A Mechanism for the Rearrangement of Unsymmetrical Tetradentate (N_2O_2) Ligands bound to Manganese(III): the Isolation and Crystal Structure of a Manganese(III) Complex containing a Ten-membered *cis*-Chelated Ring†

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The unsymmetrical Schiff-base ligand L^1 (where H_2L^1 is the condensation product of 8-amino-4-methyl-5-azaoct-3-en-2-one and 3-ethoxysalicylaldehyde) has been found to rearrange into the symmetrical ligand L^2 [H_2L^2 = *N,N'*-bis(3-ethoxysalicylidene)propane-1,3-diamine] in the presence of manganese(III). The manganese(III) complexes of both the unsymmetrical and symmetrical ligands have been characterised by elemental analyses, infrared spectroscopy, magnetic susceptibility measurements and fast atom bombardment (FAB) mass spectrometry and have been assigned the stoichiometries $[Mn(HL^1)_2][ClO_4]\cdot H_2O$ and $[MnL^2][ClO_4]\cdot 3H_2O$ based on these data. The FAB mass spectrum of the former exhibits an interesting phenomenon, with two distinct metal co-ordination environments being observed. The ion of $[Mn(HL^1)_2]^+$ at *m/z* 661 is observed, as would be expected from the experimental data; however, the parent ion peak at *m/z* 357 corresponds to the monomeric $[ML^1]^+$ ion with the amine nitrogen atom of the ligand deprotonated. The manganese(III) complex of the unsymmetrical ligand $[Mn(HL^1)_2][ClO_4]$ has been crystallographically characterised, no water of crystallisation being observed in the selected crystal. This monomeric complex consists of a pseudo-octahedral metal centre with an N_2O_4 donor environment. The non-co-ordination of the amine nitrogen atom, confirmed by the Mn $\cdots$ N(2) separation of 3.51 Å, produces a ten-membered chelate ring about the manganese ion, believed to be the first example of such a system. The crystal structure has enabled a mechanism for the rearrangement of Schiff bases about manganese(III) to be proposed. It involves a series of reversible hydrolysis reactions which are stabilised by manganese(III) acting as a template.

There is currently much interest in the chemistry of manganese, partly due to its involvement in a number of biological systems.[1] Of these the most important is undoubtedly the oxygen evolving complex of photosystem II (PS II) found in green plants. It is now well established that for high rates of dioxygen evolution from PS II four manganese atoms are essential, although their precise configuration is not yet known.[2,3] As a result of this, many model complexes have been synthesised containing mono-,[4] di-[5–7] and multi-nuclear manganese centres in a variety of oxidation states (II–IV).[8,9] Since Calvin[10] presented his dinuclear model of PS II, a number of complexes have been prepared containing μ-oxo[11] and di-μ-carboxylate bridges,[12] but to date only our group has produced molecular oxygen from water *via* the light activation of the dimeric species $[Mn(salpn)(H_2O)]_2[ClO_4]_2$ [H_2salpn = *N,N'*-bis(salicylidene)propane-1,3-diamine].[13] As a result of this, our studies were extended to the use of unsymmetrical Schiff-base ligands with an N_2O_2 donor set and these too proved to be of great interest. We have reported the synthesis of the unsymmetrical Schiff-base ligand H_2L^3, derived from the condensation of 7-amino-4-methyl-5-azahept-3-en-2-one and salicylaldehyde, and the preparation of the manganese(III) complex $[\{MnL^3(H_2O)\}_2][ClO_4]_2\cdot 4H_2O$.[14] To our surprise we found that upon irradiation of an aqueous solution of this complex for 6 h ligand rearrangement occurred and the manganese(III) complex of the symmetrical ligand salen [H_2salen = *N,N'*-bis(salicylidene)ethane-1,2-diamine] was isolated in *ca.* 40% yield.[14] We have since also isolated the complex $[Mn(HL^4)(H_2O)_2][ClO_4]_2\cdot 2H_2O$, where H_2L^4 is the condensation product of 7-amino-4-methyl-5-azahept-3-en-2-one and α-methylsalicylaldehyde, from the facile rearrangement of $[MnL^5]ClO_4\cdot H_2O$ in acetonitrile[15] [H_2L^5 = *N,N'*-bis(α-methylsalicylidene)ethane-1,2-diamine].

