Crystal and Molecular Structure and some Properties of Pyridinium μ-Oxo-bis[trichloroferrate(III)]–Pyridine

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The crystal structure of the title complex, $[Hpy]_2[Cl_3Fe-O-FeCl_3]\cdot py$, prepared by hydrolysis of $FeCl_3$ in aqueous ethanol–pyridine, has been determined. Crystals are monoclinic with $a = 8.532(6)$, $b = 13.914(11)$, $c = 10.597(11)$ Å, $\beta = 110.8(1)°$, $Z = 2$, and space group $P2_1/m$. The structure has been solved by Patterson and Fourier methods and refined by full-matrix least squares to R 0.056 for 1 236 independent above-background reflections measured by diffractometer. In the complex anion which has crystallographically imposed C_s symmetry, the two equivalent $FeOCl_3$ units are bridged by the oxygen atom *via* short Fe–O bonds [1.755(3) Å], the Fe–O–Fe angle being 155.6(7)°. The geometry about each metal is close to tetrahedral, the Cl–Fe–Cl and Cl–Fe–O angles being 108—111°. The Fe–Cl distances (2.208—2.219 Å) are somewhat lengthened with respect to those in $[FeCl_4]^-$. Strong antiferromagnetic coupling between the $S = \frac{5}{2}$ spins in the binuclear anion is observed. The coupling constant, $J = -92$ cm^{-1}, is not appreciably different from values reported for other binuclear μ-oxo-complexes in which the iron(III) ions are in a square-pyramidal or octahedral environment. Infrared and Mössbauer spectra are reported.

OXO-BRIDGED complexes of iron(III) are of considerable interest and importance. First, they constitute a convenient class of compound for the study of magnetic-exchange interaction between paramagnetic centres.[1-5] Secondly, the aqueous chemistry of Fe^{III} is dominated by its tendency to undergo hydrolytic polymerization.[6,7] Thirdly, antiferromagnetically coupled Fe^{III} is believed to occur in a number of iron-transport and iron-storage proteins.[7,8] Moreover, μ-oxo-di-iron(III) complexes appear to be the end products of the autoxidation of natural and synthetic iron(II)–dioxygen carriers.[9]

A number of μ-oxo-iron(III) complexes have been studied in some detail, particularly in regard to their magnetic properties and electronic and Mössbauer spectra, and several have been structurally analyzed by single-crystal X-ray methods.[10] All these are chelate complexes in which the co-ordination geometry is square pyramidal, octahedral, or, in a very few cases, pentagonal bipyramidal. In this paper we describe the structure and properties of the complex pyridinium μ-oxo-bis-[trichloroferrate(III)]–pyridine, $[Hpy]_2[Cl_3Fe-O-FeCl_3]\cdot py$, the first example of a μ-oxo-di-iron(III) complex in which all the non-bridging ligands are unidentate and where the metal ions are tetrahedrally co-ordinated. This complex is of some biochemical interest in the light of the recent suggestion,[7,8] based on electronic spectra, that the green form of iron(III) phosvitin, a phosphoglycoprotein, contains polynuclear clusters of tetrahedrally co-ordinated iron(III) ions linked by oxygen bridges. A study of this complex also allows a determination of the influence, if any, of the tetrahedral symmetry about the metal on the structural and magnetic parameters associated with the Fe–O–Fe bridging unit.

