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Synthesis and crystal structure of the iron(II)–iron(III) complex [FeL][FeCl$_4$]Cl [L = 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane]*

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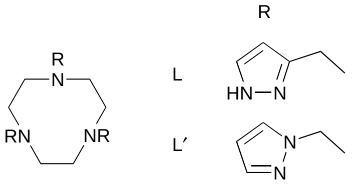
The pyrazole-functionalized macrocycles 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane, L, and 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane, L′, gave mixed-valence iron complexes of formulae [FeL][FeCl$_4$]Cl and [FeL′][FeCl$_4$]Cl, which are considered to contain the high-spin iron(II) [FeL]$^{2+}$ and, respectively, [FeL′]$^{2+}$ cations, besides [FeCl$_4$]$^-$ and Cl$^-$ anions. The diamagnetic compound [FeL′][ClO$_4$]$_2$ has also been obtained. There is evidence for the iron(II) contained in [FeL][FeCl$_4$]Cl being formed in the reduction of iron(III), accomplished by primary alcohols in the presence of L·6HCl. The assignment of the [FeL][FeCl$_4$]Cl formula to the L derivative is supported by the results of an X-ray structural determination. The iron(II) in the [FeL]$^{2+}$ cation is in a six-co-ordinate environment formed by the donor nitrogen atoms of the L ligand. The Fe–N bond distances are 2.274(4) Å (macrocycle nitrogens) and 2.120(4) Å (pyrazole nitrogens). Comparison with the much shorter distances detected for the diamagnetic compound [FeL′][ClO$_4$]$_2$ by a (poor-quality) structure determination supports the assignment of the iron(II) high-spin nature to the metal ion in the [FeL]$^{2+}$ cation.

We have recently reported the synthesis and characterization of some transition-metal complexes with the functionalized macrocycle L = 1,4,7-tris(pyrazol-3-ylmethyl)-1,4,7-triazacyclononane.[1] One of the goals of the synthesis of L was to avoid bond cleavage in the pendant arms of the substituted macrocycle, a process which had occurred upon formation of some metal complexes when the related 1,4,7-tris(pyrazol-1-ylmethyl)-1,4,7-triazacyclononane (L′)[2] or another substituted macrocycle was used.[3] Single-crystal X-ray analyses of the two complexes [ML][ClO$_4$]$_2$·nH$_2$O (M = Ni, n = 0.5; M = Zn, n = 1) revealed co-ordination geometries intermediate between trigonal prismatic and octahedral.[1]

In the course of our efforts to prepare iron(III) complexes with L we obtained, in addition to [FeL][ClO$_4$]$_3$·H$_2$O, previously reported,[1] a compound which analysed as Fe$_2$LCl$_5$, apparently containing both iron-(II) and -(III) in spite of its preparation from FeCl$_3$. Now we report on the synthesis and characterization of this compound, which has been assigned the formula [Fe^{II}L][Fe^{III}Cl$_4$]Cl, on the basis of a single-crystal X-ray analysis and spectral and magnetic data. There is experimental evidence for iron(II) being formed in the reduction of iron(III) by primary alcohols, according to a process which has previously been reported very rarely. In order to resolve possible ambiguities in the formula of the above compound, structural comparisons were sought with complexes formed by L or L′, of the type reported in refs. 1 and 2, unambiguously containing either iron-(III) or -(II). In spite of many attempts, poor-quality crystals were only obtained for the low-spin compound [FeL′][ClO$_4$]$_2$, whereas the above L derivative is high spin. The results of a structural investigation on this L′ complex, although inaccurate from the viewpoint of present standards, allow significant and chemically useful comparisons between the overall dimensions of the co-ordination in these two iron derivatives, helping to clarify the nature of the compound [FeL][FeCl$_4$]Cl.

Experimental

All chemicals were reagent grade. Solvents, when required by the synthetic procedures, were dried according to standard methods just before use. The compound L·6HCl was prepared as previously described.[1] Anhydrous FeCl$_3$ (Merck) was used as received; FeCl$_2$·4H$_2$O (Merck) was recrystallized from ethanol under a nitrogen atmosphere.



Synthesis of the complexes

[FeL][FeCl$_4$]Cl. A compound having elemental analyses corresponding to this formula can be prepared using different procedures and reactants (Scheme 1). Details of typical synthetic procedures are reported.

