Eight-co-ordination in Manganese(II) and Iron(II) Complexes with a Pyrazole-functionalised Tetraazamacrocycle *

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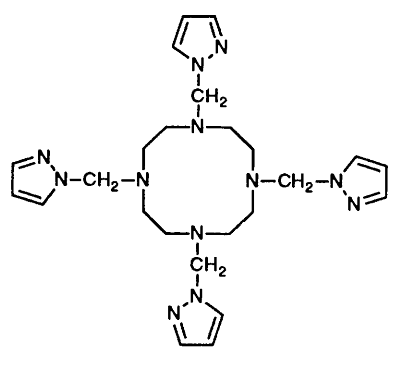
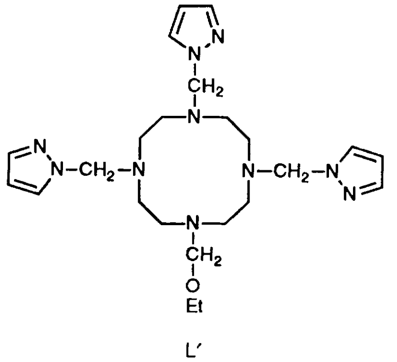
The potentially octadentate ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane (L) gives with manganese(II) the complex $[MnL][PF_6]_2\cdot(CH_3)_2CO$ and with iron(II) species of formula $[FeL_xL'_{1-x}][PF_6]_2\cdot$solvent where the ligand L′ originates from L by substitution of an ethoxy group for a pyrazolyl group in one of the pendant arms of the macrocycle. The crystal structure of $[MnL][PF_6]_2\cdot(CH_3)_2CO$ has been determined by X-ray diffraction: orthorhombic, space group *Pcab*, with a = 15.801(6), b = 17.973(4), c = 26.793(3) Å and Z = 8. The manganese(II) atom is co-ordinated by the eight nitrogen atoms of the L ligand. X-Ray analyses on the isomorphous crystals of the iron(II) species have shown that these contain both eight- and seven-co-ordinate iron(II) in complex cations respectively formed by the L and L′ ligands.

The co-ordination properties of macrocycles bearing pendant donor groups have recently attracted much interest which has produced a rapid advance in the field of both biomimetic models and abiotic systems.[1] In the growing class of such molecules the potentially octadentate ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane (L), which provides four nitrogen atoms in a flexible macrocyclic ring and the remaining four N donors on the pendant arms, has been found to present interesting features both regarding its co-ordinating ability and its chemical behaviour.[2] It yields complexes with co-ordination numbers of six or eight, according to the stereochemical requirements of the metal ions involved. The metal ion is always bound to the four nitrogen atoms of the macrocycle, whose bonding cavity is too small to accommodate cations, and completes its co-ordination sphere with two[2b] or four[2a] additional N donors from the dangling groups. The macrocycle folds to yield six-co-ordinate complexes, but it remains planar in the eight-co-ordinate species. A relevant chemical feature of the ligand is that it may undergo substitution by an ethoxy group for the pyrazolyl group in one of its pendant arms under very mild conditions.[2b] Reporting on the co-ordinating and chemical behaviour of the L ligand toward the cations Ni^{2+}, Cu^{2+} and Zn^{2+}, we anticipated that the iron derivative might have a co-ordination number higher than six.[2b]

Now we report on the synthesis and structural characterization of the compound $[MnL][PF_6]_2\cdot(CH_3)_2CO$ containing eight-co-ordinate manganese(II). We also give general structural information about the species $[FeL_xL'_{1-x}][PF_6]_2\cdot$solvent, where L′ = 1-ethoxymethyl-4,7,10-tris(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane, which consists of solid solutions containing both cations with iron(II) eight-co-ordinated by the intact L ligand and cations with iron(II) seven-co-ordinated by the L′ ligand originating from L by the replacement of one pendant pyrazole by an ethoxy group. A preliminary account of part of this work has appeared.[2d] Complexes with co-ordination numbers exceeding six are uncommon for manganese(II) and iron(II) and have generally been obtained with ligands having donor sets formed by oxygen atoms.[3]



