# Magnetic Properties and Crystal and Molecular Structure of μ-Oxo-bis-[bis-(2-methyl-8-hydroxyquinolinato)iron(III)]–Chloroform

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The crystal structure of the title compound has been established by three-dimensional $X$-ray single crystal analysis. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, in a cell of dimensions $a = 18{\cdot}29(3)$, $b = 11{\cdot}52(2)$, $c = 13{\cdot}13(2)$ Å, $\alpha = 89{\cdot}72(20)$, $\beta = 127{\cdot}25(20)$, $\gamma = 110{\cdot}95(20)°$. Atomic co-ordinates were obtained by Fourier methods and refined by full-matrix least-squares calculations to $R$ 0·126 for 2289 independent reflections. Fe–O–Fe is 151·6°, and with this geometry a pair of 2-methyl-8-hydroxyquinolinato ligands adopt a parallel arrangement. The mean magnetic susceptibilities of the title compound and of the corresponding unsolvated species are discussed in terms of a spin–spin coupling model involving two spin-free iron(III) ions.

In recent years there has been considerable interest in the structures of molecules containing metal–oxygen–metal bridges, and in particular, because of their possible importance in biological system, iron(III) complexes have been subjected to numerous investigations.[1] Recent $X$-ray structural determinations [1,2–6] have revealed quite a marked variation in the Fe–O–Fe bridging angle in various complexes (for some examples see later, Table 5). The factors affecting this bridging angle could be electronic or steric and it has been suggested [1a] that the variations are primarily due to steric factors. The study on the present compound should enable some useful comments to be made on the relative importance of steric effects *vs.* the demands of σ and π bonding within the oxo-bridge, since the corresponding $Al^{III}$ complex has been shown to have a linear Al–O–Al bridging arrangement.[7]

## EXPERIMENTAL

*Preparation.*—Fe(2-Mequin)$_2$Cl (2-Mequin = 8-hydroxy-2-methylquinolinato-) was first prepared as a black solid by treating stoicheiometric amounts of 8-hydroxy-2-methylquinoline and anhydrous iron(III) chloride in ethanol. Fe(2-Mequin)$_2$Cl dissolved in ethanol was treated with triethylamine to produce [Fe(2-Mequin)$_2$]$_2$O which was recrystallised from chloroform (Found: C, 56·1; H, 4·0; Cl, 12·4; Fe, 12·2; N, 6·1. Calc. for $C_{41}H_{33}Cl_3Fe_2N_4O_5$: C, 55·7; H, 4·2; Cl, 12·0; Fe, 12·6; N, 6·3%).

*Crystal Data.*—$(C_{10}H_8NO)_4Fe_2O,CHCl_3$, $M = 879{\cdot}8$, Triclinic, $a = 18{\cdot}29(3)$, $b = 11{\cdot}52(2)$, $c = 13{\cdot}13(2)$ Å, $\alpha = 89{\cdot}72(20)$, $\beta = 127{\cdot}25(20)$, $\gamma = 110{\cdot}95(20)°$, $U = 1972$ Å$^3$, $D_m = 1{\cdot}46$, $Z = 2$, $D_c = 1{\cdot}481$, $F(000) = 900$. Space group $P\bar{1}(C_i^1)$ from the structure refinement. Cu-$K_\alpha$ radiation, $\lambda = 1{\cdot}542$ Å; $\mu$(Cu-$K_\alpha$) = 83 cm$^{-1}$.

*Crystallographic Measurements.*—Unit-cell dimensions were obtained from zero-level Weissenberg photographs taken with Cu-$K_\alpha$ radiation and from precession photographs taken with Mo-$K_\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). A crystal of dimensions 0·10 × 0·20 × 0·60 mm was used for the collection of 0—13$kl$ layer data which were estimated visually from equi-inclination multiple-film Weissenberg photographs. In all, 2289 independent structure amplitudes were derived from the intensity estimates after corrections were applied for spot-shape and the usual Lorentz and polarization factors. Absorption was neglected.

*Structure Analysis.*—Initial co-ordinates for the iron atoms were derived from the three-dimensional Patterson synthesis. Approximate co-ordinates for the other non-hydrogen atoms were obtained from an iron-phased ($R$ 0·58) three-dimensional $F_o$ Fourier synthesis calculated with weighted coefficients.[8] Inclusion of the fifty-three atoms in the structure-factor calculations decreased $R$ to 0·38. Atomic positional and isotropic thermal parameters were then adjusted for several rounds of full-matrix least-squares calculations which reduced $R$ to 0·176. During these iterations the paremeters of 35 atoms were varied in any one cycle, and the atoms being refined were rotated in successive cycles. The iron and chlorine atoms were then allowed to assume anisotropic thermal parameters and four cycles of least-squares calculations decreased $R$ to 0·129. Evaluation of a difference-Fourier revealed significant density in those regions where the quinolinium hydrogen atoms were calculated to lie, but the methyl hydrogen atoms could not be placed with certainty. Fixed contributions for twenty hydrogen atoms were included in the remaining iterations, and two more cycles on all the other atoms resulted in convergence at $R$ 0·126.

For all structure-factor calculations, scattering factors for neutral atoms taken from ref. 9 were employed. During the least-squares iterations weights $w$ were assigned according to $\sqrt{w} = 1$ for $|F_o| \leqslant 23{\cdot}0$ and $\sqrt{w} = 23{\cdot}0/|F_o|$ for $|F_o| > 23{\cdot}0$ and $\Sigma w\Delta^2$ was minimized. Analysis of $\langle w\Delta^2\rangle$ in ranges of sin θ and $|F_o|$ showed no systematic dependence.