Method A. A warm ethanol solution (20 cm^3) of anhydrous FeCl$_3$ (162 mg, 1.00 mmol) and a warm methanol solution (30 cm^3) of L·6HCl (294 mg, 0.50 mmol) were mixed. The resulting orange-yellow solution was concentrated until a brown crystalline product had formed. The solid was filtered off, washed with ethanol and diethyl ether and dried in a vacuum oven. Yield 10–30% (Found: C, 32.9; H, 4.25; Cl, 27.3; Fe, 17.3; N, 19.1. Calc. for C$_{18}$H$_{27}$Cl$_5$Fe$_2$N$_9$: C, 32.8; H, 4.15; Cl, 26.9; Fe, 16.9; N, 19.2%). If the same synthesis was carried out using acetonitrile, acetone, *tert*-butyl alcohol, or their mixtures as solvents, this compound could not be obtained unless either methanol, ethanol or propan-1-ol was subsequently added to the mixture of reactants.

Method B. The following reactions were carried out under strictly anaerobic conditions under a prepurified nitrogen atmosphere and using solvents appropriately freed from oxygen prior to use. An ethanol solution (15 cm^3) of FeCl$_2$·4H$_2$O (99 mg, 0.50 mmol) was added to a warm methanol solution (20 cm^3) of L·6HCl (294 mg, 0.50 mmol). To the resulting colourless solution was added FeCl$_3$ (81 mg, 0.50 mmol) dissolved in ethanol (15 cm^3). The yellow solution was concentrated until a brown crystalline product was obtained (yield 20–30%). The elemental analysis of the product matched that from method A. Identical results were obtained when FeCl$_3$ was added first to L, before adding FeCl$_2$·4H$_2$O and concentrating the solution.

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* *Non-SI unit employed*: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

Method C. The same compound was obtained in greater yield (30–50%) when $FeCl_2·4H_2O$ (198 mg, 1.00 mmol) and L·6HCl (294 mg, 0.50 mmol) in ethanol–methanol (2:1 v/v) were allowed to react in the air.

[FeL′][FeCl$_4$]Cl.[4] An ethanol solution (20 cm^3) of L′ (185 mg, 0.50 mmol) was added to a warm methanol solution (20 cm^3) containing both $FeCl_3$ (81 mg) and $FeCl_2·4H_2O$ (99 mg) in equimolar amounts (0.50 mmol). By concentrating the solution a brown crystalline product was obtained (Found: C, 32.9; H, 4.15; N, 18.9. Calc. for $C_{18}H_{27}Cl_5Fe_2N_9$: C, 32.8; H, 4.15; N, 19.2%). The reaction of L′·6HCl with $FeCl_3$ under the same experimental conditions as for [FeL][FeCl$_4$]Cl (method A) gave yellow compounds of iron(III) which were not characterized further.

[FeL′][ClO$_4$]$_2$. The reaction was carried out under strictly anaerobic conditions under a prepurified nitrogen atmosphere and using solvents carefully deaerated with a nitrogen flow prior to use. A warm water solution (20 cm^3) of $NaClO_4·H_2O$ (211 mg, 1.5 mmol) was added to a warm ethanol solution (30 cm^3) containing both $FeCl_2·4H_2O$ (99 mg) and L′ (185 mg) in equimolar amounts (0.50 mmol). By concentrating the solution a purple crystalline product was obtained (Found: C, 34.4; H, 4.3; N, 19.9. Calc. for $C_{18}H_{27}Cl_2FeN_9O_8$: C, 34.6; H, 4.35; N, 20.2%).

Physical measurements

Electronic spectra were recorded in the range 300–2000 nm with a Perkin-Elmer Lambda 9 spectrometer. The concentration of the solution in acetonitrile was about 10^{-3} mol dm^{-3}. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer as Nujol mulls between KBr plates. Variable-temperature magnetic susceptibility measurements were made on solid samples using a fully automatized Aztec DSM5 susceptometer equipped with an Oxford CF 1200 S continuous-flow cryostat and a Bruker B-E15 electromagnet. The apparatus was calibrated with a pure sample of $(NH_4)_2Mn(SO_4)_2·6H_2O$ at several temperatures. Diamagnetic corrections were estimated from Pascal's constants. Cyclic voltammetry was carried out with an electrochemical unit formed by an Amel 553 potentiostat equipped with 863, 560/A and 568 elements, 731 integrator and a standard three-component system consisting of a platinum-microsphere working electrode, platinum-disc auxiliary electrode and a standard calomel reference electrode (SCE). The ferrocenium–ferrocene couple was used to monitor the reference electrode and was obtained to lie at +0.345 V *vs.* SCE. Electrochemical measurements were made on a deaerated acetonitrile solution of [FeL][FeCl$_4$]Cl at room temperature with 0.1 mol dm^{-3} NBu_4PF_6 as supporting electrolyte.