Thus we have shown that manganese(III) complexes of tetradentate N_2O_2 donor-set Schiff bases are of interest, not only for their ability to evolve dioxygen from co-ordinated water, but also for their ability to facilitate the rearrangement of the ligands. However, no mechanism for this rearrangement has been proposed. Herein we report a further example of the rearrangement of an unsymmetrical ligand H_2L^1 (obtained by the condensation of 8-amino-4-methyl-5-azaoct-3-en-2-one with 3-ethoxysalicylaldehyde) in the presence of manganese(III) to form the symmetrical ligand *N,N'*-bis(3-ethoxysalicylidene)-

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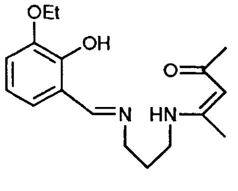
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

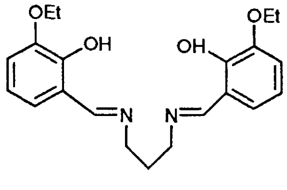
propane-1,3-diamine, H_2L^2, which is isolated in the complex $[MnL^2]ClO_4{\cdot}3H_2O$. The manganese(III) complex of the unsymmetrical ligand has also been isolated and crystallographically characterised as $[Mn(HL^1)_2]ClO_4$. It is the crystallographic characterisation of this compound that has enabled us to propose a mechanism for the rearrangement.

Results and Discussion

The manganese(III) complexes of both the unsymmetrical ligand H_2L^1, and the symmetrical ligand H_2L^2, have been synthesised by a modification of the method first proposed by Boucher and Coe:[16] the reaction of the dianion of the unsymmetrical ligand with manganese(II) perchlorate in air. Both complexes generally exhibit similar characteristics. The complex of the symmetrical ligand $[MnL^2]ClO_4{\cdot}3H_2O$, shows infrared bands typical of Schiff-base ligands co-ordinated to manganese(III).[13] A broad band centred at 3370 cm^{-1} can be assigned to a combination of the ν(OH) modes of co-ordinated and lattice water. A shift to lower energy in the ν(C=N) bond is observed at 1605 cm^{-1} (from 1634 cm^{-1} in the free ligand) and the broad band at 1080 cm^{-1} is characteristic of non-co-ordinated perchlorate. The presence of the symmetrical ligand complex is confirmed by the FAB mass spectrum which show a peak at *m/z* 423 (70%) attributable to $[MnL^2]^+$; no fragments corresponding to unsymmetrical ligand or to an unsymmetrical ligand complexed with manganese are observed. The complex exhibits a room-temperature magnetic moment of $4.75\mu_B$ and a plot of $1/\chi_m$ *vs.* T in the range 77–292 K gives a straight line which almost goes through the intercept, indicative of the absence of an antiferromagnetic interaction.



H_2L^1



H_2L^2

The complex of the unsymmetrical ligand $[Mn(HL^1)_2]ClO_4{\cdot}H_2O$ also shows similar bands in the infrared region, ν(OH) centred at 3450 cm^{-1} and ν(C=N) shifted to 1610 cm^{-1} (from 1630 cm^{-1} in the free ligand). A broad band at 1090 cm^{-1} is similarly attributable to unco-ordinated perchlorate. The FAB mass spectrum of the complex exhibited a quite interesting phenomenon. Whilst single-crystal X-ray diffraction shows (see below) the complex to be a monomer, with two ligands encapsulating the metal centre and the amine nitrogen atoms unco-ordinated, the FAB mass spectrum gives a parent-ion peak at *m/z* 357. This corresponds to the monomeric $[ML^1]^+$ ion with the amine nitrogen atom deprotonated. The $[Mn(HL^1)_2]^+$ ion is observed at *m/z* 661 and concurs with the crystallographic description of the structures with two non-co-ordinated amine groups in the structures.

