Synthesis and Structure of Tetradentate Amido-phenolate Manganese(III) Complexes; Precursors for High-valent Manganese Chelate Complexes

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Abstract

The synthesis and electrochemical properties of a range of manganese(III) complexes of a planar tetraanionic amido-phenolate ligand are described. The complexes are of general formula $[MnL(A)(B)]^-$ where L^{4-} = 1,2-bis(2-hydroxy-benzamido) benzene anion; A and B are H_2O or pyridine-type bases. The crystal structure of the six coordinate $[MnLpy_2]^-$ moiety is described in the complex $[Mn^{II}py_4(H_2O)_2][(Mn^{III}Lpy_2)_2]py_2$. The magnetic moment of the latter complex is 9.10 BM which is indicative of uncoupled $\{Mn^{II}, Mn^{III}, Mn^{III}\}$ centres. The other complexes show $S = 2$ magnetic behaviour. Cyclic voltammetric studies on DMF solutions of the complexes show a reversible Mn^{III}/Mn^{IV} wave at +0.67 V (relative to SCE) indicating that an oxidizing agent is required to obtain Mn(IV) species.

Introduction

There is currently a resurgence of interest in the chemistry of the higher oxidation states of manganese, largely because of the occurrence of $Mn^{II/III/IV}$ states in biological sites such as the water oxidation centre of Photosystem II [1, 2] and in other Mn enzymes [3, 4], but also because of the intermediate formation of $[Mn^VO]^{3+}$ or $[Mn^{IV}O]^{2+}$ moieties in olefin oxidations or epoxidations catalysed by Mn complexes [5, 6].

We are involved in studies of both these areas of Mn chemistry using, amongst other tactics, bi-nucleating ligands to stabilize Mn_2 or higher oligomeric species, and highly negatively charged ligands to stabilize high oxidation state mononuclear species. This present communication deals with the latter aspect and contains a preliminary account of the synthesis and structures of some new Mn^{III} chelates formed with the tetradentate amido-phenolate ligand, L^{4-}.

L^{4-}

$(L')^{2-}$
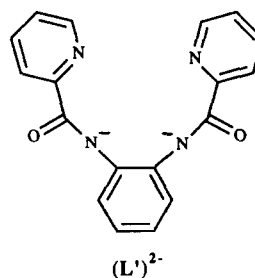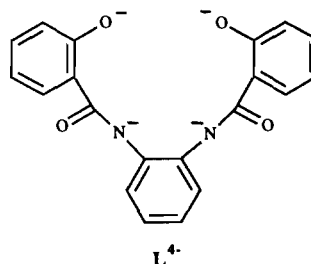
We are exploring the use of these compounds to obtain high-valent Mn compounds and to catalyse olefin oxidation reactions. While the present paper was being written a communication by Collins and Gordon-Wylie [7] has appeared which describes similar studies on a ligand system related to L^{4-} but containing amido-alcoholate groups. These workers were able to crystallize and structurally characterize a Mn^VO chelate formed by reaction of the Mn^{III} precursor with neat t-butylhydroperoxide. Two other recent papers of note include a description of some bis-tridentate Mn^{IV} amido-phenolate species [8] and the use of Mn^{III} complexes of the amido-pyridyl type (shown) Mn(L')X, to catalyse olefin epoxidation in the presence of PhIO [9].

Results and Discussion

Alcoholic solutions of the ligand, LH_4 [10], react readily with manganese(II) acetate tetrahydrate, in air, in the presence of bases such as KOH, NaOH or pyridine to yield the range of complexes given in Table 1. Microanalytical data were satisfactory

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TABLE 1. Tetradentate manganese(III) amido-phenolate complexes

Complex	Colour of crystals	Magnetic moment (BM, 295 K)	Vis–UV (MeOH) (nm) (ϵ(l mol^{-1} cm^{-1}))
K[Mn^{III}L]H$_2$O	yellow	4.62	492(326), 306(22600), 219(51300), 202(53800)
K[Mn^{III}L]py$_3$	red	4.80[c]	484(383), 306(26300), 261sh(26200), 254sh(32800), 248sh(36600), 242sh(39000), 219(48380), 202(38800)
Na[Mn^{III}L]py$_2$H$_2$O	brown	4.79	488(370), 305(26200), 263sh(24100), 255sh(29900), 248sh(33600), 218(47800), 204sh(34900)
Na[Mn^{III}L](β-pic)(H$_2$O)[a]	brown	4.84	486(573), 307(24900), 269sh(22000), 220(46800)
[Mn^{II}py$_4$(H$_2$O)$_2$][(Mn^{III}Lpy$_2$)$_2$]py$_2$	brown	9.10[b, c]	488(836[b]), 306(47800), 263sh(56900), 255sh(65600), 249sh(80000), 243sh(83600), 218(98700), 203(82800)