X-Ray crystallography

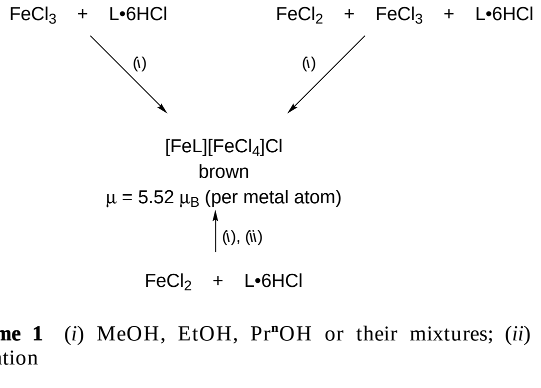
Crystals of [FeL][FeCl$_4$]Cl **1** in the form of flat trigonal prisms, suitable for X-ray analysis, were obtained by slow evaporation in air of a water–ethanol solution of the complex. Crystals of [FeL′][ClO$_4$]$_2$ **2**, obtained by slow evaporation at room temperature of an acetonitrile–ethanol solution, were elongated, ill formed and diffracted poorly. The results reported here for **2** were obtained with the best set of data available. All operations were performed at 293 K using an Enraf-Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα ($\lambda = 0.710\,69$ Å) radiation. Lattice constants were calculated by least-squares refinement of the setting angles of 24 reflections with $12 < \theta < 17$ (**1**) and $9 < \theta < 13°$ (**2**). A summary of crystal data and details of the data collections and structure determinations are given in Table 1. No decay was revealed by the intensities of three (**1**) and two (**2**) standard reflections during data collections. An empirical absorption correction[5] was applied to the data for **1** (maximum, minimum correction factors 1.11, 0.92) after structure solution at isotropic convergence, with a triclinic model, followed by data merging. In the case of **2** absorption corrections by the above procedure or based on ψ scans had insignificant effects and were not applied. The principal computer programs used in the crystallographic calculations are listed in refs. 5–9. The atomic scattering factors were from ref. 6.

Both structures were solved by direct and heavy-atom methods. The unit cell of complex **1** contains one formula unit, crystallographic three-fold symmetry being imposed on each of the three constituent ions. That of **2** contains three symmetry-independent cations, each possessing three-fold crystallographic symmetry, and six anions, two of which are independent. Least-squares refinements were performed on F^2 for both structures. In the final model for **1** all non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms, located from Fourier-difference maps, were assigned an overall thermal parameter and their positions refined. Owing to the bad quality of the data for **2** many restraints had to be imposed on bond distances between light atoms in order to prevent some of them from attaining chemically unreasonable values. Each ClO_4^- anion in that structure was modelled by two tetrahedra of fractional oxygen atoms surrounding the chlorine atom. The two tetrahedra had complementary occupancy factors and equal Cl–O distances. All non-hydrogen atoms of **2**, including the fractional ClO_4^- oxygens but excluding the nitrogen atoms (which were less affected than the other light atoms by thermal motion or disorder) were refined anisotropically. Hydrogen atoms were allowed to ride on the carrier C atoms with $U_H = 1.2U_C$. The absolute configuration could be assigned in each case, with a value of the Flack parameter differing from zero by less than 1σ (**1**) or 2σ (**2**).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/421.

