Chemistry of Polydentate Ligands. Part 7.[1] Synthesis, Characterisation, and Properties of some Manganese(II) Complexes of Quinquedentate Macrocyclic Ligands based on 1,10-Phenanthroline. Crystal and Molecular Structure of a Complex with Pentagonal-pyramidal Co-ordination Geometry about the Mn^{II}

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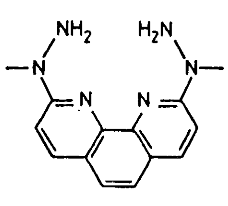
Complexes of quinquedentate macrocyclic ligands with Mn^{II} have been prepared by condensation of 2,6-diformylpyridine and 2,6-diacetylpyridine with 2,9-di(1-methylhydrazino)-1,10-phenanthroline monohydrochloride in the presence of manganese(II) templates. Electrical conductivity and i.r. spectra are reported and evaluated to distinguish between ring closure and polymer formation, while magnetic susceptibility data show the complexes to be high spin. Evidence is presented for co-ordination of unidentate ligands in one axial site thereby completing the pentagonal-pyramidal co-ordination geometry about the Mn^{II} ions. This is confirmed by a single-crystal *X*-ray structure determination of [MnC$_{23}$H$_{21}$N$_7$Cl][BF$_4$], which is monoclinic with a = 11.717(8), b = 14.403(9), c = 15.316(9) Å, β = 116.42(6)°, Z = 4, space group $P2_1/n$. Metal–donor nitrogen bond lengths are 2.167(11), 2.168(11), 2.204(11), 2.312(11), and 2.348(11) Å and the metal–chlorine distance is 2.353(6) Å. The Mn^{II} is 0.53 Å out of the N$_5$ donor plane, towards the chlorine. The structure is compared with other pentagonal pyramids and distortions from the symmetric shape are discussed. Structural similarities between the current ligand and porphyrins, particularly in cavity sizes, are noted.

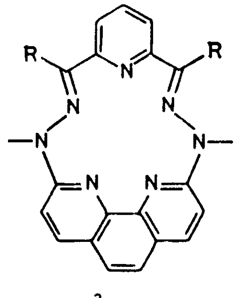
THE number of transition-metal ions found to be capable of acting as templates for ring closure with 2,6-diacetylpyridine, to yield quinquedentate macrocyclic ligands, is small. Requisite cations, including Group 2B ions in the list, are high-spin Mn^{II},[2] Fe^{II},[3] and Fe^{III}[4] along with Ag^{I},[5] Zn^{II},[6] Cd^{II},[5] and Hg^{II},[5] all of which, with the exception of Fe^{II}, have symmetric d^5 or d^{10} outer-electron configurations. An earlier paper in this series reported the formation of macrocycles L^2 and L^3 from the linear quadridentate ligand L^1, with Zn^{II}, Cd^{II}, and Hg^{II} ions as templates; the resemblance of these macrocyclic ligands to porphyrins was noted.[1] This paper, which describes the extension of the investigation to a manganese(II) template, provides further evidence of similarity between porphyrins, and L^2 and L^3. The two types of compound are planar, relatively rigid, and have potential π-electron delocalisation extending around the macrocyclic rings. The crystal structure of [Mn(L^3)Cl][BF$_4$], a preliminary report of which has appeared,[7] shows that L^3 also has a similar cavity size to that found in manganese(II) porphyrin complexes. Differences between the types of ligand include the number of donor atoms, and the charge present (dinegative for porphyrins and neutral for L^3).



L^1

RESULTS AND DISCUSSION

Manganese(II) readily acts as a template in the ring-closure reaction of 2,9-di(1-methylhydrazino)-1,10-phenanthroline monohydrochloride, L^1·HCl, with 2,6-diformylpyridine and 2,6-diacetylpyridine to yield complexes of L^2 and L^3 respectively. The condensations do not require any acid catalyst, in contrast to the same cyclisations around Group 2B templates,[1] although addition of several drops of a dilute mineral acid does hasten the reactions. Yields of the orange manganese(II) complexes are *ca.* 80%.



L^2: R = H

L^3: R = Me

Analytical, electrical conductance and, where measured, magnetic data for the complexes are contained in Table 1. The compounds appear to be indefinitely stable both in the solid state and in solution. Magnetic moments, recorded at room temperature (293 K), are typical of high-spin d^5 systems, where the predicted spin-only value is 5.90 B.M.[8,†] The analytical data demonstrate that, as with the zinc(II) complexes, addition of a large anion, like BF$_4^-$ or ClO$_4^-$, to a solution of [Mn(L)Cl$_2$] (L = L^2 or L^3) yields a precipitate in which a chloro-ligand is retained. The analyses by themselves could apply equally to polymeric chains and monomeric macrocycles. Evidence for cyclisation comes from (*i*) the crystal structure of [Mn(L^3)Cl][BF$_4$] (see below), (*ii*) the i.r. spectra of the complexes, with their similarity to that of the known macrocyclic compound, and (*iii*) the

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[†] Throughout this paper: 1 B.M. = 9.27 × 10^{-24} A m^2.

