

A Remarkably Stable Mononuclear Manganese(III) Hydroxide Complex: [L¹Mn^{III}(OH)] [H₂L¹ = bis(2-hydroxy-5-nitrobenzyliminopropyl)methylamine]

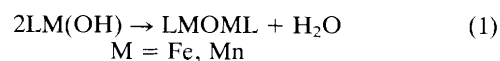
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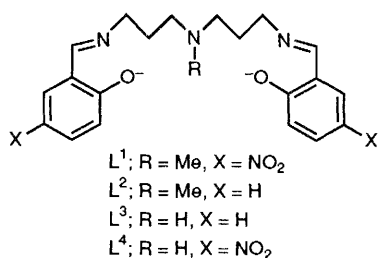
A mononuclear manganese(III) hydroxide complex of a pentadentate Schiff base ligand has been prepared and characterized using X-ray crystallography and magnetic susceptibility, ¹H NMR, and UV-VIS measurements.

Interest in the oxo and hydroxo coordination chemistry of manganese has intensified significantly as it has become clear that photosynthetic water oxidation takes place at a polynuclear manganese aggregate within the oxygen evolving complex of photosystem II.^{1,2} Numerous oxo-bridged binuclear, trinuclear and tetranuclear species have been characterized.^{2,3} On the other hand, complexes with terminal oxo or hydroxo ligation are much less common. There is only one example of a structurally characterized complex containing a Mn=O moiety⁴ and a single case of terminal OH⁻ ligation in a binuclear Mn^{IV}Mn^{IV} species⁵ has been demonstrated. One might assume that the paucity of mononuclear Mn-OH species is due to the tendency of such moieties to dehydrate,

giving oxo-bridged complexes [eqn. (1)], a reaction type that is well known for Fe^{III}.⁶ Contrary to this expectation, we have discovered that a family of pentadentate Schiff base ligands (see below) support the formation of the first fully documented examples of mononuclear [LMn^{III}(OH)] species. These hydroxy complexes show no tendency to condense to μ-oxo species in CH₂Cl₂ solution under ambient conditions.



While Coleman and Taylor previously postulated that a species formed by the treatment of L¹Mn^{II} with dioxygen in toluene is [L¹Mn(OH)],⁷ they were unable to obtain crystallo-



graphic verification and thus alternative formulations cannot be ruled out unequivocally. Our method for the synthesis of $[L^1Mn(OH)]$ involves the rapid stirring of a CH_2Cl_2 solution of $[L^1MnCl]^\dagger$ with an aqueous NaOH solution ($\sim 0.02 \text{ mol dm}^{-3}$). Within a few minutes the yellow-green colour of the organic layer gives way to a red-brown colour. Dark-red crystals of $[L^1Mn(OH)]$ suitable for elemental analyses and physical measurements, ‡ were grown from a mixture of CH_2Cl_2 and hexanes at 4°C (yield: ca. 10%).

An X-ray structure determination § did indeed confirm the monomeric nature of the reaction product. The solid state structure of $[L^1Mn(OH)]$ is presented in Fig. 1. The proton of the coordinated hydroxide group was located on a difference Fourier map (O-H, 1.0 Å) and included in structure factor calculations, however, its position was not refined. The Schiff base ligand is coordinated with the three nitrogen atoms oriented meridionally and with the phenolate oxygen donors positioned *cis* to each other. The hydroxide group is situated *trans* to one of the phenolate groups. The methyl group bound to N(1) is directed away from the OH moiety. The structural isomer observed is in agreement with the prediction made by Coleman and Taylor. 7 There is no evidence for a steric interaction that would block formation of the oxo-bridged species $L^1MnOMnL^1$. As shown in Fig. 2, the compound crystallizes with two molecules in the asymmetric unit that are associated by a hydrogen-bonding interaction between the hydroxide group of one molecule and a phenolate oxygen atom of another [O(1)⋯O(D1) 2.825(4), Mn⋯Mn 5.251 Å]. A similar hydrogen-bonded dimer was observed by Ashmaw *et al.* 8 Each monomer has a pseudo-octahedral coordination environment with a Jahn-Teller elongation along the N(1)-Mn-O(A1) axis. The bond lengths for $[L^1Mn(OH)]$ are consistent with those found for other Mn^{III} Schiff base complexes. 9 The Mn-OH bond length of 1.827(6) Å is somewhat longer than the average Mn-O distance reported for $[Mn_2O(5-NO_2\text{saldien})_2]$ [$H_25-NO_2\text{saldien} = \text{bis}(5\text{-nitrosalicylidene})\text{diethylenetriamine}$] (1.754 Å) 3 and significantly

