The Reaction of 1,1′-Biphenyl-2,2′-diol with Iron(III) and the Crystal Structure of Piperidinium Bis[μ-(1,1′-biphenyl-2,2′-diolato-*O*,μ-*O*′)-(1,1′-biphenyl-2,2′-diolato-*O*,*O*′)ferrate(III)]–Ethanol(1/2) †

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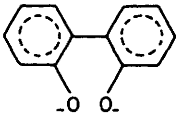
The interaction of 1,1′-biphenyl-2,2′-diol (H_2L) with iron(III) perchlorate in the presence of piperidine yields the title complex $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$, the crystal and molecular structure of which has been determined by single-crystal *X*-ray diffraction techniques. Crystals of the complex are triclinic, space group $P\bar{1}$, with a = 14.058(2), b = 9.976(1), c = 12.517(1) Å, α = 73.41(1), β = 65.29(1), γ = 61.48(1)°, and Z = 1. After full-matrix least-squares refinement the final R value is 0.052 for 3 473 observed reflections. The complex contains $[(FeL_2)_2]^{2-}$ dimers with seven-membered chelate rings, as well as piperidinium ions and ethanol molecules of crystallization. Each Fe^{III} is bonded to five oxygen atoms from L^{2-} ligands to give a distorted trigonal-bipyramidal co-ordination. The iron atoms are bridged by phenolate oxygens. The ethanol molecules, piperidinium ions, and L^{2-} ligands are linked by hydrogen bonds. Spectroscopic and magnetic data are in keeping with the dimeric $[(FeL_2)_2]^{2-}$ structure, with weak antiferromagnetic coupling *via* the bridging oxygen atoms. Spectroscopic evidence indicates that the dimers are dissociated by nitrogen-donor solvents.

As part of our interest in the iron tyrosinate protein, human lactoferrin,[1] we have been studying the interaction of phenolates with iron(III).[2] Although it is well known that simple uni- and bi-dentate phenols give intensely coloured solutions with iron(III) salts, it is only with catechol that the isolation of crystalline complexes has been achieved.[3,4] In this paper therefore, we report that 1,1′-biphenyl-2,2′-diol, H_2L, in the presence of piperidine, reacts with iron(III) perchlorate to yield the title complex $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$. Since the early work of Brady and Hughes,[5] 1,1′-biphenyl-2,2′-diolato, L^{2-}, complexes have been reported for a variety of metals especially by Andrä and co-workers,[6] however no structural data are available for the co-ordinated L^{2-} ion, which would be expected to form seven-membered chelate rings.


L^{2-}

Results and Discussion

Synthesis of $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$.—The interaction of H_2L with iron(III) perchlorate in ethanol yields an intense blue-black solution, with an e.s.r. spectrum dominated by a strong resonance at g = 4.31, indicative of high-spin iron(III) in a rhombic environment.[1,7] In view of the high stability[8] of the monoprotonated anion, HL^-, it is suggested that the blue-black species may be a $[Fe(HL)_n]^{(3-n)+}$ solvated complex. Addition of the base piperidine causes an immediate colour change of the solution to dark red, and allows the isolation of the complex $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ as air-stable crystals.

