

New Mononuclear Manganese(III) Complexes with Hexadentate (N_4O_2) Schiff Base Ligands: Synthesis, Crystal Structures, Electrochemistry, and Electron-Transfer Reactivity towards Hydroxylamine

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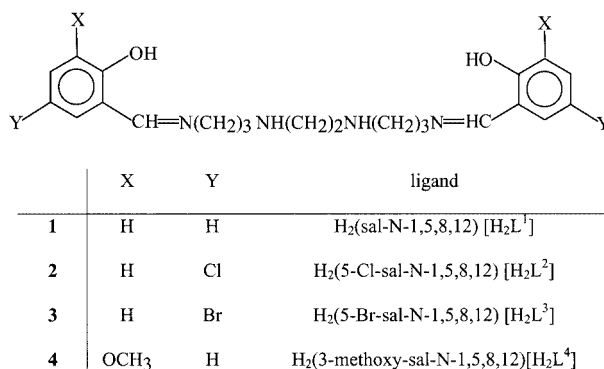
Four new manganese(III) complexes of hexadentate Schiff base ligand obtained from *N,N'*-bis(3-aminopropyl)ethylenediamine and salicylaldehyde, or salicylaldehyde derivatives having N_4O_2 donor sets – [Mn(sal-N-1,5,8,12)]ClO₄ (**1**), [Mn(5-Cl-sal-N-1,5,8,12)]ClO₄ (**2**), [Mn(5-Br-sal-N-1,5,8,12)]ClO₄ (**3**), and [Mn(3-methoxy-sal-N-1,5,8,12)]ClO₄·H₂O (**4**) – have been synthesized and characterized. The crystal structures of **1** and **4** have been determined, and the kinetics of the electron-transfer reactions between these complexes and

hydroxylamine hydrochloride have been followed spectrophotometrically in the 5.5–8.0 pH range. Similar kinetic reactivities of all the complexes towards a particular species of the reductant were noted. Hydrogen-bonded adduct formation between the reactants prior to electron transfer seems to be a possible reaction pathway, according to analysis of the experimental data.

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Introduction

An important area of investigation in the bioinorganic chemistry of manganese is the study of the structures and reactivities of manganese(III) complexes incorporating biologically relevant heteroatom donor ligands. In this regard, syntheses and characterization of manganese(III) complexes with polydentate Schiff base ligands^[1–6] have been an ongoing theme. In this communication we report the synthesis of a series of manganese(III) complexes with hexadentate Schiff base ligands possessing N_4O_2 donor sets (Scheme 1): [Mn(sal-N-1,5,8,12)]ClO₄ (**1**), [Mn(5-Cl-sal-N-1,5,8,12)]ClO₄ (**2**), [Mn(5-Br-sal-N-1,5,8,12)]ClO₄ (**3**), and [Mn(3-methoxy-sal-N-1,5,8,12)]ClO₄·H₂O (**4**). Of these compounds, **1** and **4** have been characterized by X-ray crystallography. A kinetic study of these complexes with hydroxylamine in aqueous solution has been carried out in order to determine the electron-transfer reactivity of these complexes. The mechanistic versatility noted in the reaction behavior of hydroxylamine is attractive in that it can act both as an oxidant or a reductant,^[7] and can coordinate through either the N- or the O-end.^[8] The estimated bond



Scheme 1

dissociation energy for the N–H moiety^[9] in hydroxylamine (92 kcal·mol^{–1}) is similar to that of the O–H group of tyrosine (85.5 kcal·mol^{–1}),^[10,11] and so proton movement – as observed with tyrosine in PSII – may have some relevance to the observed reactions with hydroxylamine.

Results and Discussion

Crystal Structures of [Mn^{III}sal-N(1,5,8,12)]ClO₄ (**1**) and [Mn(3-methoxy-sal-N(1,5,8,12))]ClO₄·H₂O (**4**)

Atom-labeling schemes and molecular views of complex **1** and **4** are shown in Figures 1 and 2, respectively, while selected bond lengths and angles are given in Tables 1 and 2, respectively. In each case the metal is in a hexadentate distorted MnN₄O₂ environment, the two phenolic oxygen

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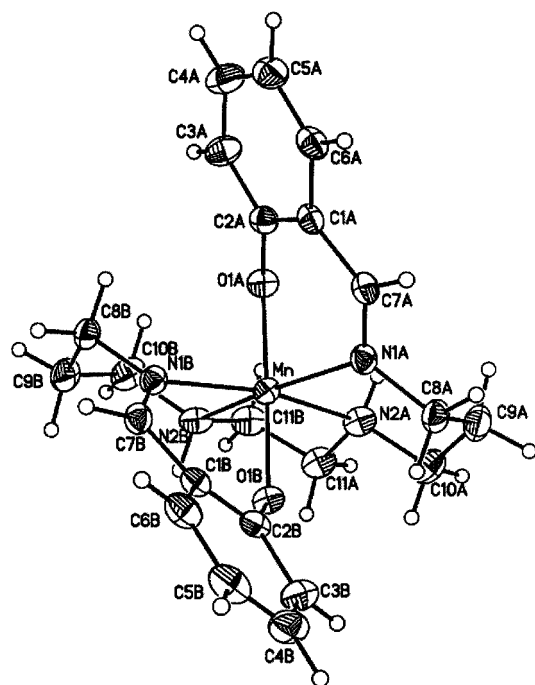