Crystal Structure of $[Mn(HL^1)_2]ClO_4$.—The co-ordination environment around the monomeric manganese(III) centre consists of a pseudo-octahedral metal centre surrounded by an N_2O_4 co-ordination sphere, made up of two ligands (Fig. 1). This is in contrast to the previously reported manganese(III) complexes of analogous unsymmetrical Schiff bases which have the structural formulation $[MnL(H_2O)_2]^+$.[17] The necessity for two ligands, rather than one, about the metal centre is created by the non-co-ordination of the amine nitrogen atoms. Although this type of behaviour is not unknown,[18,19] it is still rare, especially in view of the stoichiometry of the reaction. The non-co-ordination of the nitrogen atom also

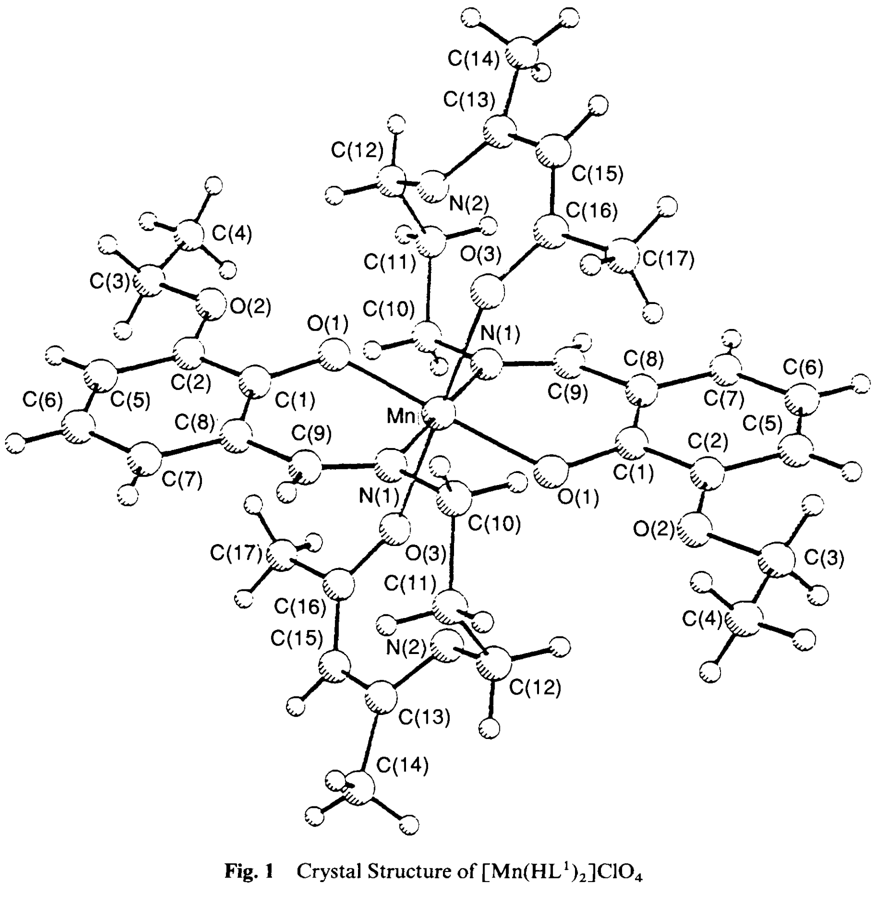


Fig. 1 Crystal Structure of $[Mn(HL^1)_2]ClO_4$

creates, to our knowledge, the first example of a ten-membered chelate ring about manganese. Positional parameters for the complex are given in Table 1 and selected bond lengths and angles are given in Table 2. High residual factors can be attributed to the poorly resolved perchlorate counter ion.

The N_2O_4 co-ordination in the x,y plane about the metal centre is almost perfectly planar, with bonds typical of manganese(III) centres, *e.g.* Mn(1)–O(1) 1.884(8) and Mn(1)–N(1) 2.06(1) Å. Elongation is observed along the z axis in the Mn–O bonds, with Mn(1)–O(3) 2.19(1) Å, which is probably due to a combination of a Jahn–Teller distortion typical of a manganese(III) d^4 ion, and the slightly weaker donor power of the ketonic oxygen atom. The short bond length C(16)–O(3) of 1.27(1) Å indicates that O(3) is a ketone donor rather than a charged donor. This is further supported by the planar nature of atoms N(2), C(13), C(15), C(16) and O(3) which implies that the system is conjugated in this region. The non-co-ordination of the N(2) amine nitrogen atom to the manganese centre is further supported by the Mn ··· N(2) separation of 3.51 Å, which indicates that there is no covalent interaction between the centres.

Proposed Mechanism of Rearrangement.—It is well known that Schiff-base condensations are subject to hydrolysis in acid or basic conditions to reform the carbonyl and amine precursors,[20] and we believe the mechanism of this hydrolysis to be the same in the presence of manganese, Scheme 1.