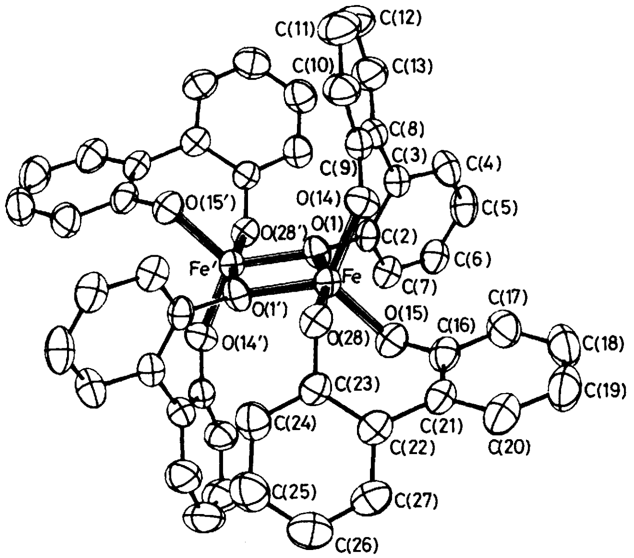


Figure 1. Structure of the $[(FeL_2)_2]^{2-}$ dimer showing atom labelling

The Structure of $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$.—The structure consists of $[(FeL_2)_2]^{2-}$ dimers containing a crystallographic centre of symmetry (Figure 1). In addition the unit-cell contains two piperidinium ions and two disordered non-co-ordinated ethanol molecules.

Each iron atom is bonded to five oxygen atoms of the L^{2-} ligands. One oxygen atom, O(1), acts as a bridging atom between the two iron atoms, which are 3.255 Å apart. The iron therefore has a distorted trigonal-bipyramidal five-fold co-ordination with Fe–O bond lengths varying from 1.851(2) to 2.056(2) Å (Table 1). The two phenyl rings of the L^{2-} ligand are twisted about their connecting bond thus reducing electron delocalization between them. The angles between the planes of the phenyl rings are 48.3 and 49.2° for the C(2)—C(13) and C(16)—C(27) rings respectively. It is this twisting which allows the formation of the apparently unstrained seven-membered chelate rings. While O(1) and O(14) lie in the

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† *Supplementary data available* (No. SUP 23588, 24 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: G = 10^{-4} T.

Table 1. Bond lengths (Å) and angles (°) for $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ with estimated standard deviations in parentheses

$[(FeL_2)_2]^{2-}$ dimer							
Fe–O(1)	2.056(2)	C(4)–C(5)	1.383(6)	C(12)–C(13)	1.384(6)	C(21)–C(22)	1.485(5)
Fe–O(1′)	1.966(2)	C(5)–C(6)	1.375(6)	C(8)–C(13)	1.402(5)	C(22)–C(23)	1.405(5)
Fe–O(14)	1.851(2)	C(6)–C(7)	1.385(5)	O(15)–C(16)	1.360(4)	O(28)–C(23)	1.356(4)
Fe–O(15)	1.896(2)	C(2)–C(7)	1.396(5)	C(16)–C(17)	1.390(6)	C(23)–C(24)	1.396(5)
Fe–O(28)	1.933(2)	O(14)–C(9)	1.347(4)	C(17)–C(18)	1.410(7)	C(24)–C(25)	1.382(6)
O(1)–C(2)	1.360(4)	C(8)–C(9)	1.391(5)	C(18)–C(19)	1.370(7)	C(25)–C(26)	1.379(6)
C(2)–C(3)	1.395(5)	C(9)–C(10)	1.411(5)	C(19)–C(20)	1.397(6)	C(26)–C(27)	1.383(6)
C(3)–C(8)	1.490(5)	C(10)–C(11)	1.381(6)	C(20)–C(21)	1.397(5)	C(22)–C(27)	1.400(5)
C(3)–C(4)	1.405(5)	C(11)–C(12)	1.374(7)	C(16)–C(21)	1.395(6)		

Piperidinium ion				Ethanol molecule	
N(29)–C(30)	1.498(6)	C(32)–C(33)	1.517(9)	O(35)–C(36)	1.443(9)
C(30)–C(31)	1.494(7)	C(33)–C(34)	1.544(8)	C(36)–C(37)	1.278(13)
C(31)–C(32)	1.511(9)	N(29)–C(34)	1.490(5)		