L



L′

Experimental

All reactions and manipulations were carried out under a purified nitrogen atmosphere. The solvents were reagent grade and were appropriately dried and freed of molecular oxygen prior to use. Magnetic susceptibilities were measured by the Faraday method with an automated DMS-5 magnetometer. Electronic spectra were recorded in the range 300–2000 nm with a Perkin-Elmer Lambda 9 spectrometer. The concentrations of the solutions in CH_3CN were about 10^{-3} mol dm^{-3}. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer on a Nujol mull and KBr plates. The ligand 1,4,7,10-tetrakis(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

(L) was prepared as previously described;[2b] $MnCl_2·4H_2O$ (Carlo Erba) and $TlPF_6$ (Strem) were used as received.

Preparation of the Complexes.—$[MnL][PF_6]_2·(CH_3)_2CO$. The salt $TlPF_6$ (0.70 g, 2 mmol) was added to a solution of $MnCl_2·4H_2O$ (0.20 g, 1 mmol) in acetone (20 cm^3). The resulting suspension was stirred at 40–50 °C for 30 min and filtered to eliminate TlCl; the ligand (0.49 g, 1 mmol) dissolved in acetone (20 cm^3) was added to the filtrate. Colourless crystals of the complex were obtained by adding ethanol (10 cm^3) and slowly concentrating the resulting solution. The solid was filtered off and washed with absolute ethanol and then light petroleum (b.p. 40–70 °C) before being dried in a stream of nitrogen. Yield *ca.* 80%. The compound crystallizes with acetone as inferred from IR data [ν(CO) 1710 cm^{-1}] and confirmed by the X-ray analysis (Found: C, 35.9; H, 4.80; N, 18.6. $C_{27}H_{42}F_{12}MnN_{12}OP_2$ requires C, 36.2; H, 4.75; N, 18.8%).

$[FeL_xL'_{1-x}][PF_6]_2$·solvent. Repeated preparations under the same reaction conditions, through the procedure described above for the manganese(II) derivative but using anhydrous $FeBr_2$, gave products whose elemental analyses were grossly in agreement with an $x = 0.3$ value in the above formula. It was evident, also from X-ray analyses performed on crystals from different batches (see below), that in the course of the preparations part of the L ligand had transformed to L′ (L′ = 1-ethoxymethyl-4,7,10-tris(pyrazol-1-ylmethyl)-1,4,7,10-tetraazacyclododecane], due to substitution by an ethoxy group for a pyrazolyl group in L. The colourless solid contained solvate acetone [ν(CO) 1710 cm^{-1}] and ethanol [ν(OH) 3340 cm^{-1}] molecules.

Crystal Structure Analysis of $[MnL][PF_6]_2·(CH_3)_2CO$—*Crystal data.* $C_{27}H_{42}F_{12}MnN_{12}OP_2$, $M = 895.6$, orthorhombic, space group *Pcab*, $a = 15.801(6)$, $b = 17.973(4)$, $c = 26.793(3)$ Å, $U = 7609(3)$ Å^3, $Z = 8$, $D_c = 1.56$ g cm^{-3}, $\lambda = 0.710\,69$ Å, $\mu = 5.1$ cm^{-1}, $F(000) = 3672$, $T = 295$ K.

An Enraf–Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα radiation were used. The prismatic crystal had dimensions 0.20 × 0.40 × 0.50 mm. Unit-cell parameters were determined from the angular settings of 24 reflections with $13 \leqslant \theta \leqslant 14°$. Reflections $+h$, $+k$, $+l$ were collected in the ω–2θ scan mode with $(1.10 + 0.35 \tan\theta)°$ scan width and variable (3–8° min^{-1}) scan speed in the $2.5 \leqslant \theta \leqslant 23°$ range; of the 4074 unique reflections collected 2617 having $I \geqslant 3\sigma(I)$ were used in the calculations. No crystal decay was detected. An empirical absorption correction was applied using DIFABS.[4] The principal computer programs used in the crystallographic calculations are given in refs. 4–8.