combination of analyses and conductivity measurements. As mentioned in Part 6,[1] the absence of N–H bending vibrations and ν(C=O) bands in the 1 600—1 750 cm^{-1} region, and of ν(N–H) signals around 3 200 cm^{-1} in the i.r. spectra does not differentiate between long polymers and macrocycles. However, the conductivity measurements, run in dimethyl sulphoxide (dmso), that fall in the range for 2 : 1 electrolytes 50—80 S cm^2 mol^{-1},[9] indicate that polymeric species cannot be present in these instances. The compounds that act as 1 : 1 electrolytes could be polymeric, but $[Mn(L^3)Cl][BF_4]$ is one of these complexes and by inference the others are also macrocycles. It is noticeable from Table 1, that only those complexes containing at least one chloride ion are 1 : 1 electrolytes. The binding of Cl^- in dmso solution is stronger than that of Br^-, NCS^-, or NO_3^- as only the chloro-ligand remains co-ordinated.

TABLE 1

Analytical and conductivity data for manganese(II) complexes

Compound	Analysis (%) Found C	H	N	Calc. C	H	N	Λ[a] S cm^2 mol^{-1}
$[Mn(L^2)Cl][BF_4]\cdot 0.5H_2O$	45.8	3.3	17.4	45.6	3.3	17.7	36
$[Mn(L^2)Cl][ClO_4]$	45.0	3.3	17.8	45.3	3.1	17.6	42
$Mn(L^2)(NCS)_2$	51.5	3.4	23.6	51.3	3.2	23.4	63
$[Mn(L^2)Cl_2]\cdot 2H_2O$	47.6	4.0	18.7	47.6	4.0	18.5	*b*
$Mn(L^2)Br_2$	42.2	3.4	17.1	42.3	3.1	16.5	55
$[Mn(L^2)Cl][NO_3]\cdot 0.75H_2O$	47.2	3.2	21.3	47.3	3.5	21.0	54
$[Mn(L^3)Cl][BF_4]$[c]	48.2	3.9	17.3	48.2	3.7	17.1	37
$[Mn(L^3)Cl][ClO_4]\cdot 0.75MeOH$	46.2	3.8	15.9	46.5	4.3	15.5	37
$Mn(L^3)(NCS)_2$	53.0	3.9	22.4	53.0	3.7	22.3	68
$Mn(L^3)Cl_2$[d]	53.5	4.1	19.2	53.0	4.1	18.8	35
$Mn(L^3)Br_2$	45.3	3.6	16.3	45.3	3.5	16.1	*b*
$Mn(L^3)(ClO_4)_2$	42.5	3.3	14.4	42.6	3.3	15.1	61
$Mn(L^3)(NO_3)_2\cdot EtOH$	48.4	4.3	19.8	48.4	4.4	20.3	49
$[Mn(L^4)Cl][BF_4]$	45.6	3.6	17.3	45.9	3.9	17.9	44
$[Mn(L^5)Cl][BF_4]$	48.2	4.4	16.5	47.9	4.4	17.0	31
$Mn(L^5)Cl_2\cdot 0.25H_2O$	51.9	4.9	18.9	52.1	4.9	18.5	

[a] Measured at 22 °C on 10^{-3} mol dm^{-3} solutions in dmso. [b] Insoluble in dmso. [c] Room-temperature magnetic moment of 6.00 B.M. [d] $\mu_{eff.}$ = 5.85 B.M. at room temperature.

The retention of a single chloride ion per molecule in many of the complexes provides non-crystallographic evidence for the Mn^{II} being six-co-ordinate, with the donor atoms at the vertices of a pentagonal pyramid. The inequivalence of the two axial sites was investigated by preparing complexes with anions other than chloride present. A surprising difference exists between the ν(C≡N) regions of the i.r. spectra of $Mn(L^3)(NCS)_2$ and $Mn(L^2)(NCS)_2$. The former contains a single resonance at 2 060 cm^{-1} while the latter consists of bands at 2 053 and 2 031 cm^{-1}, the second of which is the sharper of the two signals. Although both values for $Mn(L^2)(NCS)_2$ are lower than usual, the signal at 2 053 cm^{-1} is assigned to an isothiocyanato-ligand and the other to an ionic NCS^- group.[10] The possibility that the band at 2 031 cm^{-1} arises from a weakly co-ordinated, rather than an ionic NCS^-, cannot be dismissed however, as the ν(C≡N) signals of $Mn^{I}(NCS)_2$ occur at 2 058 and 2 038 cm^{-1} and yet the crystal structure shows both anions to be co-ordinated.[11] Replacing L^2 with L^3 is unlikely to alter the difference between the axial sites much, and the sole ν(C≡N) band with $Mn(L^3)(NCS)_2$ is probably the result of accidental degeneracy. The i.r. signals from the nitrate groups in $Mn(L^3)(NO_3)_2$ occur at 1 420, 1 360, 1 303, 1 050, and 832 cm^{-1} which, by comparison with other recorded spectra,[10] can be assigned to one ionic nitrate and one unidentate nitrato-ligand per molecule. Again this is indicative of six-co-ordinate manganese(II).