*Magnetic Susceptibility Measurements.*—The mean mag-

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[1] P. Coggon, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc.* (*A*), 1971, 1014. (*b*) H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 2683. (*c*) A. B. Hoffman, D. M. Collins, V. W. Day, E. B. Fleischer, T. S. Srivastava, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1972, **94**, 3620, and references therein.

[2] S. J. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, 1967, **6**, 1825.

[3] M. Gerloch, E. D. McKenzie, and A. D. C. Towl, *J. Chem. Soc.*, (*A*) 1969, 2850.

[4] E. B. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, 1967, **89**, 720.

[5] E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, 1969, **91**, 2403.

[6] J. E. Davies and B. M. Gatehouse, *Cryst. Struct. Comm.*, 1972, **1**, 115.

[7] Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, 1970, **92**, 91.

[8] G. A. Sim in ' Computing Methods and the Phase Problem in $X$-Ray Crystal Analysis,' ed. R. Pepinsky, J. M. Robertson, and J. C. Speakman, Pergamon Press, Oxford, 1961, p. 227.

[9] ' International Tables for $X$-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

metic susceptibilities were determined as described previously.[1] The results are given in Table 1.

TABLE 1

Mean magnetic susceptibilities (c.g.s. units)

(*a*) $[Fe(2\text{-}Mequin)_2]_2O,CHCl_3$

| | | | | | |
|---|---|---|---|---|---|
| $T/°K$ | 294·1 | 259·9 | 239·2 | 212·5 | 194·4 |
| $10^6\chi_{Fe}$ | 1918 | 1859 | 1815 | 1770 | 1735 |
| $T/°K$ | 170·3 | 150·8 | 130·5 | 105·6 | 90·0 |
| $10^6\chi_{Fe}$ | 1635 | 1558 | 1411 | 1178 | 1006 |

(*b*) $[Fe(2\text{-}Mequin)_2]_2O$

| | | | | | | |
|---|---|---|---|---|---|---|
| $T/°K$ | 293·1 | 273·1 | 264·0 | 242·4 | 215·5 | 201·7 |
| $10^6\chi_{Fe}$ | 1791 | 1762 | 1735 | 1711 | 1676 | 1699 |
| $T/°K$ | 194·3 | 180·2 | 177·4 | 153·3 | 130·0 | 111·4 |
| $10^6\chi_{Fe}$ | 1667 | 1668 | 1668 | 1565 | 1476 | 1360 |
| $T/°K$ | 92·4 | 83·5 | | | | |
| $10^6\chi_{Fe}$ | 1286 | 1243 | | | | |

## RESULTS AND DISCUSSION

*Crystal and Molecular Structure.*—Final atomic coordinates and temperature factor parameters, with their estimated standard deviations, are listed in Table 2.* The atom numbering scheme employed is shown in Figure 1, and a view of the molecule is presented in Figure 2. Interatomic distances and angles are provided in Table 3. Displacements of some atoms from various least-squares planes calculated through groups of atoms are given in Table 4.

The mean bond lengths involving only C, N, and O are C–C(aromatic) 1·40, C($sp^2$)–C($sp^3$) 1·50, C($sp^2$)–N 1·35, and C($sp^2$)–O 1·34 Å, all in satisfactory agreement with accepted values.[1a] Although chemically equivalent bonds have a range of values, none may be considered to deviate significantly from the average.

The mean bond lengths around the iron atoms are Fe–O(quinolinato) 1·918, Fe–O(bridging) 1·780, and Fe–N 2·190 Å. Those to the oxygen atoms agree very well with the corresponding lengths in other oxo-bridged iron(III) compounds: $[Fe(salen)]_2O,CH_2Cl_2$ [1a] 1·922 and 1·794,† $[Fe(salen)]_2O$,2pyridine [2] 1·918 and 1·797, and μ-oxo-bis-[bis-*N*-n-propylsalicylideneiminatoiron(III)] [6] 1·93 and 1·77 Å. The shorter bonds to the bridging oxygen atom may be attributed to π-bonding.[1a] The Fe–N bonds are significantly longer than the corresponding distances in $[Fe(salen)]_2O,CH_2Cl_2$ [1a] 2·105, $[Fe(salen)]_2O$,2pyridine [3] 2·087, $[Fe(salen)Cl]_2$ [10] 2·095, μ-oxo-bis[α,β,γ,δ-tetraphenylporphinatoiron(III) [1c] 2·087, and chlorobis(*N*-n-propylsalicylaldiminato)iron(III) [11] 2·096 Å, all of which involve a six-membered chelate ring with mean angles in the range 85·8—87·0° subtended at the iron atom. In the present complex five-membered chelate rings are formed and the associated smaller N–Fe–O angles average 79·0°.