The structure of the compound was solved by heavy-atom and direct methods using SIR[5] and refined by full-matrix least squares, with the final weighting scheme $w = [\sigma^2(F_o) + 0.0010F_o^2]^{-1}$. One of the PF_6^- anions, affected by orientational disorder, was refined as two regular octahedra of F sites, with a common P atom position and complementary occupancy factors but independent P–F parameters. The disordered acetone solvate molecule was refined as a triangular array of C atoms surrounding a carbon centre, with one C–C parameter. The cation H atoms were introduced in calculated positions (C–H 0.96 Å) with $U_H \approx 1.2U_C$. Anisotropic thermal parameters were assigned to the Mn, P and F atoms (except for the fluorine sites of the less-populated octahedron in the model for the disordered PF_6^- anion), as well as to those of the acetone model. Refinement on 344 parameters converged at $R = 0.079$ and $R' = 0.084$. Final difference electron-density maps showed no feature outside the range +0.50 to −0.40 e Å^{-3}. The atomic scattering factors were taken from ref. 9. Table 1 contains a list of atomic positional parameters, Table 2 selected bond distances and angles.

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

Structural Investigations on $[FeL_xL'_{1-x}][PF_6]_2$·solvent.—Crystals of the iron(II) derivative were isomorphous to those of the manganese(II) complex. Structural analyses performed on various crystals from different batches revealed that the crystals were solid solutions containing complex cations with eight-co-ordinate iron(II) formed by the unchanged L ligand, as well as cations with seven-co-ordinate iron(II), formed by the transformed L ligand. The occupancy factors could be refined, the best set of data (final $R = 0.075$ for 1664 reflections and 330 parameters) yielding the formula $[FeL_{0.31}L'_{0.69}][PF_6]_2·0.5(CH_3)_2CO·0.5C_2H_5OH$.

We are not reporting here the full and lengthy details of the structure refinement procedure or the structural parameters for the iron(II) compound; these are included in the supplementary material and will be made available by us on request. The results of this structural study are useful for general considerations and to perform gross comparisons, but their use for accurate comparisons is prevented by the small amount of disorder in the structure conceivably induced by the isomorphous replacement described above.

Results and Discussion

The reaction of the L ligand with Mn^{2+} in the presence of the PF_6^- anion in acetone–ethanol solution affords the complex $[MnL][PF_6]_2·(CH_3)_2CO$. Under the same experimental conditions, however with Fe^{2+} instead of Mn^{2+}, crystalline products were obtained which may be formulated as $[FeL_xL'_{1-x}][PF_6]_2$·solvent where solvent = acetone and ethanol (see Experimental section). The L′ macrocycle with mixed pendant arms originates from L by substitution by an ethoxy group for a pyrazolyl group. Such a displacement reaction has already been reported to occur when the ligand L is allowed to react with Ni^{2+} and Zn^{2+} in an acetone–ethanol solution in the presence of BPh_4^-.[2b] Based on the information currently available, the solvolysis of ligand L exhibits two peculiar aspects: (*a*) it involves only one pyrazolyl group and (*b*) it occurs in the presence of specific metal ions. As regards point (*a*) we note that even under forcing reaction conditions, such as prolonged heating of the reaction mixture, the detachment of only one pyrazolyl group has been detected. As far as point (*b*) is concerned, the Mn^{2+} cation does not promote detachment of the pyrazolyl group under reaction conditions identical to those in which the Fe^{2+} ion does.

The electronic spectra of both complexes are essentially featureless in the range 500–2000 nm. The magnetic moments at room temperature are 5.79 and 4.94 μ_B for the complexes of Mn^{2+} and Fe^{2+}, respectively. On the basis of these data alone we could not assign a definite stereochemistry to either complex; in the case of the iron(II) complex even the formula could not be assigned exactly on the basis of elemental analyses alone. Consequently, a complete X-ray investigation on the manganese(II) complex $[MnL][PF_6]_2·(CH_3)_2CO$ **1** was carried out and the nature of the iron(II) species $[FeL_xL'_{1-x}][PF_6]_2$·solvent **2** was elucidated, as outlined in the Experimental section, by diffraction methods.