This hydrolysis reaction can then be applied to the products isolated from the reactions of manganese(III) Schiff-base complexes that we have observed, Scheme 2. We have recently crystallographically characterised compound **I** ($n = 2$)[17] and the crystallographic characterisation of $[Mn(HL^1)_2]ClO_4$ reported in this paper confirms that the non-co-ordination of an amine nitrogen atom about a manganese(III) centre in a chelate ring, as in **II**, can exist.

We have also previously observed the isolation of 3-aminopropylammonium perchlorate and propane-1,3-diammonium diperchlorate from the hydrolysis of a tris [*N*-(pyrrol-2-ylmethylene)propane-1,3-diamine]manganese(III) complex.[21] In addition, the visible-light induced hydrolysis and recondensation of H_2L^3 to form the symmetrical salen ligand in the presence of manganese(III), **VI**, has been reported by us.[14] Thus, we have now isolated all possible combinations of aldehyde and amine except the symmetrical combinations of pent-3-en-2-one, **VII**. The intermediates **III** and **IV** have not been isolated although they are implied by the mechanism.

We believe the rearrangements proceed *via* a series of reversible reactions which result in the formation of a manganese(III) 'template' complex, **IV**. Recondensation with a salicylaldehyde derivative and an acetylacetone derivative results in the reformation of starting material, **I**. However, recondensation with two salicylaldehyde derivatives produces the symmetrical Schiff-base manganese(III) complex, **VI**.[4] The production of these symmetrical ligand complexes containing the salicylaldehyde unit and the failure to isolate complexes of the acetylacetone unit, **VII**, could be attributed to the greater chelation properties of the salicylaldehyde-based ligands and the poorer co-ordination of the acetylacetone unit to manganese(III).

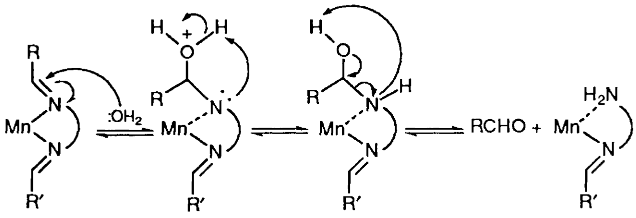
Secondary hydrolysis to produce the diamine also results in the formation of $Mn^{3+}(aq)$ which disproportionates to $Mn^{2+}(aq)$ and MnO_2, driving the equilibrium in this direction. The isolation of an insoluble black precipitate in all reactions is indicative of manganese dioxide formation, whilst the presence of the mildly acidic $[Mn(OH_2)_6]^{2+}$ could serve to produce the diammonium perchlorate salt.

Table 1 Positional parameters for $[Mn(HL^1)_2][ClO_4]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Mn	0.5	0.5	0.5
O(1)	0.6177(5)	0.5289(8)	0.6343(6)
O(2)	0.7800(6)	0.468(1)	0.8070(7)
O(3)	0.5021(6)	0.3334(9)	0.5582(7)
N(1)	0.4668(7)	0.605(1)	0.5422(8)
N(2)	0.3596(8)	0.393(1)	0.475(1)
C(1)	0.654(1)	0.546(1)	0.726(1)
C(2)	0.741(1)	0.514(2)	0.818(1)
C(3)	0.866(1)	0.428(2)	0.897(1)
C(4)	0.893(1)	0.375(2)	0.866(1)
C(5)	0.782(1)	0.536(2)	0.916(1)
C(6)	0.740(1)	0.586(2)	0.922(1)
C(7)	0.654(1)	0.619(1)	0.832(1)
C(8)	0.610(1)	0.595(1)	0.732(1)
C(9)	0.521(1)	0.633(1)	0.639(1)
C(10)	0.379(1)	0.659(1)	0.459(1)
C(11)	0.324(1)	0.608(2)	0.457(1)
C(12)	0.289(1)	0.481(1)	0.412(1)
C(13)	0.393(1)	0.328(2)	0.555(1)
C(14)	0.349(1)	0.325(2)	0.573(2)
C(15)	0.469(1)	0.268(1)	0.624(1)
C(16)	0.524(1)	0.276(1)	0.629(1)
C(17)	0.612(1)	0.216(1)	0.714(1)
Cl	1.0	0.4303(8)	0.75
O(4)	0.937(2)	0.518(3)	0.693(2)
O(5)	1.016(2)	0.409(3)	0.836(2)
O(6)	1.042(2)	0.322(3)	0.813(2)
O(7)	1.079(3)	0.469(4)	0.801(4)

