Synthesis of a Macrocyclic Metal Complex incorporating Peripheral Hydroxyethyl Tails: The *X*-Ray Structure of $[Mn(L^1)Cl][BF_4]\cdot4H_2O$ †

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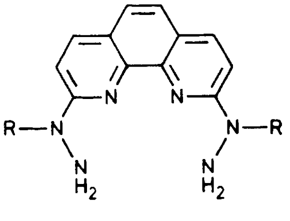
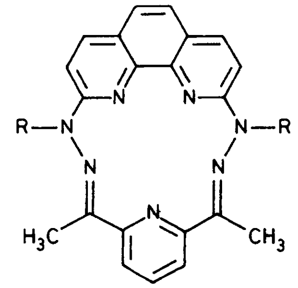
Reaction of 2,9-dichloro-1,10-phenanthroline with 2-hydroxyethylhydrazine leads to the isolation of 2,9-di(*N*-2′-hydroxyethylhydrazino)-1,10-phenanthroline in moderate yield. This species undergoes a template condensation reaction with 2,6-diacetylpyridine in the presence of $MnCl_2\cdot4H_2O$ to give the title complex of the macrocyclic ligand L^1. The *X*-ray structure of the complex shows the six-co-ordinate nature of the metal ion which is bound by five N-donors of the macrocycle and is displaced 0.51 Å towards the axial chlorine ligand. The hydroxyethyl tails extend up on the same side of the ligand as the axial chlorine. The complex crystallises in orthorhombic space group *Pnma* with a = 13.225(4), b = 25.011(4), and c = 17.343(4) Å. The structure was refined to R = 0.103 for 1 323 reflections.

The chemistry of quinquedentate macrocyclic ligands incorporating nitrogen donor atoms has been a continuing subject of study in this laboratory. Ligands of the type L^2 have been synthesised [1] from (1b) and 2,6-diacetylpyridine as a range of bivalent metal complexes and their properties studied by a variety of techniques, including *X*-ray diffraction. Compound (1b) itself is prepared from 2,9-dichloro-1,10-phenanthroline and methylhydrazine. One possible progression of the work was the structural development of the macrocyclic periphery in order to facilitate the eventual attachment of pendant groups to the ligand framework. Such experiments have received wide attention [2] in recent years.

In this paper we report the synthesis of the new phenanthroline dihydrazine (1a) and the *X*-ray structure of the macrocyclic condensation product formed from (1a), $MnCl_2\cdot4H_2O$, and 2,6-diacetylpyridine.



(1a) $R = CH_2CH_2OH$
(1b) $R = CH_3$



L^1 $R = CH_2CH_2OH$
L^2 $R = CH_3$

Results and Discussion

Reaction of 2,9-dichloro-1,10-phenanthroline with commercially available 2-hydroxyethylhydrazine under conditions of rigorous air exclusion gives the dihydrazine (1a) as its yellow monohydrochloride salt in yields of the order of 50% after recrystallisation. Reaction of (1a) with $MnCl_2\cdot4H_2O$ and 2,6-diacetylpyridine under conditions identical to those reported [3] for the synthesis of $[Mn(L^2)Cl][BF_4]$ gives an orange powder upon completion. Recrystallisation from water gives large, well formed red crystals suitable for diffraction studies.

The *X*-ray structure of the complex proves its macrocyclic nature, and that the Mn^{II} is six-co-ordinate, bound by five nitrogens from the macrocycle and sitting 0.51 Å out of their least-squares plane towards the chlorine atom in the axial (sixth) site. In these and other respects the structure resembles that of $[Mn(L^2)Cl][BF_4]$.[3] The Figure shows the cation with hydrogen atoms omitted for clarity. Also apparent is the doming of the macrocycle away from the axial ligand. The atoms of the N_5 donor set deviate from coplanarity by less than 0.2 Å. The atoms of the phenanthroline subunit remain approximately coplanar, as do those of the pyridine subunit (maximum deviations <0.05 and <0.03 Å respectively). The angles subtended by the adjacent nitrogen donor atoms at the manganese fall in the range 68—73°. The bond lengths from all the donor atoms are the same, within the estimated standard deviation (e.s.d.s), as found for $[Mn(L^2)Cl][BF_4]$, ranging from 2.269(19) and 2.306(19) Å for the Mn–N-

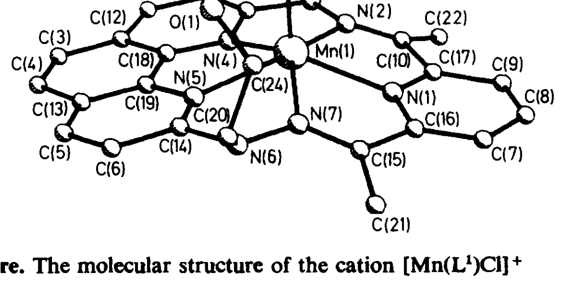


Figure. The molecular structure of the cation $[Mn(L^1)Cl]^+$

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† Chloro[2,6-diacetylpyridine *NN*′-bis(2′-hydroxyethyl)-*NN*′-1,10-phenanthroline-2,9-diyldihydrazone]manganese tetrafluoroborate tetrahydrate.