The manganese atom in the $[MnL]^{2+}$ cation is eight-co-ordinated by the four N atoms (N_{ma}) of the macrocycle and the four nitrogens (N_{pz}) of the dangling pyrazole groups (Fig. 1) arranged at the corners of a square prism with the basal faces rotated by approximately 24° with respect to each other about the pseudo-four-fold axis. Each set of N atoms is planar, with deviations < 0.01 Å from the respective least-squares plane, the two planes being essentially parallel, with a 0.3(2)° angle between their normals. The co-ordination geometry is similar to that found about the Na^+ cation in the compound $[NaL]BPh_4$[2a] **3** where, however, the basal faces of the prism are rotated by 31.4° with respect to each other. Additional differences between the complex cations in compounds **1** and **3** are due to the different sizes of the metal ions involved, both the $Mn-N_{ma}$ and the $Mn-N_{pz}$ distances in **1** (Table 2) being shorter,

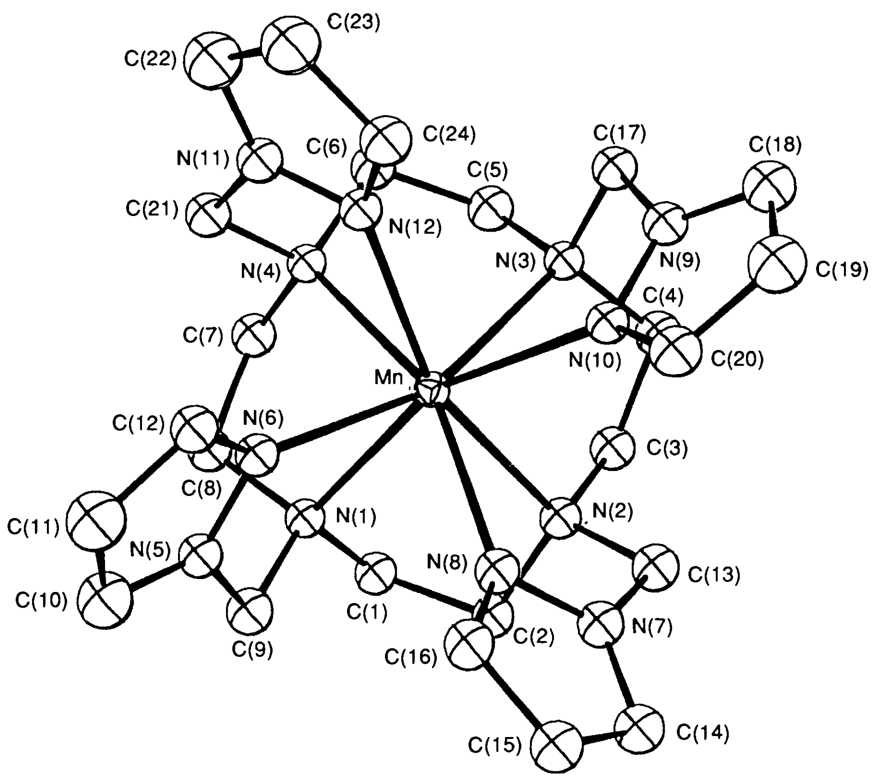

Fig. 1 A view of the cation in the structure of $[MnL][PF_6]_2\cdot(CH_3)_2CO$, with 20% probability ellipsoids

