Hydroxide-bridged Diiron(III) Complexes of Tetraaminodiphenol Macrocyclic Ligands: Structure and Properties†

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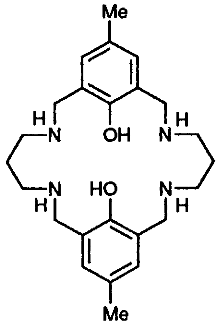
Some dinuclear iron(III) complexes derived from two tetraaminodiphenol macrocyclic ligands, one (H_2L^1) contains two $-NH(CH_2)_3NH-$ and the other (H_2L^2) one $-NH(CH_2)_3NH-$ and one $-NH(CH_2)_2NH-$ units, and an acyclic tetradentate ligand {H_2L^3 *N,N'*-bis(2-hydroxybenzyl)-1,3-diaminopropane} have been synthesised and studied. In all of the macrocyclic complexes $[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**, $[Fe_2(\mu\text{-}OH)_2L^1{}_2]\cdot 2H_2O$ **2**, $[Fe(H_2L^1)(H_2O)_2][ClO_4]_3\cdot H_2O$ **3**, $[Fe_2(\mu\text{-}OH)_2(H_2L^2)_2][ClO_4]_4\cdot 2H_2O$ **4**, $[Fe_2(\mu\text{-}OH)_2L^2{}_2]\cdot 2H_2O$ **5** and $[Fe_2(\mu\text{-}OH)_2L^3{}_2]$ **6** only N_2O_2 donation to the metal centres occurs, while the two unco-ordinated amino nitrogens either remain singly protonated (**2** and **5**) or one (**1**) or both of these (**3** and **4**) is doubly protonated. Variable-temperature magnetic susceptibility data for **1**, **4** and **6** indicate weak antiferromagnetic-exchange interactions in each case with *J* values of: −5.5 (**1**), −7.3 (**4**) and −11.8 cm^{-1} (**6**). The isomer-shift and quadrupole-splitting values for **1** at 77 K are 0.46 and 0.43 mm s^{-1}, respectively. The redox chemistry of **1** has been studied by cyclic voltammetry and its crystal structure has been determined: monoclinic, space group $P2_1/c$, $a = 13.448(1)$, $b = 14.847(1)$, $c = 13.442(1)$ Å, $\beta = 91.48(1)°$, $Z = 2$, $R = 0.048$ and $R' = 0.050$. The two edge-sharing FeO_4N_2 octahedra are distorted and connected by a centre of inversion.

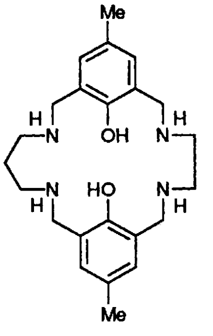
The chemistry of homo- and hetero-dinuclear metal complexes of Schiff-base type tetraazadiphenol macrocyclic ligands[1-12] has contributed much to our understanding of the behaviour of coupled metal systems. Although these compounds are customarily synthesized by one- or two-step template-condensation reactions, in the last few years we have widened the scope of these studies by introducing more flexible preformed tetraaminodiphenol ligands,[13] H_2L^1 and H_2L^2. The similar use of preformed unsaturated[14] or saturated[15] tetraaza diphenol macrocyclic ligands in the designed synthesis of metal complexes has also been reported recently. A common aspect of these dinuclear complexes is that they are all derived from dipositive metal cations, at least initially. Although the dicopper(II)[13b,c] and dinickel(II)[13f,h,i] complexes of H_2L^1 can be electrochemically oxidized, in a stepwise fashion, to M^{II}–M^{III} and M^{III}–M^{III} species, the higher-valent M^{III}–M^{III} species are not sufficiently stable for isolation in the solid state. Furthermore, while bromine oxidation of the dicobalt(II)[4b,13l] and dimanganese(II)[6c,13l] complexes of Schiff-base type macrocycles as well as H_2L^1 afford stable mixed-valence M^{II}–M^{III} complexes, again the corresponding M^{III}–M^{III} species have not been isolated. Prompted by the dearth of dinuclear trivalent metal-ion complexes and anticipating their rich co-ordination chemistry, we have embarked upon a study with 3d trivalent cations. Our first choice is iron(III) complexes because dinuclear iron centres occur widely in biology.[16] We report here the synthesis, characterization, structure, redox and magnetic properties of hydroxide-bridged diiron(III) complexes of H_2L^1 and H_2L^2.

Experimental

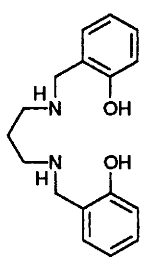
Materials.—All chemicals were reagent grade and used as received. The macrocyclic ligands H_2L^1 [ref. 13(*a*), (*b*)] and H_2L^2 [ref. 13(*g*)] were prepared according to the reported methods. Crystals of $Fe[ClO_4]_3\cdot 6H_2O$ were obtained by reacting chloride-free freshly precipitated iron(III) hydroxide with perchloric acid.