RESULTS AND DISCUSSION

The complex $[Hpy]_2[Fe_2OCl_6]\cdot py$ was prepared by hydrolysis of $FeCl_3$ in ethanol–pyridine solvent mixtures. The $FeCl_3$: py ratio and the concentration of water were quite critical. Best results (see Experimental section) were obtained when the pyridine : metal ratio was between 1.5 and 3.0 : 1 and the water concentration did not exceed *ca.* 2%. Reaction of $FeCl_3$ with neat anhydrous pyridine yielded red crystals which are probably the same as those described by Cotton and Gibson [11] as *fac*-$Fe(py)_3Cl_3\cdot py$. We did not investigate this complex further except to observe that on exposure to air it appeared to lose py and to absorb moisture with accompanying formation of a μ-oxo-species as judged by the development of a strong band at 860 cm^{-1} in the i.r. spectrum. Reaction of $FeCl_3$ with 1 molar proportion of py in ethanol (not rigorously dried) yielded a complex of stoicheiometry $[Hpy]_3[Fe_2Cl_9]$. Infrared spectra of this complex confirmed the presence of the pyridinium ion and the absence of an Fe–O–Fe bridge. A strong band at 385 cm^{-1} is attributable to ν(Fe–Cl) of the tetrahedral $[FeCl_4]^-$ anion. This complex is almost certainly that examined by Ginsberg and Robin [12] who showed that it did not contain any binuclear species, only $[FeCl_4]^-$. All the other products isolated from $FeCl_3$–pyridine–ethanol mixtures containing small amounts of water indicated, from i.r. spectra, the presence of both the Fe–O–Fe unit and of the $[Hpy]^+$ ion (see later). However, they varied in com-

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[1] E. Sinn, *Co-ordination Chem. Rev.*, 1970, **5**, 313; P. W. Ball, *ibid.*, 1969, **4**, 361.

[2] J. Lewis, F. E. Mabbs, and A. Richards, *J. Chem. Soc.* (*A*), 1967, 1014.

[3] H. J. Schugar, G. R. Rossman, C. G. Barraclough, and H. B. Gray, *J. Amer. Chem. Soc.*, 1972, **94**, 2683.

[4] A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, 1971, **5**, 45.

[5] R. L. Martin, in 'New Pathways in Inorganic Chemistry,' eds. E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Cambridge University Press, Cambridge, 1968, p. 175.

[6] S. A. Cotton, *Co-ordination Chem. Rev.*, 1972, **8**, 185.

[7] J. Webb, in 'Techniques and Topics in Bioinorganic Chemistry,' ed. C. A. McAuliffe, Macmillan, London, 1973, p. 271.

[8] H. B. Gray, in 'Proteins of Iron Storage and Transport in Biochemistry and Medicine,' ed. R. R. Crichton, North Holland, Amsterdam, 1975, p. 3.

[9] J. M. Pratt, ref. 7, p. 146.

[10] For a recent review, see K. S. Murray, *Co-ordination Chem. Rev.*, 1974, **12**, 1.

[11] S. A. Cotton and J. F. Gibson, *J. Chem. Soc.* (*A*), 1971, 1696.

[12] A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, 1963, **2**, 817.

position according to the amount of excess of pyridine, with respect to $FeCl_3$, present in the solutions from which they were prepared. All the analytical data could be fitted to the formula $[Hpy]_2[Fe_2OCl_6]\cdot x$py ($x$ = *ca.* 0.5—2.5), but only when $x = 1$ did the product consist of large well formed crystals. Thermogravimetric analysis (t.g.a.) confirmed the authenticity of the 1 : 1 pyridine adduct as a distinct chemical species rather than a mixture of other complexes of different pyridine contents. All the products were yellow-orange. This observation, together with information derived from i.r. spectra and t.g.a. experiments, suggested that in all these products the pyridine is unco-ordinated. Although t.g.a. showed a discontinuity in the rate of loss of pyridine from the 1 : 1 adduct at a composition corresponding to pyridine-free $[Hpy]_2[Fe_2OCl_6]$, attempts to isolate this complex in a pure form were not successful.

Crystal Data.—$C_{15}H_{17}Cl_6Fe_2N_3O$, $M = 578.3$, Monoclinic, $a = 8.532(6)$, $b = 13.914(11)$, $c = 10.597(11)$ Å, $\beta = 110.8(1)°$, $U = 1\,177.5$ Å^3, $D_m = 1.62$, $Z = 2$, $D_c = 1.63$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 19.3$ cm^{-1}. Space group $P2_1/m$ from systematic absences $0k0$ ($k = 2n + 1$) and the successful structure determination.