TABLE 2

Fractional atomic co-ordinates (× $10^4$) and thermal parameters, with estimated standard deviations in parentheses

| Atom | $x/a$ | $y/b$ | $z/c$ | $B/Å^2$ |
|---|---|---|---|---|
| Fe(1) | 4384(2) | 2035(3) | 1814(2) | * |
| Fe(2) | 1839(2) | 863(3) | −1016(2) | * |
| N(1) | 4123(8) | 3410(12) | 2552(10) | 4·4(3) |
| C(2) | 3928(10) | 4436(16) | 2117(14) | 4·9(4) |
| C(3) | 3684(12) | 5053(19) | 2662(17) | 6·7(5) |
| C(4) | 3540(13) | 4663(19) | 3501(17) | 7·0(6) |
| C(5) | 3719(11) | 3654(17) | 3965(15) | 5·6(5) |
| C(6) | 3669(13) | 3205(19) | 4927(17) | 7·1(6) |
| C(7) | 3912(13) | 2208(19) | 5296(17) | 6·6(5) |
| C(8) | 4180(13) | 1586(19) | 4787(17) | 6·9(5) |
| C(9) | 4258(10) | 1999(16) | 3805(14) | 5·0(4) |
| C(10) | 4031(10) | 3032(14) | 3469(13) | 4·1(4) |
| O(11) | 4525(7) | 1465(10) | 3292(9) | 5·4(3) |
| C(12) | 4036(13) | 4795(19) | 1076(17) | 7·1(6) |
| N(13) | 5093(8) | 881(11) | 1780(10) | 3·9(3) |
| C(14) | 4848(10) | −373(15) | 1687(13) | 4·7(4) |
| C(15) | 5386(11) | −955(17) | 1557(15) | 5·9(5) |
| C(16) | 6143(12) | −170(18) | 1561(16) | 6·5(5) |
| C(17) | 6460(11) | 1146(16) | 1732(14) | 5·1(4) |
| C(18) | 7201(13) | 2003(19) | 1748(17) | 6·9(5) |
| C(19) | 7409(13) | 3247(19) | 1918(17) | 6·9(5) |
| C(20) | 6862(13) | 3810(19) | 1961(17) | 7·1(6) |
| C(21) | 6053(12) | 2971(18) | 1891(15) | 6·1(5) |
| C(22) | 5857(10) | 1627(14) | 1787(12) | 4·0(4) |
| O(23) | 5491(8) | 3359(12) | 2014(10) | 6·5(3) |
| C(24) | 3973(13) | −1211(20) | 1659(18) | 7·6(6) |
| N(1′) | 1494(8) | 1055(11) | 285(10) | 4·3(3) |
| C(2′) | 1516(12) | 327(17) | 1105(16) | 6·0(5) |
| C(3′) | 1234(12) | 700(17) | 1861(15) | 5·7(5) |
| C(4′) | 1033(12) | 1663(18) | 1838(16) | 6·0(5) |
| C(5′) | 1016(12) | 2380(18) | 940(16) | 6·4(5) |
| C(6′) | 809(13) | 3434(19) | 792(17) | 6·9(5) |
| C(7′) | 816(14) | 4090(22) | −102(19) | 8·4(6) |
| C(8′) | 1060(11) | 3775(16) | −863(14) | 5·4(4) |
| C(9′) | 1263(10) | 2699(15) | −696(13) | 4·8(4) |
| C(10′) | 1265(10) | 2046(15) | 189(14) | 4·8(4) |
| O(11′) | 1533(7) | 2320(10) | −1351(9) | 5·2(3) |
| C(12′) | 1823(11) | −732(16) | 1234(15) | 5·5(5) |
| N(13′) | 1505(7) | 454(11) | −2935(10) | 3·9(3) |
| C(14′) | 1872(10) | 1246(15) | −3437(14) | 4·8(4) |
| C(15′) | 1552(12) | 718(17) | −4708(15) | 6·1(5) |
| C(16′) | 884(12) | −567(18) | −5399(16) | 6·7(5) |
| C(17′) | 551(11) | −1358(16) | −4845(14) | 5·3(4) |
| C(18′) | −132(14) | −2754(21) | −5461(18) | 7·9(6) |
| C(19′) | −460(14) | −3472(21) | −4836(19) | 7·9(6) |
| C(20′) | −67(12) | −2887(17) | −3548(15) | 6·0(5) |
| C(21′) | 548(10) | −1582(15) | −2955(13) | 4·8(4) |
| C(22′) | 871(9) | −805(13) | −3571(12) | 3·6(4) |
| O(23′) | 914(7) | −933(10) | −1762(9) | 5·4(3) |
| C(24′) | 2632(12) | 2616(19) | −2622(16) | 6·8(5) |
| O(25) | 3154(6) | 1267(9) | 159(8) | 3·9(3) |
| Cl(1) | 2805(5) | 7324(7) | 3220(6) | * |
| Cl(2) | 2304(6) | 5840(9) | 4585(7) | * |
| Cl(3) | 2479(6) | 8473(8) | 4741(7) | * |
| C(26) | 2909(16) | 7370(25) | 4580(22) | 7·7(7) |

* Anisotropic thermal parameters in the form:

$\exp(-B\sin^2\theta/\lambda^2) = \exp-[(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ were used, with parameters $b_{ij}$ (× $10^4$).

| Atom | $b_{11}$ | $b_{22}$ | $b_{33}$ | $b_{12}$ | $b_{13}$ | $b_{23}$ |
|---|---|---|---|---|---|---|
| Fe | 67(1) | 124(3) | 98(2) | 88(3) | 83(2) | 51(4) |
| Fe′ | 60(1) | 150(3) | 75(2) | 91(3) | 71(2) | 38(4) |
| Cl(1) | 285(4) | 349(7) | 346(7) | 493(8) | 507(7) | 483(12) |
| Cl(2) | 260(5) | 261(12) | 342(7) | 166(13) | 479(7) | 184(16) |
| Cl(3) | 229(5) | 328(8) | 220(7) | 393(8) | 273(8) | 220(14) |

The five-co-ordinate iron atoms are in environments intermediate between square pyramidal and trigonal bipyramidal geometries, configurations between which there is only a small energy difference.[12] For a comparison of the geometry with those of similar complexes

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* Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20734 (15 pp., 1 microfiche). For details, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue.

