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Influence of second sphere hydrogen bonding interaction on a manganese(II)-aquo complex†

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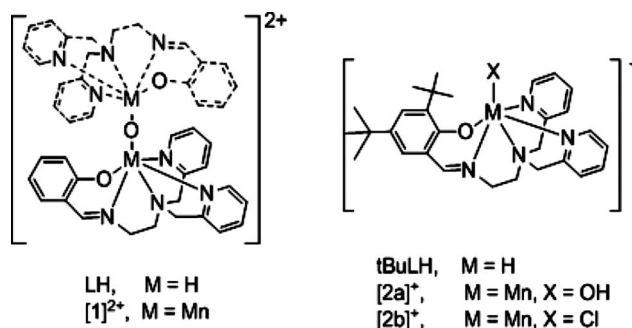
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We have developed a pentadentate N₄O ligand scaffold with a benzimidazole group placed in a rigid fashion to develop hydrogen bonding interaction with the ligand in the sixth position. The mononuclear Mn(II) complex with a water molecule was isolated and characterized. We discuss the role of the outer sphere ligand in stabilising a Mn(II)-aquo complex.

During these past few years, there has been a growing recognition for the role of outer sphere ligands on the structure/reactivity relationship of several active sites of metalloenzymes.¹ For instance, different amino acid residues often located in the surrounding of the metal ion provide additional control in the binding and activation of small molecules and also offer ways to modulate the chemical reactivity of the metal ion through hydrogen bonding. Introducing such a degree of sophistication in synthetic models is a challenging task for a synthetic chemist. Remarkable effects have already been observed on the metal activation of dioxygen and water through the judicious positioning of a hydrogen bonding network in the second coordination sphere of both manganese and iron based complexes.² Collman and colleagues have been pioneers in the design of hydrogen bonded cavities on the porphyrin core to stabilise the dioxygen adduct.³

In the course of our study on manganese complexes, we have shown that the pentadentate N₄O monoanionic ligand LH, (Scheme 1) leads to the formation of a mono-μ-oxo dinuclear manganese(III) complex [1]²⁺.⁴ All attempts to isolate the mononuclear manganese species, either in the +II or +III oxidation states with an axially bound water molecule, have proved unsuccessful. In a more recent study, we have shown that adding a bulky *tert*-butyl



Scheme 1

group in the *ortho*- and *para*-positions of the phenol (tBuLH, Scheme 1), we could isolate a manganese(III) complex bearing a hydroxo ligand in the available sixth coordination site on the metal centre, complex [2a]⁺. Electrochemical study indicates a reversible Mn^{III/II} process on a cyclic voltammogram scale at quite a negative potential ($E^{\circ}_{\text{Mn}^{\text{III}}\text{OH}+\text{H}_2\text{O}/\text{Mn}^{\text{II}}\text{OH}_2+\text{OH}^-} = -0.35 \text{ V vs. SCE}$) in the presence of water.⁵ It has been argued that hydrogen bonding in the second coordination sphere can also help to prevent the formation of the M–O–M motif and at the same time stabilise highly oxidised Metal–Oxo units.^{6–8}

With the aim to understand the stepwise activation of a manganese bound water molecule, we reasoned that the N₄O ligand skeleton stands as a good candidate to implement a functional group that could develop hydrogen bonding with a bound water molecule. We report here on the synthesis of a novel derivative of the N₄O ligand covalently assembled with a benzimidazole as a potential donor for hydrogen bonding. The crystallographic structure of the mononuclear Mn(II) complex with a bound water molecule evidenced a hydrogen bonding interaction between the water and the protonated form of the benzimidazole unit. We also report on the spectroscopic characterisation and electrochemical properties of the analogous chloro Mn(II) derivative. Further comparison with compounds [2a]⁺ and [2b]⁺ helps to account for the contribution of the second coordination sphere.

The synthetic pathway leading to the target ligand (LH₂) is presented in Scheme 2. The benzimidazole fragment was positioned in an *ortho* position of the phenol group (compound (a)) and was obtained in good yield by reaction of one equivalent of 1,2-diamino benzene with 5-*tert*-Butyl-2-hydroxybenzaldehyde in the presence of benzofuroxane.⁹ The introduction of a formyl group on (a), was realised by the Duff procedure, treatment with

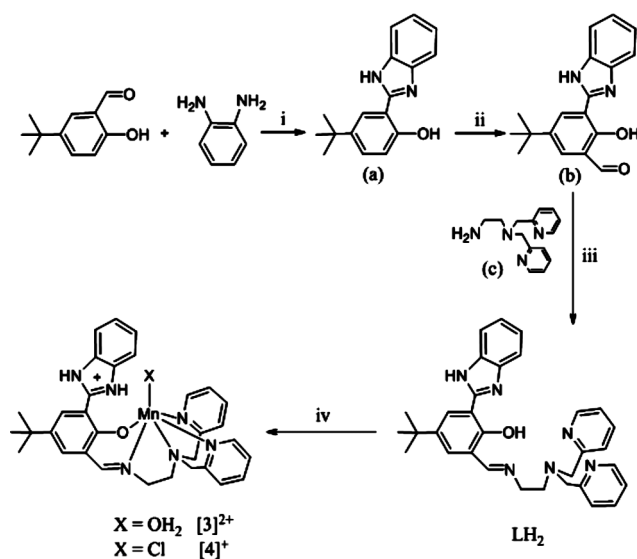
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Scheme 2 (i) 1 eq of benzofuroxane/methanol/60 °C 4h; (ii) HMT/TFA reflux 2 days; (iii) (c)/ethanol under argon, (iv) ethanol, $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ for $[3]^{2+}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}/\text{NaPF}_6$ for $[4]^+$.