H_2L^1



H_2L^2



H_2L^3

Synthesis.—H_2L^3. A mixture of salicylaldehyde (4.2 g, 40 mmol) and 1,3-diaminopropane (1.6 g, 20 mmol) in MeOH (100 cm^3) was refluxed for 1 h. The solution was cooled to room temperature and treated with small portions of an aqueous solution of $NaBH_4$ and stirring was continued for 1 h; the reduction was considered complete when the yellow solution became colourless. A major part of the solvent was removed on a rotary evaporator, diluted with water (250 cm^3), acidified with HCl (6 mol dm^{-3}) to *ca.* pH 2 and the solution was kept at room temperature for 30 min. It was then treated slowly with ammonia to pH ≈10 and extracted with $CHCl_3$ (2 × 50 cm^3). The $CHCl_3$ layer was dried over Na_2SO_4 and evaporated to dryness, and the white residue was recrystallized from $CHCl_3$–MeOH (1 : 1), m.p. 108 °C; yield 4.69 g (80%) (Found: C, 71.6; H, 7.75; N, 9.7. $C_{17}H_{22}N_2O_2$ requires C, 71.35; H, 7.7; N, 9.8%).

Dedicated to the memory of Dr. K. Venkatsubramanian, a friend and collaborator, who passed away on November 22, 1993.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, p. xxv–xxx.

$[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**. To a MeOH solution (50 cm^3) of H_2L^1 (0.82 g, 2 mmol) and NEt_3 (0.4 g, 4 mmol), a solution of $Fe[ClO_4]_3{\cdot}6H_2O$ (0.92 g, 2 mmol) was added dropwise with stirring. After 3 h the product deposited was collected by filtration, washed with MeOH and dried under vacuum. On recrystallization from MeCN–EtOH (1 : 2) purple red crystals were obtained; yield 0.87 g (75%) (Found: C, 49.8; H, 6.25; N, 9.45. $C_{48}H_{72}Cl_2Fe_2N_8O_{14}$ requires: C, 49.35; H, 6.15; N, 9.6%). $\tilde{\nu}/cm^{-1}$ (KBr) 3260 [ν(NH)], 3180 [ν(OH)], 1610 [δ(NH)], 1470 [ν(C=C), aryl], 1100 and 630 [$\nu(ClO_4^-)$]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeOH–H_2O (1 : 1)] 470 (4200), 275 (22 750) and 235 (27 700).

$[Fe_2(\mu\text{-}OH)_2L^1{}_2]{\cdot}2H_2O$ **2**. Complex **1** (1.17 g, 1 mmol) was first dissolved in *N*,*N*-dimethylformamide (dmf) (50 cm^3) and then diluted with an equal volume of water. To this solution aqueous NaOH solution (20 cm^3) (0.1 mol dm^{-3}) was added slowly with stirring. A deep red compound that separated out over 3 h was filtered off and washed with MeOH and MeCN, and dried over P_2O_5 *in vacuo*. The material was extracted with MeOH in a Soxhlet apparatus and the solution, upon slow evaporation, afforded magenta crystals; yield 0.58 g (60%) (Found: C, 57.8; H, 7.25; N, 11.05. $C_{48}H_{74}Fe_2N_8O_8$ requires: C, 57.5; H, 7.4; N, 11.2%). $\tilde{\nu}/cm^{-1}$ (KBr) 3400 [ν(OH), H_2O], 3280 [ν(NH)], 3110 [ν(OH)], 1605 [δ(NH)] and 1470 [ν(C=C), aryl]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeOH–H_2O (1 : 1)] 465 (4350), 275 (22 500) and 235 (28 000).

$[Fe(H_2L^1)(H_2O)_2][ClO_4]_3{\cdot}H_2O$ **3**. Complex **1** (0.58 g, 0.5 mmol) was dissolved in MeCN (10 cm^3), diluted with MeOH (30 cm^3) and then treated with aqueous $HClO_4$ (2 cm^3, 1.0 mol dm^{-3}). The solution changed from deep red to blue-violet. The solution was reduced to *ca.* 5 cm^3 on a rotary evaporator and then added to Et_2O (100 cm^3). A dark blue compound separated, which was recrystallized from EtOH–hexane; yield 0.78 g (quantitative) (Found: C, 35.6; H, 5.05; N, 6.7. $C_{24}H_{42}Cl_3FeN_4O_{17}$ requires: C, 35.1; H, 5.1; N, 6.85%). $\tilde{\nu}/cm^{-1}$ (KBr) 3450 (br) [ν(OH), H_2O], 3200 (br) [ν(NH)], 1610 [δ(NH)], 1470 [ν(C=C) aryl], 1100 and 630 [$\nu(ClO_4)$]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeOH–H_2O (1 : 1)] 530 (4400), 320 (sh), 290 (21 400) and 230 (26 000).