† Salen = *NN′*-ethylenebis-salicylideneiminato. † Hedta = ethylenediaminetetra-acetic acid.

[10] M. Gerloch and F. E. Mabbs, *J. Chem. Soc.* (*A*), 1967, 1900.

[11] J. E. Davies and B. M. Gatehouse, *Chem. Comm.*, 1970, 1166.

[12] E. L. Mutterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 245.

which have been discussed in terms of distorted square-planar co-ordination, we evaluated the displacements of the iron atoms from the least-squares planes through the quinolinato-donor atoms. The iron atoms are displaced 0·63 and 0·64 Å from the calculated planes towards the bridging oxygen atom. As reported in these other studies, the donor atoms are again not coplanar and the displacements found here are greater than in $[Fe(salen)]_2O,CH_2Cl_2$,[1a] mean 0·56, and $[(Hedta)_2Fe_2O]^{2-}$,* 0·36 Å.[2] Hence, the geometry approaches more closely a trigonal bipyramidal arrangement with the basal plane defined by the oxygen atoms, and the nitrogen atoms occupy apical positions.

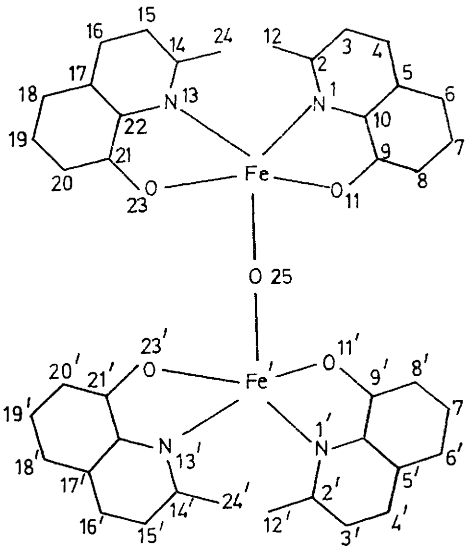

FIGURE 1 Atom numbering scheme

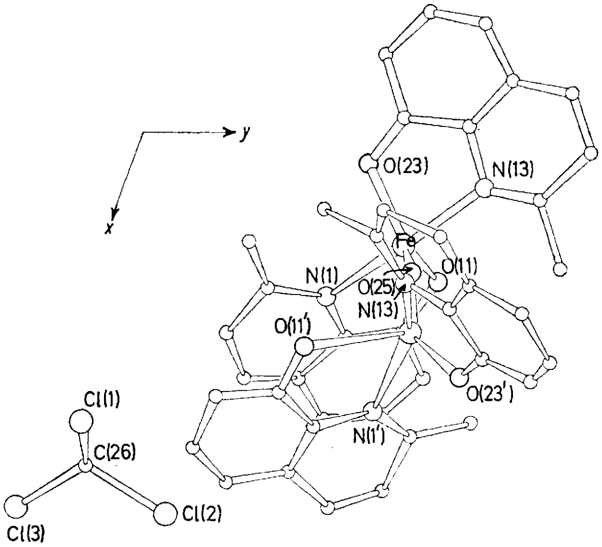

FIGURE 2 Atomic arrangement, viewed in projection along the $c^*$ axis

TABLE 3

Interatomic distances (Å) and valency angles (deg.), with estimated standard deviations in parentheses