Figure 1. Molecular structure of complex **1** showing atom-labeling scheme

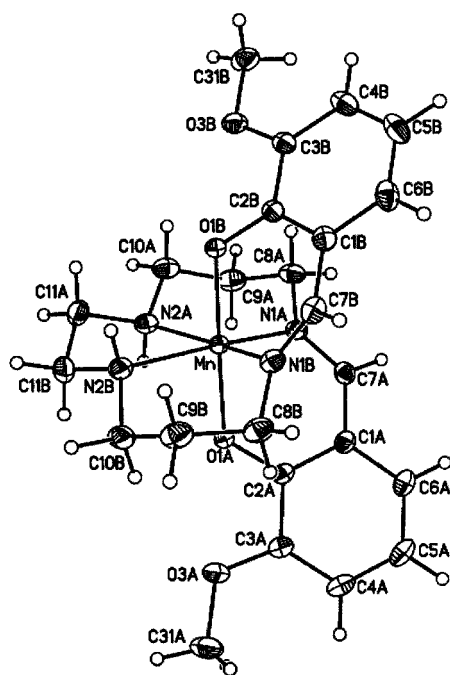


Figure 2. Molecular structure of complex **4** showing atom-labeling scheme

atoms are in a *trans* configuration, and the two coordinating ONN ligand halves are facial. The mean deviations of the manganese atom from the equatorial plane are 0.10 Å in **1** and 0.08 Å in **4**. The bond lengths are quite similar (Tables 1 and 2), the Mn–O(phenolic) lengths being 1.869(4) and 1.878(4) Å in **1** and 1.869(15) and 1.873(15) Å in **4**, the Mn–N(imine) bond lengths being 2.098(4) and

2.102(4) in **1** and 2.054(19) and 2.104(2) Å in **4**, and the Mn–N(amine) lengths being 2.207(4)/2.239(5) and 2.163(2)/2.174(2) Å, respectively. These are consistent with those reported for manganese(III) Schiff base complexes.^[1,3–5] Both the lattices are hydrogen bonded, although the hydrogen bonding is less extensive in **1**. The intramolecular hydrogen bonding here involves the N–H moiety and the phenolic oxygen of the ligand and O of the perchlorate anion. The N–H···O(phenolic) distances are 3.199(12) and 3.387(12) Å, whereas N–H···O(perchlorate) is 3.098(18) Å. In **4**, on the other hand, the coordinated water molecule, together with the phenolic oxygen, amine nitrogen (N–H), and perchlorate anion, constitute a network (Figure 3). Both intra- and intermolecular hydrogen bonding are observed, the O(1W)–H···O(phenolic) distances being 2.858(3) and 2.837(7) Å, whereas the O(1W)–H···O(perchlorate) distances are 2.638(10), 3.196(8), and 3.227(7) Å. The amine hydrogen also enters into intramolecular hydrogen bonding with the oxygen of –OCH₃ in the aromatic ring, as well as with the H₂O molecule.

Table 1. Selected bond lengths [Å] and angles [°] for complex **1**

Mn–O(1A)	1.869(4)	Mn–O(1B)	1.878(4)
Mn–N(1A)	2.098(4)	Mn–N(1B)	2.102(4)
Mn–N(2B)	2.207(4)	Mn–N(2A)	2.239(5)
O(1A)–Mn–O(1B)	175.50(15)	O(1A)–Mn–N(1A)	87.06(16)
O(1B)–Mn–N(1A)	90.99(17)	O(1A)–Mn–N(1B)	90.41(17)
O(1B)–Mn–N(1B)	86.39(16)	N(1A)–Mn–N(1B)	109.09(17)
O(1A)–Mn–N(2B)	90.37(16)	O(1B)–Mn–N(2B)	92.52(16)
N(1A)–Mn–N(2B)	165.30(17)	N(1B)–Mn–N(2B)	85.38(17)
O(1A)–Mn–N(2A)	95.25(18)	O(1B)–Mn–N(2A)	88.65(18)
N(1A)–Mn–N(2A)	85.77(18)	N(1B)–Mn–N(2A)	164.39(17)
N(2B)–Mn–N(2A)	80.05(18)		

Table 2. Selected bond lengths [Å] and angles [°] for complex **4**

Mn–O(1B)	1.8692(15)	Mn–O(1A)	1.8733(15)
Mn–N(1A)	2.0544(19)	Mn–N(1B)	2.104(2)
Mn–N(2B)	2.163(2)	Mn–N(2A)	2.174(2)
O(1B)–Mn–O(1A)	178.49(7)	O(1B)–Mn–N(1A)	92.42(7)
O(1A)–Mn–N(1A)	86.07(7)	O(1B)–Mn–N(1B)	87.44(8)
O(1A)–Mn–N(1B)	92.98(8)	N(1A)–Mn–N(1B)	104.02(8)
O(1B)–Mn–N(2B)	93.08(7)	O(1A)–Mn–N(2B)	88.40(8)
N(1A)–Mn–N(2B)	169.31(9)	N(1B)–Mn–N(2B)	85.39(9)
O(1B)–Mn–N(2A)	87.56(7)	O(1A)–Mn–N(2A)	92.36(8)
N(1A)–Mn–N(2A)	89.59(8)	N(1B)–Mn–N(2A)	165.69(8)
N(2B)–Mn–N(2A)	81.49(8)		

UV/Visible and IR Spectroscopy

The electronic absorption spectra for all the complexes **1–4** were recorded in acetonitrile, and data are given in Table 3. All the complexes exhibit similar spectral features. There are four important regions in the UV/Vis spectra for this set of complexes. The least intense bands appear in the 630–660 nm range, while another band of higher intensity is observed in the 510–540 nm range. The UV/Vis spectra