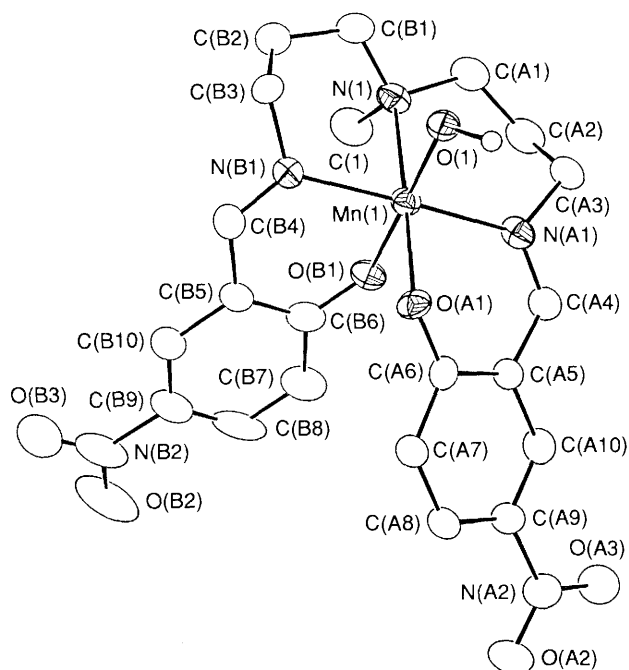


Fig. 1 Structure of one molecule of $[L^1Mn(OH)]$ showing the 50% thermal ellipsoids and the atom-labelling scheme. Hydrogen atoms are omitted for clarity, except for the hydroxide hydrogen atom, which is shown with arbitrary radius. Selected interatomic distances (Å) and angles ($^\circ$) are as follows: Mn-O(1) 1.827(3), Mn-O(A1) 2.127(3), Mn-O(B1) 1.920(3), Mn-N(1) 2.414(4), Mn-N(A1) 2.058(4), Mn-N(B1) 2.036(4), O(1)-H(O1) 0.998; O(1)-Mn-O(B1) 179.1(2), N(1)-Mn-O(A1) 177.4(1), N(A1)-Mn-N(B1) 174.9(2), O(1)-Mn-N(1), 87.7(1). The other molecule in the asymmetric unit has similar bond lengths and angles.

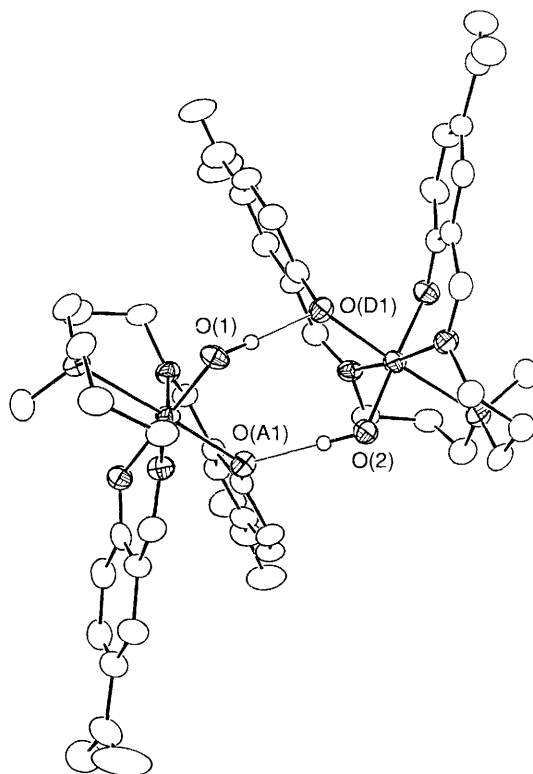


Fig. 2 Structure of $[L^1Mn(OH)]$ showing the 50% thermal ellipsoids for the hydrogen-bonded dimer comprising the asymmetric unit. Hydrogen atoms are omitted, except for the hydroxide hydrogen atoms, which are included with arbitrary radii. Pertinent interatomic distances (Å) are as follows: O(1)⋯O(D1) 2.824(4), O(2)⋯O(A1) 2.827(4), Mn(1)⋯Mn(2) 5.251(1).

† D. M. Eichhorn and W. H. Armstrong, unpublished results. The precursor to 1, $[L^1MnCl]$ was prepared by treatment of $(Et_4N)_2[MnCl_4]$ in MeCN with a MeCN solution of H_2L^1 in a 1:1 molar ratio. After stirring for 1 h, the solvent was removed and the resulting green-black solid was extracted into CH_2Cl_2 . Removal of solvent gave $[L^1MnCl]$ in adequate purity for use in the next reaction.

‡ Satisfactory elemental analyses (C, H, N) were obtained. 1H NMR: $CDCl_3$; positive shifts are downfield of Me_4Si δ 173, 108, 73, 42, 23, 16, -2, -6, -11, -14, -39 and -75.