A crystal with dimensions *ca.* 0.3 × 0.7 × 0.3 mm was mounted with the 010 planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities and cell dimensions (*via* a least-squares treatment of 2θ values of high-angle reflections). The instrument was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered Mo-K_α radiation was used with the stationary-crystal–stationary-counter method, a 4° take-off angle, and a counting time of 10 s. Individual backgrounds were taken for reflections whose counts were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of backgrounds against 2θ. Several standard reflections were monitored during the course of the experiment and showed no significant changes in intensity. No absorption or extinction corrections were applied. Of 1 620 independent reflections measured with $2\theta < 45°$, 1 236 with $I > \sigma(I)$ were used in subsequent calculations.

Structure Determination.—The structure was determined from Patterson and Fourier syntheses and refined by full-matrix least squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and $\sin\theta/\lambda$, was $w^{\frac{1}{2}} = 1$ for $F_o < 60$ and $w^{\frac{1}{2}} = F_o/60$ for $F_o > 60$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre using published programs.[13] Atomic-scattering factors used were taken from ref. 14 as were the anomalous dispersion corrections for Fe and Cl. The anisotropic thermal parameter is defined as $\exp(-2\pi^2\Sigma_i\Sigma_jU_{ij}b_ib_jh_ih_j)$ (i, j = 1—3) where b_i is the ith reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2\sin^2\theta/\lambda^2)$. A difference-Fourier map based on the heavy atoms gave the positions of the hydrogen atoms of the pyridine rings. In two of the three rings the nitrogen atoms had a hydrogen atom attached and are thus identified as $[Hpy]^+$, the other being solvent py.* Only the hydrogen atoms of one ring could be refined; the others were given fixed parameters in trigonal positions and with a thermal parameter equivalent to that of the atom to which they were bonded. The final R value was 0.056. A subsequent difference-Fourier map showed no significant peaks, and the zero-weighted reflections had no serious discrepancies. In the final cycle no shift was greater than 0.1σ. Final positional co-ordinates are given in Table 1, bond lengths and angles in Table 2. Thermal parameters and observed and calculated structure factors are given in Supplementary Publication No. SUP 22141 (6 pp.).†

TABLE 1

Positional parameters (× 10^4; H, × 10^3) with estimated standard deviations in parentheses

Atom	x	y	z
Fe	1 344(2)	3 732(1)	2 922(1)
Cl(1)	−1 256(3)	4 173(2)	1 715(3)
Cl(2)	1 913(4)	4 070(2)	5 074(2)
Cl(3)	3 024(3)	4 594(2)	2 188(3)
O	1 592(13)	2 500 [a]	2 698(9)
N(11)	4 149(16)	7 500 [a]	4 294(13)
C(12)	3 807(14)	6 665(8)	4 752(11)
C(13)	3 158(13)	6 642(8)	5 764(11)
C(14)	2 803(21)	7 500 [a]	6 264(15)
N(21)	4 947(15)	2 500 [a]	7 947(12)
C(22)	4 783(14)	3 314(9)	8 535(11)
C(23)	4 430(15)	3 311(9)	9 704(12)
C(24)	4 214(19)	2 500 [a]	10 274(15)
N(31)	0 587(17)	7 500 [a]	0 740(13)
C(32)	0 319(13)	6 651(7)	1 287(10)
C(33)	−0 247(13)	6 666(7)	2 339(10)
C(34)	−0 498(16)	7 500 [a]	2 848(12)
H(11)	463(21)	750 [a]	380(17)
H(12)	415(13)	609(8)	444(11)
H(13)	289(8)	607(6)	607(8)
H(14)	194(20)	750 [a]	659(17)
H(22) [b]	493	399	809
H(23) [b]	433	399	1 017
H(24) [b]	387	250	1 116
H(31) [b]	097	750	−004
H(32) [b]	055	597	088
H(33) [b]	−049	600	276
H(34) [b]	−092	750	369

[a] Parameter fixed. [b] All parameters fixed.