Fe–O(1)–Fe′	108.0(4)	C(3)–C(8)–C(9)	124.6(3)	C(16)–C(21)–C(20)	118.2(4)
O(1)–Fe–O(1′)	72.0(1)	C(3)–C(8)–C(13)	117.3(3)	C(20)–C(21)–C(22)	118.9(4)
O(1)–Fe–O(14)	91.5(1)	C(9)–C(8)–C(13)	118.0(3)	C(21)–C(22)–C(23)	122.1(3)
O(1)–Fe–O(15)	91.6(1)	C(8)–C(9)–O(14)	124.1(3)	C(21)–C(22)–C(27)	119.6(3)
O(1)–Fe–O(28)	166.1(1)	C(8)–C(9)–C(10)	119.4(3)	C(23)–C(22)–C(27)	118.2(4)
O(1′)–Fe–O(14)	123.7(1)	C(10)–C(9)–O(14)	116.4(3)	C(22)–C(23)–C(24)	119.6(3)
O(1′)–Fe–O(15)	120.9(1)	C(9)–C(10)–C(11)	120.8(4)	C(22)–C(23)–C(28)	121.2(3)
O(1′)–Fe–O(28)	94.3(1)	C(10)–C(11)–C(12)	120.2(4)	C(24)–C(23)–C(28)	119.1(3)
O(14)–Fe–O(15)	112.8(1)	C(11)–C(12)–C(13)	119.1(4)	C(23)–C(24)–C(25)	121.1(4)
O(14)–Fe–O(28)	97.9(1)	C(12)–C(13)–C(8)	122.3(4)	C(24)–C(25)–C(26)	119.7(4)
O(15)–Fe–O(28)	94.0(1)	Fe–O(14)–C(9)	134.2(2)	C(25)–C(26)–C(27)	120.1(4)
Fe–O(1)–C(2)	118.1(2)	Fe–O(15)–C(16)	119.5(2)	C(26)–C(27)–C(22)	121.4(4)
O(1)–C(2)–C(3)	120.0(3)	O(15)–C(16)–C(17)	118.0(4)	Fe–O(28)–C(23)	122.6(2)
O(1)–C(2)–C(7)	118.7(3)	O(15)–C(16)–C(21)	121.2(3)	C(30)–N(29)–C(34)	113.0(4)
C(3)–C(2)–C(7)	121.2(3)	C(17)–C(16)–C(21)	120.7(4)	N(29)–C(30)–C(31)	111.3(4)
C(2)–C(3)–C(4)	117.0(3)	C(16)–C(17)–C(18)	120.0(4)	C(30)–C(31)–C(32)	110.5(5)
C(2)–C(3)–C(8)	123.4(3)	C(17)–C(18)–C(19)	119.7(4)	C(31)–C(32)–C(33)	111.2(5)
C(4)–C(3)–C(8)	119.3(3)	C(18)–C(19)–C(20)	119.8(4)	C(32)–C(33)–C(34)	111.1(5)
C(3)–C(4)–C(5)	121.5(4)	C(19)–C(20)–C(21)	121.5(4)	C(33)–C(34)–N(29)	109.8(4)
C(4)–C(5)–C(6)	120.5(4)	C(16)–C(21)–C(22)	122.9(3)	O(35)–C(36)–C(37)	120.7(10)
C(5)–C(6)–C(7)	119.4(4)				
C(6)–C(7)–C(2)	120.2(4)				

planes of their respective phenyl rings (Δd = 0.01 and 0.02 Å respectively), O(15) and O(28) deviate somewhat more from their phenyl-ring planes (Δd = 0.10 and 0.07 Å respectively).

The oxygen atom of the ethanol molecule is well defined by the crystal-structure analysis but the two carbon atoms of the ethanol molecule are not. The oxygen atom, O(35), is hydrogen bonded to H(29A) of the piperidinium ion and the other

$$\mathrm{O(35)} \overset{1.78\,Å}{\cdots} \mathrm{H(29A)} \overset{167}{} \overset{1.05\,Å}{\text{——}} \mathrm{N(29)}$$
$$\longleftarrow 2.81\,Å \longrightarrow$$

hydrogen of the piperidinium nitrogen, N(29B), is hydrogen bonded to O(28) of the ligand. A further hydrogen bond is

$$\mathrm{O(28)} \overset{1.70\,Å}{\cdots} \mathrm{H(29B)} \overset{175°}{} \overset{1.05\,Å}{\text{——}} \mathrm{N(29)}$$
$$\longleftarrow 2.75\,Å \longrightarrow$$

indicated by a peak in the final difference Fourier, corresponding to the hydrogen connected to the ethanol oxygen O(35). This is confirmed by the known O(35) $\cdots$ O(15) distance of 2.76 Å. In this way the structure forms hydrogen-bonded chains in the [010] direction.