| (*a*) Interatomic distances | Unprimed | Primed |
|---|---|---|
| Fe–N(1) | 2·188(14) | 2·186(14) |
| Fe–O(11) | 1·940(12) | 1·920(12) |
| Fe–N(13) | 2·180(13) | 2·211(13) |
| Fe–O(23) | 1·910(14) | 1·901(13) |
| Fe–O(25) | 1·801(11) | 1·760(11) |
| N(1)–C(2) | 1·37(2) | 1·33(2) |
| N(1)–C(10) | 1·36(2) | 1·35(2) |
| C(2)–C(3) | 1·37(3) | 1·46(3) |
| C(2)–C(12) | 1·52(3) | 1·52(3) |
| C(3)–C(4) | 1·32(3) | 1·35(3) |
| C(4)–C(5) | 1·36(3) | 1·38(3) |
| C(5)–C(6) | 1·40(3) | 1·35(3) |
| C(5)–C(10) | 1·42(3) | 1·43(3) |
| C(6)–C(7) | 1·36(3) | 1·33(3) |
| C(7)–C(8) | 1·36(3) | 1·40(3) |
| C(8)–C(9) | 1·44(3) | 1·39(3) |
| C(9)–C(10) | 1·38(2) | 1·45(3) |
| C(9)–O(11) | 1·30(2) | 1·35(3) |
| N(13)–C(14) | 1·35(2) | 1·34(2) |
| N(13)–C(22) | 1·33(2) | 1·34(2) |
| C(14)–C(15) | 1·49(3) | 1·44(3) |
| C(14)–C(24) | 1·48(3) | 1·49(3) |
| C(15)–C(16) | 1·28(3) | 1·37(3) |
| C(16)–C(17) | 1·43(3) | 1·37(3) |
| C(17)–C(18) | 1·38(3) | 1·47(3) |
| C(17)–C(22) | 1·41(3) | 1·45(2) |
| C(18)–C(19) | 1·40(3) | 1·40(4) |
| C(19)–C(20) | 1·41(3) | 1·42(3) |
| C(20)–C(21) | 1·40(3) | 1·37(3) |
| C(21)–C(22) | 1·38(3) | 1·41(2) |
| C(21)–O(23) | 1·36(2) | 1·36(2) |
| C(26)–Cl(1) | 1·68(3) | |
| C(26)–Cl(2) | 1·72(3) | |
| C(26)–Cl(3) | 1·79(3) | |
| (*b*) Valency angles | | |
| N(1)–Fe–O(11) | 78·0(5) | 78·7(5) |
| N(1)–Fe–N(13) | 160·9(5) | 156·2(5) |
| N(1)–Fe–O(23) | 93·9(6) | 90·6(5) |
| N(1)–Fe–O(25) | 99·3(5) | 101·3(5) |
| O(11)–Fe–N(13) | 89·7(5) | 91·4(5) |
| O(11)–Fe–O(23) | 123·4(6) | 128·7(5) |
| O(11)–Fe–O(25) | 118·8(5) | 114·8(5) |
| N(13)–Fe–O(23) | 80·5(5) | 78·7(5) |
| N(13)–Fe–O(25) | 99·5(5) | 102·5(5) |
| O(23)–Fe–O(25) | 117·8(5) | 116·5(5) |
| Fe–N(1)–C(2) | 129·4(12) | 127·5(12) |
| Fe–N(1)–C(10) | 110·3(10) | 109·8(11) |
| C(2)–N(1)–C(10) | 119·9(14) | 122·7(16) |
| N(1)–C(2)–C(3) | 117·2(17) | 114·5(17) |
| N(1)–C(2)–C(12) | 117·4(16) | 121·2(18) |
| C(3)–C(2)–C(12) | 125·5(18) | 124·3(18) |
| C(2)–C(3)–C(4) | 123·9(20) | 125·7(19) |
| C(3)–C(4)–C(5) | 120·7(21) | 116·5(20) |
| C(4)–C(5)–C(6) | 126·5(20) | 123·6(20) |
| C(4)–C(5)–C(10) | 116·6(18) | 119·6(18) |
| C(6)–C(5)–C(10) | 116·8(17) | 116·8(19) |
| C(5)–C(6)–C(7) | 117·7(20) | 120·0(21) |
| C(6)–C(7)–C(8) | 125·3(21) | 124·3(22) |
| C(7)–C(8)–C(9) | 120·2(19) | 114·4(18) |
| C(8)–C(9)–C(10) | 113·4(17) | 122·0(17) |
| C(8)–C(9)–O(11) | 123·6(17) | 119·9(16) |
| C(10)–C(9)–O(11) | 123·0(17) | 118·0(15) |
| N(1)–C(10)–C(5) | 121·4(15) | 120·9(17) |
| N(1)–C(10)–C(9) | 112·1(15) | 116·6(16) |
| C(5)–C(10)–C(9) | 126·5(17) | 122·5(17) |
| Fe–O(11)–C(19) | 115·4(11) | 116·9(10) |
| Fe–N(13)–C(14) | 130·5(12) | 129·8(11) |
| Fe–N(13)–C(22) | 109·2(10) | 108·3(10) |
| C(14)–N(13)–C(22) | 120·2(15) | 121·9(14) |
| N(13)–C(14)–C(15) | 120·2(17) | 118·7(16) |
| N(13)–C(14)–C(24) | 119·8(17) | 118·5(16) |
| C(15)–C(14)–C(24) | 120·0(17) | 122·8(17) |
| C(14)–C(15)–C(16) | 117·4(18) | 120·8(19) |
| C(15)–C(16)–C(17) | 124·1(20) | 119·2(19) |

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* Salen = *NN′*ethylenebis-salicylideneiminato. † Hedta = ethylenediaminetetra-acetic acid.

TABLE 3 (*continued*)

(*b*) Valency angles

| | | |
|---|---|---|
| C(16)–C(17)–C(18) | 128·4(19) | 124·3(19) |
| C(16)–C(17)–C(22) | 114·7(17) | 119·1(17) |
| C(18)–C(17)–C(22) | 116·7(17) | 116·6(17) |
| C(17)–C(18)–C(19) | 120·8(21) | 120·0(21) |
| C(18)–C(19)–C(20) | 126·7(22) | 120·5(21) |
| C(19)–C(20)–C(21) | 115·5(20) | 121·1(19) |
| C(20)–C(21)–C(22) | 118·2(18) | 120·3(17) |
| C(20)–C(21)–O(23) | 123·7(18) | 125·1(17) |
| C(22)–C(21)–O(23) | 117·9(17) | 114·7(15) |
| N(13)–C(22)–C(17) | 123·1(15) | 120·2(15) |
| N(13)–C(22)–C(21) | 115·2(15) | 118·4(14) |
| C(17)–C(22)–C(21) | 121·7(17) | 121·3(15) |
| Fe–O(23)–C(21) | 116·6(12) | 119·7(12) |
| Fe–O(25)–Fe′ | 151·6(7) | |
| Cl(1)–C(26)–Cl(2) | 110·9(17) | |
| Cl(1)–C(26)–Cl(3) | 110·8(17) | |
| Cl(2)–C(26)–Cl(3) | 113·4(18) | |

