Influence of the Electrochemical Conversion of [(LH)Mn^{II}Cl$_2$] into [(L)Mn^{III}Cl]$^+$ on the Protonic State of a Phenol-Containing Ligand

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A bischloromanganese(II) complex [(LH)MnCl$_2$] (**1**), where LH is the pentadentate ligand *N,N*-bis(2-pyridylmethyl)-*N′*-salicylidene-ethane-1,2-diamine, has been synthesized. Elemental analysis, UV–visible, and cyclic voltammetry experiments showed that the phenol function of the ligand LH remains protonated. Exhaustive electrolysis at 1.0 V vs SCE led to the formation of the Mn^{III} derivative [(L)MnCl]$^+$ (**3**) with the concomitant expulsion of H$^+$ and Cl$^-$. The formation of the Mn^{III} species was confirmed by UV–visible spectroscopy and X-ray crystallography. Complex **1** could be regenerated by the reduction of complex **3** in the presence of H$^+$ and Cl$^-$.

Perhaps one of the most challenging tasks for bioinorganic chemists is to provide structural or functional models of the solar-powered Mn-based cluster (oxygen-evolving complex, OEC) of photosystem II, termed the "engine of life" by Barber.[1] Indeed, the OEC wrests four electrons and four protons from two molecules of water, yielding O$_2$ as the byproduct.[2,3] Mn, Cl, and Ca ions are essential cofactors for the proper functioning of the system, and proton-coupled electron transfer is the basis for the electron trade within.[4,5] Mn compounds known to oxidize water are scarce and still under debate.[6–9] Hereby, we report the electrochemical behavior of a mononuclear Mn complex where Cl$^-$ ions and the protonic state of a phenol-containing ligand, two important parameters to disentangle the chemistry of the OEC, have been analyzed.

For the majority of phenol-containing ligands that have been used in the development of Mn chemistry, this coordinating group is in a deprotonated form and is bound to the metal ion. Recently, a few structures of Mn^{II} complexes with noncoordinated or coordinated phenol groups have been reported.[10] For one of them, the corresponding Mn^{III} complex with bound phenolato has also been characterized.[10] In our laboratory, we have developed several families of ligands bearing a phenol group, to tackle the highly demanding task of providing biomimetic models for the OEC.[11] However, little attention was given to the synthesis of Mn complexes where the phenol group remains protonated. In this paper, we described the synthesis of a Mn^{II} complex with ligand LH (where LH stands for the *N,N*-bis(2-pyridylmethyl)-*N′*-salicylideneethane-1,2-diamine ligand; Chart 1) in a one-pot synthesis under an inert atmosphere.

Chart 1. Ligand LH
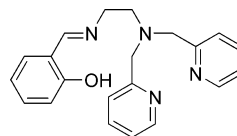
The addition of MnCl$_2$·4H$_2$O to an ethanolic solution of ligand LH in a 1:1 ratio leads to the rapid precipitation of a white powder of complex **1**, which we formulate as [(LH)MnCl$_2$] based on elemental analysis and on electrochemical investigations described below.[12] According to the work of Rompel et al.,[10] two forms are possible, one with a coordinated phenol and the other one with an uncoordinated