Results and Discussion

The reaction of anhydrous $FeCl_3$ and L·6HCl (Scheme 1) in primary alcohol solutions (methanol, ethanol, propan-1-ol and their mixtures) gives a brown compound which analyses as Fe_2LCl_5. The compound has a magnetic moment at 280 K of 5.52 μ_B per metal atom, which does not change significantly down to 64 K (5.46 μ_B). The electronic spectra of the compound in the solid state and in acetonitrile solution are essentially featureless in the range 800–1700 nm and dominated by a very strong absorption in the near-UV region, which is centred at 360 nm ($\varepsilon = 7.0 \times 10^3$ cm^2 $mmol^{-1}$) for a 0.85×10^{-3} mol dm^{-3} solution in acetonitrile. On the basis of its chemical formula the compound appears to contain both iron-(II) and -(III), in spite of its formation in the air from pure $FeCl_3$. This hypothesis is reinforced by the experimental evidence that the same compound can be obtained by using equimolar amounts of iron-(II)



Scheme 1 (*i*) MeOH, EtOH, Pr^{n}OH or their mixtures; (*ii*) aerial oxidation

and -(III) salts (it was checked that the solids from the different preparation procedures are indeed isostructural). If the strong absorption at 360 nm is assigned to the tetrahedral $[FeCl_4]^-$ species,[10] the complex cation in the compound may be assumed to contain iron(II). The alternative (less likely) formulation of the compound as $[Fe^{III}L][Fe^{II}Cl_4]Cl$ would be based on the assumption that the tetrahedral anion is $[FeCl_4]^{2-}$, which is rather unstable in solution in the air. Then, by assigning a magnetic moment of 5.92 μ_B at room temperature to $[FeCl_4]^-$,[11] a value of 5.1 μ_B can be computed for the magnetic moment of the $[FeL]^{2+}$ cation. This is slightly lower than the value found for the $[FeL^1][BPh_4]_2$ complex[2] [5.34 μ_B; L^1 = 1,4,7-tris-(1-methylimidazol-2-ylmethyl)-1,4,7-triazacyclonane] but is indicative of a high-spin configuration for iron(II).

Many experiments (see the Experimental section) have shown that the compound Fe_2LCl_5 can be obtained from $FeCl_3$ provided that primary alcohols (methanol, ethanol, propan-1-ol or their mixtures) are used as solvents. On the other hand, the above compound could not be obtained when acetonitrile, acetone or *tert*-butyl alcohol were used in combination with $FeCl_3$ and L·6HCl. It therefore appears that the reduction of iron(III) is carried out by the primary alcohols employed as solvents. Moreover, the presence of the L·6HCl species seems to be of crucial importance for the process to occur: when the same reaction with $FeCl_3$ was carried out using L′·6HCl or free L′ the corresponding compound $Fe_2L'Cl_5$ could not be obtained. This, on the other hand, could be obtained from equimolar amounts of iron-(II) and -(III) salts and free L′ (see Experimental section). It exhibits magnetic and spectral properties quite similar to those of $[FeL][FeCl_4]Cl$ and may be reasonably assumed to have similar structural features as far as the co-ordination is concerned. Reverting to the L ligand, also the acidic conditions provided by the L·6HCl species are of importance, as the neutral L was found not to be capable of promoting iron(III) reduction. Finally, water in the solvent mixture is found to inhibit the reduction of iron(III). The oxidation of alcohols by iron(III) in the presence of L·6HCl appears to be stoichiometric, not catalytic (see below). Consequently the oxidation products are too scarce, and presumably too volatile, to be detected. Once formed, the $[Fe^{II}L]^{2+}$ species is stable in solution towards oxidation by O_2: when methanol solutions of the compound $[FeL][FeCl_4]Cl$ obtained from different preparations were flushed with O_2 for 24 h the starting compound was recovered unchanged from these solutions.

The cyclic voltammogram of a deaerated acetonitrile solution of $[FeL][FeCl_4]Cl$ at 298 K displays two well resolved reversible one-electron redox processes at −0.37 and 0.19 V *vs.* ferrocenium–ferrocene (0.03 and 0.59 V *vs.* normal hydrogen electrode, NHE). The above values can be assigned to the reduction of $[FeCl_4]^-$ and $[FeL]^{3+}$, respectively. The potential of the $[FeL]^{3+}$–$[FeL]^{2+}$ couple indicates that the remarkable stability of the $[FeL]^{2+}$ species with respect to its oxidation by O_2 must be due to kinetic factors. The X-ray structural analysis (see below) has shown that the iron atom in the above complex cation is efficiently screened by the macrocyclic ring and by the pyrazole groups. This prevents access of oxygen to the metal centre and iron(II) oxidation. Owing to its substantial inertness toward oxidation by O_2, the $[FeL]^{2+}$ species cannot act as a catalyst of alcohol oxidation by molecular oxygen.