Supplementary data available (No. SUP 23440, 27 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected cation bond lengths (Å) and angles (°)

Mn(1)-Cl(1)	2.372(7)	Mn(1)-N(1)	2.216(15)	C(24)-O(1)	1.43(3)	N(6)-C(14)	1.44(3)
Mn(1)-N(2)	2.269(19)	Mn(1)-N(4)	2.212(18)	C(14)-N(5)	1.32(3)	N(5)-C(19)	1.36(3)
Mn(1)-N(5)	2.210(17)	Mn(1)-N(7)	2.306(19)	C(18)-C(19)	1.39(3)	N(4)-C(18)	1.35(3)
N(2)-N(3)	1.436(25)	N(6)-N(7)	1.396(25)	N(4)-C(11)	1.31(3)	N(3)-C(11)	1.41(3)
N(7)-C(15)	1.33(3)	C(25)-O(2)	1.40(3)	N(3)-C(23)	1.50(3)	C(23)-C(25)	1.54(3)
N(1)-C(16)	1.39(3)	C(15)-C(16)	1.43(3)	N(2)-C(10)	1.24(3)	C(10)-C(17)	1.53(3)
N(6)-C(20)	1.48(3)	C(20)-C(24)	1.49(3)	N(1)-C(17)	1.32(3)		
N(1)-Mn(1)-N(2)	71.8(7)	N(2)-Mn(1)-N(4)	68.2(6)	C(14)-N(5)-Mn(1)	122(1)	Mn(1)-N(5)-C(19)	117(1)
N(4)-Mn(1)-N(5)	72.1(6)	N(5)-Mn(1)-N(7)	68.1(6)	N(5)-C(19)-C(18)	115(2)	C(19)-C(18)-N(4)	118(2)
N(7)-Mn(1)-N(1)	69.9(6)	Cl(1)-Mn(1)-N(1)	108.6(5)	C(18)-N(4)-Mn(1)	116(1)	Mn(1)-N(4)-C(11)	122(1)
Cl(1)-Mn(1)-N(2)	101.8(5)	Cl(1)-Mn(1)-N(4)	106.4(5)	N(4)-C(11)-N(3)	116(2)	C(11)-N(3)-N(2)	111(2)
Cl(1)-Mn(1)-N(5)	101.8(4)	Cl(1)-Mn(1)-N(7)	97.6(5)	C(11)-N(3)-C(23)	116(2)	C(23)-N(3)-N(2)	117(2)
N(1)-C(16)-C(15)	113(2)	C(16)-C(15)-N(7)	117(2)	N(3)-C(23)-C(25)	110(2)	C(23)-C(25)-O(2)	115(2)
C(15)-N(7)-Mn(1)	118(1)	Mn(1)-N(7)-N(6)	119(1)	N(3)-N(2)-Mn(1)	118(1)	Mn(1)-N(2)-C(10)	120(2)
N(7)-N(6)-C(14)	110(2)	N(7)-N(6)-C(20)	120(2)	N(2)-C(10)-C(17)	114(2)	C(10)-C(17)-N(1)	116(2)
C(20)-N(6)-C(14)	117(2)	N(6)-C(20)-C(24)	111(2)	C(17)-N(1)-Mn(1)	116(1)	Mn(1)-N(1)-C(16)	120(1)
C(20)-C(24)-O(1)	113(2)	N(6)-C(14)-N(5)	117(2)				