$$\mathrm{C(36)} \overset{1.443\,Å}{\text{——}} \overset{115°}{\mathrm{O(35)}} \overset{1.20\,Å}{\text{——}} \overset{150}{\mathrm{H(35)}} \overset{1.65\,Å}{\cdots} \mathrm{O(15)}$$
$$\longleftarrow 2.76\,Å \longrightarrow$$

The Fe–O bond lengths span the range found in other iron(III) complexes with phenolate-type ligands,[2–4,9] however the individual distances are influenced by the observed hydrogen-bonding pattern. The shortest Fe–O bond length is Fe–O(14) at 1.851(2) Å. This is considerably shorter than Fe–O(15) and Fe–O(28) [1.896(2) and 1.933(2) Å] which are both hydrogen bonded (to ethanol and the piperidinium ion respectively). The remaining pair of Fe–O bonds are Fe–O(1′) and Fe–O(1), at 1.966(2) and 2.056(2) Å, but these are now bridging rather than terminal. The shortest O–C(phenyl) bond is O(14)–C(9) at 1.347(4) Å, and the others are all longer [1.356(4), 1.360(4), and 1.360(4) Å]. All other bond lengths and angles are normal and there are only van der Waals contacts between the [010] columns.

Physicochemical Studies of $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$.—Magnetic and spectroscopic data obtained on the solid-state complex are in keeping with the dimeric $[(FeL_2)_2]^{2-}$ structure, with weak antiferromagnetic coupling *via* the bridging oxygen atoms. The room-temperature magnetic moment for the complex is 4.73 μ_B per iron atom, and is considerably lower than the spin-only value for five unpaired electrons (5.92 μ_B). The magnetic moment drops to 3.02 μ_B at 101 K. Experimental magnetic susceptibility data over the temperature range 101—273 K could be fitted to the equation[10] for binuclear complexes of metal ions with $S = \frac{5}{2}$ by a $|J|$ value of 14 ± 1 cm^{-1}. The $|J|$ value falls within the range 7—17 cm^{-1} found for other iron(III) dimers with similar Fe–O–Fe bridging angles (103—111°) and Fe–O(bridging) distances (1.93—2.00 Å).[11]

The ^{57}Fe Mössbauer spectrum, recorded at room temper-

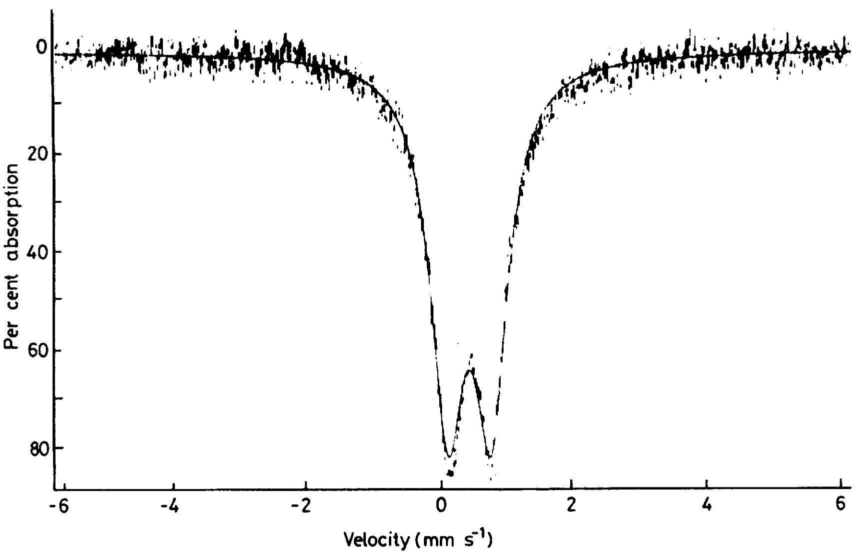

Figure 2. Room-temperature ^{57}Fe Mössbauer spectrum of powdered $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$