While the oxidation of primary alcohols by a variety of cations such as Co^{III},[12] Mn^{III}[13] and Ru^{IV}[14] is well documented, alcohol oxidation by iron(III) is quite rare. To the best of our knowledge, only two compounds, $[FeL^2_3][FeCl_4]_2$ (L^2 = 3,3′-bipyridazine)[15] and $[FeL^3_2][FeBr_4]Br$ [L^3 = 2,6-di(benzothiazol-2-yl)pyridine],[16] have been reported to form from the reaction of an iron(III) halide and the respective pro-ligand in hot ethanol solution. In both cases the formulation as mixed-valence iron(II)–iron(III) complexes was based on the magnetic moment values and on the Mössbauer and electronic spectra; no comment concerning their formation was reported.

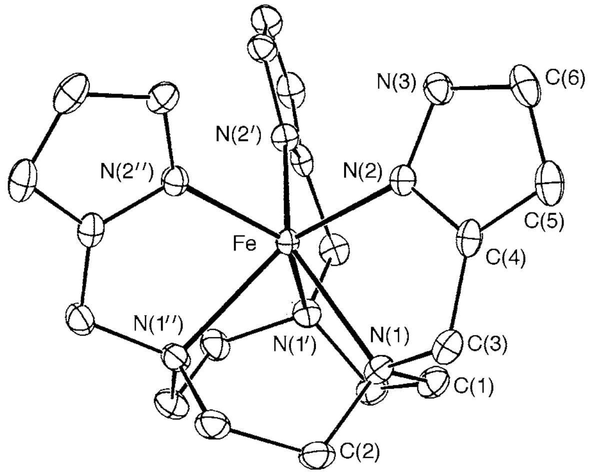


Fig. 1 View of the $[FeL]^{2+}$ cation in the structure of complex **1**. Primed atoms are related to unprimed ones by a three-fold axis

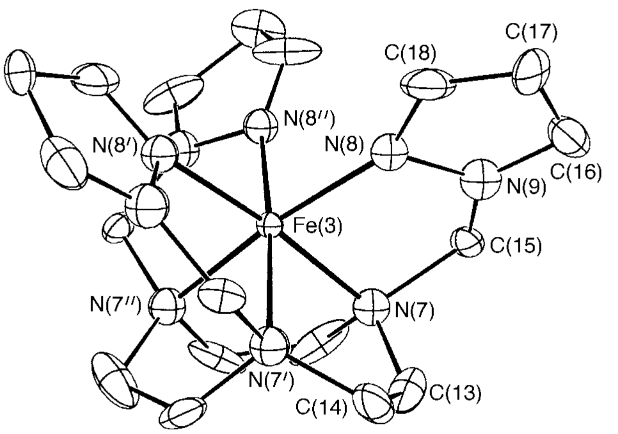


Fig. 2 View of one of the $[FeL']^{2+}$ cations in the structure of complex **2**. Primed atoms are related to unprimed ones by a three-fold axis. The other two independent cations in the unit cell are substantially isostructural with that shown

The reaction of $FeCl_2·4H_2O$ and L′ with an excess of $NaClO_4$ in a water–ethanol mixture and under strictly anaerobic conditions gives the purple, diamagnetic, complex $[FeL'][ClO_4]_2$. This is at variance with the presence of the high-spin $[FeL']^{2+}$ cation in the solid compound $[FeL'][FeCl_4]Cl$. The attainment of two different spin states by the $[FeL']^{2+}$ cation suggests that it is at the verge of the high spin–low spin transition for six-co-ordinated iron(II). Solid-state effects due to the different anions employed may then be decisive in determining the spin state of iron(II).

The structure of the compound $[FeL][FeCl_4]Cl$ **1**, as revealed by the X-ray analysis, consists of isolated $[FeL]^{2+}$, $[FeCl_4]^-$ and Cl^- ions. The rhombohedral unit cell contains one formula unit, the constituent ions being aligned along the symmetry axis, so that three-fold symmetry is imposed on each of them. The iron(II) in the complex cation is co-ordinated by the six nitrogen-donor atoms of the L ligand (Fig. 1 and Table 2), with a geometry grossly similar to that of the nickel(II) **3** and zinc(II) **4** complexes[1] formed by the same ligand as well as to that of a nickel(II)[17] or of a lithium[4] complex formed by related ligands. There are no non-bonded interactions involving atoms of the $[FeCl_4]^-$ anion shorter than 3.54 Å. The chloride ion, on the other hand, lies at 3.158(5) Å from the non-co-ordinating N atoms of the pyrazole groups and at 2.479(8) Å from their H atoms, possibly giving rise to hydrogen-bond interactions [Cl(3)···H(3N)–N(3) 150(6)°]. The long distance [4.660(3) Å] of the chloride ion from the metal centre reveals that access to