hexamethyltetramine in trifluoroacetic acid followed by hydrolysis in basic medium gave (b).¹⁰ The condensation of the aldehyde derivative (b) on the primary amine (c) in ethanol under argon leads to ligand LH_2 , which was isolated as a brown oil. The metallation was performed in ethanol upon treatment of the ligand LH_2 with the manganese(II) perchlorate salt yielding the complex $[3]^{2+}$ as a pale yellow solid. The same synthesis was also realised with MnCl_2 with the aim to have a chloride ligand in the sixth position, complex $[4]^+$ (see ESI†).

X-band EPR spectra obtained on the isolated powders exhibit broad resonances over a wide range of magnetic field, supporting a Mn(II) complex and excluding a mononuclear manganese in a +III oxidation state which would be EPR silent under these conditions (*vide infra* and ESI†). The X-ray analysis of complex $[3](\text{ClO}_4)_2$ (Fig. 1) points to several structural features that need to be mentioned. Two perchlorate ions accompany each manganese unit. Given the monoanionic nature of the N_4O ligand, the +2 charge of the manganese complex can be explained by the

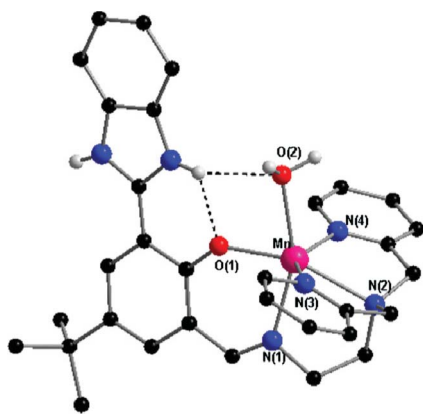


Fig. 1 Crystal structure of $[3]^{2+}$. Hydrogen atoms counter anions and solvent molecules were omitted for clarity. Selected metric distances (Å): Mn–N(1) 2.233(5), Mn–N(2) 2.363(5), Mn–N(3) 2.164(4), Mn–N(4) 2.190(4), Mn–O(1) 2.056(4), Mn–O(2) 2.292(4).

presence of the protonated form of the benzimidazole. This stems from the deprotonation of the phenol group upon metallation with the manganese(II) ion performed in the absence of external base. The manganese(II) ion is wrapped by the N_4O ligand and a water molecule completes the coordination sphere. The mean Mn–N bond distance is 2.2 Å while the water molecule is at 2.291 Å from the manganese.¹¹

A noticeable feature of this structure is the presence of a bifurcated hydrogen bond between the proton from the $\text{N}^+\text{–H}$ group of the benzimidazolium fragment with the oxygen atom of the phenolate group on one side and the oxygen of the metal bound water molecule on the other. The former hydrogen bond being the major component, with the $\text{N–H} \cdots \text{O}(1)$ distance of 2.53 Å and the latter as the minor component with the $\text{N–H} \cdots \text{O}(2)$ distance of 3.23 Å respectively. The presence of the hydrogen bond between the metal bound water molecule and the hydrogen donor group, the $\text{N}^+\text{–H}$ group of the benzimidazolium fragment leads to a pronounced tilt of the water molecule towards hydrogen donor component. This is clearly evidenced by the angle sustained at the metal ion by the O(1) atom of the phenol and O(2) of the water molecule found at 77.7°¹² while a value of 94.1° was found for the angle of the Mn(III) derivative $[2a]^+$ with an axial hydroxo group.⁵

The electrochemical behaviour of the manganese complexes $[3]^{2+}$ and $[4]^+$ was studied in acetonitrile (Fig. 2) and compared to the corresponding derivative with a *tert*-butyl group ($[2a]^+$ and $[2b]^+$).^{5,13} The cyclic voltammogram of compound $[4]^+$ shows one quasi-reversible anodic wave at 0.5 V vs. SCE that was assigned to the $\text{Mn}^{\text{III/II}}$ process.

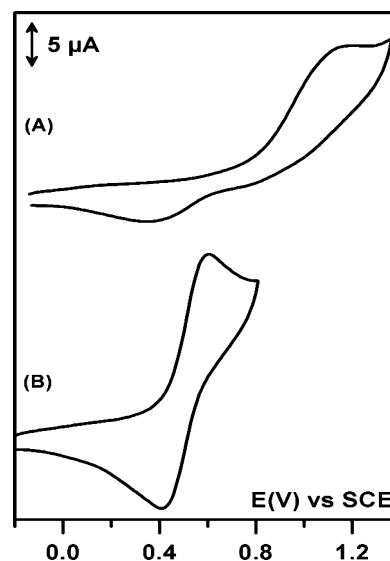


Fig. 2 Cyclic voltammetry of (2 mM) solution in acetonitrile at 0.1 V s^{-1} , $T = 273 \text{ K}$, on a glassy carbon electrode (0.1 M NBu_4PF_6), (A) $[3](\text{ClO}_4)_2$, (B) $[4](\text{PF}_6)$.