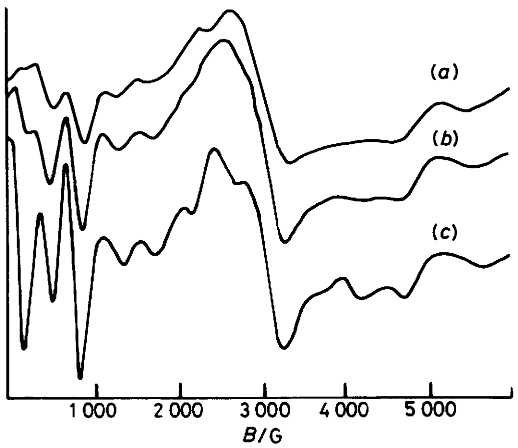

Figure 3. *X*-Band e.s.r. spectra of powdered $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ at +20 (*a*), −70 (*b*), and −120 °C (*c*)

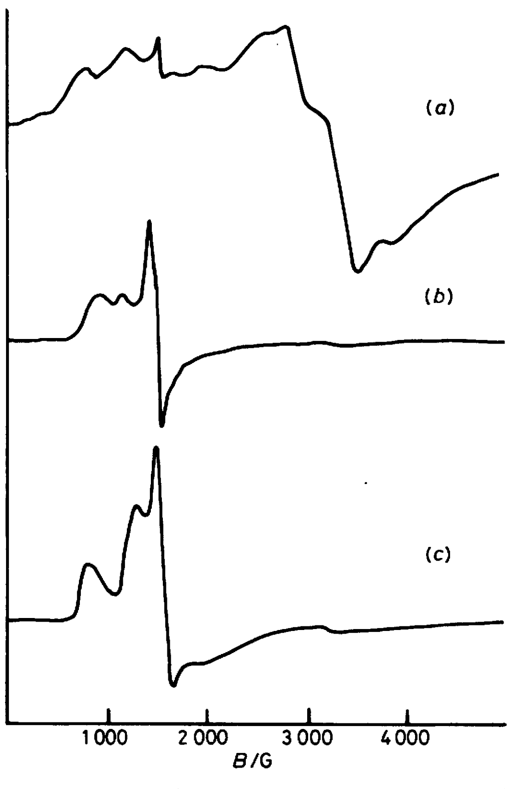

Figure 4. Frozen-solution e.s.r. spectra of $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ in $CHCl_3$ (*a*), pyridine (*b*), and 1-methylimidazole (*c*)

ature (Figure 2), clearly indicates that the complex contains high-spin iron(III) irons [12] and yields the following parameters: isomer shift (*vs.* iron metal), 0.46 mm s^{-1}; quadrupole splitting, 0.65 mm s^{-1}. Although high-spin iron(III) complexes can exhibit quadrupole splittings of 1 mm s^{-1} or greater, the lower value obtained for $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ is still a reflection of a relatively unsymmetrical ligand field about the metal ion.

The *X*-band e.s.r. spectrum of the powdered complex recorded at room temperature and below (Figure 3) is complicated, but is in line with the dimeric nature of the $[(FeL_2)_2]^{2-}$ unit. Complex e.s.r. spectra have been reported previously by Wollmann and Hendrickson [13] for a series of complexes [{Fe(salen)X}$_2$] [salen = *N*,*N*′-ethylenebis(salicylideneiminate), X = anion] which were postulated to have dimeric structures. As pointed out by these authors such dimeric iron(III) complexes would have a number of electronic states giving rise to e.s.r. signals and these would be further complicated by single-ion and dipolar zero-field interactions. Dissolving $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ in $CHCl_3$ yields a spectrum at low temperature not unlike its room-temperature solid-state spectrum (*e.g.* a broad resonance between 3 000 and 5 000 G) (Figure 4) indicating the dimeric structure is retained. However, the use of nitrogen-donor solvents (pyridine, 1-methylimidazole, and piperidine) gives rise to spectra which have a strong signal with $g \approx 4.3$ and weaker ones at higher g values (Figure 4 and Table 2). Such spectra are typical of monomeric iron(III) ($S = \frac{5}{2}$) complexes in a rhombic environment [2,7] and point to a breaking up of the $[(FeL_2)_2]^{2-}$ moiety. It may be noted that in $CHCl_3$ a weak signal is seen at $g \approx 4.3$ (Figure 4) showing that, even in this