The Structure.—The unit cell in the c projection is shown in Figure 1. It contains independent $[Hpy]^+$ and $[Fe_2OCl_6]^{2-}$ ions and py solvent, all of which have crystallographically imposed C_s symmetry. In the complex anion two $FeOCl_3$ tetrahedra are bridged *via* the

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* It is possible that the N(31) site is really C and the C(34) site N. We refined both arrangements and chose the most likely one. Disorder between N and C over these two sites is also possible for this ring but not for the other two because of the strong hydrogen bond between them.

† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[13] ' X-Ray ' system of progams, ed. J. M. Stewart, University of Maryland, Computer Science Center, Technical Report TR 192, 1972.

[14] ' International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

oxygen atom. There have been quite a few structural determinations of the tetrahedral $[FeCl_4]^-$ anion. Among the most accurate are those of $[PCl_4][FeCl_4]$[15] and $[Fe(NCMe)_6][FeCl_4]_2$[16] in which the Fe–Cl bond lengths are 2.182—2.187(1) and 2.180—2.186(2) Å, respectively. In the present molecule the Fe–Cl bond lengths are slightly longer (Table 2) than these, presumably because of the strong Fe–O bond. The O–Fe–Cl and Cl–Fe–Cl angles are all close to the tetrahedral value, with the mean value for the former being just slightly greater and the mean value of the latter slightly smaller. Of particular interest are the Fe–O distance and the Fe–O–Fe bond angle. A recent review[10] on binuclear μ-oxo-di-iron(III) complexes lists eight examples on which crystal structure data are available. In these complexes, in which the metal ion is five-, six-, or seven-co-ordinate, the Fe–O bond lengths range from 1.76 to 1.82 Å, and the Fe–O–Fe angles vary widely between 139 and 178°, with no apparent correlation between the two parameters (Table 4). In the present complex the Fe–O bond length [1.755(3) Å] is the shortest yet known for a μ-oxo-di-iron(III) complex. However, the Fe–O–Fe angle [155.6(7)°] falls in the middle of the range of angles referred to above. Packing effects, the anion having C_s symmetry, preclude a much smaller angle in this particular case.

TABLE 2

Bond lengths (Å) and angles (°)

(*i*) The anion			
Fe–O	1.755(3)	O–Fe–Cl(1)	109.7(3)
Fe–Cl(1)	2.219(3)	O–Fe–Cl(2)	110.8(3)
Fe–Cl(2)	2.208(3)	O–Fe–Cl(3)	110.9(3)
Fe–Cl(3)	2.212(3)	Cl(1)–Fe–Cl(2)	110.2(1)
		Cl(1)–Fe–Cl(3)	106.7(1)
Fe–O–Fe^{I}	155.6(7)	Cl(2)–Fe–Cl(3)	108.4(1)
(*ii*) The cations and solvent			
N(11)–C(12)	1.331(14)	C(12^{II})–N(11)–C(12)	121.6(14)
C(12)–C(13)	1.371(19)	N(11)–C(12)–C(13)	120.5(12)
C(13)–C(14)	1.384(15)	C(12)–C(13)–C(14)	118.9(12)
		C(13)–C(14)–C(13^{II})	119.4(16)
N(21)–C(22)	1.324(15)	C(22^{I})–N(21)–C(22)	117.6(13)
C(22)–C(23)	1.376(20)	N(21)–C(22)–C(23)	121.0(12)
C(23)–C(24)	1.323(17)	C(22)–C(23)–C(24)	121.6(13)
		C(23)–C(24)–C(23^{I})	117.1(16)
N(31)–C(32)	1.371(13)	C(32^{II})–N(31)–C(32)	119.1(13)
C(32)–C(33)	1.364(18)	N(31)–C(32)–C(33)	119.5(10)
C(33)–C(34)	1.329(13)	C(32)–C(33)–C(34)	120.1(10)
		C(33)–C(34)–C(33^{II})	121.7(13)