$[Fe_2(\mu\text{-}OH)_2(H_2L^2)_2][ClO_4]_4{\cdot}2H_2O$ **4**. An MeOH solution (30 cm^3) containing H_2L^2 (0.4 g, 1 mmol), NEt_3 (0.2 g, 2 mmol) and $Fe[ClO_4]_3{\cdot}6H_2O$ (0.46 g, 1 mmol) was stirred for 2 h. The solution was filtered and evaporated to near dryness on a rotary evaporator. The semi-solid product on stirring with CH_2Cl_2 (20 cm^3) became a rusty solid, which on recrystallization from Me_2CO–hexane (5 : 1) produced dark red crystals; yield 0.48 g (70%) (Found: C, 39.7; H, 5.45; N, 8.2. $C_{46}H_{74}Cl_4Fe_2N_8O_{24}$ requires: C, 40.1; H, 5.35; N, 8.15%). $\tilde{\nu}/cm^{-1}$ (KBr) 3420 (br) [ν(OH), H_2O], 3290, 3250 [ν(NH)], 3150 (br) [ν(OH)], 1615 [δ(NH)], 1470 [ν(C=C), aryl], 1100 and 640 [$\nu(ClO_4)$]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeOH] 450 (4800), 290 (21 400) and 226 (26 700).

$[Fe_2(\mu\text{-}OH)_2L^2{}_2]{\cdot}2H_2O$ **5**. The compound was prepared similarly to **2** (Found: C, 56.5; H, 7.1; N, 11.25. $C_{46}H_{70}Fe_2N_8O_8$ requires: C, 56.7; H, 7.2; N, 11.5%). $\tilde{\nu}/cm^{-1}$ (KBr) 3420 [ν(OH), H_2O], 3280 [ν(NH)], 3120 [ν(OH)], 1615 [δ(NH)] and 1470 [ν(C=C), aryl]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeOH] 450 (5500), 290 (22 500) and 226 (28 000).

$[Fe_2(\mu\text{-}OH)_2L^3{}_2]$ **6**. A mixture of H_2L^3 (0.57 g, 2 mmol), NEt_3 (0.4 g, 4 mmol) and $Fe[ClO_4]_3{\cdot}6H_2O$ (0.92 g, 2 mmol) in MeOH (30 cm^3) was stirred for 1 h. The solution upon concentration to *ca.* 10 cm^3 deposited a red-brown solid, which was recrystallized from MeOH; yield 0.4 g (56%) (Found: C, 57.65; H, 5.9; N, 7.6. $C_{34}H_{42}Fe_2N_4O_6$ requires: C, 57.15; H, 5.9; N, 7.85%). $\tilde{\nu}/cm^{-1}$ (KBr) 3450 [ν(OH), H_2O], 3100 [ν(OH)], 1595 [δ(NH)], 1480 and 1455 [ν(C=C), aryl]; λ_{max}/nm (ε/$dm^3\ mol^{-1}\ cm^{-1}$) [MeCN] 485 (2600), 277 (6900), 232 (10 500) and 221 (10 600).

CAUTION: All the perchlorate salts reported here are potentially explosive and therefore should be handled with care.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using KBr discs and electronic spectra on a Shimadzu UV-160A spectrophotometer. The electrochemical measurements were carried out under O_2-free conditions using a Bioanalytical Systems BAS 100B electrochemical analyser. A three-electrode assembly (BAS) comprising a Pt working electrode, a Pt auxiliary electrode and a Ag–AgCl reference electrode with a salt bridge separated by a porous Vycor tip and heat-shrinkage tubing was used. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte. Variable-temperature magnetic-susceptibility data were obtained in the range 85–300 K by using a PAR 155 vibrating-sample magnetometer in combination with a Janis 153N cryostat and a Lake Shore DRC-70C controller. To achieve better accuracy, a *ca.* 60 mg sample was packed in a Teflon capsule. The magnetometer was calibrated with $[HgCo(NCS)_4]$ and susceptibility data were corrected for diamagnetism using Pascal constants. Mössbauer spectra were recorded at 77 K on a 2 × 256 channel multiscalar confined to a constant-acceleration drive system. The source used was 3.7×10^{11} Bq ^{57}Co in Rh matrix. The C, H and N analyses were performed on a Perkin-Elmer model 240C elemental analyser; iron was estimated volumetrically after decomposition with mineral acids.

Crystal Structure Determination of $[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**.—Crystals suitable for structure determination were obtained by diffusing Et_2O to a solution of **1** in MeCN.