Table 2. E.s.r. and electronic spectral data for the complex $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$

Solvent	*g* [a]	$\lambda_{max.}$ [b]/nm
$CHCl_3$	*c*	420 (sh) (1 600)
Pyridine	6.99, 5.69, 4.30, ≈2.00	485 (*ca.* 1 600)
1-Methylimidazole	8.08, 5.03, 4.20, ≈2.02	535
Piperidine [d]	6.81, 5.39, 4.26, ≈1.99	438

[a] At −160 °C. [b] Absorption coefficients ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) per iron are given in parentheses; sh = shoulder. [c] See Figure 4. [d] Freshly prepared solution.

solvent, slight dissociation has occurred. The e.s.r. spectra of the pyridine and 1-methylimidazole solutions remain virtually unchanged with time, however the spectrum of the piperidine solution gradually develops a resonance at $g = 2.02$, indicative of the formation of a low-spin iron(III) species. After 4 d the signal at $g = 4.26$ has virtually disappeared.

Further support for the dissociation of the $[(FeL_2)_2]^{2-}$ unit in N-donor solvents comes from electronic spectral measurements. The visible spectrum of $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ in both the solid state and $CHCl_3$ is dominated by a broad shoulder at *ca.* 420 nm which can be assigned [2,14] to a ligand-to-metal charge-transfer (c.t.) transition involving the p_π phenolate oxygen orbitals and the half-filled d_π^* orbitals on the Fe^{III}. Since the wavelength of this type of c.t. band is sensitive to the nature of the Fe–O(phenoxide) bonding,[2] and the complex contains both terminal and bridged phenoxides, as well as a wide variation in Fe–O bond lengths [1.851(2)—2.056(2) Å], the band would be expected to contain several components. In the nitrogen-donor solvents the c.t. band becomes a clearly resolved maximum in line with the formation of a monomeric species such as $[FeL_2(solv)_2]^-$ (solv = pyridine, 1-methylimidazole, or piperidine). It has not been possible to isolate any complexes from these solutions, however Andrä and co-workers [6] have isolated stoicheiometrically similar L^{2-} ligand complexes with Sn^{IV} and Ti^{IV}, *e.g.* $SnL_2(py)_2$ and $TiL_2(py)_2$ (py = pyridine).

Experimental

Physical measurements were made as described previously.[2] Microanalyses were by Professor A. D. Campbell, University of Otago. The protonated ligand, 1,1′-biphenyl-2,2′diol, was used as purchased from Aldrich Chemical Co. E.s.r. spectra in piperidine were recorded on degassed solutions under dinitrogen.

Synthesis of the Complex $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$.—To the diol H_2L (4.6 g, 25 mmol), dissolved in ethanol, was added iron(III) perchlorate hexahydrate (4.6 g, 10 mmol) dissolved in the same solvent, giving a total ethanol volume of *ca.* 200 cm³. Excess of piperidine (5 cm³, 50 mmol) was then added to the resulting blue-black solution causing an immediate colour change to dark red. After filtration, the solution was refluxed gently for 1 h, cooled, and allowed to stand for 2 h. The dark red-brown crystals of the *product* were filtered off, washed with ethanol, and air dried. Yield 4.3 g (78%) (Found: C, 66.2; H, 6.0; N, 2.6. $C_{31}H_{34}FeNO_5$ requires C, 66.9; H, 6.2; N, 2.5%). The complex slowly loses ethanol on standing in air. The same complex results when the H_2L : Fe ratio is increased to 3 : 1.