Oxygenation of the complex ion $[Mn(L^3)]^{2+}$ was attempted to investigate whether the structural similarity between the ligand and porphyrins results in chemical similarities. The compound [Mn(tpp)]* undergoes reversible oxygenation [12] in toluene at −79 °C but the interaction is irreversible at room temperature.[13] No reaction occurs when an axial ligand is present. Some indication as to the nature of the product from the irreversible process is provided by a similar reaction of [Mn(pc)]* in the presence of pyridine [14] to yield the oxo-bridged dimer $[\{Mn(pc)(py)\}_2O]$. Removal of the chloride ions from $Mn(L^3)Cl_2$ was achieved by refluxing a methanolic solution of this compound with silver perchlorate and filtering off the AgCl. However, no reaction occurred with oxygen, as the product is $Mn(L^3)(ClO_4)_2$. The necessary presence of anions, for electrical neutrality, with the cation $[Mn(L^3)]^{2+}$ provides groups which, by occupying the axial co-ordination site, may block oxygenation. Co-ordination of the ClO_4^- groups is established by the i.r. spectrum of the product as the ν_3 perchlorate band is split into three signals.[10] The approximate equivalence of the perchlorate ligands is difficult to reconcile with the differing axial environment about $[Mn(L^3)]^{2+}$, although another example of this behaviour exists. The first report of the synthesis of (2) noted that the perchlorate ions are co-ordinated,[2] whereas subsequent papers provide evidence for inequivalent axial sites when a chloride ion is present.[11,15]

Efforts were made to isolate L^3 free of a metal ion by adding $S(NH_4)_2$ to a solution of $[Mn(L^3)Cl][BF_4]$. The dark green solid, MnS, was filtered off and the solvent

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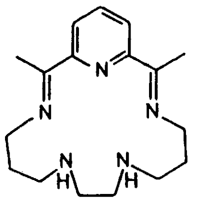
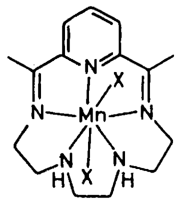
* tpp is 5,10,15,20-Tetraphenylporphyrin, pc is phthalocyanine, and py is pyridine.

then evaporated off to leave a pale yellow solid. The absence of a peak corresponding to the free macrocycle (*m*/*e* 388) in the mass spectrum indicates that the ligand decomposes when the metal ion is removed. All attempts at isolating the similar compound (3) free of a template ion, have also failed.[16]

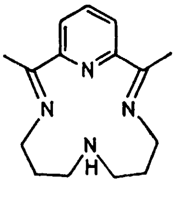


(1)



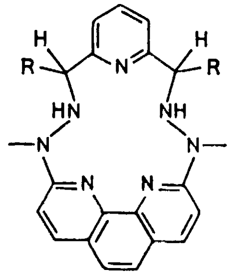
(2)

X = ClO_4^-,Cl



(3)

Reduction of the hydrazone bonds in manganese(II) complexes of L^2 and L^3, to yield complexes with L^4 and L^5 respectively, was accomplished by adding an excess of $Na[BH_4]$ to aqueous solutions of the compounds, and then acidifying. If necessary, the salt of a large anion was added to obtain a precipitate. Hydrogenation of the hydrazone groups is confirmed by N–H stretching bands at 3 300 and 3 200 cm^{-1}, and the bending mode at 1 640 cm^{-1} in the i.r. spectra. Analytical and conductivity data for the complexes are contained in Table 1; the solids are 1 : 1 electrolytes in dmso. The retention of a chloride ion, coupled with the conductivity measurements provide strong evidence that the manganese(II) ions are still six-co-ordinate. By analogy with the zinc(II) complexes of L^4 and L^5, the co-ordination geometry about the central cations is between pentagonal pyramidal and octahedral.[1]



L^4 : R = H
L^5 : R = Me

Crystal and Molecular Structure Determination of $[Mn(L^3)Cl][BF_4]$.—*Crystal data.* $[C_{23}H_{21}N_7ClMn][BF_4]$, $M = 572.7$, Monoclinic, $a = 11.717(8)$, $b = 14.403(9)$, $c = 15.316(9)$ Å, $\beta = 116.42(6)°$, $U = 2\,314.8$ Å^3, $D_c = 1.64$ g cm^{-3}, $Z = 4$, space group $P2_1/n$. Graphite monochromated Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 6.82$ cm^{-1}.

A block-shaped crystal with dimensions *ca.* 0.28 × 0.175 × 0.14 mm was mounted on a Syntex $P2_1$ four-circle diffractometer, and accurate cell parameters obtained from the 2θ values of 15 strong reflections ($20 < 2\theta \leqslant 30°$). A total of 6 314 intensity data with $3.0 \leqslant 2\theta \leqslant 55.0°$ were collected with a 96 step θ—2θ scan procedure; the scan rate varying between 1.00 and 29.3° min^{-1}. Two standard reflections measured periodically showed no significant variation. Data were corrected for Lorentz and polarisation effects but not for absorption. The 1 709 unique reflections with $I > 2.5\sigma(I)$ were used in the structure analysis.