(*c*) Some intramolecular distances $<3{\cdot}7$ Å

| | | | |
|---|---|---|---|
| N(1) ··· N(1′) | 3·57 | C(6) ··· C(4′) | 3·62 |
| C(2) ··· C(9′) | 3·57 | C(9) ··· C(2′) | 3·61 |
| C(2) ··· C(10′) | 3·65 | C(9) ··· C(12′) | 3·61 |
| C(4) ··· C(5′) | 3·49 | C(10) ··· N(1′) | 3·64 |
| C(4) ··· C(6′) | 3·62 | C(10) ··· C(2′) | 3·61 |
| C(5) ··· C(4′) | 3·55 | O(11) ··· C(12′) | 3·62 |
| C(5) ··· C(5′) | 3·67 | C(12) ··· O(11′) | 3·51 |
| C(6) ··· C(3′) | 3·69 | | |

(*d*) Intermolecular separations $\leqslant 3{\cdot}7$ Å

| | | | |
|---|---|---|---|
| C(4′) ··· O(23′$^{\mathrm{II}}$) | 3·29 | C(16) ··· O(25$^{\mathrm{I}}$) | 3·61 |
| Cl(3) ··· C(16′$^{\mathrm{IV}}$) | 3·28 | N(1′) ··· C(14′$^{\mathrm{II}}$) | 3·62 |
| N(13) ··· C(16$^{\mathrm{I}}$) | 3·43 | C(2′) ··· C(5′$^{\mathrm{II}}$) | 3·62 |
| C(15) ··· C(22$^{\mathrm{I}}$) | 3·43 | C(16) ··· C(14′$^{\mathrm{I}}$) | 3·63 |
| C(15) ··· C(17$^{\mathrm{I}}$) | 3·45 | C(18) ··· C(21′$^{\mathrm{I}}$) | 3·64 |
| C(15) ··· C(17$^{\mathrm{I}}$) | 3·49 | C(14) ··· C(16$^{\mathrm{I}}$) | 3·65 |
| Cl(1) ··· C(24′$^{\mathrm{III}}$) | 3·49 | C(18) ··· C(22′$^{\mathrm{I}}$) | 3·65 |
| C(18) ··· C(24$^{\mathrm{I}}$) | 3·53 | C(16) ··· N(13′$^{\mathrm{I}}$) | 3·67 |
| C(14) ··· C(18$^{\mathrm{I}}$) | 3·54 | Cl(2) ··· C(20′$^{\mathrm{II}}$) | 3·68 |
| C(2′) ··· C(4′$^{\mathrm{II}}$) | 3·54 | Cl(2) ··· C(17′$^{\mathrm{II}}$) | 3·70 |
| N(1′) ··· C(3′$^{\mathrm{II}}$) | 3·57 | Cl(1) ··· C(4) | 3·70 |
| C(3′) ··· C(10′$^{\mathrm{II}}$) | 3·60 | | |

Roman numeral superscripts refer to the following transformations of the co-ordinates of Table 2:

I $1 - x, -y, -z$
II $-x, -y, -z$
III $x, 1 + y, z$
IV $x, 1 + y, 1 + z$

TABLE 4

(*a*) Displacements (Å) of some atoms from various least-squares planes. Atoms not included in the derivation of the plane are italicized

Plane (A): N(1) 0·28, O(11) −0·29, N(13) 0·28, O(23) −0·27, *Fe* 0·63, *O(25) 2·43*

Plane (B): N(1′) 0·19, O(11′) −0·19, N(13′) 0·19, O(23′) −0·19, *Fe′ 0·64, O(25) 2·40*

Plane (C): N(1) 0·00, C(2) −0·01, C(3) −0·05, C(4) 0·02, C(5) 0·03, C(6) 0·01, C(7) −0·03, C(8) −0·01, C(9) 0·00, C(10) 0·01, O(11) 0·00, C(12) 0·01, *Fe 0·28*

Plane (D): N(1′) 0·02, C(2′) 0·01, C(3′) 0·03, C(4′) −0·01, C(5′) 0·01, C(6′) −0·02, C(7′) −0·01, C(8′) −0·01, C(9′) 0·03, C(10′) 0·01, O(11′) 0·00, C(12′) −0·05, *Fe′ 0·00*

Plane (E): N(13) 0·00, C(14) −0·02, C(15) 0·01, C(16) 0·04, C(17) −0·02, C(18) 0·00, C(19) −0·05, C(20) 0·00, C(21) 0·04, C(22) 0·02, O(23) 0·00, C(24) −0·02, *Fe 0·13*

Plane (F): N13′) 0·02, C(14′) 0·01, C(15′) 0·03, C(16′) −0·01, C(17′) 0·01, C(18′) −0·02, C(19′) −0·01, C(20′) −0·01, C(21′) 0·03, C(22′) 0·01, O(23) 0·00, C(24) −0·05, *Fe′ 0·00*

(*b*) Dihedral angles (deg) between the planes

| | | | |
|---|---|---|---|
| (*C*)–(*D*) | 1 | (*D*)–(*F*) | 59 |
| (*C*)–(*E*) | 44 | (*E*)–(*F*) | 52 |

The atoms in each of the quinolinato-ligands are coplanar (Table 3). In one half of the complex the iron atom is in the same plane as the bidentate ligand atoms while in the other half it is displaced significantly by unequal amounts from the corresponding planes. Consequently, the complex does not possess exact $C_2$ symmetry.