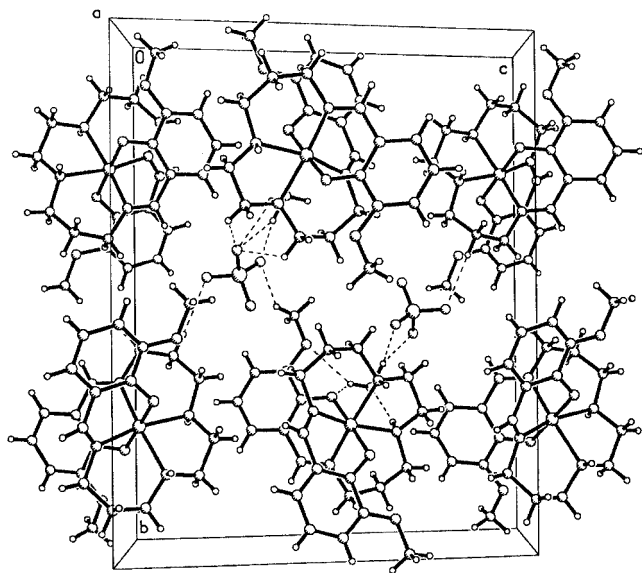


Figure 3. Molecular packing of **4** showing both intra- and inter-molecular hydrogen bonding

Table 3. UV/Visible spectroscopic data for the complexes **1–4**

Complex	$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
1	640 sh (245), 512 (881), 342 sh (5670), 271 (22390), 226 (36180)
2	653 sh (209), 516 (773), 332 sh (5670), 268 sh (17250), 223 (43580)
3	656 sh (212), 517 (820), 335 sh (6090), 269 sh (17970), 226 (43440)
4	660 sh (403), 534 (1270), 364 sh (5670), 284 (21640), 231 (46260)

of all the complexes show ligand to metal charge-transfer bands in the 330–370 nm region. These bands are similar to those reported for hexacoordinate $[\text{Mn}^{\text{III}}(\text{BBPEN})](\text{PF}_6)$ [$\text{H}_2\text{BBPEN} = N,N'$ -bis(2-hydroxybenzyl)- N,N' -bis(2-methylpyridyl)ethylenediamine] with N_4O_2 donor sets.^[12] The intense higher-energy bands in the region 220–280 nm are usually attributed to intraligand $\pi \rightarrow \pi^*$ transitions, as observed previously for manganese(III) ions in octahedral environments.^[6,12–15] It is interesting to note that all the bands are affected by the benzene ring substitution, which indicates that the frontier molecular orbitals of the high-spin manganese(III) complexes possess significant contribution from the ligands.

In order to provide some insight into the nature of redox and spectroscopically relevant orbitals, extended Hückel MO calculations, using the crystallographic parameters of **1** and **4**, were performed with the aid of the CACAO program (Figure S1 and Figure S2 in the Supplementary Material, see footnote on the first page of this article).^[16] The lowest unoccupied molecular orbital (LUMO) of **1** was found to be strongly delocalized, with 61% metal contribution and 29% ligand contribution. The HOMO, on the other hand, is predominantly metal-based (84%), with little contribution from the ligand (6%). The closely spaced

($\Delta E = 0.036 \text{ eV}$) HOMO-1 also has the same character, but with less contribution from the metal orbitals (72% metal and 17% ligand). In **4**, the LUMO is also strongly delocalized, with a little more contribution from the ligand (58% metal and 33% ligand) relative to **1**. Two closely spaced ($\Delta E = 0.071 \text{ eV}$) HOMO (83% metal and 7% ligand) and HOMO-1 (64% metal and 30% ligand) orbitals are also delocalized, with a greater contribution from the metal in the former than in the latter.

The EHMO calculations indicate that the frontier molecular orbitals are predominantly metal-based, but with significant contributions from the ligands. The bands in the 630–660 nm range can therefore be assigned as predominantly d-d with some admixed MLCT character. These bands are similar to those reported previously for manganese(III)–Schiff base complexes.^[6,12,13,17] The bands in the 510–540 nm range have previously been attributed to phenolato-to-manganese(III) LMCT for similar Mn^{III} complexes.^[8,14,15,17] The EHMO calculations, however, indicate that all the frontier MOs are predominantly metal-based with significant contribution from the ligands, so the above assignment is not unambiguous. From the X-ray crystal data, the observed $\text{Mn}^{\text{III}}\text{–O}(\text{phenolate})$ average bond lengths are 1.873 Å for **1** and 1.871 Å for **4**, which is quite short in comparison with the reported values for manganese(III) complexes.^[5,14,15,18] The shift of the 510–540 nm bands to much lower energy compared to those (ca. 480–490 nm) reported earlier indicates stronger interaction between the phenolato(O) and manganese(III) center^[12] and supports the assignment of the 510–540 nm bands as LMCT from phenolato-to- Mn^{III} .

All the complexes show similar IR spectral features, each exhibiting a strong band attributable to $\nu(\text{CN})$ between 1620–1627 cm^{-1} . All of them also show broad unsplit bands at 1081–1095 cm^{-1} , together with bands at 626–627 cm^{-1} indicative of the presence of a noncoordinated perchlorate counterion. As well as these, **4** exhibits a broad band at 3550 cm^{-1} due to the presence of a non-coordinated water molecule in the crystal, which is consistent with the molecular structure.