Table 1 Crystallographic data for $[FeL][FeCl_4]Cl$ **1** and $[FeL'][ClO_4]_2$ **2**

	1	**2**
Formula	$C_{18}H_{27}Cl_5Fe_2N_9$	$C_{18}H_{27}Cl_2FeN_9O_8$
M	658.44	624.24
Crystal system	Rhombohedral	Trigonal
Space group	$R3$ (no. 146)	$P3$ (no. 143)
a^a/Å	9.287(7)	16.621(4)
c/Å		7.594(3)
α/°	69.02(6)	
U/Å^3	673.6(9)	1816.8(9)
Z	1	3
D_c/g cm^{-3}	1.623	1.712
$F(000)$	335	966
Crystal size/mm	0.10 × 0.20 × 0.20	0.07 × 0.15 × 0.60
μ/mm^{-1}	1.60	0.91
Scan type	ω–2θ	ω–2θ
Scan width^b/°	1.00	1.00
Scan speed/° min^{-1}	2–5	1–4
Collection range/°	$5 \leqslant 2\theta \leqslant 54$	$5 \leqslant 2\theta \leqslant 46$
Data collected	$\pm h, \pm k, \pm l$	$\pm h, \pm k, +l$
No. measured reflections	5528	5474
No. unique data^c	1954	1830
No. parameters	131	374
Weighting coefficients a, b, f^d	0.0486, 0.00, 0.33	0.1264, 34.33, 0.33
Goodness of fit	1.016	1.056
$R1 = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert^e$	0.036	0.105
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{\frac{1}{2}}$	0.087	0.283
Largest features in final difference map/e Å^{-3}	0.23, −0.29	1.04, −1.06

^{a} For complex **1**, $a = b = c$, $\alpha = \beta = \gamma$; **2**, $a = b$, $\alpha = \beta = 90$, $\gamma = 120°$. ^{b} Value of a in the formula $(a + 0.35 \tan \theta)°$ for the scan width. ^{c} R_{int} 0.05 (**1**) and 0.06 (**2**). ^{d} Weighting scheme $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [f \max(0, F_o^2) + (1 - f)F_c^2]$. ^{e} Based on the 1708 (**1**) and 1618 (**2**) reflections having $F_o > 4\sigma F_o$; $R1 = 0.045$ (**1**) and 0.119 (**2**) for all unique reflections.

Table 2 Selected bond distances (Å) and angles (°) for $[FeL][FeCl_4]Cl$ **1***

Fe(1)–N(1)	2.274(4)	Fe(2)–Cl(1)	2.207(3)
Fe(1)–N(2)	2.120(4)	Fe(2)–Cl(2)	2.179(2)
N(1)–Fe(1)–N(1^{I})	78.9(2)	N(2)–Fe(1)–N(2^{I})	94.95(13)
N(1)–Fe(1)–N(2)	75.2(2)	Cl(1)–Fe(2)–Cl(2)	108.95(5)
N(1)–Fe(1)–N(2^{I})	140.19(13)	Cl(2)–Fe(2)–Cl(2^{I})	109.99(5)
N(1)–Fe(1)–N(2^{II})	123.92(13)		

* Atoms Fe(1), Fe(2) and Cl(1) lie on a three-fold axis; Fe(1) and the N atoms belong to the $[FeL]^{2+}$ cation, whereas Fe(2) and the Cl atoms form the $[FeCl_4]^-$ anion. Symmetry operations: I z, x, y; II y, z, x.