Table 1 Atomic coordinates (× 10^4) for $[MnL][PF_6]_2\cdot(CH_3)_2CO$ *

Atom	x	y	z	Atom	x	y	z
Mn	2952(1)	519(1)	3584(1)	C(19)	4387(9)	1591(7)	2320(5)
N(1)	2680(5)	−282(4)	4322(3)	C(20)	4327(8)	1444(7)	2821(5)
N(2)	3806(5)	−650(5)	3505(3)	C(21)	1001(7)	905(6)	3795(4)
N(3)	2546(5)	−121(5)	2781(3)	C(22)	899(10)	2183(8)	3399(5)
N(4)	1412(5)	227(4)	3609(3)	C(23)	1461(9)	2613(8)	3161(5)
N(5)	2942(5)	863(5)	4731(3)	C(24)	2213(8)	2207(6)	3123(5)
N(6)	2824(5)	1220(5)	4297(3)	P(1)	1426(2)	2146(1)	1533(1)
N(7)	4933(6)	188(5)	3694(3)	P(2)	8377(2)	737(2)	3949(1)
N(8)	4359(5)	673(5)	3876(3)	F(1A)	889(6)	1817(4)	1975(2)
N(9)	3324(5)	891(5)	2455(3)	F(2A)	2161(4)	2339(5)	1908(2)
N(10)	3658(5)	1008(4)	2903(3)	F(3A)	1964(5)	2473(4)	1090(2)
N(11)	1313(6)	1533(5)	3505(3)	F(4A)	692(4)	1950(5)	1158(3)
N(12)	2112(5)	1554(5)	3346(3)	F(5A)	1831(5)	1357(2)	1441(3)
C(1)	3022(7)	−1027(6)	4248(4)	F(6A)	1023(5)	2934(2)	1626(3)
C(2)	3871(7)	−1043(6)	3984(4)	F(1B)	528(3)	2248(10)	1614(8)
C(3)	3453(7)	−1128(6)	3122(4)	F(2B)	1248(12)	1533(8)	1199(5)
C(4)	3176(7)	−712(6)	2663(5)	F(3B)	1393(13)	2657(9)	1116(5)
C(5)	1680(7)	−443(7)	2834(5)	F(4B)	1603(12)	2758(8)	1866(6)
C(6)	1075(7)	59(6)	3113(4)	F(5B)	1458(13)	1634(9)	1949(5)
C(7)	1243(7)	−370(6)	3968(4)	F(6B)	2323(3)	2043(10)	1451(8)
C(8)	1761(7)	−305(7)	4441(4)	F(7)	7681(5)	944(6)	3553(3)
C(9)	3115(7)	74(6)	4740(4)	F(8)	7878(5)	9(5)	4045(4)
C(10)	2966(8)	1334(8)	5116(6)	F(9)	9069(5)	511(5)	4336(3)
C(11)	2850(8)	2026(8)	4924(5)	F(10)	8865(5)	1474(5)	3849(4)
C(12)	2761(7)	1939(6)	4411(4)	F(11)	8919(4)	342(5)	3530(3)
C(13)	4660(7)	−382(6)	3362(4)	F(12)	7835(4)	1133(4)	4367(3)
C(14)	5725(8)	344(7)	3857(5)	C(25)	4458(11)	2054(9)	284(6)
C(15)	5666(8)	948(7)	4147(5)	C(26)	4250(14)	2736(9)	128(6)
C(16)	4809(7)	1143(7)	4149(4)	C(27)	4169(14)	1804(10)	723(7)
C(17)	2546(7)	461(6)	2403(4)	C(28)	5019(20)	1650(14)	27(10)
C(18)	3769(8)	1226(7)	2089(5)				

* Atoms F(*n*A) and F(*n*B) belong to the two regular octahedra forming the model for the disordered PF_6^- anion; these have population parameters of 0.76(1) and 0.24(1). Atoms C(25)–C(28) belong to the model for the solvate molecule.

respectively by 0.20 and 0.24 Å in the mean, than the corresponding distances in 3. The ability of the ligand to adapt to such changes in the dimensions of the cage about the metal ion for a given co-ordination geometry, as well as its ability to

Table 2 Selected bond distances (Å) and angles (°) for $[MnL][PF_6]_2\cdot(CH_3)_2CO$