Table 2 Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses

Mn–O(1)	1.884(8)	O(1)–C(1)	1.34(1)
Mn–O(3)	2.19(1)	O(3)–C(16)	1.27(1)
Mn–N(1)	2.06(1)		
O(1)–Mn–O(1)	180.00	O(3)–Mn–O(3)	180.00
O(1)–Mn–O(3)	91.1(4)	O(3)–Mn–N(1)	91.6(4)
O(1)–Mn–N(1)	89.8(4)	N(1)–Mn–N(1)	180.00



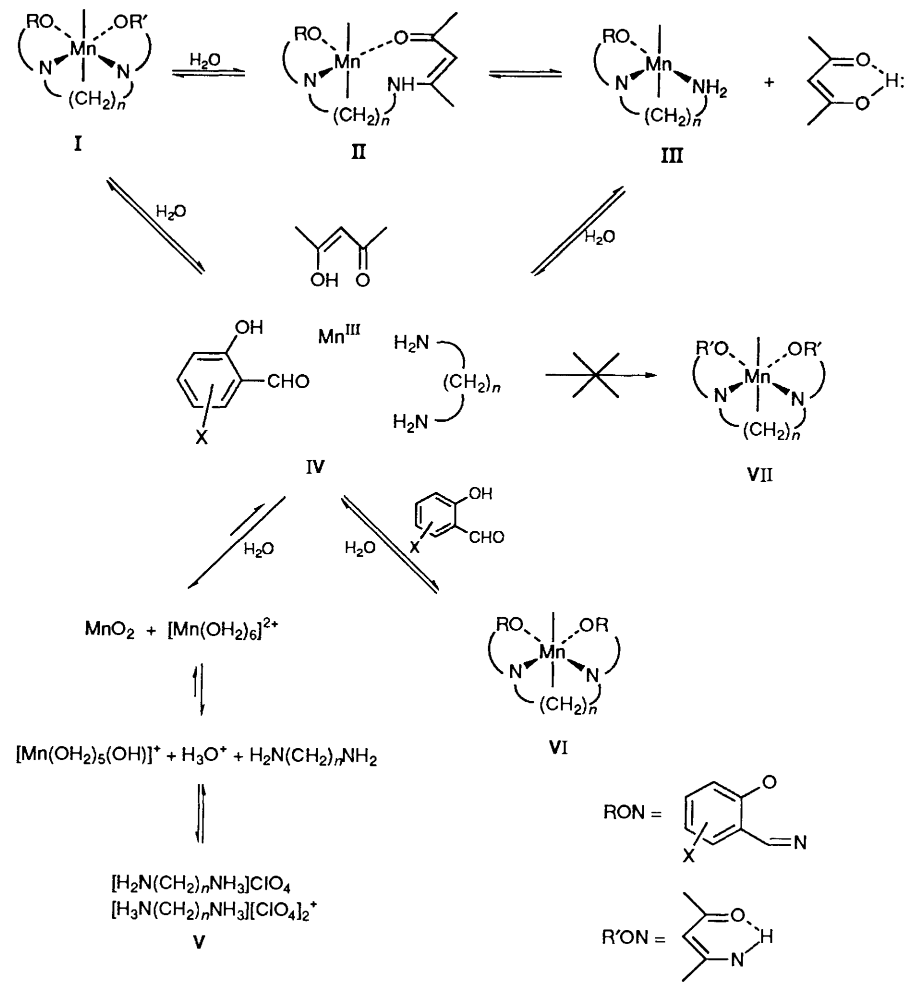
Scheme 1 Proposed mechanism for the hydrolysis of an imine bond when co-ordinated to manganese, R,R′ = alkyl or aryl

Conclusion

The rearrangement of unsymmetrical Schiff-base ligands appears to proceed *via* a series of reversible hydrolysis steps and most combinations of the rearrangement process have now been crystallographically characterised. We believe the failure to isolate the acetylacetone-based symmetrical Schiff-base manganese(III) complex can be attributed to the poorer co-ordination of the 'softer' ketonic donor atoms to manganese(III) and hence the low stability of a template complex. The isolation of the complex $[Mn(HL^1)_2]ClO_4$ further highlights the variety of structural possibilities that are available to manganese(III), differing from the manganese(III)–ligand co-ordination environment that we have previously reported for other unsymmetrical Schiff-base ligands.[17]