Table 2. Fractional atomic co-ordinates

Atom	x	y	z
Mn(1)	0.312 4(2)	0.002 3(1)	0.652 9(2)
Cl(1)	0.135 0(4)	0.015 4(2)	0.645 3(3)
N(1)	0.357 2(12)	0.001 8(7)	0.776 0(8)
N(2)	0.367 4(12)	0.085 5(7)	0.684 3(10)
N(3)	0.388 6(15)	0.122 3(7)	0.622 9(10)
N(4)	0.378 7(13)	0.044 2(7)	0.552 6(10)
N(5)	0.338 1(11)	−0.057 4(7)	0.561 1(9)
N(6)	0.297 9(14)	−0.126 3(7)	0.648 6(11)
N(7)	0.309 5(13)	−0.083 8(7)	0.700 2(9)
C(1)	0.416 5(16)	0.124 4(10)	0.486 0(12)
C(2)	0.423 5(16)	0.095 4(9)	0.417 3(13)
C(3)	0.408 5(14)	0.004 2(10)	0.349 2(13)
C(4)	0.389 2(16)	−0.047 3(9)	0.353 8(14)
C(5)	0.340 3(16)	−0.126 1(9)	0.437 5(14)
C(6)	0.316 4(19)	−0.146 0(10)	0.508 6(14)
C(7)	0.353 4(16)	−0.038 4(9)	0.898 3(13)
C(8)	0.372 3(16)	0.011 1(9)	0.932 0(14)
C(9)	0.389 4(17)	0.056 1(10)	0.890 0(13)
C(10)	0.397 3(18)	0.094 7(10)	0.751 0(16)
C(11)	0.390 7(16)	0.096 3(9)	0.550 7(12)
C(12)	0.407 0(15)	0.039 4(8)	0.413 1(12)
C(13)	0.365 2(16)	−0.072 3(8)	0.426 6(12)
C(14)	0.315 7(16)	−0.108 5(8)	0.571 0(12)
C(15)	0.326 7(17)	−0.091 0(9)	0.774 8(12)
C(16)	0.345 6(17)	−0.044 1(10)	0.820 0(13)
C(17)	0.378 6(16)	0.048 8(8)	0.807 2(11)
C(18)	0.381 4(13)	0.015 9(8)	0.486 4(11)
C(19)	0.363 4(15)	−0.038 6(8)	0.490 4(12)
C(20)	0.216 2(15)	−0.165 8(9)	0.660 2(13)
C(21)	0.333 0(18)	−0.144 8(9)	0.814 6(13)
C(22)	0.452 0(19)	0.142 5(10)	0.780 9(14)
C(23)	0.334 7(15)	0.174 8(8)	0.625 1(12)
C(24)	0.118 6(19)	−0.138 8(11)	0.679 2(14)
C(25)	0.221 1(16)	0.166 8(10)	0.610 0(12)
O(1)	0.082 5(12)	−0.105 4(7)	0.618 4(10)
O(2)	0.195 6(12)	0.158 2(6)	0.532 7(9)
O(3)	−0.006 4(14)	0.157 1(7)	0.505 8(11)
O(4)	0.257 3(21)	0.2500	0.456 3(17)
O(5)	−0.119 2(20)	0.2500	0.511 2(15)
O(6)	−0.486 9(30)	0.2500	0.249 3(26)
B(1)	−0.322 4(13)	0.2500	0.678 8(10)
F(1)	−0.277 7(21)	0.2500	0.607 5(12)
F(2)	−0.425 4(14)	0.2500	0.670 4(17)
F(3)	−0.293 2(16)	0.294 7(1)	0.718 5(11)
B(2)	−0.519 2(16)	0.2500	0.357 8(11)
F(4)	−0.424 3(20)	0.2500	0.326 1(18)
F(5)	−0.511 5(24)	0.2500	0.436 6(11)
F(6)	−0.570 4(19)	0.205 3(1)	0.334 3(14)
F(4a)	−0.619 2(18)	0.2500	0.337 1(19)
F(6a)	−0.473 2(20)	0.294 8(1)	0.328 9(13)

(hydrazone) to 2.212(18) and 2.210(17) Å for the Mn–N(phenanthroline) distances and 2.216(15) Å for the Mn–N(pyridine) distance. The Mn–Cl bond length is 2.372(7) Å. A selection of bond lengths and angles is given in Table 1. Table 2 gives a list of atomic co-ordinates for the structure.

A major point of interest in the structure is the orientation and environment of the hydroxyethyl tails. The structure shows both to be displaced above the Mn atom on the side of the axial chlorine ligand, and twisted slightly back over the phenanthroline. Both methyl groups on the pyridine hydrazones are displaced on the other side of the molecule and by analogy with $[\mathrm{Mn}(\mathrm{L}^2)\mathrm{Cl}][\mathrm{BF}_4]$ this is assigned to a non-bonded interaction between these groups and the hydroxyethyl carbons C(20) and C(23). The distances between C(20) and C(21) and C(22) and C(23) (3.24 and 3.22 Å) are well within the sum of the formal van der Waals radii, 4.00 Å. Studies of models indicate that only a few orientations of the hydroxyethyl tails are sterically feasible, which may partly account for their not being disordered over several sites. Hydrogen bonding between the oxygen atom O(1) and the axial chlorine ligand is inferred from their separation of 3.1 Å.