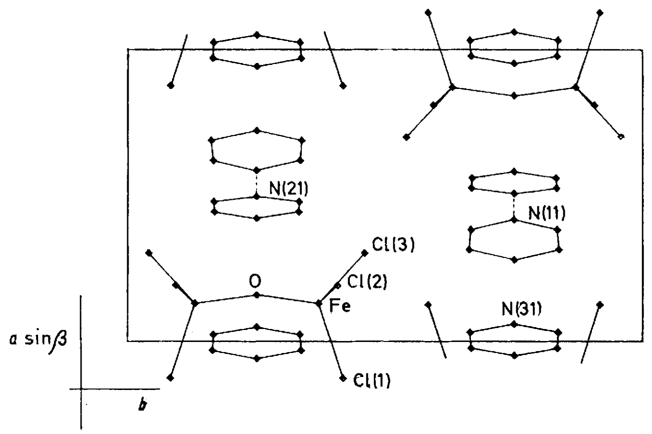

FIGURE 1 Unit cell in the *c* projection. Broken lines represent the proposed hydrogen-bonding scheme

The geometry of the $[Hpy]^+$ ions and the py molecule are as expected. There is just one short intermolecular contact, *viz.* N(11) · · · N(21) 2.747 Å, which must represent a strong hydrogen bond between $[Hpy]^+$ and py; the N–H · · · N angle is 160°. The remaining contacts are given in Table 3.

TABLE 3

Intermolecular distances, excluding those to hydrogen less than 3.60 Å

C(12) · · · C(33)	3.50		N(21) · · · N(31^{III})	3.56
N(21) · · · N(11^{III})	2.75		N(21) · · · C(12^{III})	3.58
C(23) · · · C(33^{IV})	3.46		Cl(1) · · · C(33)	3.58
O · · · N(31^{V})	3.45		N(21) · · · C(34^{IV})	3.58
C(32) · · · Cl(3)	3.59			

* Roman numerals as superscripts refer to the following equivalent positions relative to the *x*, *y*, *z* set in Table 1:

I $x, \frac{1}{2} - y, z$
II $x, \frac{3}{2} - y, z$
III $1 - x, 1 - y, 1 - z$
IV $-x, 1 - y, 1 - z$
V $-x, 1 - y, -z$

Infrared Spectra.—The most striking feature of the i.r. spectrum is an intense broad band at 860 cm^{-1}. Strong absorption in this region is a characteristic of μ-oxo-di-iron(III) complexes[10] and we therefore assign this band to the Fe–O–Fe antisymmetric stretch; significantly, it is absent in the spectrum of $[Hpy]_3[Fe_2Cl_9]$. It occurs at somewhat higher energy than in most other μ-oxo-dimers of Fe^{III} (see Table 4) and this may be due to a stronger than usual Fe–O interaction, a view consistent with the shorter than usual Fe–O distance.

The local symmetry about each iron(III) atom is C_{3v} and, accordingly, two i.r.-active Fe–Cl stretching vibrations, *e* and a_1, are expected. We identify these as the strong band (doubly degenerate antisymmetric Cl–Fe–Cl stretch) occurring at 360 cm^{-1} and the medium-intensity band at 311 cm^{-1} (symmetric stretch). In the tetrahedral anion $[FeCl_4]^-$ the single i.r.-active Fe–Cl stretch occurs at 385 cm^{-1}. The shift to lower energy in the present complex is once again consistent with the crystallographic data, the strong Fe–O interaction serving both to weaken and lengthen the Fe–Cl bond. None of the three bands (at 860, 360, and 311 cm^{-1}) discussed above is present in the spectrum of $[Hpy]_3[Fe_2Cl_9]$, or in that of the red complex $Fe(py)_3Cl_3 \cdot py$.