[a]β-pic = β-picoline. [b]For Mn$_3$. [c]Curie temperature dependence in the range 300–20 K.

for all compounds (see 'Supplementary Material'). Yellow needles of K[MnL]H$_2$O can be converted to red crystals of K[Mn^{III}L]py$_3$ by dissolution in MeOH/pyridine. It is likely, by reference to the crystal structure described below, that two of the py molecules in K[MnL]py$_3$ are bonded to Mn*. At the outset of the work it seemed feasible to obtain planar Mn^{IV} chelates of L^{4-}, i.e. [Mn^{IV}L] under the present reaction conditions, since di-negative-tridentate amide or Schiff base ligand systems are known to be capable of stabilizing Mn^{IV} [8, 12]. However, it is clear from analytical and structural data on the crystalline products that oxidation has stopped at the Mn^{III} stage in the present system, and that Mn^{III} has a general tendency to achieve a coordination number of six (or five). It is possible that the complexes containing H$_2$O and base have coordinated H$_2$O since Mn^{III} is known to readily bind water [13].

A most interesting compound, obtained by reaction of Mn^{II}acetate with LH$_4$ in neat pyridine, contains a [Mn^{II}py$_4$(H$_2$O)$_2$]$^{2+}$ cation for every two [Mn^{III}Lpy$_2$]$^-$ anions, the crystal lattice being further stabilized by solvated py molecules interacting in a π-bonding fashion to coordinated py groups. Dark brown crystals of this material, viz. [Mn^{II}py$_4$(H$_2$O)$_2$][(Mn^{III}Lpy$_2$)$_2$]py$_2$, possess the molecular structure shown in Fig. 1.

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*A recent crystal structure on this complex confirms this. The geometric features around Mn^{III} are similar to those in Fig. 1. The crystals contain a novel pentacoordinate K$^+$ ion bonded to four O atoms from surrounding [MnL] groups and one N atom from the solvated py [11].

The [Mn^{III}Lpy$_2$]$^-$ moieties display a trans-py$_2$ coordination, while the aromatic rings of the tetradentate L^{4-} ligand are non-coplanar. Pertinent bond distances are given in Fig. 1. The general coordination geometry around Mn^{III} is similar to that observed in a planar coordinated [OsN(L)]$^-$ nitrido complex [14]. Mn–N bond lengths to L^{4-} are similar to the corresponding dimensions in the recently reported Mn^{V}O analogue [7] but considerably shorter than the Mn–N(py) axial distances.

The magnetic moment of this complex, 9.10 BM per 3 Mn, is as calculated for three non-interacting S = 2, 5/2, 2 centres ($\sqrt{83}$ BM), and compatible with the lack of any direct bridging between the Mn atoms. It shows Curie behaviour in the range 300–20 K. The room temperature moments of the other complexes given in Table 1 are generally typical of S = 2 Mn^{III} values, although the small reduction observed for K[MnL]H$_2$O might be indicative of a bridged structure incorporating a hydrogen-bonded H$_2$O group. Further investigations are warranted in this case. The UV–Vis spectra of the complexes in methanol show a charge-transfer band (perhaps with d–d character) at ~490 nm and intra-ligand bands below 306 nm, with vibrational structure being evident on the latter bands for the py and β-pic adducts.

