Manganese(iv)–Amide Binding: Structural Characterisation and Redox Stability of a Hexadentate Complex

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The hexadentate diamide ligand H_4L (1), formed from ethyl salicylate and triethylenetetramine, affords $MnL \cdot 4H_2O$ which has a *trans–cis–cis* $Mn^{IV}N_2$(amide)N_2(amine)O_2(phenol) co-ordination sphere and a low Mn^{IV}/Mn^{III} reduction potential.

Manganese(iv) is an uncommon oxidation state. In O- and/or non-porphyrinic N-co-ordination this state is implicated in photosystem II.[1] Carboxylato and phenolato functions of amino acid residues could account for the O-binding.[2] If N-binding does occur, it could well involve the amide function. Very little is known about manganese(iv)–amide

binding, however.[3] Herein we describe the first structural characterisation of such binding as well as of the binding of manganese(iv) by an aliphatic amine function.

The ligand H_4L (1) was synthesised by condensing ethyl salicylate and triethylenetetramine. Upon reaction with manganese-(ii) or -(iii) acetate in methanol in air, a reddish brown

(1)
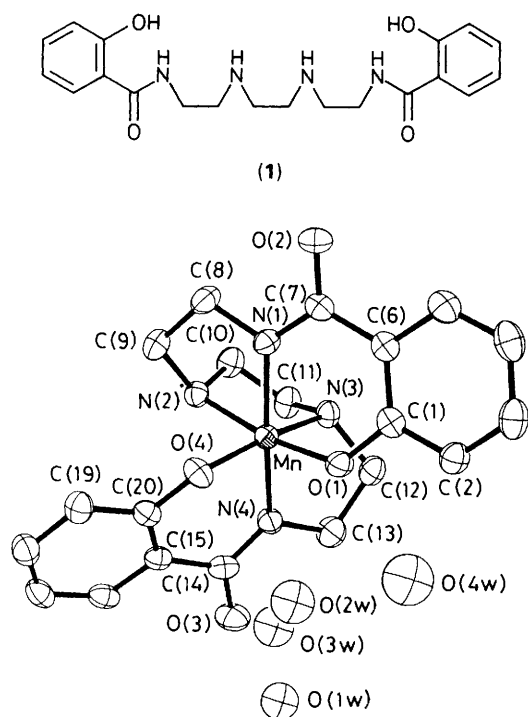
Figure 1. An ORTEP projection of MnL·4H$_2$O. Non-hydrogen atoms are depicted as 50% probability ellipsoids. Pertinent distances (Å) and angles (°): Mn–N(1), 1.956(3); Mn–N(4), 1.955(3); Mn–O(1), 1.838(3); Mn–O(4), 1.855(3); Mn–N(2), 2.033(3); Mn–N(3), 2.038(4); O(1)–Mn–O(4), 93.2(1); O(4)–Mn–N(1), 96.0(1); O(4)–Mn–N(2), 91.6(1); O(1)–Mn–N(3), 92.7(1); N(1)–Mn–N(3), 94.3(1); O(1)–Mn–N(4), 91.4(1); N(3)–Mn–N(4), 78.7(1); O(1)–Mn–N(1), 91.5(1); N(1)–Mn–N(2), 80.7(1); N(2)–Mn–N(3), 84.0(1); O(4)–Mn–N(4), 90.7(1); N(2)–Mn–N(4), 95.9(1); N(1)–Mn–N(4), 172.6(1); O(4)–Mn–N(3), 168.0(1); O(1)–Mn–N(2), 171.2(1).

solution was rapidly formed. Removal of solvent and re-crystallisation from aqueous methanol afforded dark crystals of composition MnL·4H$_2$O in 85% yield.

The structure of MnL·4H$_2$O is shown in Figure 1.† The ligand is hexadentate and the distorted octahedral MnN$_4$O$_2$ co-ordination sphere consists of two amide N atoms, two amine N atoms, and two phenolic O atoms in a *trans–cis–cis* configuration. The Mn–N(amide) bonds are significantly shorter than the Mn–N(amine) bonds. Previously reported bonds of the latter type have involved aromatic amines such as pyridine[6] or 2,2'-bipyridine.[2] The Mn–O(phenolic) distances

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† *Crystal data*: C$_{20}$H$_{30}$MnN$_4$O$_8$, M = 509.4, monoclinic, space group $P2_1/n$, Z = 4, a = 8.778(3), b = 21.559(8), c = 11.882(3) Å, β = 99.40(2)°, U = 2218.4(12) Å^3, T = 295 K, D_c = 1.525 g cm^{-3}, μ (Mo-K_α) = 6.23 cm^{-1}, crystal dimensions 0.16 × 0.14 × 0.40 mm; data were collected in the range 2.0 ≤ 2θ ≤ 55.0° on a Nicolet R3m/V four-circle diffractometer. 5090 Independent reflections were collected using graphite-monochromated Mo-K_α radiation and the ω scan technique; 3216 reflections with I > 3σ(I) were used for structure solution. All calculations used the SHELXTL-Plus[4] program package. The metal atom was located by Patterson synthesis and the remaining non-hydrogen atoms by difference Fourier maps and least-squares analyses. Complex atomic scattering factors were used in refinement.[5] Non-hydrogen atoms including the solvent molecules were refined with anisotropic thermal parameters. Hydrogen atoms were included at calculated positions with fixed U values of 0.08 Å^2. The structure refined to R = 0.0514 and R_w = 0.0592. The largest non-solvent residual was 0.18 e/Å^3. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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in MnL·4H$_2$O compare well with the few others that are known.[2,6–8] The complex provides the first example of hexadentate chelation and non-porphyrinic N$_4$O$_2$ co-ordination for manganese(IV).

The co-ordinated amide functions are planar; *e.g.* the mean deviation from the best Mn–N(4)–C(13)–O(3)–C(14) plane is 0.01 Å. This contrasts with complexes of highly oxidised metal ions, in which the amide function may be nonplanar.[9] The water oxygen atoms O(1w) and O(3w) are hydrogen bonded to the amide oxygen O(3) [av. O···O 2.854(5) Å], whereas O(2), O(2w), and O(4w) are not involved in hydrogen bonding. In agreement with this MnL·4H$_2$O loses water quantitatively in two discrete steps at 360 and 395 K in differential thermogravimetric analysis.

The magnetic moment of MnL·4H$_2$O is 4.05 μ$_B$ (298 K). Its X-band powder ESR spectrum (77 K) displays signals at g 2.015 (strong) and 3.829 (weak). This corresponds to[10] small zero-field splitting, 2D ≪ 0.3 cm^{-1}.

Cyclic voltammetry of MnL·4H$_2$O in methanol solution (0.1 M Et$_4$NClO$_4$; platinum working electrode; 298 K) shows a quasi-reversible Mn^{IV}L + e ⇌ Mn^{III}L$^-$ couple ($E°$ 0.01 V *vs.* saturated calomel electrode). The Mn^{III}/Mn^{II} couple lies below the solvent cut-off potential (−0.5 V). The low reduction potential explains the rapid formation of MnL·4H$_2$O from H$_4$L and manganese salts in air; the complex is not formed under nitrogen. Amide binding may explain the low reduction potential of MnL·4H$_2$O. If this is so, such binding may not be important in the active site of photosystem II, where high potentials are required for water splitting.

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