 (2)
N	−0·01 (2)	0·07 (2)	−0·02 (2)	−0·11 (2)
	Plane *A*2	*B*2	*C*2	*D*2
C(8)	0·01 (2)	−0·01 (2)	0·02 (3)	0·02 (3)
C(9)	−0·02 (3)	0·01 (2)	0·01 (3)	−0·01 (3)
C(10)	0·00 (3)	−0·02 (3)	−0·03 (3)	−0·01 (3)
C(11)	0·02 (3)	0·04 (3)	0·03 (3)	0·01 (3)
C(12)	−0·02 (2)	−0·05 (3)	−0·01 (3)	0·00 (3)
C(13)	0·01 (2)	0·03 (2)	−0·02 (3)	−0·01 (3)
N*	−0·07 (2)	0·05 (2)	0·05 (2)	−0·15 (2)
Cl*	−0·06 (1)	−0·19 (1)	0·01 (1)	−0·10 (1)

(*b*) Plane equations (defined such that *X*, *Y*, *Z* are coordinates n Å relative to the orthogonal crystal axes *a*, *b*, *c*).

Plane	Equation			
*A*1	0·9672*X*	−0·2109*Y*	−0·1417*Z*	−4·4767 = 0
*A*2	−0·6030	−0·0520	−0·7961	+7·4011
*B*1	−0·9630	−0·1729	−0·2067	+9·7874
*B*2	0·6278	−0·0247	−0·7780	+1·7796
*C*1	−0·9655	0·1359	−0·2219	+2·2303
*C*2	−0·5688	0·0233	−0·8222	+4·4287
*D*1	0·9694	0·2043	−0·1358	−3·3467
*D*2	0·5583	−0·0349	−0·8289	+4·5817

* Planes *A*1, *A*2 refer to ligand *A*; *B*1, *B*2 to ligand *B*, *etc.* Atoms not used to define the plane are indicated by an asterisk.

significant and that instead they reflect the overall accuracy of the structure determination. The standard deviations from the block-diagonal least-squares refinement are almost certainly underestimated and more realistic values for these standard deviations may be two to three times those quoted in Table 3.

The geometry of the Fe–O–Fe bridge is of particular interest. Within the errors of this determination the two Fe–O(bridge) bond lengths are equal ($1\cdot76_5$ Å) and are typical of the short Fe–O(bridge) distances observed in all other oxo-bridged iron(III) structures which have so far been studied (Table 1). Despite the constancy of the Fe–O(bridge) bond lengths, the Fe–O–Fe angles listed in Table 1 show marked angular differences which have been the subject of much speculation and discussion. The degree of π-bonding with the oxygen atom (which should make the system more linear as the degree increases) is certainly of some relevance to the problem, although it is difficult to explain why there is no apparent tendency for the Fe–O(bridge) distances to decrease with increasing Fe–O–Fe angle. The 25° difference between the Fe–O–Fe angles in $[Fe(salen)]_2O.2py$ and $[Fe(N\text{-n-propyl-sal})_2]_2O$ (Table 1) is also difficult to explain by purely π-bonding arguments because with such similar ligands, one would perhaps expect similar angles.