Electrochemical Studies

Cyclic voltammograms of all the Mn^{III} complexes were recorded in acetonitrile solution with TEAP as supporting electrolyte in the potential range from –1.2 to +1.2 V vs. SCE. The results are summarized in Table 4. As the cyclic voltammetric features of all the complexes are similar, a representative profile for **3** is shown in Figure 4. A notable feature for all the complexes is that an electrochemically quasi-reversible anodic wave and two well defined irreversible cathodic waves are detected. The anodic process corresponds to the $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ couple, and the peak-to-peak separation lies between 80 mV to 120 mV, slightly above the value expected for a one-electron electrochemically reversible process.^[19] The first irreversible cathodic process can be attributed to the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ couple, in line with previously reported complexes of similar ligand environment.^[1,13] The irreversibility of the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ couple might be due to the

Table 4. Cyclic voltammetric results^[a] for manganese(III) complexes at 298 K

Complex ^[a]	Mn ^{IV} /Mn ^{III} <i>E</i> _{pa} /V	Mn ^{III} /Mn ^{II} <i>E</i> _{pc} /V	Δ <i>E</i> _p /V	(<i>E</i> _{1/2})/V	<i>E</i> _{pc} /V
1	0.66	0.54	0.12	0.60	−0.60
2	0.78	0.68	0.10	0.67	−0.52
3	0.78	0.70	0.08	0.70	−0.54
4	0.64	0.55	0.09	0.59	−0.58

^[a] Solvent: acetonitrile; working electrode: platinum; reference electrode: SCE; *E*_{pa} and *E*_{pc} are anodic and cathodic peak potentials respectively; *E*_{1/2} = 0.5(*E*_{pa} + *E*_{pc}); Δ*E*_p = *E*_{pa} − *E*_{pc}; scan rate: 50 mV·s^{−1}.

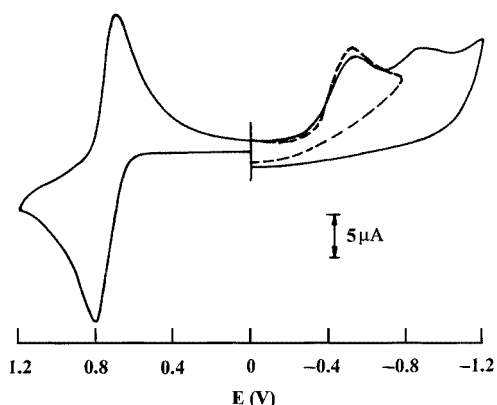


Figure 4. Cyclic voltammogram (scan rate 50 mV·s^{−1}) of complex 3 in acetonitrile at a platinum electrode with ferrocene as internal standard and TEAP as supporting electrolyte

instability of the formally Mn^{II} species.^[20] The second cathodic process is very difficult to assign. It has been observed that the cyclic voltammogram of the free ligands features an irreversible reduction at about −1.0 V. The more negative (ca. −0.88 V) cathodic process in the complex is close to that observed for the free ligand. This chemical environment is not suitable to stabilize the Mn(I) state, and Mn^{II}/Mn^I couples are not usually observed for this type of complexes.^[14] Because of the instability of the formally Mn^{II} species, there might be free ligand (probably protonated) available in the solution, resulting in the second irreversible cathodic wave.^[20] The electrochemical results are consistent with those observed previously for manganese(III) complexes.^[1,12,21] In the group of complexes at hand, both the *E*_{pc} and *E*_{1/2} values are sensitive to substitution, both increasing with increasing electron-withdrawing power of the substituents. The standard extended Hückel MO calculation indicates that the frontier molecular orbitals are predominantly metal-based with significant contribution from the ligands. The ligand contribution both to the HOMO and to the LUMO is reflected in the change in the redox potentials with substitution in the benzene ring.

Electron-Transfer Reactivity

The electron-transfer reactivities of all four complexes were studied in the 5.5–8.0 pH range, with hydroxylamine

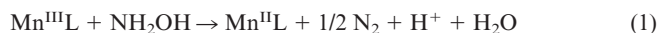
as the reducing agent. The redox chemistry of hydroxylamine in solution is very complicated, due to its oxidation to various products depending upon the nature of the oxidants. It has been observed that the most common oxidation products of hydroxylamine are N₂O and N₂,^[8,22–24] oxidation of hydroxylamine to NO₂[−], NO₃[−], and NO^[22–24] being relatively rare.

Stoichiometry

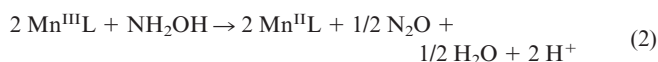
Because of the formation of various products and the complicated redox chemistry involved, variable stoichiometry has usually been encountered for the oxidation of hydroxylamine by various oxidants.^[8,22,23] The stoichiometry was therefore examined very carefully in the presence both of excess reductant and of excess oxidant. In the presence of excess hydroxylamine over the complexes, the stoichiometry was determined by bromatometric estimation of the unchanged reductant,^[25] whereas in the presence of excess oxidant, the stoichiometry was measured spectrophotometrically with the aid of the known extinction coefficient of the complex (*λ*_{max} = 517 nm, ε = 820 dm³ mol^{−1}·cm^{−1} for complex 3). The results in Table 5 also imply a variable stoichiometry in our system. Thus, under the kinetic reaction conditions, the “putative first step” of the reaction may be given as shown in the following equations.