Intensity data were collected with an Enraf-Nonius CAD4 diffractometer at 293 K using graphite-monochromatized Cu-Kα radiation. Pertinent crystallographic data are summarized in Table 1. Three standard reflections were monitored after every 100 and no significant variations in intensities were observed. The intensity data were corrected for Lorentz-polarization effects and for absorption by an empirical method.[17]

The structure was solved by the heavy-atom method. A three-dimensional Patterson map gave the positions of the heavy atoms. The remaining non-hydrogen atoms were located through Fourier-difference syntheses, alternated by least-squares refinements. Hydrogen atoms were positioned geometrically, but not refined. A unit-weighting scheme with a Dunitz–Seiler factor[18] was used in the final stage of the refinement.

The refinement of **1** converged to $R = 0.048$ and $R' = 0.050$. The shift-to-error ratio in the final cycle was less than 0.03 and the difference map at this stage showed ripples ranging between

Table 1 Crystal data for $[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**

Formula	$C_{48}H_{72}N_8Cl_2Fe_2O_{14}$
M	1166.7
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	13.448(1)
b/Å	14.847(1)
c/Å	13.442(1)
β/°	91.48(1)
U/Å^3	2683.3(6)
Z	2
D_c/g cm^{-3}	1.372
λ(Cu-Kα)/Å	1.540 18
μ(Cu-Kα)/cm^{-1}	29.38
Transmission (%)	98.16, −71.48
Crystal size/mm	0.32 × 0.33 × 0.22
Reflections measured	4574
Reflections observed [$I > 3\sigma(I)$]	2083
θ Range/°	4–130
R^a	0.048
R'^b	0.050

^{a} $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R'(F_o) = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$

+0.7 and −0.6 e Å^{-3}. The atomic scattering factors were taken from ref. 19. All computations were carried out using the structure determination package[20] available with Enraf-Nonius PDP-11/73. Drawings of the structure were generated with the ORTEP program.[21]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Characterization.—When a methanolic solution of the macrocyclic ligand H_2L^1 (1 equivalent) was treated with iron(III) perchlorate (1 equivalent) the solution became intensely blue violet, which, on treatment with triethylamine (2 equivalents), turned to blood red. Complex **1** was isolated from the solution and gave an empirical composition $[FeL^1(H_2O)][ClO_4]$. Based on the high-spin magnetic moment of this compound monomeric square-pyramidal geometry was ruled out and two alternative formulations, *viz.* $[Fe_2(\mu-H_2O)_2L^1{}_2][ClO_4]_2$ and $[Fe_2(HL^1)_2(\mu-OH)_2][ClO_4]_2$, were considered. Although the formation of two aqua bridges is unusual and not consistent with the known aqueous chemistry of iron, this could not be entirely ruled out on the basis of the crystal structure (see later) since the hydrogen atoms neither in the bridging oxygens nor in the non-co-ordinated amine nitrogens could be located. It should be noted that the composition $[Fe_2(\mu-OH)_2(HL^1)_2][ClO_4]_2$ would require protonation of one of the two non-co-ordinated amine nitrogens of the ligand anion $(L^1)^{2-}$. In order to ascertain the structure unambiguously, spectrophotometric titrations of a series of solutions of **1** with varying amounts of $HClO_4$ and NaOH were carried out. Fig. 1 shows that the incremental addition of NaOH had practically no effect on the spectrum of **1**. Under preparative conditions, addition of two equivalents of NaOH to a solution of **1** in dmf–H_2O led to the isolation of the neutral complex $[Fe_2(\mu-OH)_2L^1{}_2]\cdot 2H_2O$ **2**. Since the conversion of **1** into **2** is not accompanied by a spectral change, the co-ordination environment around the metal centres in these two compounds must be identical. On the other hand, Fig. 1 shows that the addition of $HClO_4$ to **1** leads to a progressive shift of the phenolate to iron(III) charge-transfer transition of **1** from 470 nm to higher wavelengths. Finally, when four equivalents of the acid were added the absorption maximum shifted to 530 nm, and thereafter no further change took place. The solution became deep blue violet and a compound of composition $[Fe(H_2L^1)(H_2O)_2][ClO_4]_3\cdot H_2O$ **3** was isolated. The occurrence of the phenolate to iron(III) charge-transfer transition at a lower energy (18 870 cm^{-1}) in **3** relative to that of **1** (21 280 cm^{-1}) may be rationalized in the following way: protonation of the basic hydroxide ligands in **1** to the neutral aqua ligands in **3** leads to an increase of the Lewis acidity of the iron(III) centre in **3** and thereby facilitates charge transfer at lower energies. Thus, **1** may be formulated as $[Fe_2(\mu-OH)_2(HL^1)_2][ClO_4]_2$.

The hydroxide-bridged diiron(III) complexes $[Fe_2(\mu-OH)_2(H_2L^2)_2][ClO_4]_4\cdot 2H_2O$ **4** and $[Fe_2(\mu-OH)_2L^2{}_2]\cdot 2H_2O$ **5** of the asymmetric macrocyclic ligand H_2L^2 were prepared in the same way as **1** and **2**, respectively. The spectrophotometric titrations of **4** with acid and alkali exhibited similar features. The difference between **1** and **4** with regard to the extent of protonation of the amino nitrogens of the ligands is noteworthy. Unlike the symmetric macrocyclic ligand H_2L^1, in H_2L^2 the iron(III) may occupy either side of the ligand. Although the structure of **4** has not been determined, it is probable that in **4** iron(III) is located in the $-NH(CH_2)_2NH-$ part of the ligand.