The atomic co-ordinates of the manganese atom were derived from a Patterson synthesis, and the remaining atoms located from successive electron-density difference maps. The structure was refined by full-matrix least squares, with anisotropic temperature factors for Mn and Cl, isotropic for C, N, and B, and common isotropic temperature factors for H(ring), H(methyl), and F atoms. Ring and methyl hydrogens were constrained to lie in geometrically idealised positions (C–H 1.08 Å), the methyl groups being treated as rigid bodies pivoted about the carbons. The BF_4^- anion is disordered about one of its ' three-fold axes '. It was successfully refined, with a site occupancy factor of 50%, by employing two sets of positions for three fluorine atoms, and treating the anion as a rigid group. The final refinement converged to $R' = \Sigma w^{\frac{1}{2}}(|F_o - F_c|)/\Sigma w^{\frac{1}{2}}|F_o| = 0.069$ with a corresponding unweighted R of 0.099. The weighting scheme was $w = 11.9/\sigma^2(F_o)$. The last difference map did not contain any peaks higher than 0.4 e Å^{-3}. Atomic co-ordinates are given in Table 2, and Table 3 contains bond lengths and angles. Structure factors and thermal parameters are contained in Supplementary Publication No. SUP 22725 (15 pp.).* Computations were made using the SHELX program[17] on the University of Cambridge IBM 370/165. Neutral-atom scattering factors were taken from ref. 18, with those for Mn and Cl corrected for both parts of anomalous dispersion. The exponential series for a spherical, bonded hydrogen atom came from ref. 19.

Discussion of the Structure.—The crystal structure of $[Mn(L^3)Cl][BF_4]$ is illustrated in Figure 1, along with the numbering scheme adopted, the BF_4^- ion having been omitted for clarity. The co-ordination geometry of the manganese is a slightly distorted pentagonal pyramid, with the chlorine in the axial position. The N_5 donor set of atoms which form the pentagon, are approximately coplanar (maximum deviation from the least-squares plane is <0.1 Å) and the Mn atom is displaced 0.53 Å from this plane towards the chlorine. An angle of 4.4° is formed between the direction of the Mn–Cl bond and the normal to this plane. The macrocycle is not planar but

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2

Atom co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom *	x/a	y/b	z/c
Mn(1)	2 278(2)	1 274(1)	1 096(1)
Cl(1)	4 342(3)	1 005(2)	2 344(2)
N(1)	1 879(8)	2 748(6)	876(7)
N(2)	1 131(8)	1 755(6)	1 942(6)
N(3)	733(8)	1 059(7)	2 346(6)
N(4)	1 181(8)	138(6)	1 326(6)
N(5)	2 122(8)	158(6)	82(6)
N(6)	2 995(9)	1 115(7)	−665(6)
N(7)	2 709(8)	1 775(6)	−160(6)
C(1)	331(11)	−631(8)	2 280(8)
C(2)	419(11)	−1 446(9)	1 912(8)
C(3)	1 085(11)	−2 365(9)	789(8)
C(4)	1 584(11)	−2 366(9)	147(8)
C(5)	2 506(11)	−1 398(9)	−787(8)
C(6)	2 863(12)	−574(8)	−988(9)
C(7)	2 096(12)	4 178(9)	173(9)
C(8)	1 621(13)	4 642(10)	728(10)
C(9)	1 285(12)	4 162(9)	1 349(9)
C(10)	967(11)	2 624(8)	1 986(8)
C(11)	769(11)	195(8)	1 994(8)
C(12)	911(11)	−1 541(8)	1 224(8)
C(13)	1 950(11)	−1 505(8)	−154(8)
C(14)	2 672(11)	225(8)	−530(8)
C(15)	2 583(11)	2 641(9)	−383(8)
C(16)	2 196(11)	3 200(9)	253(9)
C(17)	1 408(11)	3 205(8)	1 410(8)
C(18)	1 254(10)	−696(8)	959(8)
C(19)	1 796(11)	−683(8)	267(8)
C(20)	4 019(11)	1 212(10)	−967(8)
C(21)	2 650(12)	3 100(8)	−1 250(8)
C(22)	255(13)	3 101(9)	2 497(9)
C(23)	537(12)	1 168(10)	3 231(9)
B(1)	−1 451(8)	−1 126(7)	3 900(7)
F(1)	−1 871(8)	−1 765(5)	3 180(5)
F(2)	−2 503(11)	−889(10)	4 063(11)
F(3)	−858(16)	−394(9)	3 808(11)
F(4)	−654(14)	−1 619(10)	4 760(8)
F(2′)	−1 963(16)	−1 148(11)	4 511(10)
F(3′)	−1 780(18)	−264(7)	3 379(10)
F(4′)	−149(9)	−1 125(13)	4 350(11)

* Primed atoms represent the second of the two sets of sites for the F atoms required by the disordered BF_4^- ion.

has the shape of a shallow dome, the distortion being away from the Cl atom. This point is illustrated by considering the angles between the planes defined by the pyridine ring, the phenanthroline group, and the nitrogen donors: the pyridine ring forms an angle of 11.0° with the N_5 plane, and 12.4° with the phenanthroline segment. Details of these least-squares planes and deviations of selected atoms from them are contained in Table 4. Bond distances indicate that the BF_4^- is unco-ordinated.