Table 5. Stoichiometry of the reduction of complex 3 by hydroxylamine hydrochloride (all concentrations are in mmol·dm^{−3}) at 30 °C

[Complex]	pH	[NH ₂ OH]	Δ[complex]/Δ[NH ₂ OH]
3.00	5.50	30.0	1.05
3.00	5.50	15.0	0.97
20.0	5.50	2.00	1.95
10.0	5.50	2.00	1.75
3.00	8.00	30.0	1.03
3.00	8.00	12.0	1.20
20.0	8.00	2.00	1.98



and with an excess of Mn^{III}



The appearance of a six-line EPR signal in the *g* = 2.0 region indicates that at least some complex is in the +2 state in the final form, thus supporting the above mechanism. The electrochemical study shows that the formally Mn^{II}L species formed upon reduction of the parent complexes are unstable and readily decompose. The decomposed species may be hydrated Mn²⁺ ion in aqueous solution, together with free ligand. The formulation of the reduced product as Mn^{II}L is therefore not unambiguous. However, externally added Mn²⁺ ion in the form of

$\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ was found to exert no effect on the rate of the reactions, indicating that the reduced product of the complexes has no influence on the electron transfer rate.

Kinetics and Mechanism

The kinetics of the oxidation of NH_2OH were observed under pseudo first-order conditions, with the reductant being maintained in large excess over the complex. At a fixed hydrogen ion concentration and ionic strength ($\text{pH} = 6.0$, $I = 0.2 \text{ mol} \cdot \text{dm}^{-3}$ (NaCl), $[\text{phosphate}] = 0.05 \text{ mol} \cdot \text{dm}^{-3}$, temperature = 30°C and $\lambda = 360 \text{ nm}$), the observed rate constants ($k_{\text{obsd.}}/\text{s}^{-1}$) [Table 6] follow rate saturation kinetics at higher values of $[\text{NH}_2\text{OH}]$ for all the complexes **1–4**. These observations are consistent with the theoretical rate law in Equation (3).

Table 6. Pseudo-first order rate constants ($k_{\text{obsd.}}/\text{s}^{-1}$) for the oxidation of NH_2OH by the complexes **1–4** at a fixed pH of 6.0 {kinetic conditions: $[\text{complex}] = 5\text{--}6 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, $I = 0.20 \text{ mol} \cdot \text{dm}^{-3}$ (NaCl), $[\text{buffer}] = 0.05 \text{ mol} \cdot \text{dm}^{-3}$ (phosphate), 30°C }

$10^3 [\text{NH}_2\text{OH}]$ [$\text{mol} \cdot \text{dm}^{-3}$]	$[\text{NaCl}]^{[a]}$ [$\text{mol} \cdot \text{dm}^{-3}$]	mol % D_2O	$10^3 k_{\text{obsd.}} [\text{s}^{-1}]$			
			1	2	3	4
0.6		0	2.86	3.88	4.01	1.36
0.6		50	2.85			
0.6		90	2.82			
0.6	0.2		3.22			
0.6	0.4		3.20			
0.6	0.8		3.20			
0.8			3.65	4.19	4.60	1.48
1.0			4.28	4.65	5.00	1.68
3.0			6.63	6.61	7.68	3.25
5.0			7.68	7.99	9.29	3.88
7.0			7.88	8.93	9.57	4.05
10			8.31	9.68	11.1	4.33

[a] $I = 1.0 \text{ mol} \cdot \text{dm}^{-3}$ (NaNO_3).

$$k_{\text{obsd.}} = (k Q [\text{NH}_2\text{OH}]) / (1 + Q [\text{NH}_2\text{OH}]) \quad (3)$$

where Q is the association constant between the complex and the reductant prior to the electron-transfer reaction, and the parameters derived by fitting the experimental data to above equation at pH 6.0 are:

- (i) $k = (9.4 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ and $Q = (791 \pm 37)$ for **1**
- (ii) $k = (1.03 \pm 0.05) \times 10^{-2} \text{ s}^{-1}$ and $Q = (820 \pm 130)$ for **2**
- (iii) $k = (1.20 \pm 0.05) \times 10^{-2} \text{ s}^{-1}$ and $Q = (792 \pm 98)$ for **3**
- (iv) $k = (5.20 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ and $Q = (527 \pm 39.8)$ for **4**

The effect of pH on the rate of reaction was studied at a constant concentration of NH_2OH ($6 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$) at which a strict first-order dependence is valid. The observed rate constants decrease with increasing pH (Table 7). Figure 5 shows the plot of k_{ox} vs. $[\text{H}^+]$. The observations are not unprecedented, similar findings having been made in the reaction between this reductant and several mononuclear and polynuclear manganese complexes reported previously,^[9,26,27] and have been attributed to the generation of more reactive aquated derivatives of the complexes. The

complexes **1–4** are octahedral, with all the coordination sites occupied by the four N atoms and the two O atoms of the ligand. An effort was made to examine the electrochemistry of the complex at different pH values in an acetonitrile/water medium, but no variance was seen. There was also no noticeable change in the electronic spectra of the complexes when recorded at different pH values. The conclusion that can be drawn from these observations is that either only one species of the Mn^{III} complexes is present, or that the reactivity of the protonated species is identical to that of the parent species, if one exists, over the pH range studied. The pH variation results are also inconsistent with those expected from the thermodynamic potential values of the reductants. It is well documented that the deprotonated forms of the reductants are more reactive than the protonated species, due to the changed oxidation potential.^[28] On protonation, the oxidation potential of the reductant decreases significantly from +3.04 V for NH_2OH to +1.87 V for NH_3OH^+ , according to^[29]