For comparison of the magnetic properties of the above complexes with that of the non-macrocyclic analogue H_2L^3, the hydroxy-bridged complex $[Fe_2(\mu-OH)_2L^3{}_2]$ **6** was also synthesized. We note that the structures and magnetic properties of the diiron complexes derived from two *N,N′*-bis(2-hydroxybenzyl)-1,2-diaminoethane derivatives have been reported.[22,23]

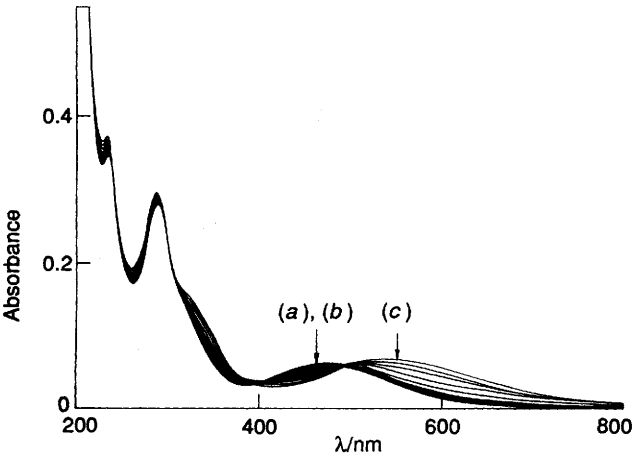


Fig. 1 UV/VIS spectral changes of $[Fe_2(\mu-OH)_2(HL^1)_2][ClO_4]_2$ **1** (1.4×10^{-5} mol dm^{-3}) in MeOH–H_2O (1 : 1) upon addition of varying amounts of NaOH and $HClO_4$ solutions: (*a*) neutral solution; (*b*) after addition of two equivalents of NaOH; (*c*) after addition of four equivalents of $HClO_4$

Structural Description of $[Fe_2(\mu-OH)_2(HL^1)_2][ClO_4]_2$ **1**.—Perspective views of the complex cation and co-ordination polyhedra of the metal centres are shown in Fig. 2. The atomic coordinates of **1** are given in Table 2, while the selected bond distances and angles are listed in Table 3.

The structure consists of two macrocyclic FeO_2N_2 co-ordination cores linked by two hydroxyl groups which, in effect, leads to edge sharing between two FeO_4N_2 octahedra. Of the six N_4O_2 donor atoms of the macrocyclic ligand only two N and two O atoms are involved in co-ordination and one of the two non-co-ordinated amine nitrogens is protonated. Thus, although both the phenols are deprotonated in **1** the ligand HL^{1-} is anionic.

The complex cation has a centrosymmetric structure and the centre of inversion is at the middle of the exactly planar four-membered Fe–O(3)–Fe′–O(3′) ring. As may be seen in Fig. 2(*b*), the macrocyclic ligand is folded in such a way that the two phenolate oxygens O(1) and O(2) are in a *cis* position. The extent of folding is evident from the dihedral angle of 72.2(2)° between the planes of the phenyl rings C(1)–C(6) and C(13)–C(18). There is no reflection plane in the two edge-sharing octahedra. The bond distances and angles given in Table 3 reveal the distorted-octahedral geometries of the iron centres. The *cis* angles vary from 79.3 to 101.5°, while the *trans* angles lie in the range 169.1–177.8°. Although the two Fe–N distances [2.221(5) and 2.231(5) Å] differ very slightly, the two Fe–O(phenolate) distances [1.891(4) and 1.954(4) Å] differ more significantly and they are shorter relative to the Fe–O(hydroxo) distance [2.002(4) Å]. The two iron centres are separated by 3.085(3) Å, with a Fe–OH–Fe bridge angle of 100.7(4)°.

Magnetochemistry.—Variable-temperature magnetic-susceptibility measurements were carried out for complexes **1**, **4** and **6** in the temperature range 85–300 K. The susceptibility data were fitted by equation (1), which is based on the general

$$\chi_M = (1 - p)[Cx(J,T)] + 4.375p/T + N_\alpha \qquad (1)$$

isotropic exchange Hamiltonian $\mathscr{H} = -2JS_1S_2$, with $S_1 = S_2 = \frac{5}{2}$. In this expression[24,25] $C = Ng^2\mu_B{}^2/kT$, $x = J/kT$ and p = mole percentage of paramagnetic impurity. The value of g was fixed at 2.0 and the temperature-independent paramagnetic susceptibility N_α was considered to be 6.0×10^{-4} cm^3 mol^{-1} in