Table 3. Final atomic co-ordinates (× 10^4) for $[C_5H_{12}N]_2[(FeL_2)_2]\cdot 2EtOH$ with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	4 503(1)	5 148(1)	1 411(1)
O(1)	5 624(2)	3 694(3)	120(2)
C(2)	6 188(4)	2 188(5)	465(3)
C(3)	7 066(4)	1 740(5)	912(4)
C(4)	7 616(4)	165(5)	1 246(4)
C(5)	7 305(5)	−895(6)	1 130(5)
C(6)	6 451(4)	−433(6)	666(4)
C(7)	5 876(4)	1 114(5)	350(4)
C(8)	7 506(4)	2 815(5)	949(4)
C(9)	6 824(4)	4 185(5)	1 462(4)
C(10)	7 350(4)	5 031(6)	1 551(5)
C(11)	8 530(5)	4 531(7)	1 115(6)
C(12)	9 210(4)	3 203(6)	574(6)
C(13)	8 698(4)	2 364(6)	494(5)
O(14)	5 671(2)	4 743(4)	1 942(2)
O(15)	3 731(3)	3 838(3)	2 225(3)
C(16)	3 307(4)	3 696(5)	3 428(4)
C(17)	3 872(5)	2 335(6)	4 032(5)
C(18)	3 411(6)	2 082(7)	5 273(5)
C(19)	2 422(6)	3 200(8)	5 883(5)
C(20)	1 878(5)	4 582(7)	5 272(4)
C(21)	2 302(4)	4 844(5)	4 040(4)
C(22)	1 655(4)	6 310(5)	3 439(4)
C(23)	2 188(4)	7 241(5)	2 602(4)
C(24)	1 527(4)	8 645(5)	2 111(4)
C(25)	353(4)	9 135(6)	2 432(5)
C(26)	−175(4)	8 221(7)	3 243(5)
C(27)	467(4)	6 826(6)	3 738(5)
O(28)	3 328(2)	8 646(3)	2 315(2)
N(29)	3 310(4)	9 066(5)	3 217(4)
C(30)	4 423(5)	8 372(7)	3 450(6)
C(31)	4 513(6)	6 986(7)	4 337(6)
C(32)	3 505(8)	7 383(9)	5 471(6)
C(33)	2 374(7)	8 077(8)	5 243(6)
C(34)	2 286(5)	9 488(7)	4 307(5)
O(35)	3 030(3)	11 913(4)	1 849(3)
C(36)	1 973(10)	13 025(13)	1 646(10)
C(37)	1 013(13)	13 335(16)	2 492(14)

Crystallography.—The crystals of the title complex are dark red-brown prisms. Preliminary photography indicated triclinic symmetry and subsequent solution and refinement confirmed the space group as $P\bar{1}$. Lattice constants and the orientation matrix used for data collection were obtained from least-squares refinement of the diffractometer settings for 12 reflections for which $16 < \theta < 20°$.

Crystal data. $C_{62}H_{68}Fe_2N_2O_{10}$, $M = 1\,112.9$, Triclinic $a = 14.058(2)$, $b = 9.976(1)$, $c = 12.517(1)$ Å, $\alpha = 73.41(1)$, $\beta = 65.29(1)$ $\gamma = 61.48(1)°$, $U = 1\,393$ Å³, $Z = 1$, $D_c = 1.33$ g cm⁻³, $F(000) = 586$, Cu-K_α radiation, $\lambda = 1.5418$ Å, μ(Cu-K_α) = 46.3 cm⁻¹, space group $P\bar{1}$.

Data collection and structure solution. Data were collected using a Hilger and Watts four-circle auto-diffractometer with a θ—2θ scan consisting of 70 steps of 0.01° with 1 s per step. The local background was measured at either side of the scan for 15 s using a stationary counter and stationary crystal. A total of 3 937 reflections for which $\theta < 57°$ were measured. The intensities of three reflections measured periodically throughout the data collection showed only random fluctuations of ±3%. Absorption corrections were applied using the analytical method,[15] the corrections ranging from 2.33 to 5.52.