Table 7. Pseudo-first order rate constants ($k_{\text{obsd.}}/\text{s}^{-1}$) for the oxidation of NH_2OH by the complexes **1–4** at different pH values (kinetic conditions: $[\text{NH}_2\text{OH}] = 6 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, $[\text{complex}] = 5\text{--}6 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$, $I = 0.20 \text{ mol} \cdot \text{dm}^{-3}$ (NaCl), $[\text{buffer}] = 0.05 \text{ mol} \cdot \text{dm}^{-3}$ (phosphate), 30°C)

pH	$10^4 k_{\text{obsd.}}/\text{s}^{-1}$			
	1	2	3	4
5.50	61.3	64.2	69.9	28.8
5.75	41.7	41.1	55.3	19.0
6.00	28.6	40.0	42.7	13.6
6.25	23.5	32.3	31.6	11.2
6.50	19.0	27.9	25.6	9.10
7.00	9.80	14.4	16.7	6.50
7.50	5.50	9.00	4.50	3.00
8.00	3.40	5.00	2.50	1.20

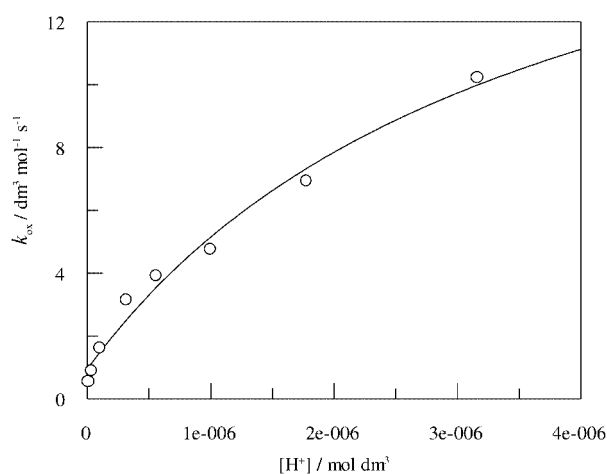
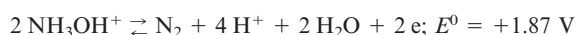
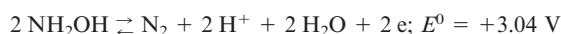
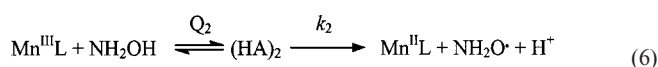
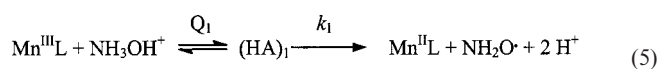


Figure 5. Plot of k_{ox} vs. $[\text{H}^+]$ for the oxidation of hydroxylamine by **1** at 30°C , $I = 0.2 \text{ mol} \cdot \text{dm}^{-3}$ (NaCl), $0.05 \text{ mol} \cdot \text{dm}^{-3}$ phosphate buffer



It is therefore unlikely that the observed decrease in k_{obsd} at higher pH values is due to the greater kinetic activity of NH_3OH^+ over NH_2OH . Rate saturation at higher $[\text{NH}_2\text{OH}]$, however, with high association constant values, and also the leveling off of rates at higher $[\text{H}^+]$, are clear indications of some sort of association between the complex and the reductant prior to the electron-transfer act. The self-exchange rate constant of the $\text{NH}_2\text{OH}/\text{NH}_2\text{OH}^+$ couple is very low ($5 \times 10^{-13} \text{ M}^{-1}\cdot\text{s}^{-1}$), with $E^0 = +0.42 \text{ V}$.^[9,22] In the absence of any accurately determined potential value for the $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}^+$ couple the self-exchange rate constant may be taken roughly as that for the $\text{NH}_2\text{OH}/\text{NH}_2\text{OH}^+$ couple.^[9] The very low self-exchange rate constant value for the $\text{NH}_3\text{OH}^+/\text{NH}_2\text{OH}^+$ couple and the poor reducing character of the protonated reductant disfavours the outer sphere electron-transfer path. The structure of the complex also discounts the possibility of the formation of a seven-coordinated adduct with the Mn^{III} center, so formation of a hydrogen-bonded adduct (HA) is more reasonable to conceive. The EHMO calculations indicate that the lowest unoccupied molecular orbitals in all the complexes are predominantly metal-based, with significant contribution from the phenoxo ligand. Initial association between the reductant and the complex could involve an interaction with the metal center in addition to hydrogen bonding with the ligand prior to the electron transfer, and would be conducive for an inner sphere mechanism. The following sequence of reactions may be proposed to explain the observed kinetics.



The termination of the free radicals for the consumption of a 1:1 ratio was reported to occur as in Equation (7).



The rate law derived from the above sequence of reactions can be given as:

$$k_{\text{ox}} = (k'_1[\text{H}^+] + k'_2K_a)/(K_a + [\text{H}^+]) \quad (8)$$

where $k_{\text{ox}} = k_{\text{obsd}}/[\text{NH}_2\text{OH}]$, $k'_1 = k_1Q_1$, and $k'_2 = k_2Q_2$.

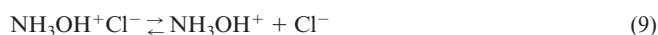
The derived kinetic parameters for all the complexes are: $k'_1 = 20.32 \pm 4.5 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k'_2 = 0.95 \pm 0.29 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ and $K_a = (3.61 \pm 0.80) \times 10^{-6}$ for **1**; $k'_1 = 13.0 \pm 1.5 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k'_2 = 1.16 \pm 0.42 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, and $K_a = (1.03 \pm 0.42) \times 10^{-6}$ for **2**; $k'_1 = 15.29 \pm 1.5 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k'_2 = 0.76 \pm 0.39 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, and $K_a =$

$(1.18 \pm 0.45) \times 10^{-6}$ for **3**; $k'_1 = 10.00 \pm 3.4 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, $k'_2 = 0.56 \pm 0.18 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$, and $K_a = (4.14 \pm 0.9) \times 10^{-6}$ for **4**.

