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Iron complexes of derivatised pentadentate macrocyclic ligands; the crystal and molecular structure of dichloro(6,13-(bis-2-hydroxyethyl)-6*H*,13*H*-tripyrido[*cd*,*fg*,*lm*][1,2,4,7,9,10,13]heptaaza-pentadecine)iron(III) chloride

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Abstract

Iron(II) complexes of planar pentadentate macrocyclic ligands containing 2,2′-bipyridine or 1,10-phenanthroline subunits have been prepared by template condensation of open-chain bis(hydrazines) with 2,6-diacetylpyridine or 2,6-pyridinedialdehyde. The complexes are seven-coordinate trigonal bipyramidal iron(II) complexes containing two axial ligands. Aerial oxidation yields iron(III) complexes, which may not be prepared directly by template condensations. The seven-coordinate iron(III) complex [FeL^4Cl_2]Cl has been structurally characterised (crystallographic data: space group $Pna2_1$, $a = 15.494(8)$, $b = 12.873(6)$, $c = 12.229(6)$ Å, $Z = 4$, 4487 reflections with $F \geqslant 3\sigma(F)$, $R = 0.0770$).

Introduction

Planar pentadentate N_5-donor macrocyclic ligands form complexes which exhibit unusual coordination geometries. We have demonstrated that macrocyclic ligands of this type are readily prepared by template or transient template condensations of hydrazino-substituted 2,2′-bipyridines, 1,10-phenanthrolines [1–25] or 2,2′:6′,2″-terpyridines [26–32] and that complexes with planar pentadentate, pentagonal-based pyramidal or pentagonal bipyramidal geometries are formed. The introduction of derivatised substituents into macrocyclic ligands allows further structural development and the design of biomimetic systems. In this paper we wish to describe the preparation of iron complexes with such ligands, and the structural characterisation of an iron(III) complex with a macrocyclic ligand bearing hydroxyethyl substituents.

Experimental

Infrared spectra were recorded in compressed KBr pellet on Perkin-Elmer FT 910 or Perkin-Elmer 983 spectrophotometers; ^{1}H NMR spectra were recorded on Brüker WM 250 or AM400 spectrometers. Fast atom bombardment (FAB) mass spectra were recorded on a Kratos MS50 mass spectrometer. Electrochemical measurements were made as previously described [25]. The macrocyclic ligands and precursors were prepared as previously described [25]. All preparations of iron(II) complexes were performed under an atmosphere of dinitrogen or argon.

Synthesis of [$FeLCl_2$]·nH_2O

A solution of $FeCl_2 \cdot 4H_2O$ (1 mmol) in degassed water (50 ml) was heated to reflux with L^1 or L^2 (1 mmol) for 10 min, after which period 2,6-diacetylpyridine or 2,6-pyridinedialdehyde (1 mmol) was added and the orange solution heated for a further 3 h. This solution was concentrated *in vacuo* to yield the chloro complex as orange microcrystals.

Treatment of aqueous solutions of the chloro complexes with excess of [NH_4][PF_6], Na[BF_4] or KSCN led to the precipitation of the appropriate complexes as orange solids.

Synthesis of [$FeLCl_2$]Cl·nH_2O

Air was bubbled through hot solutions of the above chloro complexes for 30 min, followed by concentration of the dark coloured solutions *in vacuo* to yield green–black crystals of the complexes. Treatment of aqueous solutions of the chloro complexes with excess of [NH_4][PF_6], Na[BF_4] or KSCN led to the precipitation of the appropriate complexes as brown solids.

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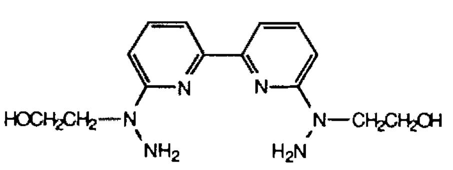
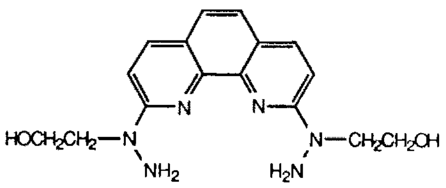


L^1



L^2

X-ray crystallography of [FeL^4Cl_2]Cl

A green–black dichroic needle obtained from water was mounted in a glass capillary. Space group and unit cell dimensions were derived from preliminary Weissenberg (Cu Kα) photography.