A mere comparison with the redox potential observed for the corresponding *tert*-butyl derivative ($[2b]^+$) (Table 1) indicates a shift of about 400 mV to more positive potentials. This can be partly due to the strong hydrogen bonding between the proton donor $\text{N}^+\text{–H}$ fragment of the benzimidazolium and the phenolate oxygen atom, thereby diminishing the donating power of the phenolate group.

Table 1 $E_{1/2}^a$ values (V vs. SCE) and E_p^a (for irreversible processes) for complexes [3](ClO₄)₂ and [4](PF₆) in acetonitrile (0.1 M Bu₄NPF₆) and related complexes

	Mn ^{III} /Mn ^{II}	Mn ^{IV} /Mn ^{III}
	$E_{1/2}(\Delta E_p/\text{mV})$	$E_{1/2}(\Delta E_p/\text{mV})$
[3] ²⁺	1.1 (irr)	—
[4] ⁺	0.50 (196)	—
[2a] ⁺	−0.35 (117) ^a	0.82 (117) ^a
[2b] ⁺	0.10 (96) ^b	1.1 (96) ^b
[2aH] ²⁺	0.32 (~200) ^{a,c}	

^a ref. 5; ^b ref. 13, ^c [2aH]²⁺ stands for the aqua form of [2a]⁺ in which the hydroxo ligand is protonated.

For compound [3]²⁺, we observed one irreversible anodic process at ca. 1.1 V vs. SCE. This value is close to the one reported in the case of [L_{N5}Mn(II)(OH₂)]²⁺ complex ($E_p^a = 1.4$ V vs. SCE) where L_{N5} stands for a pentadentate nitrogen containing ligand.¹⁴ In the present case, the destabilisation of the Mn(III) oxidation state, contrary to the previously reported Mn(III)-aqua complex [2c]⁺ agrees with the decrease of the donating power of the phenolate group. The irreversibility of the process is characteristic of an EC mechanism¹⁵ as reported for complex [L_{N5}Mn(II)(OH₂)]²⁺¹⁴ this irreversibility is attributed to arise from the deprotonation of a bound water molecule upon oxidation.

A controlled potential coulometric experiment at 1.3 V vs. SCE confirmed a one-electron oxidation process and was monitored by EPR spectroscopy (see Fig. 3).

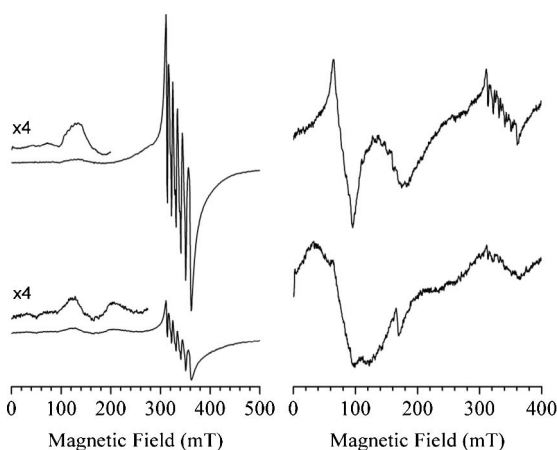


Fig. 3 EPR spectra recorded in the perpendicular (left panel) and parallel (right panel) mode for [3](ClO₄)₂ before (bottom spectra) and after (top spectra) exhaustive oxidative electrolysis at 1.3 V vs. SCE at 273 K in acetonitrile.

Before electrolysis, the perpendicular mode EPR spectrum exhibits large resonances in the 0–300 mT range comparable to what was observed in the powder (see ESI†) and attributable to the mononuclear Mn(II) complex (the 6-line pattern at $g = 2$ is due to free Mn(II) impurities which was estimated to be about 12% of the total amount of Mn present). Upon exhaustive oxidation, the EPR signal of the initial Mn(II) complex disappears in favor of a mixture of Mn(IV) complex detected in perpendicular mode with a

characteristic signal above 100 mT¹⁶ and Mn(III) complex detected in parallel mode with a signal below 100 mT. We also note an increase in free Mn(II) content. Taken together these results agree with the formation of a Mn(III) complex upon electrolysis that further chemically reacts, likely by dismutation, as supported by the irreversibility of the wave observed in the cyclic voltammetry.

We have reported here on the functionalisation of the second coordination sphere of a manganese complex. We have shown that the presence of an imidazolium group in hydrogen bonding interaction with a manganese bound water molecule shifts the redox potential to more positive values. The irreversible nature of the one electron oxidised species leading to the Mn(III) species was explained by a dismutation reaction. Further efforts to design more robust manganese based systems introducing at the same time a second coordination sphere to understand the initial steps of water activation are going on in our laboratory.

Acknowledgements

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