The Fe–O–Fe angle (151·6°) is intermediate between the values (142·2 and 139°) in [Fe(salen)]$_2$O,CH$_2$Cl$_2$ [1a] and [Fe(salen)]$_2$O,2pyridine,[3] and the corresponding angles (165·0 and 164°) in [(Hedta)$_2$Fe$_2$O]$^{2-}$ (ref. 2) and μ-oxo-bis[bis-*N*-n-propylsalicylideneiminatoiron(III)].[6] In all these complexes the bridging Fe–O lengths are not significantly different. We suggested earlier that the different angles at the bridging oxygen atoms were due to steric factors, and the results of the present analysis support this contention. In the complex, one pair of ligands adopts a parallel arrangement resulting in an interplanar separation of 3·52 Å and appreciable ligand overlap (Figure 3). The geometry adopted represents a potential-energy minimum in which the repulsive intramolecular ligand–ligand interactions are balanced by the van der Waals attractive forces. The orientation here contrasts strongly with the 90° staggered arrangement reported recently for μ-oxo-bis[bis-*N*-n-propylsalicylideneiminatoiron(III)] [6] in which the van der Waals attractions are apparently not sufficient to overcome the repulsive interactions, and consequently the Fe–O–Fe angle is larger. Since the Fe–O–Fe angle in [Fe(salen)]$_2$O,CH$_2$Cl$_2$ is smaller than that found in the present study, we anticipate that if the foregoing holds true then a similar attractive interaction should exist in this complex. A view of the projection on to the plane through part of one of the ligands in [Fe(salen)]$_2$O is shown in Figure 4 where a significant amount of overlap is indeed shown to be present.

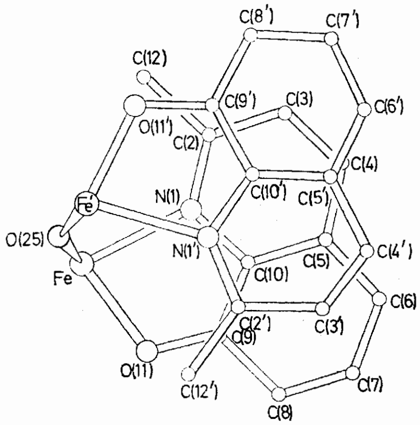

FIGURE 3 Mutual orientation of a pair of 8-hydroxy-2-methylquinolinato-ligands in the complex viewed normal to the plane through one of the ligands

In the corresponding complex [7] with Al$^{\mathrm{III}}$, the Al–O and Al–N distances are all *ca.* 0·10 Å shorter than the corresponding Fe–O and Fe–N in the present work. This implies that the bond orders in both complexes must be similar and in particular, that the degree of $\pi$-bonding in the linear Al–O–Al bridge bonds must be similar to that in the bent Fe–O–Fe bridge. Consequently, the difference in angles subtended at the bridging oxygen atoms cannot be explained by differences in $\pi$-bonding, and the observed linear geometry in the aluminium complex must be ascribed to the fact that the smaller $Al^{III}$ radius produces a smaller than acceptable ligand–ligand separation if the Al–O–Al angle is less than 180°.

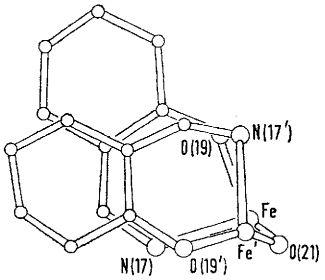

FIGURE 4 Mutual orientation of ligands in $Fe(salen)_2O$,[3] viewed normal to the plane through one of the ligands

The mean dimensions of the chloroform molecule of solvation (C–Cl 1·73 Å, and Cl–C–Cl 111·7°) are satisfactorily close to the uncorrected values reported for Co(salen),$CHCl_3$[13] (C–Cl 1·77 Å, Cl–C–Cl 109·7°), and are in good agreement with other recorded values.[14] The mean temperature factor ($B$ 14·3 $Å^2$) for the chlorine atoms is significantly greater than for atoms in the $\mu$-oxo-complex, and this may indicate either some randomness in their position or perhaps that some solvent is lost during prolonged exposure. Certainly the latter is very possible for there are channels along which the chloroform molecules may diffuse out of the crystal.

The crystal structure, viewed in projection along $c^*$, is illustrated in Figure 5. In the crystal the $\mu$-oxo-complexes lie in rows along the $a$ direction, and around the centres of symmetry at 0,0,0 and 1/2,0,0 parallel pairs of quinolinato-ligands have short interplanar separations and a significant amount of overlap. Not dissimilar stacking of phenyl rings has been noted in other crystal studies.[15] The chloroform solvate molecules lie between the rows of complex molecules with the shortest distance of approach Cl(3) · · · C(16') 3·38 Å representing a normal van der Waals separation.