The crystal was aligned about the *a* axis and accurate unit cell dimensions obtained from zero-layer ω-angle and μ-angle measurements. Lorentz and polarisation effects were allowed for on the 5356 recorded intensity data (layers 18, $0-k$, 1) and a numerical absorption correction was applied. The crystal was bound by the planes $\{011\}$, $\{0\bar{1}1\}$, $\{01\bar{1}\}$, $\{0\bar{1}\bar{1}\}$, $\{100\}$ and $\{\bar{1}00\}$. Transmission factors ranged from 0.8904 to 0.7944 for the full data set. Equivalent reflections were averaged leaving 4487 unique observed reflections with $F \geqslant 3\sigma(F)$. Pertinent crystallographic data are given in Table 1. Calculations were carried out using the program SHELX [33] on the University of Cambridge IBM 370/165 computer.

All the non-hydrogen atoms were located by direct methods followed by Fourier difference syntheses. Methyl, methylene and aromatic hydrogen atoms were placed in idealised positions 1.08 Å from the relevant carbon atom, and each type was assigned a common isotropic thermal factor. The hydroxyl hydrogen atoms were not located. All non-hydrogen atoms were refined anisotropically. The final difference Fourier map had no peaks larger than 0.88 e/Å^3. Positional parameters are presented in Table 2 and bond distances and bond angles are given in Table 3.

TABLE 1. Crystal data for [FeL^4Cl_2]Cl

Formula	$C_{23}H_{25}Cl_3FeN_7O_2$
Formula weight	593.71
Space group	*Pna*2_1
a (Å)	15.494(8)
b (Å)	12.873(6)
c (Å)	12.229(6)
V (Å^3)	2439
Z	4
F(000)	1228
D_{calc} (g/cm^3)	1.616
Crystal size (mm)	0.8×0.3×0.3
μ (Mo Kα) (cm^{-1})	9.34
Data collection instrument	Stoe STAD-2
Radiation	Mo Kα (λ=0.71069 Å)
Temperature (°C)	20
No. of unique data	5356
Total with F$\geqslant$3σ(F)	4487
R[a]	0.0770
Largest peak (e/Å^3)	0.88

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.

TABLE 2. Positional parameters ($\times 10^4$) and their e.s.d.s. for [FeL^4Cl_2]Cl

	x	*y*	*z*
Fe(1)	3320	6342	3566
N(1)	1960(3)	6142(3)	3511(8)
C(1)	1546(8)	6037(10)	2573(10)
C(2)	634(8)	5932(9)	2504(11)
C(3)	216(4)	5887(5)	3403(7)
C(4)	657(7)	5958(7)	4477(9)
C(5)	1538(5)	6080(5)	4489(7)
C(6)	2129(6)	6094(8)	5556(8)
C(7)	1733(8)	5765(10)	6614(11)
N(2)	2893(6)	6332(7)	5256(6)
N(3)	3454(5)	6428(6)	6088(6)
C(8)	3392(7)	7135(11)	7046(9)
C(9)	3364(9)	8297(11)	6711(12)
O(1)	4255(6)	8593(6)	6452(8)
N(4)	4398(5)	6381(5)	4585(6)
C(10)	4302(6)	6379(8)	5712(8)
C(11)	5090(7)	6301(9)	6366(7)
C(12)	5876(6)	6269(8)	5939(8)
C(13)	5934(5)	6203(7)	4761(7)
C(14)	5185(6)	6296(8)	4127(7)
C(15)	5241(5)	6285(6)	2913(7)
C(16)	5962(7)	6290(8)	2273(9)
C(17)	5829(7)	6257(10)	1199(9)
C(18)	5015(6)	6351(7)	705(8)
C(19)	4354(5)	6387(6)	1426(6)
N(5)	4441(5)	6340(6)	2488(6)
N(6)	3533(5)	6392(7)	989(6)
C(20)	3259(7)	7173(10)	118(9)
C(21)	3370(7)	8276(10)	456(10)
O(2)	4195(5)	8594(7)	712(5)
N(7)	2872(5)	6330(5)	1815(6)
C(22)	2043(5)	6116(7)	1682(7)
C(23)	1707(8)	5843(11)	539(9)
Cl(1)	3380(1)	4510(1)	3561(3)
Cl(2)	3121(1)	8146(1)	3579(3)
Cl(3)	4810(1)	1796(1)	3561(3)