Cyclic voltammograms have been measured on DMF solutions of a number of the complexes in Table 1 using Pt, glassy carbon or gold working electrodes and a SCE reference electrode calibrated relative to ferrocene/ferrocenium ($E_{1/2}$ = 0.49 V). A typical CV is shown in Fig. 2. The voltammograms
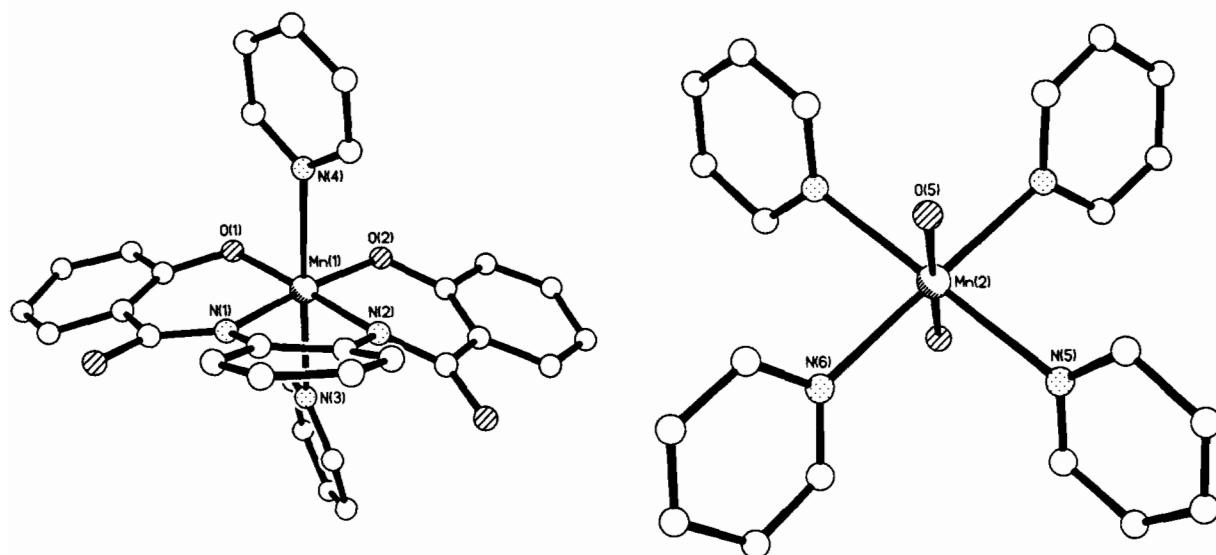
Fig. 1. Molecular structure and numbering scheme of $[Mn^{II}py_4(H_2O)_2][(Mn^{III}Lpy_2)_2]py_2$. Selected bond distances: Mn(1)–N(1) 1.98(2), Mn(1)–N(2) 1.94(2), Mn(1)–N(3) 2.48(2), Mn(1)–N(4) 2.42(2), Mn(1)–O(1) 1.86(2), Mn(1)–O(2) 1.91(2), Mn(2)–O(5) 2.19(2), Mn(2)–N(5) 2.36(2), Mn(2)–N(6) 2.30(2) Å.
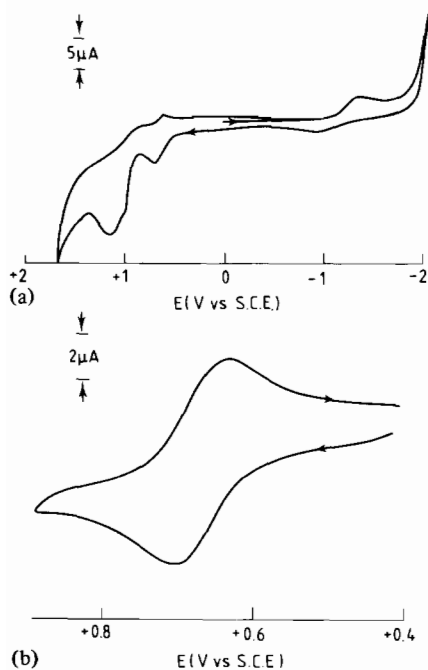

Fig. 2. Cyclic voltammogram of $K[Mn^{III}L]H_2O$ in DMF: gold button working electrode, voltages relative to SCE; scan speed 100 mV/S, temperature 25 °C, supporting electrolyte $(Bu_4N)(ClO_4)$ (0.1 M); (a) full sweep, (b) wave at +0.672 V.