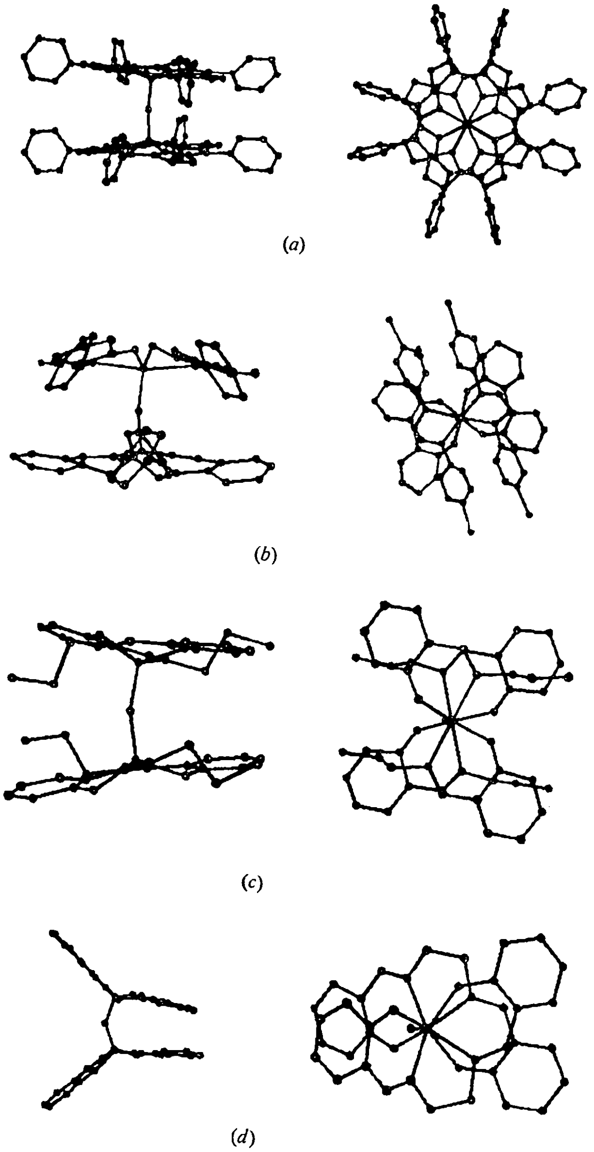

Fig. 8 (*a*) $[Fe(TPP)]_2O$ (Hoffman, Collins, Day, Fleischer, Scrivastava & Hoard, 1972). (*b*) $[Fe(N\text{-}p\text{-chlorophenyl-sal})_2]_2O$ (this work). (*c*) $[Fe(N\text{-n-propyl-sal})_2]_2O$ (Davies & Gatehouse, 1972*b*). (*d*) $[Fe(salen)]_2O.2py$ (Gerloch, McKenzie & Towl, 1969). In each case, the diagram on the left is drawn with the Fe–O–Fe plane parallel to the plane of the paper and that on the right is drawn looking down the Fe-Fe direction.

Intermolecular (crystal-packing) forces also do not seem to be a dominant factor, at least in the case of $[Fe(salen)]_2O$, since this molecule has virtually the same Fe–O–Fe angle in three completely different environments (Table 1). Furthermore, in these three different crystal structures, the conformations of the $[Fe(salen)]_2O$ molecules are almost identical, each consisting of two umbrella shaped Fe(salen) moieties linked by the oxygen atom bridge (Fig. 8). This is in contrast with the conformations of $[Fe(TPP)]_2O$, $[Fe(N\text{-n-propyl-sal})_2]_2O$ and $[Fe(N\text{-}p\text{-chlorophenyl-sal})_2]_2O$ which all contain two approximately planar moieties arranged parallel to each other (Fig. 8). This suggests a rationalization of the Fe–O–Fe angles in these compounds in terms of the observed ligand conformations. The 'clothes-peg' shape of $[Fe(salen)]_2O$ allows the Fe–O–Fe angle to be as small as 140° in this molecule whereas such an angle in, for example, $[Fe(TPP)]_2O$ would presumably cause large intramolecular interactions.

The Fe–O–Fe angle in these compounds therefore seems to depend primarily on the conformation of the ligands attached to the iron atoms. This suggests that in a molecule such as $[Fe(sal\text{-}o\text{-phen})]_2O$,* where the Fe(sal-*o*-phen) moieties are almost certainly planar, the observed Fe–O–Fe angle will be close to 180°.

The conformational differences between $[Fe(salen)]_2O$ and $[Fe(N\text{-n-propyl-sal})_2]_2O$ are difficult to explain, however, for if an Fe–O–Fe angle of approximately 140° is favoured, then one might expect the salicylaldimine residues in the n-propyl compound to have umbrella conformations as they do in chlorobis-$(N\text{-n-propyl-sal})_2Fe(III)$ (Davies & Gatehouse, 1972*a*). It must be stressed, therefore, that the rationalization of the Fe–O–Fe angles proposed here is only in terms of the *observed* ligand conformations.

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* sal-*o*-phen = *N*,*N'*-*o*-phenylenebis(salicylaldiminato).

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Crystal Structure of 3,5-Dimethyl-4-nitrobenzoic Acid

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The crystals have the space group $P2_1/a$ with four molecules per unit cell and $a = 11{\cdot}965$, $b = 10{\cdot}207$, $c = 8{\cdot}364$ Å, $\beta = 110°36'$. The structure was solved by direct methods and hydrogen atoms were located in a differential synthesis. Refinement by full-matrix least-squares methods resulted in a final R value of 0·088 for 1409 observed reflexions. The structure consists of dimers linked together by hydrogen bonds. The benzene ring is planar and C–C distances average 1·391 Å. The carboxyl group is twisted 18°04′ from this plane and the nitro group, 86°16′ from the same plane.

Introduction

The study of the crystalline structure of 3,5-dimethyl-4-nitrobenzoic acid has been carried out in an attempt to reveal the interaction between methyl groups and the carboxyl group, together with the influence of the nitro group in the molecular packing.

Molecular structures of derivatives of benzoic acids have been studied by Anca, Martínez-Carrera & García-Blanco (1967), Martínez-Perez & Martínez-Carrera (1967), Florencio & Smith (1970), Smith, Florencio & García-Blanco (1971), Cano, Martínez-Carrera & García-Blanco (1970), and this work was undertaken as a continuation of these previous studies.

Experimental

Crystals of 3,5-dimethyl-4-nitrobenzoic acid were recrystallized from an ethanolic solution. The density was measured by flotation in an aqueous potassium iodide solution.

Crystal data

$a = 11{\cdot}965$, $b = 10{\cdot}207$, $c = 8{\cdot}364$ Å, $\beta = 110°36'$, $D_m = 1{\cdot}36$ g cm^{-3}, $D_x = 1{\cdot}356$ g cm^{-3}, $Z = 4$, $F(000) = 408$, $\mu(\text{Cu } K\alpha) = 9{\cdot}329$ cm^{-1}. Systematic absences are: $0k0$ with $k = 2n+1$ and $h0l$ with $h = 2n+1$, and the space group is $P2_1/a$.

The three-dimensional data were obtained with Cu $K\alpha$ radiation and the multiple-film integrated Weissenberg procedure for nine layers with the crystal oscillated about the unique b axis and for six layers with oscillation about the c axis. The intensities of 1944

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