Table 3. Bond distances (Å) and bond angles (°) for [FeL^{4}Cl$_2$]Cl

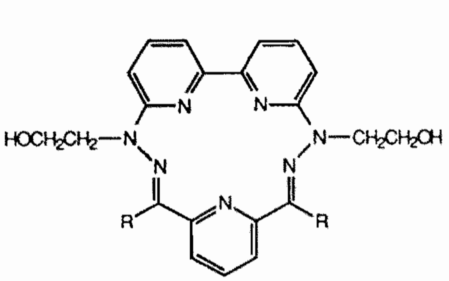
Fe(1)–N(1)	2.124(5)	Fe(1)–N(2)	2.170(8)
Fe(1)–N(4)	2.085(7)	Fe(1)–N(5)	2.181(7)
Fe(1)–N(7)	2.252(8)	Fe(1)–Cl(1)	2.360(1)
Fe(1)–Cl(2)	2.343(1)	N(1)–C(1)	1.321(15)
N(1)–C(5)	1.365(12)	C(1)–C(22)	1.339(15)
C(1)–C(2)	1.421(18)	C(2)–C(3)	1.278(16)
C(3)–C(4)	1.484(14)	C(4)–C(5)	1.373(13)
C(5)–C(6)	1.595(13)	N(2)–C(6)	1.276(12)
C(6)–C(7)	1.494(16)	N(2)–N(3)	1.343(11)
N(3)–C(10)	1.394(12)	N(3)–C(8)	1.486(15)
C(8)–C(9)	1.552(20)	C(9)–O(1)	1.466(14)
N(4)–C(10)	1.386(12)	N(4)–C(4)	1.346(12)
C(10)–C(11)	1.462(14)	C(11)–C(12)	1.326(14)
C(12)–C(13)	1.446(12)	C(13)–C(14)	1.400(12)
C(14)–C(15)	1.488(12)	C(15)–C(16)	1.364(14)
C(15)–N(5)	1.344(11)	C(16)–C(17)	1.329(15)
C(17)–C(18)	1.404(15)	C(18)–C(19)	1.353(12)
C(19)–N(5)	1.307(10)	C(19)–N(6)	1.380(11)
N(6)–C(20)	1.525(15)	N(6)–N(7)	1.441(11)
C(20)–C(21)	1.488(19)	C(21)–O(2)	1.380(14)
N(7)–C(22)	1.323(11)	C(22)–C(23)	1.533(15)
N(1)–Fe(1)–N(2)	74.2(4)	N(1)–Fe(1)–N(4)	144.8(3)
N(1)–Fe(1)–N(5)	140.5(3)	N(1)–Fe(1)–N(7)	70.3(3)
N(1)–Fe(1)–Cl(1)	85.3(1)	N(1)–Fe(1)–Cl(2)	89.4(1)
N(2)–Fe(1)–N(4)	71.0(3)	N(2)–Fe(1)–N(5)	144.9(3)
N(2)–Fe(1)–N(7)	144.3(3)	N(2)–Fe(1)–Cl(1)	90.5(3)
N(2)–Fe(1)–Cl(2)	87.7(3)	N(4)–Fe(1)–N(5)	73.9(3)
N(4)–Fe(1)–N(7)	144.7(3)	N(4)–Fe(1)–Cl(1)	89.7(2)
N(4)–Fe(1)–Cl(2)	94.4(2)	N(5)–Fe(1)–N(7)	70.8(3)
N(5)–Fe(1)–Cl(1)	88.1(2)	N(5)–Fe(1)–Cl(2)	96.3(2)
N(7)–Fe(1)–Cl(1)	90.2(2)	N(7)–Fe(1)–Cl(2)	88.4(2)