The $\text{p}K_a$ values obtained from kinetic experiments are in good agreement with that reported for NH_2OH ($\text{p}K_a = 6.0$).^[30] The composite parameters obtained from the above rate equation are indicative of the similar kinetic reactivity of all the complexes towards a particular species of the reductant. This is also reflected in the potential values of the complexes, which fall in a narrow range. The hydrogen-bonding association between the complex and the reductant species probably occurs through the phenoxo-O of the Schiff base and the hydrogen atom of the reductant. The low association constant ($Q = 5.27 \times 10^2$) encountered in complex **4** is probably a reflection of hindered hydrogen bonding involving the phenoxo-O and the reductant species.

Effect of Chloride Ions

Salem^[27] observed that rate of the reaction between hydroxylamine and Mn^{III} -salen complex decreases considerably with increasing chloride ion concentration. It has been claimed that this is due to the lowering of redox potential as well as to the common ion effect, both of which shift the equilibrium according to Equation (9) to the left-hand side.



To examine any influence of chloride ions in our systems, we varied its concentration at a fixed ionic strength but no $[\text{Cl}^-]$ effect was observed (Table 6). We also carried out some kinetic experiments with hydroxylamine nitrate in place of hydroxylamine hydrochloride; the rate constant values were found to be unaffected. The lowering of redox potential is quite understandable for Mn^{III} -salen complex, since the Cl^- ion can occupy the axial position of Mn^{III} and produce an effect on redox potential, but this is impossible in the hexacoordinate complexes under study.

Solvent Isotope Effect

The rate saturation kinetics and pH dependence on the rate of the reaction indicate the formation of hydrogen-bonded precursor complexes between the Mn^{III} complexes and the reductant prior to the electron-transfer process. These facts prompted us to examine whether the electron-transfer path is coupled with proton movement, as in the case of tyrosine in PS II. We measured the rate constants in aqueous medium partially substituted with D_2O at a fixed concentration of NH_2OH and pH $\{[\text{NH}_2\text{OH}] = 6 \cdot 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$, $\text{pH} = 6.0$, $[\text{buffer}] = 0.05 \text{ mol}\cdot\text{dm}^{-3}$ (phosphate), $I = 0.2 \text{ mol}\cdot\text{dm}^{-3}$ (NaCl) and temp. 25°C \}. The observed rate constants in pure water are almost the same as those in a 90% D_2O /water mixture (Table 6), which rules out proton-coupled electron-transfer paths in this study.

Conclusions

The synthesis and characterization of four new manganese(III) complexes with hexadentate Schiff base ligands

with N_4O_2 donor sets – derived from N,N' -bis(3-aminopropyl)ethylenediamine and salicylaldehyde, or salicylaldehyde derivatives – are reported. Two of them have been characterized by X-ray crystallography, which shows two phenolic oxygen atoms in *trans* configurations and the two coordinating ONN ligand halves facial. Both the lattices are stabilized through extended hydrogen bonding. The ligand contribution both to the HOMO and to the LUMO is reflected in the change in the redox potentials as well as the shifting of UV/Vis spectra with substitution in benzene ring. The electron-transfer reactivities of all the complexes towards hydroxylamine in the 5.5–8.0 pH range are almost identical, as reflected in the evaluated kinetic parameters. It is also notable that the hydrogen-bonding association between the manganese(III) complexes and the reductant species probably occurs through the phenoxo-O of the Schiff base and the hydrogen atom of hydroxylamine. Chloride ion has no effect on the electron-transfer act, which contrasts with Salem's observations^[27] for an almost identical reaction with hydroxylamine. Since the estimated bond dissociation energy for the N–H of hydroxylamine is similar to that of the O–H in tyrosine, an attempt was made to examine the possibility of proton movement during the electron-transfer act. The results of solvent isotope effect studies with variable mixtures of D_2O and water do not indicate any proton-coupled electron-transfer path.

Experimental Section

Materials: Hydroxylamine hydrochloride, N,N' -bis(3-aminopropyl)ethylenediamine, salicylaldehyde, 5-bromosalicylaldehyde, 5-chlorosalicylaldehyde, and *o*-methoxysalicylaldehyde were of analytical reagent grade (Aldrich) and were used without further purification. All other chemicals – manganese perchlorate hexahydrate, NaCl, NaH_2PO_4 , acetonitrile, methanol, sodium hydroxide, and hydrochloric acid – were of reagent grade. Solvent isotope effects were examined with deuterium oxide, 99 atom% D (Aldrich).

Syntheses: All the complexes reported here were synthesized by air oxidation of solutions made up from $Mn(ClO_4)_2 \cdot 6H_2O$ and the Schiff base, by the same general procedure. A typical preparation is outlined below. (**Caution!** Although no problems have been encountered in this work, perchlorates are potentially explosive and should be handled with care and only in small quantities).