Preliminary studies of the reactivity of the hydroxyethyl tails are currently being pursued in this laboratory. That both tails are displaced on the same side of the macrocycle would seem to bode well for future reaction with a suitable difunctional species to incorporate a bridging group spanning the top of the macrocycle. Complementary work aimed at expanding the range of metals incorporated is also underway.

Experimental

2-Hydroxyethylhydrazine was purchased from the Aldrich Chemical Co. and used without further purification. 2,9-Dichloro-1,10-phenanthroline was prepared as previously reported.[1]

*2,9-Di(*N*-2′-hydroxyethylhydrazino)-1,10-phenanthroline Hydrochloride.*—2,9-Dichloro-1,10-phenanthroline (4.0 g, 0.016 mol) was added to a flask containing 2-hydroxyethylhydrazine (30 cm^3, excess) at 140 °C, which had been thoroughly degassed with nitrogen before addition of the phenanthroline species. The flask was kept at this temperature for 2 h after which time the excess of 2-hydroxyethylhydrazine was distilled off under vacuum. The red oil remaining was allowed to cool under nitrogen before being dissolved in methanol (50 cm^3) and kept in a refrigerator at 4 °C overnight. The yellow precipitate was then filtered off, recrystallised from methanol with cooling to 4 °C overnight, and dried to give (1a) as its HCl salt (2.98 g, 51%) (Found: C, 52.5; H, 5.6; N, 22.6. Calc. for $C_{16}H_{21}ClN_6O_2$: C, 52.7; H, 5.8; N, 23.0%). The compound was best stored in the dark under nitrogen and was seen to discolour after several weeks standing. Attempting the preparation in the presence of air gave intractable tars.

Macrocyclic Complex $[Mn(L^1)Cl][BF_4]\cdot 4H_2O$.—The synthesis was essentially as reported [3] for the analogous complex of L^2 giving a yield of 55% of an orange powder, Λ (10^{-3} mol dm^{-3} solution in dimethyl sulphoxide) 37 ohm^{-1} cm^2 mol^{-1}. Recrystallisation from water gave large well formed crystals suitable for diffraction studies (Found: C, 42.3; H, 4.3; N, 14.2. Calc. for $C_{25}H_{33}BClF_4MnN_7O_6$: C, 42.6; H, 4.7; N, 13.9%).

X-Ray Structure Determination.—A suitable crystal of dimensions 0.27 × 0.17 × 0.12 mm was chosen. Preliminary cell parameters were determined *via* Weissenberg photography, and the crystal system assigned as orthorhombic. Systematic absences indicated that the space group was either *Pnma* or *Pna*2_1: it was shown to be *Pnma* by structure refinement. The crystal was mounted on a Stöe automatic four-circle diffractometer (Mo-K_α radiation, $\lambda = 0.710\,69$ Å) operated with a 140-step ω—θ scan technique. 3 160 Intensities were measured in the range $5 < 2\theta < 50°$. Lorentz polarisation and empirical absorption corrections were applied and the data averaged to give 1 323 unique intensities, $F > 5\sigma(F)$.

Crystal data. $C_{25}H_{33}BClF_4MnN_7O_6$, $M = 704.5$, Orthorhombic, space group *Pnma*, $a = 13.225(4)$, $b = 25.011(4)$, $c = 17.343(4)$ Å, $\alpha = \beta = \gamma = 90.00°$, $Z = 8$, $D_c = 1.59$ g cm^{-3}, $U = 5\,736.1$ Å^3, μ(Mo-K_α) = 5.82 cm^{-1}, $F(000) = 2\,912$, $R = 0.103$, $R' = 0.105$.

The position of the manganese atom was found from a Patterson map and the remaining non-hydrogen atoms from subsequent electron-density difference maps. The structure was refined by full-matrix least-squares techniques, with anisotropic thermal parameters assigned to Mn, Cl, and all N atoms. Common isotropic thermal parameters were assigned to fluorine atoms and ring, aliphatic, and aromatic hydrogens, which were constrained to lie in geometrically idealised sites 1.08 Å from the parent carbon. The methyl groups were treated as rigid bodies. The $[BF_4]^-$ counter ion was severely disordered over two major sites. The disorder model used fixed the occupancy of the boron atom at 0.5 in each and assigned occupancies to the fluorines to give a sum total of two atoms around each boron site. Tetrahedral constraints were applied to the counter ion, with B–F and F $\cdots$ F distances fixed at 1.37 and 2.237 Å respectively. In the later stages of refinement the weighting scheme $w = 1/(\sigma^2F + 0.001F^2)$ was introduced. Neutral-atom scattering factors were taken from ref. 4. All crystallographic calculations were performed using SHELX.[5]

Acknowledgements

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