TABLE 2. Cyclic voltammetric data[a]

Complex	$E_{1/2}$ (V)	ΔE_p (mV)	i_{p_a}/i_{p_c}
$K[MnL]H_2O$	1.2[b]		
	1.12[b]		
	1.02[b]		
	0.672	64	1.00
	−1.16[c]	478	0.14
$K[MnL]py_3$	1.25[b]		
	1.12[b]		
	1.02[b]		
	0.657	78	~1
	−1.15	400	~0.15
$Na[MnL](\beta\text{-pic})(H_2O)$	1.22		
	1.12		
	1.02		
	0.666	60	0.81
	−1.14	445	0.29
$[Mnpy_4(H_2O)_2][(MnLpy_2)_2]py_2$	1.22		
	1.10		
	1.02		
	0.656	74	1.49
	−1.2		
	−1.5		

[a]Measured in purified DMF on a gold button electrode relative to SCE with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. Scan rate 100 mV/s; this rate was varied between 50–500 mV/s for reversible waves. [b]These are E_{p_a} values of irreversible anodic waves. [c]This wave becomes more reversible on a glassy carbon electrode.

are generally similar in all cases (Table 2) suggesting the presence of a common $[Mn^{III}L]^-$ species, probably solvated by DMF rather than by water or pyridine. Taking $K[MnL]H_2O$ as an example, a reversible wave is observed at $E_{1/2}$ = 0.672 V (Au relative to SCE), together with stronger irreversible anodic waves at E_{p_a} = 1.2, 1.12 and 1.02 V, and a quasi-reversible cathodic wave at $E_{1/2}$ = −1.16 V. The 0.672 V wave is logically assigned to Mn^{IV}/Mn^{III},

in line with the observed stability of the Mn^{III} state, while the -1.16 V wave may be due to Mn^{III}/Mn^{II}. Comparison to the CV of the free ligand suggests that the $+1.2$ V wave may be a ligand-based process, however LH_4 is essentially not electroactive in the DMF potential window and thus these waves may involve oxidation of Mn to higher oxidation states*. Somewhat similar behaviour has recently been reported for a tetranuclear $[Mn_2^{II}Mn_2^{III}]$ complex [19]. The Mn^{IV}/Mn^{III} potential is similar to those observed for [Mn(salicylate)$_2$(bipy)] [20] and [Mn(triazacyclononane)(N$_3$)$_3$] [4] but is much more positive than those reported for bis-tridentate Mn^{IV} amido-phenolate [8] and salicylideneimine alcoholate complexes [12]. These differences may reflect the effect of stereochemistry on manganese $E_{1/2}$ values. Indeed, the details of redox tuning of Mn chelates of the present general type await a fuller study of variations in in-plane and axial ligands, coordination geometries and perhaps in counter-cation, in order to rationalize or predict the stability and reactivity of high-oxidation state oxo— or non-oxo—Mn species. Clearly, a chemical (or electrochemical) oxidant is required to convert the present Mn^{III} complexes to the Mn^{IV} or Mn^V states.

Crystal Structure Determination on
$[Mn^{II}py_4(H_2O)_2]/[(Mn^{III}Lpy_2)_2]py_2$

Cell dimensions: $a = 16.145(3)$, $b = 12.861(3)$, $c = 19.997(7)$ Å, $\beta = 99.20(2)°$, $U = 4098.8$ Å^3, $Z = 4$, $D_c = 1.36$, $D_m = 1.35(2)$ g cm^{-3} (by flotation), space group $P2_1/c$. Single crystal X-ray diffraction data were collected on a Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation for reflections with $6° < 2\theta < 50°$. A total of 1862 data with $F > 6\sigma(F)$ was used in the solution and partial refinement of the crystal structure. The structure was solved by direct methods and refined isotropically to 0.109 (Mn anisotropic). This unusually high R factor is the result of severe decomposition

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*Sawyer *et al.* [15] have recently suggested that many, if not all, $[Mn^{III}$ ligand$_x]/[Mn^{II}$ ligand$_x]$ couples are better assigned to $[Mn^{II}(ligand^+)_x]/[Mn^{II}$ ligand$_x]$. These claims need to be checked by EPR and other methods since $[Mn^{III}$ ligand$_x]$ species are known to be obtainable from $[Mn^{II}$ ligand$_x]$ precursors. Oxidations of $[Co^{III}L]^-$, $[Ni^{II}L]^{2-}$ and $[Cu^{II}L]^{2-}$ complexes are undoubtedly metal centred; see refs. 16–18.

(>50%) during data collection due to loss of pyridine solvate, and bad crystal quality. We are endeavouring to overcome these problems.

Supplementary Material

Crystallographic details on $[Mn^{II}py_4(H_2O)_2]$-$[(Mn^{III}Lpy_2)_2]py_2$ are available on request from K.S.M.

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