These bands apart, the spectrum of $[Hpy]_2[Fe_2OCl_6]$ is very similar to the spectra of pyridinium salts such as [Hpy]Cl and including $[Hpy]_3[Fe_2Cl_9]$, except in the 2 000—4 000 cm^{-1} region. The few extra bands

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[15] T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, 1968, **7**, 2150.

[16] G. Constant, J-C Daran, and Y. Jeannin, *J. Organometallic Chem.*, 1972, **44**, 353.

in the spectrum of the μ-oxo-complex can be identified as due to the pyridine adduct molecule. In the 2 000—4 000 cm^{-1} region the present complex shows an N–H stretching vibration as a moderately strong, slightly broad, band at 3 235 cm^{-1}; a weaker absorption at 3 170 cm^{-1} may be an overtone or combination band. In contrast, [Hpy]Cl displays a very intense and very broad absorption centred at *ca.* 2 700 cm^{-1}. The complex $[Hpy]_3[Fe_2Cl_9]$ shows a similar intense broad band at 2 780 cm^{-1}. Both these may be assigned to ν(N–H) in the N–H · · · Cl^- hydrogen bond. It is surprising that ν(N–H) in the present complex is so little affected by hydrogen bonding to the pyridine nitrogen, particularly since the structural data suggest a strong interaction.

TABLE 4

Comparison of some structural, magnetic, and Mössbauer parameters for $[Hpy]_2[Fe_2OCl_6]\cdot py$ with those[a] for other μ-oxo-di-iron(III) complexes

Complex	Fe–O distance (Å)	Fe–O–Fe angle (°)	$-J$/cm^{-1}	δ[b]/mm s^{-1}		ΔE_Q/mm s^{-1}	
				r.t.	77 K	r.t.	77 K
$[Hpy]_2[Fe_2OCl_6]\cdot py$	1.755(3)	155.6(7)	92	0.46	0.60	1.26	1.29
$[Hen]_2[\{Fe(Hedta)\}_2O]\cdot 6H_2O$	1.79	165	95	0.63	0.75	1.69	1.75
$[\{Fe(salen)\}_2O]$	1.77	144	95	0.58	0.56	0.92	0.92
$[\{Fe(salen)\}_2O]\cdot 2py$	1.82	139		0.71	0.79	0.92	0.88
$[\{Fe(salen)\}_2O]\cdot CH_2Cl_2$	1.79	142	87				
$[\{Fe(N\text{-}Pr^n\text{-}sal)_2\}_2O]$	1.77	164	*ca.* 100	0.54	0.58	0.88	0.94
$[\{Fe(N\text{-}p\text{-}ClC_6H_4\text{-}sal)_2\}_2O]$	1.76	175	*ca.* 100				
$[\{Fe(tpp)\}_2O]$	1.763	174.5	100	0.55		0.62	
$[\{Fe(dpop)(OH_2)\}_2O][ClO_4]$	1.8	178	100	0.81		0.62	

en = Ethylenediamine, edta = ethylenediaminetetra-acetate, salen = *NN'*-ethylenebis(salicylideneiminate), sal = salicylaldehydate, tpp= tetraphenylporphyrin, dpop = 2,13-dimethyl-3,6,9,12,18-penta-azabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene.

[a] From data collected in ref. 10. [b] Relative to $Na_2[Fe(CN)_5(NO)]$.