§ *Crystal data* for $[L^1MnOH]$: the complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.621(1)$, $b = 15.432(3)$, $c = 17.853(2)$ Å, $\alpha = 83.54(1)$, $\beta = 78.205(9)$, $\gamma = 70.07(1)^\circ$, $V = 2690.0(7)$ Å³ and $Z = 4$ with two monomers in the asymmetric unit, along with one H_2O and two disordered hexane molecules per asymmetric unit. Data collection at -103°C for $3 \leq 2\theta \leq 45^\circ$ yielding 5508 reflections with $I \geq 3\sigma(I)$. The structure was solved by direct methods (SHELXS-86, G. Sheldrick) and 685 parameters were refined to final $R(R_w)$ values of 4.8% (6.3%) (Molen crystal structure determination package, Delft Instruments, X-ray Diffraction B.V., 1990). Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

shorter than the Mn–OH distances observed for $[\text{Mn}_2\text{O}_2(\text{OH})_2(\text{tacn})_2]^{2+}$ (tacn = 1,4,7-triazacyclononane) (1.881 Å).⁵

Several physical techniques were used to characterize the title complex. The ^1H NMR spectrum of $[\text{L}^1\text{Mn}(\text{OH})]$ in CDCl_3 displays 12 well-resolved resonances over the range δ –75 to 173.‡ In contrast, under the same conditions the spectrum of the chloride precursor $[\text{L}^1\text{MnCl}]$ has no readily discernible resonances downfield of 16 ppm or upfield of Me_4Si . The existence of $[\text{L}^n\text{Mn}(\text{OH})]$ species for $n = 2-4$ (see above) was confirmed by ^1H NMR spectroscopy. The electronic spectrum of $[\text{L}^1\text{Mn}(\text{OH})]$ is dominated by an intense charge transfer transition at 363 nm ($\epsilon = 23\,000\text{ mol dm}^{-3}\text{ cm}^{-1}$). Room temperature solid state magnetic susceptibility measurements give an effective magnetic moment of $5.07\ \mu_{\text{B}}$ for $[\text{L}^1\text{Mn}(\text{OH})]$, consistent with a high-spin d^4 electronic configuration and a weak magnetic interaction at best between the hydrogen-bonded pair of monomers. As is typical of $S = 1$ species, no EPR signal was detected for $[\text{L}^1\text{Mn}(\text{OH})]$ at room temperature or at 77 K in CH_2Cl_2 .

To our knowledge $[\text{L}^1\text{Mn}(\text{OH})]$ is the first example of a structurally characterized mononuclear manganese hydroxide complex. The only other structurally characterized manganese complex with terminal hydroxide ligands is $[\text{Mn}_2(\mu\text{-O})_2(\text{OH})_2(\text{tacn})_2]^{2+}$,⁵ in which the OH^- groups adopt an *anti* orientation. Wieghardt and coworkers postulated¹⁰ that base treatment of $[\text{Mn}(\text{tacn})(\text{acac})(\text{OH}_2)]^{2+}$ (Hacac = pentane-2,4-dione) results in the formation of a mononuclear hydroxide species, although this has not been established definitively. It should also be noted that Dey *et al.* formulated a manganese piperazine-di-biguanide (pipzbig) species as $[\text{Mn}^{\text{III}}(\text{OH})(\text{H}_2\text{O})(\text{pipzbig})]$.¹¹

The stability of $[\text{L}^1\text{Mn}(\text{OH})]$ with respect to dehydration and μ -oxo dimer formation is somewhat unexpected as this process is generally thought to be facile for manganese and iron. One explanation for the increased stability of the manganese complex relative to corresponding iron species derives from consideration of their electronic structures. In a recent report of studies of the conversion of mononuclear porphyrin iron(III) hydroxide complexes to oxo-bridged binuclear species it was postulated that the rate-limiting step in the process is Fe–OH bond cleavage.^{6c} The crystal structure of $[\text{L}^1\text{Mn}(\text{OH})]$ reveals a short Mn–OH bond and Jahn–Teller elongation along an axis (z) perpendicular to the Mn–OH bond. Thus the empty $d_{x^2-y^2}$ orbital has one of its lobes

directed at the hydroxide group. In contrast, for the high-spin $d^5\text{Fe}^{\text{III}}$ case the antibonding $d_{x^2-y^2}$ orbital would be occupied and presumably the Fe^{III}–OH bond is significantly weaker than the corresponding Mn^{III}–OH bond, rendering Fe–OH bond cleavage more facile.

In conclusion, a mononuclear manganese(III) complex bearing terminal hydroxide ligation has been isolated and characterized. The stability of this species with respect to dehydration will permit us to examine whether or not intermolecular O–O bond formation, yielding hydrogen peroxide, can be driven oxidatively. A related reaction may take place in the course of photosynthetic water oxidation.

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