Table 3 Selected bond distances (Å) and angles (°) for $[FeL'][ClO_4]_2$ **2***

Fe(1)–N(1)	1.97(2)	Fe(2)–N(5)	1.905(11)
Fe(1)–N(2)	1.946(11)	Fe(3)–N(7)	1.98(2)
Fe(2)–N(4)	2.02(2)	Fe(3)–N(8)	1.966(13)
N(1)–Fe(1)–N(1^{I})	86.0(7)	N(4)–Fe(2)–N(5^{IV})	89.7(5)
N(1)–Fe(1)–N(2)	88.1(5)	N(5)–Fe(2)–N(5^{III})	95.1(5)
N(1)–Fe(1)–N(2^{I})	173.8(6)	N(7)–Fe(3)–N(7^{VI})	86.3(8)
N(1)–Fe(1)–N(2^{II})	91.8(6)	N(7)–Fe(3)–N(8)	87.4(6)
N(2)–Fe(1)–N(2^{I})	93.8(5)	N(7)–Fe(3)–N(8^{V})	173.5(7)
N(4)–Fe(2)–N(4^{III})	84.9(7)	N(7)–Fe(3)–N(8^{VI})	91.8(7)
N(4)–Fe(2)–N(5)	89.9(6)	N(8)–Fe(3)–N(8^{V})	94.3(6)
N(4)–Fe(2)–N(5^{III})	172.8(6)		

* Atoms Fe(1), N(1) and N(2), Fe(2), N(4) and N(5), and Fe(3), N(7) and N(8) belong to three symmetry-independent $[FeL']^{2+}$ cations, each possessing three-fold crystallographic symmetry. Symmetry operations: I $-y, x - y, z$; II $-x + y, -x, z$; III $1 - y, x - y, z$; IV $1 - x + y, 1 - x, z$; V $-x + y, 1 - x, z$; VI $1 - y, 1 + x - y, z$.

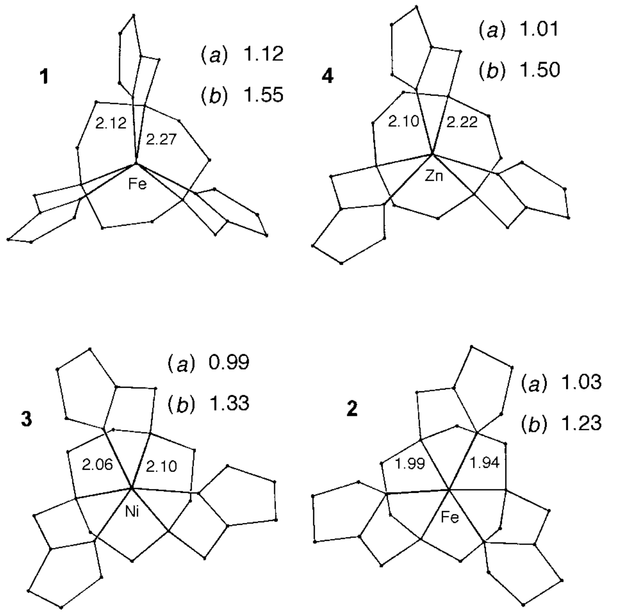


Fig. 3 Schematic views of the cations in compounds **1**–**4** along their three-fold or pseudo-three-fold axis. The mean values of the distances (Å) to the metal formed by the macrocycle nitrogens (N_m) and by the pyrazole nitrogens (N_p) are shown in each drawing. The distances of the metal atom from the planes of the N_p (*a*) and the N_m (*b*) atoms are also given. The ionic radii (Å) of the six-co-ordinate metal cations from ref. 18 (values for metal oxides; their differences are substantially unchanged in other ionic compounds) are, in the order of the above drawings: Fe^{2+} (high spin) 0.770, Zn^{2+} 0.745, Ni^{2+} 0.700 and Fe^{2+} (low spin) 0.61

the metal by O_2 should be difficult, as anticipated. Moreover, a system of hydrogen bonds formed by O_2, similar to that mentioned above, should disfavour the detachment of chelating arms.