Cl(1)–Fe(1)–Cl(2)	174.7(1)	Fe(1)–N(1)–C(1)	121.5(7)
Fe(1)–N(1)–C(5)	117.0(6)	C(1)–N(1)–C(5)	121.5(7)
N(1)–C(1)–C(2)	122.9(11)	N(1)–C(1)–C(22)	114.8(10)
C(2)–C(1)–C(22)	122.1(11)	C(1)–C(2)–C(3)	117.2(11)
C(2)–C(3)–C(4)	121.7(9)	C(3)–C(4)–C(5)	118.3(9)
N(1)–C(5)–C(4)	118.2(8)	N(1)–C(5)–C(6)	116.2(6)
C(4)–C(5)–C(6)	125.5(8)	C(5)–C(6)–C(7)	118.0(8)
C(5)–C(6)–N(2)	107.5(8)	N(2)–C(6)–C(7)	134.3(9)
Fe(1)–N(2)–C(6)	123.9(7)	Fe(1)–N(2)–N(3)	121.6(6)
C(6)–N(2)–N(3)	113.8(8)	N(2)–N(3)–C(8)	127.7(8)
N(2)–N(3)–C(10)	110.8(8)	C(8)–N(3)–C(10)	110.4(8)
N(3)–C(8)–C(9)	112.6(10)	C(8)–C(9)–O(1)	106.4(10)
Fe(1)–N(4)–C(10)	120.5(6)	Fe(1)–N(4)–C(14)	118.4(6)
C(10)–N(4)–C(14)	120.8(8)	N(3)–C(10)–N(4)	115.4(8)
N(3)–C(10)–C(11)	127.6(8)	N(4)–C(10)–C(11)	117.0(8)
C(10)–C(11)–C(12)	123.7(9)	C(11)–C(12)–C(13)	116.8(9)
C(12)–C(13)–C(14)	119.6(8)	N(4)–C(14)–C(13)	121.8(8)
N(4)–C(14)–C(15)	117.9(8)	C(13)–C(14)–C(15)	120.2(8)
C(14)–C(15)–C(16)	128.3(8)	C(14)–C(15)–N(5)	109.4(7)
C(16)–C(15)–N(5)	122.2(8)	C(15)–C(16)–C(17)	116.1(10)
C(16)–C(17)–C(18)	124.1(10)	C(1)–C(18)–C(19)	123.1(10)
C(18)–C(19)–N(5)	124.6(8)	C(18)–C(19)–N(6)	116.5(8)
N(5)–C(19)–N(6)	118.7(7)	Fe(1)–N(5)–C(15)	120.1(5)
Fe(1)–N(5)–C(19)	121.2(5)	C(15)–N(5)–C(19)	118.8(7)
C(19)–N(6)–C(20)	122.0(8)	C(19)–N(6)–N(7)	112.6(7)
C(20–N(6)–N(7)	109.1(7)	N(6)–C(20)–C(21)	113.8(9)
C(20)–C(21)–O(2)	116.9(10)	Fe(1)–N(7)–N(6)	116.5(5)
Fe(1)–N(7)–C(22)	114.7(6)	N(6)–N(7)–C(22)	128.0(7)
C(1)–C(22)–N(7)	118.3(9)	C(1)–C(22)–C(23)	122.0(9)
N(7)–C(22)–C(23)	119.3(8)		