The structure was solved by direct methods [16] and refined to convergence with anisotropic thermal parameters for all non-hydrogen atoms except those of the occluded ethanol molecule, which were refined with isotropic thermal parameters. Structure factors for Fe were taken from ref. 17, otherwise the values present in the program were used.[16] Hydrogen atoms were placed in calculated positions verified from a difference Fourier synthesis and not refined ($U_H = 0.08$ Å^2). Atoms C(35) and C(36) of the ethanol molecule were not well defined and hydrogen atoms associated with them were not included in the final cycle. The refinement converged at $R = 0.052$ and $R' = 0.059$ for the 3 473 reflections for which $I > 2.5\sigma(I)$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma_F)^2$. A final difference Fourier synthesis showed peaks in the vicinity of the obviously disordered ethanol molecule, but no other peaks of any chemical significance. Due to the high cost of refinement (*ca.* $300 per cycle) we did not try further to resolve the disorder of the ethanol molecule. Final atomic co-ordinates are listed in Table 3. Local programs were used for data reduction; otherwise SHELX 76, G. M. Sheldrick, University of Cambridge, 1976 was used.

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References

1 E. W. Ainscough, A. M. Brodie, and J. E. Plowman, *Inorg. Chim. Acta*, 1979, **33**, 149; E. W. Ainscough, A. M. Brodie, J. E. Plowman, S. J. Bloor, J. S. Loehr, and T. M. Loehr, *Biochemistry*, 1980, **19**, 4072.

2 E. W. Ainscough, A. M. Brodie, J. E. Plowman, K. L. Brown, A. W. Addison, and A. R. Gainsford, *Inorg. Chem.*, 1980, **19**, 3655.

3 B. F. Anderson, D. A. Buckingham, G. B. Robertson, J. Webb, K. S. Murray,and P. E. Clark, *Nature (London)*, 1976, **262**, 722.

4 K. N. Raymond, S. S. Isied, L. D. Brown, F. R. Fronczek, and J. H. Nibert, *J. Am. Chem. Soc.*, 1976, **98**, 1767.

5 O. L. Brady and E. D. Hughes, *J. Chem. Soc.*, 1933, 1227.

6 See, for example, K. Andrä, *Chem. Ber.*, 1968, **101**, 1013; K. Andrä and H. R. Hoppe, *Z. Anorg. Allg. Chem.*, 1975, **413**, 97; K. Andrä and F. Fleischer, *ibid.*, 1982, **485**, 210.

7 J. F. Gibson, 'ESR and NMR of Paramagnetic Species in Biological and Related Systems,' eds. I. Bertini and R. S. Drago, D. Reidel, Holland, 1979, p. 225.

8 I. Leupold and H. Musso, *Liebigs Ann. Chem.*, 1971, **746**, 134; J. E. Gordon and S. L. Johnson, *J. Phys. Chem.*, 1962, **66**, 534.

9 J. E. Davies and B. M. Gatehouse, *Acta Crystallogr., Sect. B*, 1972, **28**, 3641; P. Coggan, A. T. McPhail, F. E. Mabbs, and V. N. McLachlan, *J. Chem. Soc. A*, 1971, 1010; N. A. Bailey, D. Cummins, E. D. McKenzie, and J. M. Worthington, *Inorg. Chim. Acta*, 1981, **50**, 111.

10 A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 1961, 396.

11 J. A. Thich, B. H. Toby, D. A. Powers, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, 1981, **20**, 3314 and refs. therein.

12 N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

13 R. G. Wollmann and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 926.

14 B. P. Gaber, V. Miskowski, and T. G. Spiro, *J. Am. Chem. Soc.*, 1974, **96**, 6868.

15 J. de Meulenaer and H. Tompa, *Acta Crystallogr.*, 1965, **19**, 1014.

16 P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. De Clercq, MULTAN 77, A System of Computer Programs for the Automatic Solution of Crystal Structures, Universities of York (England) and Louvain (Belgium), 1977.

17 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1968, vol. 3.

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