Mn–N(1)	2.484(8)	Mn–N(6)	2.298(9)
Mn–N(2)	2.506(8)	Mn–N(8)	2.373(9)
Mn–N(3)	2.522(9)	Mn–N(10)	2.313(9)
Mn–N(4)	2.489(8)	Mn–N(12)	2.373(8)
N(1)–Mn–N(2)	71.0(3)	N(10)–Mn–N(12)	76.1(3)
N(2)–Mn–N(3)	71.5(3)	N(6)–Mn–N(12)	75.2(3)
N(3)–Mn–N(4)	71.2(3)	N(6)–Mn–N(10)	119.3(3)
N(1)–Mn–N(4)	71.8(3)	N(8)–Mn–N(12)	121.4(3)
N(1)–Mn–N(3)	111.8(3)	N(1)–Mn–N(6)	68.9(3)
N(2)–Mn–N(4)	110.6(3)	N(2)–Mn–N(8)	67.7(3)
N(6)–Mn–N(8)	75.2(3)	N(3)–Mn–N(10)	67.9(3)
N(8)–Mn–N(10)	76.3(3)	N(4)–Mn–N(12)	68.0(3)

yield both six-[2b] and eight-co-ordinate complexes, are indicative of a considerable flexibility. The transition-metal ion in **1** occupies a closer position to the macrocycle cavity than the larger alkali-metal ion in **3**: on going from **1** to **3** the distance of the metal ion from the plane through the N_{ma} atoms increases from 1.413(2) to 1.627(3) Å, whereas the distance from the plane through the N_{pz} atoms decreases from 1.163(2) to 1.029(3) Å. To our knowledge, no other manganese(II) complex with a N_8 donor set is available for detailed comparison. In the structure of an eight-co-ordinate manganese(II) derivative formed by two 12-crown-4 (1,4,7,10-tetraoxacyclododecane) ligands,[3b] with an O_8 donor set and antiprismatic co-ordination geometry, the Mn–O distances average 2.31 Å, smaller than the mean (2.42 Å) of the Mn–N distances in **1**.

The iron(II) derivative **2** corresponding to the formula $[FeL_{0.31}L'_{0.69}][PF_6]_2\cdot0.5(CH_3)_2CO\cdot0.5C_2H_5OH$, essentially assigned on the basis of the X-ray structural investigation, consists of a solid solution of the compounds $[FeL][PF_6]_2$ and $[FeL'][PF_6]_2$ in a 0.31(1):0.69(1) ratio and of interspersed solvent molecules. The metal atom is eight-co-ordinated in the $[FeL]^{2+}$ cation and seven-co-ordinated in the $[FeL']^{2+}$ one, with nitrogen donor sets in each case. The two complex cations have essentially the same overall conformation, as the ethoxy group of each $[FeL']^{2+}$ cation fits easily into the cavity ideally left by the pyrazolyl group for which it is substituted in the L to L′ transformation. It should be noted by contrast that in the structure of the purely seven-co-ordinate compound $[ZnL'][BPh_4]_2\cdot(CH_3)_2CO$ [2b] **4** the ethoxy group of L′ points farther away from the co-ordination sphere than in the structure of **2** and the other three dangling groups of the L′ ligand in **4** rearrange slightly from the conformation which is typical of the eight-co-ordinate complexes formed by L, such as **1** and **3**. Both the Fe–N_{ma} and the Fe–N_{pz} distances are shorter (respectively by 0.13 and 0.04 Å, in the mean) than the corresponding distances in **1**. Moreover, the Fe^{2+} ion in **2** is definitely closer (by 0.14 Å) to the plane through the N_{ma} atoms than to the plane defined by the N_{pz} donors, at variance with the arrangements found for **1** or **3** but consistent with the position of the comparatively small metal ion in **4**. The solid solution **2** contains one of the first eight-co-ordinate iron(II) complexes with an entirely nitrogen donor set, the structure of a sandwich iron(II) complex of this type, formed by a tetraazamacrocycle, having been recently reported.[10]

Acknowledgements

We thank the Italian Ministero dell' Universita e della Ricerca Scientifica e Tecnologica for financial support.

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Received 29*th October* 1991; *Paper* 1/05485F