Results and discussion

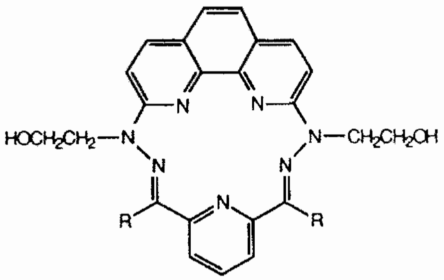
The planar pentadentate macrocyclic ligands L^3–L^6 (generically L) may be prepared by template or transient template condensations of the appropriate hydrazines (L^1 or L^2) with 2,6-pyridinedialdehyde or 2,6-diacetylpyridine [25]. These ligands are of particular interest in bearing a functionalised substituent which may be further derivatised to yield encapsulating or capped macrocycles. The open-chain ligands L^1 and L^2 are prepared by the reaction of a 6,6′-dihalo-2,2′-bipyridine or 2,9-dichloro-1,10-phenanthroline with 2-hydroxyethylhydrazine. The free ligands L^3 and L^5 are prepared by a transient template condensation of L^1 or L^2 with 2,6-pyridinedialdehyde in the presence of chromium(III) chloride [25], although the hindered compounds L^4 and L^6 cannot be prepared by this method.

The template condensation of L^1 or L^2 with 2,6-pyridinedialdehyde or 2,6-diacetylpyridine proceeds smoothly in the presence of iron(II) chloride in aqueous conditions under an inert atmosphere. The use of the one-pot template condensation does not require the isolation of the intermediate [FeL^{1}Cl$_2$] or [FeL^{2}Cl$_2$] species, which we have previously shown to undergo photochemically initiated loss of dinitrogen, to yield 2,2′-bipyridine or 1,10-phenanthroline complexes [7]. Concentration of the dark coloured solution so obtained results in the separation of orange microcrystalline solids. The chloro complexes so obtained contain varying amounts of water (see Table 4). In view of the vast amount of data we have obtained concerning first row transition metal complexes of related planar pentadentate ligands [1–32], we are confident that these compounds contain a pentagonal bipyramidal seven-coordinate iron(II) centre. There is an ambiguity about the relative numbers of coordinated water and chloride ligands in the various complexes, but the general formulation [FeL(H$_2$O)$_{2-n}$Cl$_n$]Cl$_{2-n}$·(H$_2$O)$_y$ is seen to be correct. Treatment of aqueous solutions of the chloro complexes with aqueous [NH$_4$][PF$_6$] or Na[BF$_4$] led to the precipitation of the appropriate [FeL(H$_2$O)$_2$][A]$_2$ salts (A = PF$_6$ or BF$_4$), although the compound with L^3 dehydrated upon drying *in vacuo*. These complexes behave as 1:2 electrolytes in dmso solution and, once again, these contain seven coordinate iron centres in the [FeL(H$_2$O)$_2$]$^{2+}$ cations. Treatment of aqueous solutions of the chloro complexes with K[SCN] resulted in the precipitation of the seven-coordinate neutral species [FeL(SCN)$_2$]. These complexes are non-conductors, and exhibit a single infrared mode in the region of 2060 cm^{-1} assignable to the coordinated thiocyanate ligand.

All of the complexes described above are paramagnetic with room temperature magnetic moments



L^3 R = H
L^4 R = Me



L^5 R = H
L^6 R = Me

TABLE 4. Analytical data

Compound	Calc.			Found		
	C	H	N	C	H	N
$[FeL^3Cl_2]$	47.6	4.0	18.5	47.2	4.0	18.9
$\{FeL^3(BF_4)_2\}$	39.8	3.3	15.5	40.0	3.3	5.35
$[FeL^3(H_2O)_2][PF_6]_2$	32.1	3.2	12.5	32.0	3.2	12.8
$[FeL^3(SCN)_2]$	43.8	3.6	21.9	43.6	3.5	22.0
$\{FeL^5Cl_2 \cdot 2H_2O\}$	46.8	4.2	16.6	46.9	4.3	16.9
$[FeL^5(H_2O)_2][BF_4]_2$	39.9	3.6	14.1	39.2	3.6	14.0
$[FeL^5(H_2O)_2][PF_6]_2$	34.9	2.9	12.4	35.2	3.0	12.6
$[FeL^5(SCN)_2]$	46.1	3.5	21.0	46.2	3.5	21.3
$\{FeL^6Cl_2 \cdot H_2O\}$	50.0	4.5	16.3	50.1	4.5	16.5
$[FeL^6(H_2O)_2][BF_4]_2$	41.6	4.0	13.6	41.8	4.0	13.7
$[FeL^6(H_2O)_2][PF_6]_2$	35.8	3.5	11.7	35.6	3.6	11.9
$[FeL^6(SCN)_2]$	47.9	4.0	20.1	48.2	4.0	20.0
$[FeL^3Cl_2]Cl$	44.6	3.7	18.8	3.7	17.4	5.85
$[FeL^3Cl_2][BF_4]$	40.9	3.4	15.9	41.0	3.4	16.0
$[FeL^3Cl_2][PF_6]$	37.3	3.1	14.5	37.4	3.0	14.6
$[FeL^4Cl_2]Cl$	46.5	4.2	16.5	46.5	4.4	16.9
$[FeL^4Cl_2][BF_4]$	42.8	3.9	15.2	42.8	4.0	15.6
$[FeL^5Cl_2]Cl$	46.8	3.5	16.6	46.7	3.5	16.6
$[FeL^6Cl_2]Cl \cdot 2H_2O$	45.9	4.4	15.0	46.0	4.4	15.2
$[FeL^6Cl_2][BF_4] \cdot 2H_2O$	42.6	4.1	13.9	42.5	4.2	14.0
$[FeL^6Cl_2][PF_6] \cdot H_2O$	40.3	3.6	13.2	40.2	3.6	13.4