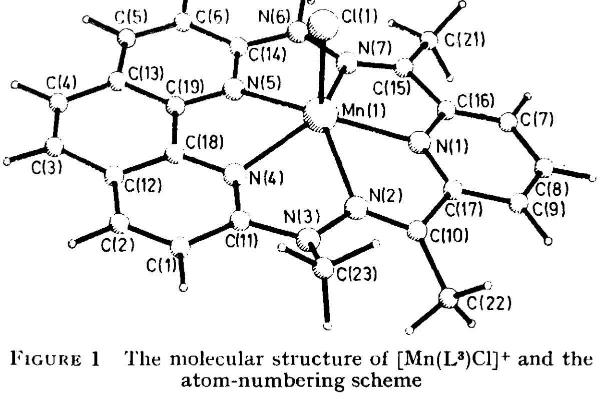

FIGURE 1 The molecular structure of $[Mn(L^3)Cl]^+$ and the atom-numbering scheme

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Lengths

Cl(1)–Mn(1)	2.353(6)	N(1)–Mn(1)	2.167(11)
N(2)–Mn(1)	2.348(11)	N(4)–Mn(1)	2.204(11)
N(5)–Mn(1)	2.186(11)	N(7)–Mn(1)	2.312(11)
C(16)–N(1)	1.338(14)	C(17)–N(1)	1.343(14)
N(3)–N(2)	1.363(12)	C(10)–N(2)	1.273(13)
C(11)–N(3)	1.364(14)	C(23)–N(3)	1.482(14)
C(11)–N(4)	1.313(13)	C(18)–N(4)	1.346(13)
C(14)–N(5)	1.356(14)	C(19)–N(5)	1.339(13)
N(7)–N(6)	1.358(12)	C(14)–N(6)	1.378(14)
C(20)–N(6)	1.472(14)	C(15)–N(7)	1.284(14)
C(2)–C(1)	1.325(15)	C(11)–C(1)	1.440(15)
C(12)–C(2)	1.415(16)	C(4)–C(3)	1.349(16)
C(12)–C(3)	1.419(16)	C(13)–C(4)	1.452(16)
C(6)–C(5)	1.340(16)	C(13)–C(5)	1.396(15)
C(14)–C(6)	1.416(16)	C(8)–C(7)	1.378(17)
C(16)–C(7)	1.414(15)	C(9)–C(8)	1.367(17)
C(17)–C(9)	1.384(15)	C(17)–C(10)	1.467(16)
C(22)–C(10)	1.537(17)	C(18)–C(12)	1.398(15)
C(19)–C(13)	1.397(14)	C(16)–C(15)	1.482(16)
C(21)–C(15)	1.516(16)	C(19)–C(18)	1.458(15)
F(1)–B(1)	1.351(9)	F(2)–B(1)	1.404(10)
F(2′)–B(1)	1.317(10)	F(3)–B(1)	1.305(10)
F(3′)–B(1)	1.434(10)	F(4)–B(1)	1.420(10)
F(4′)–B(1)	1.367(10)		