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(1) Barber, J. *Photosynth. Res.* **2004**, *80*, 137–144.
(2) Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S. *Science* **2004**, *303*, 1831–1838.
(3) Rutherford, A. W.; Boussac, A. *Science* **2004**, *303*, 1782–1784.
(4) Hoganson, C. W.; Babcock, G. T. *Science* **1997**, *277*, 1953–1956.
(5) Tommos, C.; Babcock, G. T. *Biochim. Biophys. Acta* **2000**, *1458*, 199–219.
(6) Naruta, Y.; Sasayama, M. A.; Sadaki, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1839–1841.
(7) Aurangzeb, N.; Hulme, C. E.; McAuliffe, C. A.; Pritchard, R. G.; Watkinson, M.; Bermejo, M. R.; Garcia-Deibe, A.; Rey, M.; Sanmartin, J.; Sousa, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1153–1155.
(8) Limburg, J.; Vrettos, J. S.; Cheng, H.; de Paula, J. C.; Crabtree, R. H.; Brudvig, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 423–430.
(9) Poulsen, A. K.; Rompel, A.; McKenzie, C. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6916–6920.
(10) Reddig, N.; Pursche, D.; Rompel, A. *J. Chem. Soc., Dalton Trans.* **2004**, 1474–1480.
(11) Hureau, C.; Sabater, L.; Anxolabéhère-Mallart, E.; Nierlich, M.; Charlot, M.-F.; Gonnet, F.; Rivière, E.; Blondin, G. *Chem.—Eur. J.* **2004**, *10*, 1998–2010.
(12) We ruled out other possible formulations such as [(LH)MnCl]Cl or [(LH)$_2$Mn$_2$Cl$_2$]Cl$_2$ based on the absence of detection of the oxidation peak of free Cl$^-$ ions by cyclic voltammetry.
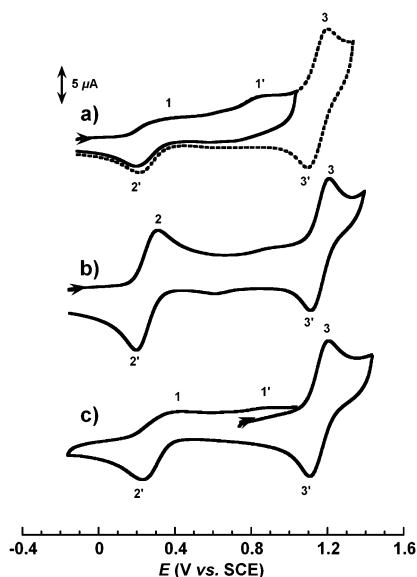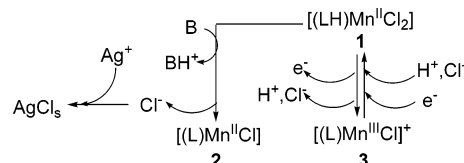
Figure 1. Cyclic voltammograms of a 0.5 mM solution of **1** in acetonitrile containing 0.1 M tetrabutylammonium perchlorate (a), in the presence of 1 equiv of 2,6-dimethylpyridine and of 1 equiv of silver perchlorate ion per Mn ion (b), and after bulk electrolysis at $E = 1.0$ V vs SCE (c). ($T = 20$ °C; scan rate = 100 mV.)

phenol.[13] Drawings of the two possible isomers are indicated in the graphical abstract. Interestingly, the electronic absorption spectrum of complex **1** exhibits an absorption band at 350 nm (Figure S1 in the Supporting Information), a value slightly lower than those observed for phenolato to Mn^{II} charge-transfer transition of related Mn^{II} complexes.[14,15] The 9.4-GHz (X-band) electron paramagnetic resonance (EPR) spectra of complex **1** in powder and solution exhibit two main transitions near 140 mT ($g = 4.7$) and 330 mT ($g = 2$), characteristic of some Mn^{II} species (Figure S2 in the Supporting Information).

The cyclic voltammetry trace of compound **1** is shown in Figure 1a. When scanning up to 1.0 V vs SCE, two anodic peaks (1 and 1′) are detected near $E^{Pa} = 0.4$ V and at $E^{Pa} = 0.85$ V vs SCE, and only one cathodic peak (2′) is detected at $E^{Pc} = 0.20$ V vs SCE on the reverse scan. It is to be noted that the value of the second anodic potential is close to the one reported for the oxidation of a similar Mn complex in a N_4Cl_2 coordination sphere.[16] Therefore, peak 1 is attributed to the isomer where the phenol is coordinated[10] to the metal center and peak 1′ to the one with an uncoordinated phenol.[10] However, if we go up to 1.4 V vs SCE, an additional reversible anodic process (peaks 3 and 3′) is detected at $E^{1/2} = 1.15$ V vs SCE. This one-electron-redox process can be attributed to the oxidation of species $[(L)MnCl]^+$ (**3**) into $[(L)MnCl]^{2+}$ based on the cyclic voltammetry signature of

(13) The possibility of a pyridinium group instead of a phenol was discarded because no cathodic peak corresponding to the reduction of a pyridinium group was observed (see ref 16).
(14) Sabater, L.; Hureau, C.; Blain, G.; Guillot, R.; Thuéry, P.; Rivière, E.; Aukauloo, A. In preparation.
(15) Horner, O.; Girerd, J.-J.; Philouze, C.; Tchertanov, L. *Inorg. Chim. Acta* **1999**, *290*, 139−144.
(16) Hureau, C.; Blondin, G.; Charlot, M.-F.; Philouze, C.; Nierlich, M.; Césario, M.; Anxolabéhère-Mallart, E. *Inorg. Chem.* **2005**, *44*, 3669−3683.

Scheme 1. Complexes **2** and **3** Obtained from Complex **1**

complex $[(L)MnCl]$ (**2**)[14] and, accordingly, the reduction process of species **3** is hereby detected at $E^{Pc} = 0.17$ V vs SCE.