The trigonal unit cell of the solid compound $[FeL'][ClO_4]_2$ **2** contains three formula units, each of the cations, which are symmetry-independent with respect to each other, possessing three-fold symmetry. The cations have closely similar co-ordination geometries (Fig. 2 and Table 3), which are also similar to those of the compounds mentioned above, however with the significant differences discussed below. In view of the bad quality of the data for **2** the structure of this compound cannot be referred to for detailed comparisons. Nevertheless it allows overall comparisons which are essential to define the nature of **1**. In particular, the Fe–N distances in **2**, mean 1.96 Å (those formed by the macrocycle nitrogens, 1.96–2.02 Å, being *ca.* 0.05 Å longer in the mean than those formed by the pyrazole nitrogens, 1.90–1.96 Å), are much shorter than the distances in **1**, 2.274(4) (macrocycle nitrogens) and 2.120(4) Å (pyrazole nitrogens). The large differences in bond distances to the metal between the two compounds support the assumption that the high-spin metal ion in the complex cation of **1** is iron(II), ruling out definitively the alternative formulation $[Fe^{III}L][Fe^{II}Cl_4]Cl$ for that compound. Indeed, according to the latter hypothesis, comparable Fe–N distances would be expected for **1** and **2**, since the ionic radius of six-co-ordinate high-spin iron(III) is only 0.03 Å larger than that tabulated for low-spin iron(II).[18] Moreover, the Fe–Cl distances [mean 2.19(1) Å] in the pseudo-tetrahedral anion of **1** match the average value reported for the dimensions of the $[FeCl_4]^-$ anion in an accurate study, based on the results of several structure determinations.[19] This value is at least 0.10 Å smaller than that expected for the $[FeCl_4]^{2-}$ anion,[19] and the difference is unchanged if corrections for thermal motion are applied.

There are structural trends among the cations in the compounds **1**–**4**, which deserve consideration. Schematic projections along the three-fold or pseudo-three-fold axis of each cation are shown in Fig. 3. The mean values of the distances to the metal formed by the macrocycle nitrogens (N_m) and by the pyrazole nitrogens (N_p) are shown, as well as the distances of the metal from the planes through the N_m and the N_p atoms. Going from **1** to **2** through **4** and **3**, in that order, a decrease in all of the above distances is observed. The overall shortening of the metal–nitrogen distances from **1** to **4** approximately corresponds to the difference between the ionic radii of the two metals,[18] although the decrease exhibited by the distances from the metal to the 'basal faces' of the co-ordination polyhedron, defined by the N_m and the N_p atoms, is higher than the decrease in ionic radii. The appreciable shortening of the polyhedron in the direction of the three-fold (or pseudo-three-fold) axis is accompanied by a rotation of the basal faces with respect to each other about that axis, which maintains the bite of the chelate rings formed by the N_m and N_p atoms at a constant value [the value of the intrachelate $N_m \cdots N_p$ distance of 2.68(1) Å in **1** matches the mean value in **4**]. As a consequence of the above rotation, the co-ordination geometry, which is close to trigonal prismatic in **1** (Fig. 3), tends to the antiprismatic arrangement in **4**. From the values in Fig. 3, this trend continues in **3** and **2**, in that order, the decrease in all of the distances considered here from the values of the previous two cations being particularly noticeable [consistently with the overall trend, the $N_m \cdots N_p$ separation remains almost constant, being 2.67(1) Å in **3** and 2.74(2) Å in **2**]. In the cations of **2** the difference between the $M-N_m$ and $M-N_p$ bond lengths is the smallest among those detected for these four compounds and the co-ordination geometry is almost antiprismatic or pseudo-octahedral. The arrangement in the cations of **3** and **2** may be dictated by the preference of the d^8 high-spin **3** and of the d^6 low-spin **2** ions for octahedral co-ordination.

Finally, the present results and additional evidence[20] suggest that both high- and low-spin complexes of iron(II) are formed by L′, depending on the conditions in the solid state, whereas only high-spin iron(II) complexes are formed by L. This might be ascribed to slightly different field strengths generated by the two ligands, due to the different mode of attachment of their pyrazole groups in the functionalized macrocycles. In order to test this hypothesis, extended-Hückel calculations[21,22] were undertaken on models of the N-substituted 1-methylpyrazole and of the C-substituted 3-methylpyrazole. Comparable atomic charges on the N donor atom were found for the two models, but in the first case (model for the pendant arms of the L′ ligand) a 20% higher contribution of the nitrogen p orbital yielding the lone pair (with appropriate choice of axes) was found for the highest occupied σ molecular orbital, compared to the other model. Moreover, a fragment analysis revealed that this p orbital mixes with different phases, in the two models, with two important (high-energy) fragment orbitals of the rest of the molecule, the ordering of which is interchanged on going from one model to the other. As a result the electron density of that nitrogen p orbital is less involved in bonding interactions with the rest of the pyrazole framework in the L′ case, which should enhance its lone-pair character. This may be at the origin of the higher field strength apparently generated by the L′ ligand.

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