(*b*) Angles

N(1)–Mn(1)–Cl(1)	111.1(4)	N(2)–Mn(1)–Cl(1)	103.6(3)
N(2)–Mn(1)–N(1)	70.1(4)	N(4)–Mn(1)–Cl(1)	102.1(3)
N(4)–Mn(1)–N(1)	130.6(4)	N(4)–Mn(1)–N(2)	67.2(4)
N(5)–Mn(1)–Cl(1)	100.8(3)	N(5)–Mn(1)–N(1)	131.7(4)
N(5)–Mn(1)–N(2)	136.2(3)	N(5)–Mn(1)–N(4)	72.4(4)
N(7)–Mn(1)–Cl(1)	101.6(3)	N(7)–Mn(1)–N(1)	71.2(4)
N(7)–Mn(1)–N(2)	139.3(3)	N(7)–Mn(1)–N(4)	136.4(3)
N(7)–Mn(1)–N(5)	67.5(4)	C(16)–N(1)–Mn(1)	118.6(9)
C(17)–N(1)–Mn(1)	120.3(9)	C(17)–N(1)–C(16)	121.0(11)
N(3)–N(2)–Mn(1)	115.4(7)	C(10)–N(2)–Mn(1)	117.1(9)
C(10)–N(2)–N(3)	127.5(11)	C(11)–N(3)–N(2)	114.5(10)
C(23)–N(3)–N(2)	124.2(11)	C(23)–N(3)–C(11)	120.2(11)
C(11)–N(4)–Mn(1)	121.4(9)	C(18)–N(4)–Mn(1)	116.5(8)
C(18)–N(4)–C(11)	119.7(11)	C(14)–N(5)–Mn(1)	121.5(9)
C(19)–N(5)–Mn(1)	117.2(8)	C(19)–N(5)–C(14)	118.6(11)
C(14)–N(6)–N(7)	114.3(10)	C(20)–N(6)–N(7)	123.7(11)
C(20)–N(6)–C(14)	116.9(11)	N(6)–N(7)–Mn(1)	117.1(7)
C(15)–N(7)–Mn(1)	118.8(9)	C(15)–N(7)–N(6)	123.9(11)
C(11)–C(1)–C(2)	119.7(12)	C(12)–C(2)–C(1)	122.5(13)
C(12)–C(3)–C(4)	122.8(13)	C(13)–C(4)–C(3)	121.1(13)
C(13)–C(5)–C(6)	123.2(13)	C(14)–C(6)–C(5)	118.2(13)
C(16)–C(7)–C(8)	118.1(14)	C(9)–C(8)–C(7)	120.2(14)
C(17)–C(9)–C(8)	119.8(15)	C(17)–C(10)–N(2)	115.3(12)
C(22)–C(10)–N(2)	126.5(12)	C(22)–C(10)–C(17)	117.9(12)
N(4)–C(11)–N(3)	116.8(11)	C(1)–C(11)–N(3)	123.8(12)
C(1)–C(11)–N(4)	119.3(12)	C(3)–C(12)–C(2)	128.5(12)
C(18)–C(12)–C(2)	113.3(12)	C(18)–C(12)–C(3)	118.2(12)
C(5)–C(13)–C(4)	127.6(12)	C(19)–C(13)–C(4)	117.4(11)
C(19)–C(13)–C(5)	115.0(12)	N(6)–C(14)–N(5)	114.6(11)
C(6)–C(14)–N(5)	120.8(12)	C(6)–C(14)–N(6)	124.5(12)
C(16)–C(15)–N(7)	112.7(12)	C(21)–C(15)–N(7)	127.7(12)
C(21)–C(15)–C(16)	119.3(12)	C(7)–C(16)–N(1)	120.5(13)
C(15)–C(16)–N(1)	117.9(12)	C(15)–C(16)–C(7)	121.5(13)
C(9)–C(17)–N(1)	120.3(13)	C(10)–C(17)–N(1)	115.9(12)
C(10)–C(17)–C(9)	123.7(14)	C(12)–C(18)–N(4)	125.2(11)
C(19)–C(18)–N(4)	115.0(11)	C(19)–C(18)–C(12)	119.8(11)
C(13)–C(19)–N(5)	124.3(11)	C(18)–C(19)–N(5)	115.0(11)
C(18)–C(19)–C(13)	120.8(11)	F(2)–B(1)–F(1)	106.3(8)
F(2′)–B(1)–F(1)	116.6(9)	F(3)–B(1)–F(1)	118.7(9)
F(3)–B(1)–F(2)	112.0(9)	F(3′)–B(1)–F(2′)	108.8(9)
F(4)–B(1)–F(1)	105.5(8)	F(4)–B(1)–F(2)	103.0(8)
F(4)–B(1)–F(3)	110.0(8)	F(4′)–B(1)–F(1)	109.4(8)
F(4′)–B(1)–F(2′)	113.7(9)	F(4′)–B(1)–F(3′)	104.1(8)

The nitrogen donor–manganese distances all lie within the range 2.16—2.35 Å, and fall into three sets; the pyridine nitrogen, Mn–N equal to 2.167(11) Å, along with the phenanthroline donors, 2.168(11) and 2.204(11) Å, and the hydrazone nitrogens, 2.312(11) and 2.348(11) Å. The normal range of Mn–N distances for high-spin six-co-ordinate Mn^{II} is 2.20—2.32 Å,[20,21] while these distances for manganese(II) complexes of more saturated quinquedentate macrocycles occur within the limits 2.22—2.30 Å,[22] 2.21—2.25 Å,[23] and 2.31—2.43 Å.[11] The generally shorter distances found here are due to the small hole size of the macrocycle, while the rigidity of the ligand causes the Mn–N hydrazone bonds to be longer than the others. A quadridentate macrocycle has the high-spin Mn^{II} out of the equatorial plane with Mn–N 2.12 Å.[24] The angles subtended at the metal ion by adjacent nitrogen donors in L^3 fall in the range 67—73°, with the two values <70° being for N(phen)–Mn–N(hydrazone) angles; again the result of the rigidity in the macrocycle. Strain in the ring system is revealed in the low N(5)–C(14)–N(6) and N(3)–C(11)–N(4) bond angles of 115(1)° and 117(1)° where the expected value for sp^2 hybridised atoms is 120°. The Mn–Cl bond length of 2.353(6) Å falls in the lower part of the range 2.34—2.51 Å found in a series of manganese(II) complexes containing a chloro-ligand.[25]

TABLE 4

Equations of least-squares planes,* with selected individual atomic deviations (Å) shown in square brackets

Plane 1: N(1), N(2), N(4), N(5), N(7)

$$7.703x - 1.311y + 5.779z = 1.687$$

[Mn(1) 0.534, Cl(1) 2.880, N(1) −0.094, N(2) 0.076, N(4) 0.030, N(5) −0.027, N(7) 0.074]

Plane 2: Mn, N(2), N(4), N(5), N(7)

$$7.622x - 2.467y + 5.715z = 1.674$$

[Mn(1) 0.374, Cl(1) 2.727, N(1) 0.420, N(2) 0.135, N(4) −0.051, N(5) −0.050, N(7) −0.139]

Plane 3: Pyridine

$$7.909x + 1.434y + 5.428z = 2.344$$

[Mn(1) 0.235, Cl(1) 2.507]

Plane 4: Phenanthroline

$$7.639x - 1.656y + 5.837z = 1.673$$

[Mn(1) 0.496, Cl(1) 2.846]

Interplanar angles (°)

2	3	4	Plane
4.6	11.0	1.4	1
	15.6	3.3	2
		12.4	3

The line joining Mn(1) to Cl(1) has direction cosines of 0.920, −0.165, 0.354.