*Magnetic Susceptibilities*.—The variation of the magnetic susceptibility of $[Fe(2\text{-Mequin})_2]_2O,CHCl_3$ is interpreted on the basis of an isotropic spin–spin interaction between two spin-free iron(III) ions ($S$ $\frac{5}{2}$) using an exchange integral $J$ $-80$ cm$^{-1}$ and $\bar{g}$ 2·00. The agreement between calculated and experimental curves are shown in Figure 6. There is a small deviation between the experimental and calculated results below *ca.* 150 K which suggests that $J$ might be larger in magnitude at the lower temperature. The interpretation of the data for the unsolvated compound is complicated by the occurrence of a constant magnetic susceptibility in the region 180—240 K, which was reproducible for two different preparations. This phenomenon suggests that

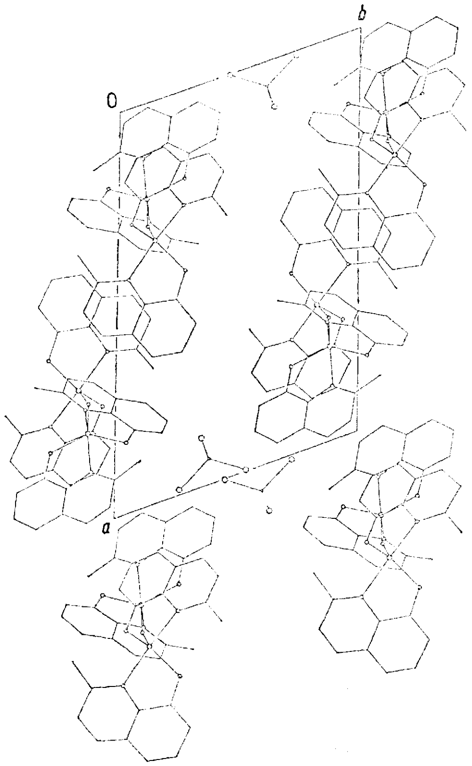

FIGURE 5 Crystal structure, viewed in projection along the $c^*$ axis

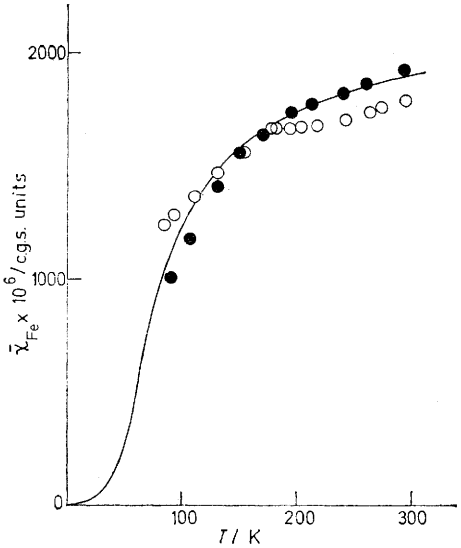

FIGURE 6 Variation of the mean magnetic susceptibilities with temperature; open circles $[Fe(2\text{-Mequin})_2]_2O,CHCl_3$, closed circles $[Fe(2\text{-Mequin})_2]_2O$. The dashed line is calculated for spin–spin interaction between two $S$ 5/2 ions with $\bar{g}$ 2·00, and $J$ $-80$ cm$^{-1}$

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[13] W. P. Schaefer and R. E. Marsh, *Acta Cryst.*, 1969, *B*, **25**, 1675.

[14] *Chem. Soc. Special Publ.*, No. 18, 1965.

[15] V. G. Albano, P. Bellon, and M. Sansoni, *J. Chem. Soc.* (*A*), 2420, and references therein.

TABLE 5

| Compound | Fe–O–Fe/ deg. | Fe–O(br)/Å | $-J$/cm$^{-1}$ |
|---|---|---|---|
| [Fe(salen)$_2$]O,pyridine | 139 | 1·80 | 80 [a] |
| [Fe(salen)$_2$]O,CH$_2$Cl$_2$ | 142 | 1·79 | 87 [a] |
| [Fe(2-Mequin)$_2$]$_2$O,CHCl$_3$ | 152 | 1·78 | 80 [b] |
| (enH)$_2$[Fe(Hedta]$_2$O,6H$_2$O | 165 | 1·80 | 95 [c] |
| [[FeB(H$_2$O)]$_2$O]ClO$_4$ * | 180 | 1·80 | 87 [d] |
| [Fe(propsal)]$_2$O † | 164 | 1·77 | 99 [e] |

[a] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1967, 1014; [b] Present work. [c] H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 2683. [d] V. N. McLachlan and F. E. Mabbs, unpublished results. [e] A. Van Den Bergen, K. S. Murray, and B. O. West, *Austral. J. Chem.*, 1968, **21**, 1517.

* B is the macrocylic ligand, 2,13-dimethyl-3,6,9,12,18-pentazabicyclo-(12.3.1)-octadeca-1(18),2,12,14,16-pentaene.

† Propsal is *N*-n-propylsalicylideneiminato.

there is a change in molecular structure in this temperature region which presumably makes a significant change in the Fe–O–Fe bridging arrangement, such that the exchange interaction is somewhat weaker below the transition region. A simple change in bond angle could occur as this seems to be the most facile distortion in these systems. However the nature of the change is difficult to infer from the magnetic results as the values of $J$ needed to account for the magnetic behaviour of a number of compounds with differing Fe–O–Fe angles show no direct correlation with this angle (see Table 5). Allowing for the possible errors in the $J$ values they are almost constant. This gives a very good empirical correlation with the Fe–O(bridging) bond lengths, which are also essentially the same. This could be interpreted on the basis that the dominant contribution to $J$ arises from exchange *via* a $\sigma$ bonding mechanism, exchange *via* $\pi$ bonding being less important.

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