[Mn(sal-N-1,5,8,12)]ClO₄ (1): N,N' -Bis(3-aminopropyl)ethylenediamine (1.74 g, 0.01 mol) was added to an ethanol (30 cm³) solution of salicylaldehyde (2.44 g, 0.02 mol). The yellowish orange solution was brought to reflux for 1 h and then allowed to cool to room temperature, which was followed by the dropwise addition of $Mn(ClO_4)_2 \cdot 6H_2O$ (3.61 g, 0.01 mol) dissolved in ethanol (20 cm³). The resulting dark brown solution was heated at reflux for 30 min. On subsequent cooling to room temperature, a microcrystalline compound separated out and was collected by filtration, washed with cold ethanol and diethyl ether, and dried under vacuum. Yield: 4.54 g, 85%. $C_{22}H_{28}ClMnN_4O_6$ (534.9): calcd. C 49.35, H 5.23, N 10.46; found C 49.21, H 5.26, N 10.28%. FTIR (KBr, cm⁻¹): $\nu(C=N)$ 1625, $\nu(C-O)$ 1280, $\nu(ClO_4^-)$ 1095 and 627. μ_{eff} 4.91 BM.

[Mn(5-Cl-sal-N-1,5,8,12)]ClO₄ (2): Yield: 4.94 g, 82%. $C_{22}H_{26}Cl_3MnN_4O_6$ (603.8): calcd. C 43.74, H 4.31, N 9.28; found C 43.63, H 4.49, N 9.19%. FTIR (KBr, cm⁻¹): $\nu(C=N)$ 1624, $\nu(C-O)$ 1281, $\nu(ClO_4^-)$ 1088 and 626. μ_{eff} 4.89 BM.

[Mn(5-Br-sal-N-1,5,8,12)]ClO₄ (3): Yield: 5.54 g, 80%. $C_{22}H_{26}Br_2ClMnN_4O_6$ (692.7): calcd. C 38.13, H 3.75, N 8.09; found C 38.23, H 3.76, N 7.89%. FTIR (KBr, cm⁻¹): $\nu(C=N)$ 1627, $\nu(C-O)$ 1283, $\nu(ClO_4^-)$ 1088 and 627. μ_{eff} 4.94 BM.

[Mn(3-methoxy-sal-N-1,5,8,12)]ClO₄·H₂O (4): Yield: 5.08 g, 83%. $C_{24}H_{34}ClMnN_4O_9$ (612.9): calcd. C 47.02, H 5.55, N 9.14; found C 47.13, H 5.49, N 9.01%. FTIR (KBr, cm⁻¹): $\nu(C=N)$ 1621, $\nu(C-O)$ 1281, $\nu(ClO_4^-)$ 1082 and 627, $\nu(O-H)$ 3550. μ_{eff} 4.92 BM.

Physical Measurements: Microanalysis (CHN) was performed in a Perkin–Elmer 240C elemental analyzer. Magnetic susceptibility measurement was carried out on a PAR 155 vibrating sample magnetometer. The EPR spectra were obtained on a Varian model 109 E-line X-band spectrometer equipped with a low-temperature quartz Dewar for measurements at 77 K. pH measurements were made with a Systronics digital pH meter (model 335, India). The observed pH was corrected by using the relationship, $pH = -\log[H^+] = pH_{obsd} \pm 0.02$. IR spectra were obtained on a Nicolet, MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Cyclic voltammetry (scan rate of 0.05 V·s⁻¹) was performed at a platinum electrode with an EG&G PARC electrochemical analysis system (model 250/5/0) in acetonitrile under dry nitrogen atmosphere in conventional three-electrode configurations.

Kinetic Measurements: Spectral and kinetic measurements were performed in an UV/Vis spectrophotometer (UV-2100, Shimadzu, Japan) with thermostatted cell compartments. The disappearance of the complex peak was monitored at 360 nm as a function of time. All the measurements were made under pseudo first-order conditions with use of an excess of hydroxylamine and a constant ionic strength of 0.2 mol·dm⁻³ (NaCl) with 0.05 mol·dm⁻³ phosphate buffer at 30 °C. The corresponding rate constants were evaluated by means of a suitable nonlinear curve fit program with data taken for at least three half-lives of the reactions. Every rate constant reported here represents the mean value of at least three determinations that fall within $\pm 5\%$.

Crystal Structure Determination and Structural Refinements of Complexes 1 and 4: Single crystals of **1** were grown from acetonitrile/ethanol solution, and single crystals of **4** were obtained from acetonitrile/methanol solution. Each crystal was then mounted on an automatic Bruker P4 diffractometer equipped with graphite monochromated Mo- K_α radiation ($\lambda = 0.71073$ Å). Unit cell dimensions and intensity data were measured at 296 K. The structure was solved by direct methods and refined by full-matrix, least-squares based on F^2 with anisotropic thermal parameters for non-hydrogen atoms by use of Bruker SHELXTL (data reduction), SHELXS^[31] (structure solution), and SHELXL^[32] (structure refinement). The hydrogen atoms were included in structure factor calculations in their idealized positions. Information concerning crystallographic data collection and refinement of the structures is compiled in Table 8.

CCDC-191275 and -191276 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44–1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 8. Crystal data and structure refinement for complexes **1** and **4**

Complex	1	4
Empirical formula	C ₂₂ H ₂₈ ClMnN ₄ O ₆	C ₂₄ H ₃₄ ClMnN ₄ O ₉
Molecular mass	534.87	612.94
Crystal system	orthorhombic	monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
a [Å]	7.800(3)	8.056(6)
b [Å]	17.359(8)	20.501(10)
c [Å]	17.891(6)	16.737(9)
β [°]	90.00	101.831(6)
V [Å ³]	2422.5(17)	2705.5(3)
Z	4	4
T [K]	296(2)	296(2)
μ(Mo-K _α) [mm ⁻¹]	0.700	0.646
Reflections collected	3957	6871
Independent reflections (R _{int})	3755 (0.0565)	6222(0.013)
Final R ₁ wR ₂	0.051 0.121	0.046 0.116
[I > 2σ(I)]		

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