Experimental

Preparation.—The unsymmetrical Schiff-base ligand H_2L^1 was prepared by standard methods as previously reported.[17]



Scheme 2 Proposed mechanism of rearrangement of manganese(III) Schiff-base complexes [n = 2 or 3; X = substituent(s) on aryl]

Both complexes were prepared as outlined below in an analogous manner by a modification of the methods originally developed by Boucher and Coe.[16]

$[MnL^2]ClO_4 \cdot 3H_2O$. To the ligand H_2L^1 (1.36 g, 4.47 mmol) dissolved in ethanol–methanol (1 : 1, 100 cm^3) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (1.62 g, 4.47 mmol) dissolved in ethanol (50 cm^3). Sodium hydroxide (0.36 g, 9 mmol) was then added in ethanol (25 cm^3) and the reaction mixture darkened rapidly. The mixture was stirred in contact with air for 5 d. The reaction mixture was filtered to remove insoluble impurities, the volume reduced to *ca.* 50 cm^3 and the green solid formed was collected by filtration and recrystallised from ethanol [Found (Calc.): C, 44.2 (43.7); H, 5.7 (5.7); Cl, 6.7 (6.3); Mn, 9.0 (9.5); N, 4.8 (4.9)%]. Mass spectrum m/z 423 (70%), $[ML^1]^+$.

$[Mn(HL^1)_2]ClO_4 \cdot H_2O$. To the ligand H_2L^1 (0.45 g, 1.48 mmol) dissolved in ethanol–methanol (1 : 1, 100 cm^3) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.53 g, 1.47 mmol) in ethanol (50 cm^3). Sodium hydroxide (0.12 g, 3 mmol) in ethanol (25 cm^3) was added and the reaction mixture darkened rapidly. The mixture was stirred in contact with air for 3 d before filtering to remove insoluble materials. The green solution was slowly evaporated producing crystals suitable for single-crystal X-ray diffraction studies. The selected crystal did not contain a water molecule of crystallisation although the infrared spectrum of the complex indicated lattice water was present [Found (Calc.): C, 52.1 (52.4); H, 6.0 (6.2); Cl, 4.1 (4.6); Mn, 6.7 (7.1); N, 7.5 (7.2)%].

Crystallographic Measurements.—For the crystal of $[Mn(HL^1)_2]ClO_4$ (0.25 × 0.17 × 0.03 mm) measurements were made on a Rigaku AFC5R diffractometer employing graphite-monochromated Cu-Kα radiation and a 12 kW rotating anode generator. Of the 2996 reflections which were collected 2911 were unique, 1180 observed [$I > 3\sigma(I)$]. All data were collected at ambient temperature using the ω–2θ scanning technique to a maximum 2θ value of 120.2°. Structure solutions were obtained by direct methods (DIRDIF).[22] All non-hydrogen atoms were subjected to anisotropic refinement (TEXSAN)[23] with hydrogen atoms included in idealised positions (C–H 0.95 Å). An empirical correction, using the program DIFABS,[24] was applied which resulted in transmission factors ranging from 0.45 to 1.25. Final residual factors were $R = 0.096$ and $R' = 0.105$; $w = 1/(F_o + 0.03F_o^2)$. Crystal data for $[Mn(HL^1)_2]ClO_4$ from least squares refinement of 25 carefully centred reflections in the range $26.34 < 2\theta < 48.11°$: $C_{34}H_{46}ClMnN_4O_{10}$, $M = 761.19$, monoclinic, space group $C2/c$ (no. 15), $a = 26.624(4)$, $b = 10.960(2)$, $c = 21.667(3)$ Å, $\beta = 144.45(2)°$, $U = 3676(3)$ Å^3, $D_c = 1.372$ g cm^{-3} ($Z = 4$), $F(000) = 1593$.

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

Physical Measurements.—Elemental analyses were performed by the Elemental Analysis services at UMIST and Santiago. Infrared spectra were recorded on a Perkin Elmer 180 spectrophotometer. Magnetic susceptibilities were measured in the temperature range 300–70 K by use of a SQUID MPMS magnetometer (Quantum), using a field of 5 T. The FAB mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS 90 data system, using *m*-nitrobenzyl alcohol as a matrix.

Acknowledgements

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