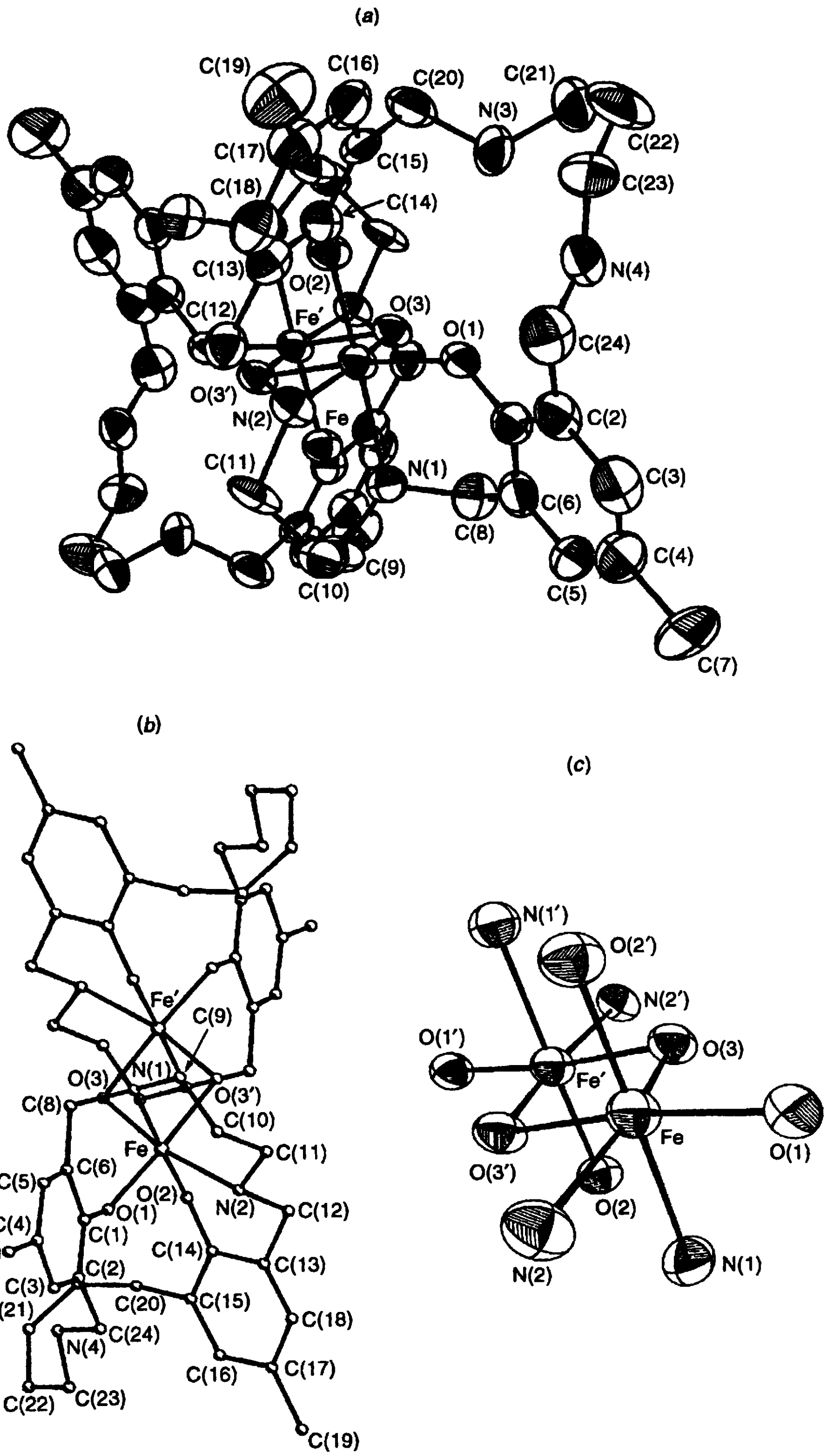


Fig. 2 (*a*) and (*b*), Perspective views of the structure of the $[Fe_2(\mu\text{-}OH)_2(HL^1)_2]^{2+}$ cation and (*c*) co-ordination polyhedra of the iron centres in complex **1**. The atom-labelling scheme corresponds to Table 2