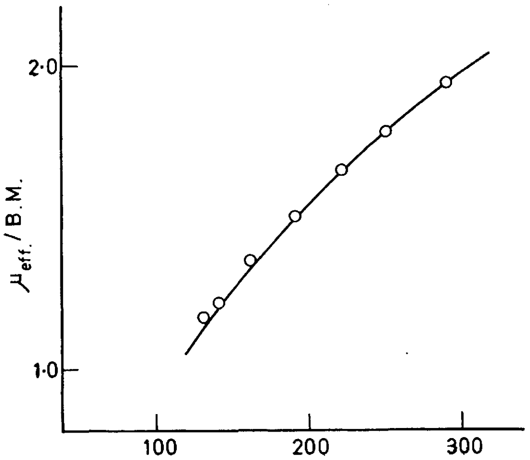

FIGURE 2 Comparison of the variation of the experimental magnetic moments (circles) with those calculated (full line); see text

Magnetic Properties.—The magnetic susceptibility of the solid complex was measured by the Gouy method between 293 and 130 K. The magnetic moment is strongly temperature dependent, decreasing from 1.94 B.M. at 293 K to 1.17 B.M. at 133 K (see Figure 2).* This behaviour, which is reversible, is typical of other μ-oxo-di-iron(III) complexes[10] and is firmly established as being due to antiferromagnetic coupling of spins across the oxygen bridge. While the data do not usually distinguish between the $S = (\frac{5}{2}, \frac{5}{2})$ and $S = (\frac{3}{2}, \frac{3}{2})$ spin states, electronic-spectral measurements[3] on some of these complexes have ruled out the case of intermediate spin, and it seems generally agreed that the interacting spins in all the systems so far studied are $\frac{5}{2}$. If this is so for octahedral and square-pyramidal Fe^{III} then it is even more likely to be so for tetrahedrally co-ordinated Fe^{III} since no case of spin pairing in such a system is known, and a $^6A_1$ ground state is therefore assumed.

Figure 2 compares the observed magnetic moments as a function of temperature with those calculated from expression (1),[10] where $x = \exp(J/kT)$, for values of the

$$\chi_A = \frac{N\beta^2 g^2(55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28})}{kT(11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30})} + N\alpha \quad (1)$$

coupling constant $J = -92$ cm^{-1}, $g = 2.00$, and $N_\alpha = 0$. The small departure of the observed from the theoretical values at the lower temperatures can be attributed to the presence of small amounts of monomeric iron(III) impurity.

Mössbauer Spectra.—Spectra at both 293 and 77 K consist of a single quadrupole-split doublet. Isomer shifts and quadrupole splittings are compared with corresponding data for other μ-oxo-systems in Table 4. Both the δ and ΔE_Q values obtained for $[Hpy]_2[Fe_2OCl_6]\cdot py$ are in the ranges associated with iron in the $S = \frac{5}{2}$ spin state, but the δ values are somewhat less positive than those of most other μ-oxo-complexes. It is commonly observed that tetrahedral complexes have a less positive isomer shift than most octahedral complexes as a result of the greater covalent character of the bonds.[17] The large quadrupole splitting (1.29 mm s^{-1} at 77 K) presumably reflects the considerable electronic asymmetry about the metal ion due to the occurrence of a strong Fe–O bond and weakened Fe–Cl bonds; in

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

[17] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' Chapman and Hall, London, 1971.

most salts of $[FeCl_4]$ the quadrupole splitting is too small to be measured.[15]

Electronic Spectra.—The electronic spectrum of the solid complex was recorded between 50 000 and 10 000 cm^{-1}. The spectrum is dominated by a strong $Cl \rightarrow Fe^{III}$ charge-transfer band at *ca.* 30 000 cm^{-1}, and at higher energies by bands due to pyridine and pyridinium ion. Weak ligand-field sextet–quartet bands have been detected in the range 22 000—27 000 cm^{-1} in the spectra of iron(III)-doped orthoclase feldspar (which contains the tetrahedral FeO_4 chromophore).[8] However, spin-forbidden bands in this region are unlikely to be detectable in the present complex although a shoulder at *ca.* 24 500 cm^{-1} was noted on the side of the charge-transfer band. However, we are unable to suggest an assignment. Spectra of solutions in methylene chloride and in ethanol differed from that of the solid and from each other. Since we have no knowledge of the nature of the species occurring in solution these spectra will not be discussed.