Angles (°) between the line and normals to the planes

Plane	1	2	3	4
Angles	4.4	1.2	15.2	3.2

* x, y, and z are fractional atomic co-ordinates.

Evidence for π-electron delocalisation around the macrocycles is provided by some bond lengths and angles in Table 3. The pyridine and phenanthroline distances and angles fall in the typical ranges observed [11,26] and it is the bonds joining these two segments which provide information pertinent to the π conjugation. The hybridisation of the atoms N(3) and N(6), which is disclosed by the sums of the bond angles subtended at these atoms, determines whether orbital overlap can occur around the ring. The experimental values of 358.9° and 354.9° suggest that the nitrogens are formally sp^2 hybridised. Non-bonded interactions between C(20) and C(21), and C(22) and C(23) are responsible for these deviations from the anticipated values of 360°. The mean distance between the pairs of methyl groups, 3.03(1) Å, is well within the sum of their van der Waals radii, 4.0 Å.[27] These interactions are partially relieved by axial distortion of the pairs of methyl groups; C(20) and C(23) are displaced towards the Cl atom and C(21) and C(22) are on the other side of the macrocycle. The average deviations from the N_5 plane are 0.57 and 0.62 Å respectively. The hydrazine bond lengths, 1.358(12) and 1.362(12) Å, fall between the N–N single bond distances of 1.45 Å in hydrazine [28,29] and 1.432(12) Å in phenylhydrazine,[30] and the typical N–N double-bond length of 1.24 Å.[29] Similar bond distances to the above are found in the zinc(II) complex of an analogous ligand to L^2.[31]

The common co-ordination geometry for six ligands is octahedral, and the pentagonal pyramidal arrangement is only rarely encountered. The simple polytopal transformation between an octahedron and a pentagonal pyramid shown in Figure 2, both raises the question of when is a distorted pentagonal pyramid in fact a distorted octahedron, and illustrates the need for criteria on which to judge the symmetry of pentagonal pyramids. Estimates of any deviations from this symmetric shape must of necessity be qualitative as the polyhedron is not one of the regular solids. The following criteria are proposed as measures of these distortions: (*a*) the maximum deviation of an equatorial donor from their least-squares plane, and (*b*) the width of the ranges of values for the equatorial donor–metal ion bond lengths and for the angles subtended at the central atom. Pentagonal pyramids have been encountered previously in five crystal structures.[5,32–34] Three of these examples involve oxygen-donor atoms and are not considered further here. The remaining two are complexes of the quinquedentate macrocycle (1). Details in keeping with the above criteria for this pair of complexes and for the current case are contained in Table 5. The data show $[Mn(L^3)Cl][BF_4]$ to be a less distorted pentagonal pyramid than the other two. The decreased flexibility of L^3 relative to (1) forces the Mn^{II} to adopt a more regular configuration.

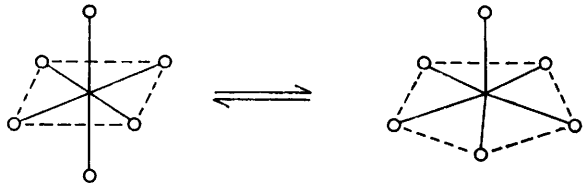

FIGURE 2 Polytopal rearrangement of an octahedron to a pentagonal pyramid

The environment of the metal ion, seated above the macrocyclic cavity and bound to a single axial ligand, bears some resemblance to that found in certain metalloporphyrins. A displacement of 0.53 Å from the donor plane here is similar to the 0.51 Å found for [Mn(mim)(tpp)] (mim = 1-methylimidazole), where the manganese(II) is also high spin.[35] The M–N distance in metalloporphyrins can be resolved into two components, the distance of M above the centre of the cavity, and the radius of the hole.[36] The exact radius of the macrocyclic hole is difficult to define when, as for L^3, pairs of donor atoms are not diametrically opposed. To obtain a comparison with the porphyrin structure, the Mn atom was assumed to sit above the centre of the cavity, and the in-plane component of the minimum Mn–N distance was taken as the hole radius for L^3. The actual value of 2.10 Å is close to the hole radius of 2.065 Å measured for tpp in [Mn(mim)(tpp)].[35]

TABLE 5

Data on deviations from the symmetric shape in pentagonal pyramids

Compound	Limits of angles (°) subtended at M by N [a]	Width of range	Limits of M–N lengths (Å)	Width of range	Maximum deviation (Å) of N from MN$_5$ plane	Angle (°) between pyridine ring and MN$_4$ plane
Cd(L)Br$_2$ [b]	64.8—75.9	11.1	2.34—2.45	0.11	0.67	48.9
Hg$_4$(L)$_2$Br$_8$ [b]	67.1—78.5	11.4	2.25—2.44	0.19	0.71	48.3
[Mn(L^3)Cl][BF$_4$]	67.2—72.4	5.2	2.17—2.35	0.18	0.09	15.6

[a] N refers to an equatorial nitrogen atom. [b] Ref. 5, L = macrocycle (1). Data obtained from the Cambridge Crystallographic Data Centre.