in the range 5.33–5.53 BM, as expected for a high-spin iron(II) centre with a quintet ground state. The complex $[FeL^3Cl_2]$ exhibits a temperature dependent magnetic susceptibility, but a plot of $1/\chi'_m$ against temperature is linear with a Weiss constant of $-35°$. This is strictly comparable to the high-spin iron(II) complexes which we have obtained with related ligands [5]. All of the complexes $[FeL(H_2O)_2][A]_2$ ($A = PF_6$ or BF_4] are redox active, and cyclic voltammograms in dmso solution reveal reversible (E_a–E_c 60–70 mV) oxidation waves (+0.22 to 0.25 V versus Ag/AgCl), a reversible reduction wave (−1.10 to 1.20 V) and a pseudo reversible reduction wave (−1.4 to 1.5 V). In some cases further irreversible reduction processes were observed. We have not investigated the reduction processes in any detail, but the oxidation is metal-centred and corresponds to the iron(II)/iron(III) couple in each case. These modest potentials suggested that the iron(III) complexes might be chemically accessible.

Iron(III) complexes were prepared cleanly by aerial oxidation of aqueous solutions of the iron(II) chloro complexes. The same products were obtained if the crude template solution or a solution of the isolated chloro complex was oxidised. It is perhaps significant to note that iron(III) salts proved to be ineffective as templates for the condensation of the open-chain precursors. Identical iron(III) complexes to those obtained by aerial oxidation were obtained by the reaction of iron(III) solutions with the preformed macrocyclic ligands (from transient template reactions). Concentration of the aqueous solutions resulted in the formation of the complexes $\{FeLCl_3\}$ as red–brown crystalline solids exhibiting a green dichroism. By analogy with the other complexes known for these ligands we consider these to be seven-coordinate iron(III) complexes of the type $[FeLCl_2]Cl$. Support for this formulation comes from the observation that the complexes behave as 1:1 electrolytes in dmso solution. It is also significant that the addition of $[NH_4][PF_6]$ or $Na[BF_4]$ to aqueous solutions of the chloro complexes results in the precipitation of the salt $[FeLCl_2][A] \cdot nH_2O$ ($A = BF_4$ or PF_6), which also behave as 1:1 electrolytes in dmso solution. The complexes $[FeL^4Cl_2]Cl$ and $[FeL^6Cl_2][BF_4] \cdot 2H_2O$ both show temperature independent magnetic moments of 5.95 ± 0.1 BM over the temperature range 93–294 K. In order to confirm the presence of the $[FeLCl_2]^+$ cation in these complexes we have determined the crystal and molecular structure of $[FeL^4Cl_2]Cl$.

The molecular structure of the $[FeL^4Cl_2]^+$ cation in $[FeL^4Cl_2]Cl$ is shown in Fig. 1. The crystal structure determination confirms the formation of the iron(III) complex of the pentadentate macrocyclic ligand. The metal is in an N_5Cl_2 pentagonal bipyramidal environment, with the two chloride ligands occupying

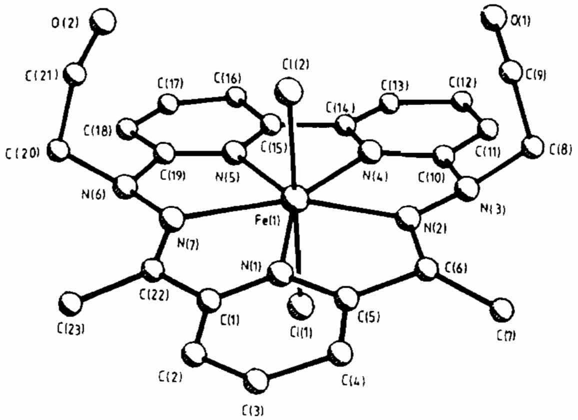


Fig. 1. The molecular structure of the $[FeL^4Cl_2]^+$ cation in $[FeLCl_2]Cl$ showing the numbering scheme adopted. Hydrogen atoms have been omitted for clarity.

the axial sites and the macrocyclic nitrogen donors the equatorial plane. The five nitrogen donor atoms of the macrocycle are approximately planar, with the greatest deviation of any of the atoms from the least-squares plane being 0.09 Å. The iron atom is located at the centre of this bonding cavity. The ligand as a whole is slightly distorted from planarity, with the pyridine and bipyridine fragments subtending angles of 3.3 and 7.0°, respectively with respect to this least-squares plane through the five nitrogen donors. This is seen in Fig. 2(a), which emphasises the slight doming of the ligand.