each case. The best-fit curves for χ_M and μ_{eff} (per iron centre) for complexes **1** and **4** are shown in Fig. 3. The theoretical least-squares fittings were obtained for **1**, **4** and **6** with the following parameters: **1**, $J = -5.5$ cm^{-1}, $p = 1.6 \times 10^{-3}$; **4**, $J = -7.3$ cm^{-1}, $p = 2.0 \times 10^{-3}$; **6**, $J = -11.8$ cm^{-1}, $p = 6.4 \times 10^{-4}$. The weak antiferromagnetic coupling constants observed for the complexes are consistent with the $-J$ values (5.5–16.5 cm^{-1}) reported for dihydroxide- or dialkoxide-bridged iron(III) complexes.[16c,22,23,25] The small, but significant difference between the J values of **1** and **4** could be due to the anticipated difference in location of the iron atoms in their respective macrocyclic ligands. Notably, exchange-coupling constants of $J = -10.4$[22] and -5.7 cm^{-1}[23] have been reported for the diiron(III) complexes $[Fe_2(\mu\text{-}OH)_2L^4{}_2]\cdot 2H_2O\cdot 2py$ [H_2L^4 = *N*,*N*′-bis(2-hydroxybenzyl)-1,2-diaminoethane, py = pyridine] and $[Fe_2(\mu\text{-}OMe)_2L^5{}_2]$ [H_2L^5 = *N*,*N*′-bis(3-*tert*-butyl-2-hydroxy-5-methylbenzyl)-1,2-diaminoethane] respectively.

The Mössbauer spectrum of **1** at 77 K is consistent with the

Table 2 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**

Atom	*x*	*y*	*z*
Fe	0.422 42(7)	0.042 05(7)	0.068 65(8)
Cl	0.827 4(1)	0.072 7(2)	0.154 0(2)
O(1)	0.284 5(3)	0.065 9(3)	0.073 2(3)
O(2)	0.414 3(3)	−0.064 5(3)	0.153 4(3)
O(3)	0.429 8(3)	−0.031 3(3)	−0.055 9(3)
O(4)	0.772 2(7)	0.001 3(6)	0.204 8(7)
O(5)	0.884 8(4)	0.116 7(6)	0.227 3(6)
O(6)	0.889 4(4)	0.037 7(5)	0.077 9(5)
O(7)	0.750 9(5)	0.129 7(5)	0.109 6(6)
N(1)	0.437 3(4)	0.162 0(4)	−0.029 9(4)
N(2)	0.445 4(3)	0.124 4(3)	0.205 2(4)
N(3)	0.203 9(5)	−0.152 0(4)	0.122 4(5)
N(4)	0.094 0(4)	0.009 2(4)	0.150 8(5)
C(1)	0.231 3(4)	0.143 5(4)	0.056 6(5)
C(2)	0.152 0(5)	0.162 3(5)	0.115 2(6)
C(3)	0.095 2(5)	0.242 1(5)	0.097 2(7)
C(4)	0.122 4(6)	0.301 2(5)	0.023 8(7)
C(5)	0.201 6(5)	0.281 7(5)	−0.032 4(6)
C(6)	0.258 6(5)	0.202 7(5)	−0.019 7(5)
C(7)	0.059 4(7)	0.386 9(6)	0.002 7(9)
C(8)	0.342 5(5)	0.179 6(5)	−0.086 4(5)
C(9)	0.488 9(5)	0.243 8(5)	0.009 6(6)
C(10)	0.461 4(5)	0.272 2(5)	0.114 0(6)
C(11)	0.505 9(5)	0.210 1(5)	0.194 2(6)
C(12)	0.488 3(5)	0.068 2(5)	0.286 7(5)
C(13)	0.411 5(5)	−0.003 1(5)	0.317 6(5)
C(14)	0.379 2(4)	−0.064 7(4)	0.242 7(5)
C(15)	0.310 6(4)	−0.129 2(4)	0.271 2(5)
C(16)	0.277 6(5)	−0.133 7(5)	0.368 7(5)
C(17)	0.310 5(5)	−0.071 2(5)	0.442 7(5)
C(18)	0.378 2(5)	−0.005 1(5)	0.412 0(5)
C(19)	0.273 8(6)	−0.075 7(6)	0.546 4(6)
C(20)	0.277 4(5)	−0.195 5(5)	0.193 1(6)
C(21)	0.100 8(6)	−0.185 5(6)	0.116 2(7)
C(22)	0.024 9(6)	−0.143 4(6)	0.179 4(7)
C(23)	0.053 2(6)	−0.054 4(6)	0.226 7(5)
C(24)	0.127 2(6)	0.098 8(6)	0.197 8(6)

Table 3 Selected bond distances (Å) and angles (°) for $[Fe_2(\mu\text{-}OH)_2(HL^1)_2][ClO_4]_2$ **1**