Conclusions.—We have shown that strong antiferromagnetic superexchange occurs between two tetrahedrally co-ordinated $S = \frac{5}{2}$ iron(III) ions linked *via* oxygen in a non-linear bridge comprising particularly short Fe–O bonds. It is pertinent to consider what relation might exist between the structures of this and other μ-oxo-complexes and the magnitude of the coupling constant J. Relevant data are collected in Table 4. We see that in fact there is little variation in J from one complex to another. The theory of the coupling of spins has been treated in some depth by several workers.[18,19] With regard to the mechanism of the exchange between two $S = \frac{5}{2}$ spins, two paths have been suggested, one involving π overlap and the other involving σ overlap, between filled $2p$ orbitals of oxygen and the half-filled $3d$ orbitals of iron, octahedral symmetry about the metal being assumed.[2,4,5,18,20] However, this model scarcely seems adequate, at least in its simple application, since in tetrahedral symmetry, as here, $3d$–$2p$ overlap will be diminished yet the J value of -92 cm^{-1} is not appreciably smaller than found for other complexes where the metal is in an octahedral or square-pyramidal environment. Moreover, there is little correlation between the magnitude of J in the different systems (Table 4) and other structural parameters, *viz.* Fe–O–Fe angles and Fe–O distances, the latter in all cases being less than terminal Fe–O bond lengths. This suggests that the mechanisms for spin–spin coupling and bond contraction need not have a common origin. In an alternative, ligand-field, approach to the structure and properties of oxo-bridged iron(III) dimers Schugar *et al.*[3] suggested that the π bonding responsible for the short Fe–O bonds must involve empty outer ($4p_\pi$ or $4d_\pi$) orbitals of the metal.

EXPERIMENTAL

Preparation of the Complex.—Several preparations were carried out using slightly different conditions, all involving 'recrystallization' of $FeCl_3$ from ethanol–pyridine mixtures. For a μ-oxo-product to be obtained the presence of water was necessary. The best results were obtained when the concentration of water was small, such as that found in absolute ethanol which had been partially dried over molecular sieves for a few hours. Under such conditions the product was obtained over several days as large well formed crystals. When larger concentrations of water were present a less crystalline product separated more quickly which showed variable elemental analysis, usually $x < 1$ in $[Hpy]_2[Fe_2OCl_6]\cdot x$py. The use of a large concentration of pyridine yielded material which contained an excess of pyridine ($x > 1$). In a typical preparation of the product used in the experiments described, $FeCl_3$ (3.2 g, 0.02 mol) was dissolved in ethanol (200 cm^3) which had been dried over molecular sieves for a few hours. Pyridine (4 g, *ca.* 0.05 mol) was added to the stirred solution which was then filtered free from some powdery yellow material. The filtrate was left to stand for 1 week in a stoppered bottle after which time the yellow-orange crystals were isolated (Found: C, 31.2; H, 3.0; N, 7.3. $C_{15}H_{17}Cl_6Fe_2N_3O$ requires C, 31.1; H, 3.0; N, 7.3%).

Physical Measurements.— Magnetic-susceptibility measurements were carried out by the Gouy method on powdered samples using a Newport Instruments variable-temperature balance. Infrared spectra, in Nujol mulls and in KBr pellets, were recorded in the range 250—4 000 cm^{-1} with a Perkin-Elmer 457 instrument. Mössbauer measurements at absorber temperatures of 293 and 77 K were made using a ^{57}Co-in-Pd source with a Harwell constant-acceleration spectrometer. The equipment was calibrated with a $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$ standard at 293 K. Absorber thicknesses were not more than 50 mg cm^{-2}. Isomer shifts and quadrupole splittings were determined by visual inspection and the values checked by repeating the measurements using different samples.

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