The Cl(1)–Fe(1)–Cl(2) bond angle is 174.7(1)°, representing a slight distortion from a regular pentagonal bipyramidal geometry. The Fe–N distances are in the range 2.08–2.26 Å, although these are partially dictated by the macrocyclic hole-size of approximately 2.1 Å. The bonded Fe–N contacts fall into two types; there are short contacts with the 2,2′-bipyridine nitrogen atoms and longer contacts to the pyridine and imine nitrogen donors. This is exactly the pattern that we have observed in other complexes with these ligands. The hydroxyethyl substituents are both folded over the same side of the macrocyclic ligand (see Fig. 2(a)), as has also been observed in the structurally characterised cations $[H_2L^3]^{2+}$, $[CrL^3]^{3+}$ [20, 25] and $[MnLCl]^+$ [18]. The hydroxyethyl substituents lie folded back over the 2,2′-bipyridyl end of the macrocyclic ligand (Fig. 2(b)). The hydroxy groups show hydrogen bonding interactions with the ionic chloride in the lattice, but not with the axial chloride ligands (see Fig. 3). The overall conformation of the complex cation is thus a compromise between a number of intermolecular hydrogen bonding interactions and intramolecular steric interactions.

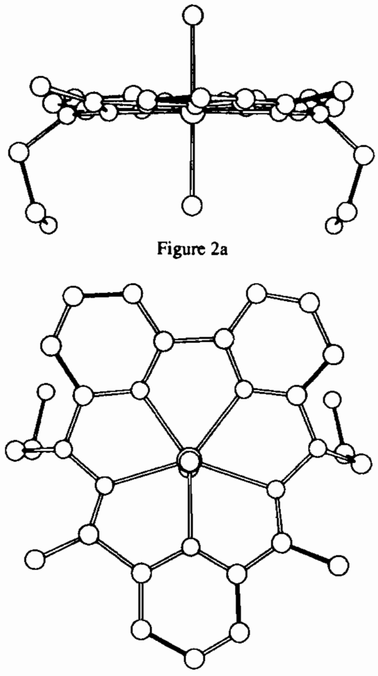


Fig. 2. (a) View of the $[FeL^4Cl_2]^+$ cation in $[FeL^4Cl_2]Cl$ showing the distortion of the ligand from planarity and the folding of the hydroxyethyl substituents. (b) View of the $[FeL^4Cl_2]^+$ cation in $[FeL^4Cl_2]Cl$ showing the arrangement of the hydroxyethyl substituents.

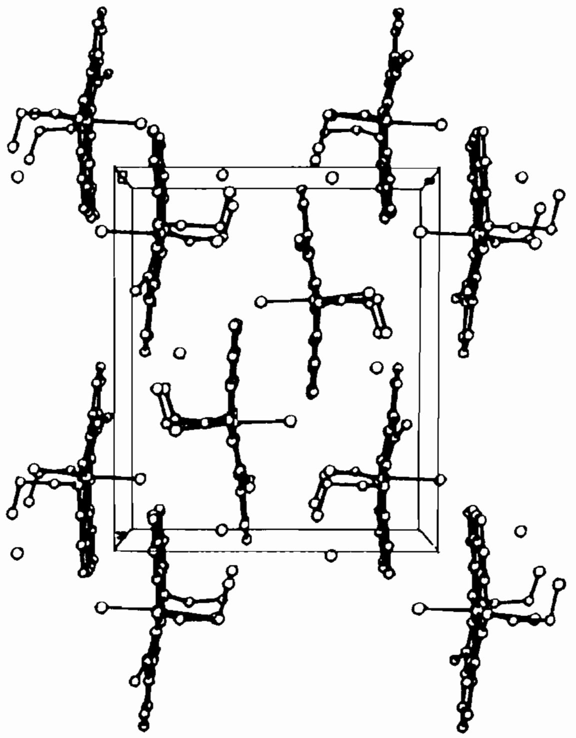


Fig. 3. Arrangement of the cations and anions in the lattice of $[FeL^4Cl_2]Cl$.

In conclusion, we have shown that derivatised planar pentadentate ligands may form stable seven-coordinate trigonal bipyramidal complexes with both iron(II) and iron(III) centres. We are currently investigating the structural development of the functionalised substituents.

Supplementary material

Tables of anisotropic displacement parameters, hydrogen atom coordinates, hydrogen atom bond angles and least-squares planes are available from the authors.

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