Structural similarities between L^3 and porphyrins therefore exist on four counts: both types of ligand (*i*) are relatively rigid, (*ii*) are planar, (*iii*) have π delocalisation around the ring, and (*iv*) have similar hole sizes.

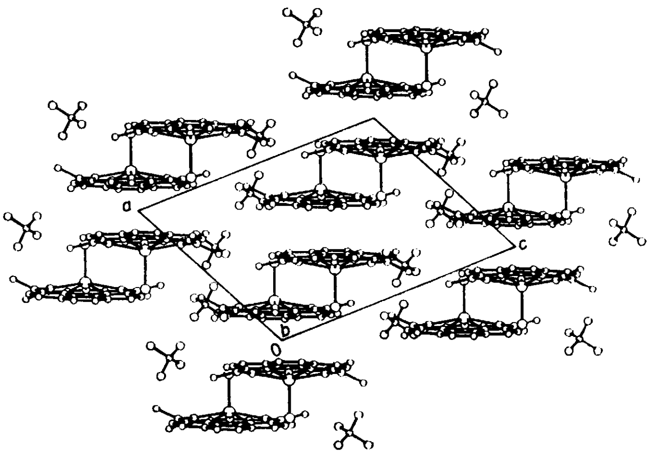

FIGURE 3 Molecular packing diagram. The unit cell is viewed along the *b* axis

The out-of-plane displacement of high-spin Mn^{II} from the porphyrin plane is thought to arise from symmetric occupation of the *d* orbitals resulting in the Mn^{II} being too big to fit into the macrocyclic hole;[35] reasoning that is equally valid for [Mn(L^3)Cl][BF$_4$]. The pentagonal-pyramidal structure of this complex is less remarkable when L^3 is regarded as a quinquedentate 'porphyrin-like' macrocycle. However, it remains an example of a macrocyclic ligand imposing an unusual co-ordination geometry on a metal ion.

A diagram of the molecular packing, viewed along the crystallographic *b* axis is shown in Figure 3. The [Mn(L^3)Cl]$^+$ units are separated by van der Waals distances. Only one intermolecular contact, between a pyridine hydrogen and a chlorine, is less than the sum of the van der Waals radii. This reflects the molecular packing where pairs of complex cations are slightly offset relative to each other with each Mn–Cl bond pointing towards the other cation in the pair. The shortest anion–cation contact, 2.185 Å, is between a phenanthroline hydrogen and a fluorine.

EXPERIMENTAL

Infrared spectra were measured as Nujol mulls supported between sodium chloride discs using Perkin-Elmer 257 and 457 spectrometers, over the range 625—4 000 cm^{-1}. Conductance measurements were made with a Wayne–Kerr Universal bridge. The magnetic moments were recorded on a Newport-Gouy balance and the readings corrected for ligand and inner-core diamagnetism by using Pascal's constants.[8] Microanalyses were performed by the University Chemical Laboratory Microanalytical Department.

Reagents, of analytical grade where possible, were used without further purification, apart from 2,6-diformylpyridine which was recrystallised from chloroform.

Manganese(II) *Complexes of* L^2 *and* L^3.—An example of the general preparative method for these complexes is the synthesis of [Mn(L^3)Cl][BF$_4$]. The ligand L^1·HCl (1 mmol) was dissolved in refluxing methanol (30 cm^3) and a solution of MnCl$_2$·4H$_2$O (1 mmol) in water (10 cm^3) added. This mixture was refluxed for 30 min before 2,6-diacetylpyridine (1 mmol) was introduced. The solution turned orange in the course of refluxing for 3 h, after which it was allowed to cool. Slow addition of a solution of Na[BF$_4$] (2 mmol) in water (5 cm^3) gave an orange solid which was filtered off, washed with water and ethanol, and recrystallised from methanol to give red crystals. Yield: 75%. The sources of Mn^{II} used were MnCl$_2$·4H$_2$O, MnBr$_2$·4H$_2$O, and Mn[NO$_3$]$_2$·4H$_2$O.

Mn(L^3)(ClO$_4$)$_2$.—The complex Mn(L^3)Cl$_2$ (0.2 mmol) was dissolved in hot degassed methanol and Ag[ClO$_4$] (0.4 mmol) added. The mixture was refluxed for 2 h and the AgCl then filtered off. After cooling, diethyl ether was added to give a yellow suspension which was filtered off, washed with diethyl ether, and dried in air. Yield: 45%.

Manganese(II) *Complexes of* L^4 *and* L^5.—The example given here is the preparation of [Mn(L^5)Cl][BF$_4$]. A tenfold excess of solid Na[BH$_4$] was added to an aqueous solution of $Mn(L^3)Cl_2$ at room temperature (23 °C). The solution was stirred for 30 min before dilute HCl was introduced to decrease the pH to <7. After filtering, an aqueous solution containing an excess of $Na[BF_4]$ was added to the mother-liquor, to produce a yellow precipitate. This solid was filtered off, washed with water, and dried in air. Yield: 45%.

Support from the S.R.C. (to T. D. O'D. and P. R. R.) is gratefully acknowledged.

[9/808 *Received*, 23*rd May*, 1979]

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