Fe–O(1)	1.891(4)	Fe–N(1)	2.231(5)
Fe–O(2)	1.954(4)	Fe–N(2)	2.221(5)
Fe–O(3)	2.002(4)	Fe ⋯ Fe′	3.085(3)
O(1)–Fe–O(2)	93.7(2)	O(2)–Fe–N(2)	88.4(2)
O(1)–Fe–O(3)	101.5(2)	O(3)–Fe–O(3′)	79.3(2)
O(1)–Fe–O(3′)	173.1(2)	O(3)–Fe–N(1)	86.0(2)
O(1)–Fe–N(1)	88.5(2)	O(3)–Fe–N(2)	169.1(2)
O(1)–Fe–N(2)	89.3(2)	O(3′)–Fe–N(1)	84.8(2)
O(2)–Fe–O(3)	93.0(2)	O(3′)–Fe–N(2)	89.9(2)
O(2)–Fe–O(3′)	93.2(2)	N(1)–Fe–N(2)	92.2(2)
O(2)–Fe–N(1)	177.8(2)	Fe–O(3)–Fe′	100.7(4)

two electronically equivalent high-spin iron(III) centres in the molecule. The values of the isomer shift δ, 0.46 mm s^{-1}, and quadrupole splitting ΔE_q, 0.43 mm s^{-1}, are reasonable for a FeO_4N_2 chromophore.[26] These values may be compared with δ values in the range 0.35–0.70 mm s^{-1} and ΔE_q values varying between 0.25 and 0.72 mm s^{-1} for μ-hydroxo-diiron(III) complexes.[16c]

Electrochemistry.—Cyclic voltammetric studies of the reduction of **1** in MeCN solutions using Pt or glassy carbon electrodes were complicated by adsorption, electrode poisoning and irreversibility, especially for scan rates less than 2 V s^{-1}. However, the spectra at higher scan rates improved significantly, particularly with a glassy carbon electrode. Fig. 4 shows the cyclic voltammogram of **1** at a scan rate of 8 V s^{-1}. A single quasi-reversible redox couple with $E_{\frac{1}{2}} = -1.42$ V *vs.* Ag–AgCl and with a peak-to-peak separation of 220 mV is observed in a potential window 0 to −2 V. Although it was not possible to determine the number of electrons involved in the redox reaction, a single step two-electron reduction $Fe^{III}_2 + 2e^- \rightleftharpoons Fe^{II}_2$ seems quite plausible.

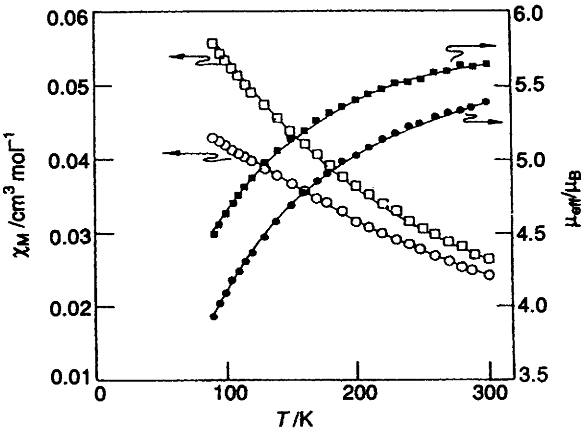


Fig. 3 Molar susceptibility χ_M and effective magnetic moment μ_{eff} per iron *vs.* temperature for complex **1** (□, ■) and **4** (○, ●). The solid lines represent least-squares fitting of the data by equation (1) (see text)

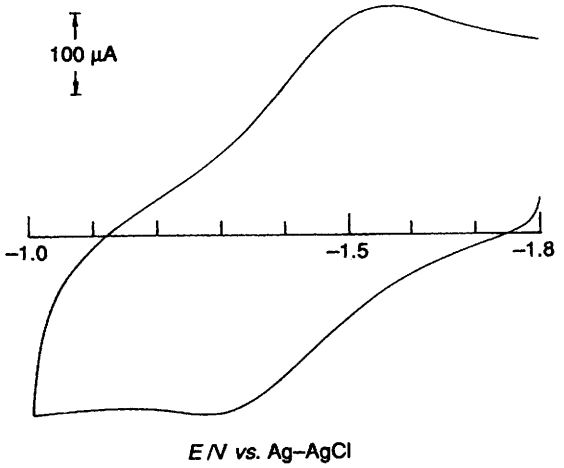


Fig. 4 Cyclic voltammogram of complex **1** in MeCN with a glassy carbon electrode at a scan rate of 8 V s^{-1}

Conclusion

The macrocyclic diiron(III) complexes reported here contribute to the developing chemistry of polyheteronuclear iron(III) complexes. The crystal structure of **1** shows that the unco-ordinated nitrogen donors in the vacant ligand compartment and the lone-pair electrons of the phenolate oxygens can be involved in the co-ordination of other di- or tri-valent metal cations through ancillary bridging groups, such as carboxylate anions. The carboxylate ions can not only provide axial donor sites to the metal centres but also partly neutralize the accumulated positive charges in the co-ordination spheres, especially when the metal cations concerned are all tripositive. Furthermore, it should be possible to deprotonate the dihydroxide bridges to generate the corresponding μ-oxo species. Indeed, our preliminary studies have shown that all these possibilities can be exploited to produce various complexes of the types $M^{II}_2Fe^{III}_2$ (M = Ni, Co, Fe or Mn), $Co^{III}_2Fe^{III}_2$ and Fe^{III}_4 and these will be the subject of future reports.

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