The cyclic voltammetry trace of complex **1** after the addition of 1 equiv of 2,6-dimethylpyridine per Mn ion shows two new anodic peaks (2 and 5) at $E^{Pa} = 0.30$ and 1.34 V vs SCE, respectively (Figure S3 in the Supporting Information). The higher anodic process is attributed to the oxidation of free Cl^- ions, while peak 2 is in accordance with the oxidation of complex $[(L)MnCl]$ (**2**).[14] Upon the addition of 1 equiv of silver perchlorate per Mn ion, peak 5 disappears because of the precipitation of the free Cl^- ions (Figure 1b). The resulting cyclic voltammetry trace is identical with the one reported for complex **2**.[14] Consequently, we suggest that the addition of a base on species **1** induces the deprotonation of ligand LH, implying the coordination of the phenolate residue and ultimately the departure of one Cl^- ion (Scheme 1, left arrow).

The cyclic voltammetry trace of compound **1** after bulk electrolysis at $E = 1.0$ V vs SCE is shown in Figure 1c. When scanning from 0.7 V vs SCE, peak 1′ is not detected, whereas peaks 2′, 3, and 3′ are still present. Anodic processes 1 and 1′ are observed on the reverse scan. The electronic absorption spectrum of the electrolyzed solution shows characteristic features of the Mn^{III} species **3**[14] and indicates that **3** was generated with a 85% yield (Figure S1 in the Supporting Information). The fact that species **3** is formed upon the metal-centered one-electron-oxidation process pertains to the simultaneous loss of one H^+ ion and one Cl^- ion (Scheme 1, right arrow). It is noteworthy that neither the H^+ ion nor the Cl^- ion could be detected by cyclic voltammetry because HCl is weakly dissociated in acetonitrile.[17,18] The observation of both peaks 1 and 1′ on the reverse scan of the cyclic voltammetry trace recorded after bulk electrolysis (Figure 1c) suggests that reduction of species **3** into species **2**, in the presence of HCl in the medium, is accompanied by the reprotonation of the coordinated phenolate group of the L^- ligand and the recoordination of the Cl^- ion. This reverse process has been confirmed by exhaustive electrolysis at $E = -0.4$ V vs SCE of the in situ generated complex **3**, which leads to the formation of species **1** (Scheme 1, right arrow).

The various chemical and electrochemical reactions involved in the different experiments are summarized in Scheme 2. All of these coupled experiments were necessary

(17) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K. J. *J. Am. Chem. Soc.* **1961**, *83*, 3927.
(18) Izutsu, K. *Acid−Base dissociation constants in dipolar aprotic solvents*; Blackwell Scientific Publications: Brookline Village, MA, 1990; Vol. 35, p 23.

Scheme 2. Chemical and Electrochemical Reactions Involved between Complexes **1**–**3**[a]
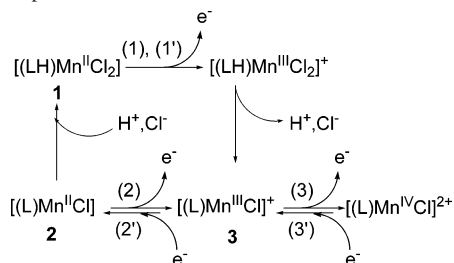
[a] The numbers in parentheses refer to the electrochemical processes observed in Figure 1 and commented on in the text.

to make conclusions on the cyclic voltammetry trace of compound **1**. Although the potential values of peaks 1 and 2 are close, peak 1 could not be attributed to the oxidation of species **2** because no equilibrium between species **1** and **2** was detected.[19] The Mn[III] complex generated by oxidation of species **1** is unstable and evolves toward the departure of HCl, through a deprotonation step of the phenol group and the exit of one metal-bonded Cl^{−} ion, to form species **3** at the electrode. This species can be reversibly oxidized into the corresponding Mn[IV] species (peaks 3 and 3′)[14] or reduced into species **2** (peak 2′).

Single crystals of species **3** were obtained from the electrolyzed solution of complex **1** and were analyzed by X-ray diffraction studies. An ORTEP view of complex **3** is shown in Figure 2. The Mn[III] ion is hexacoordinated by the N$_4$O ligand L[−] and by one exogenous Cl^{−} ion. A similar coordination sphere with ligand L[−] was previously observed for the Fe[III] complex.[20] The two pyridine arms are in the *trans* position, as observed for other Mn complexes obtained with ligand L[−].[14,21] The Jahn−Teller elongation axis is along the pyridine−Mn−pyridine axis. The Mn−N$_{imine}$ and Mn−N$_{phenolate}$ bond lengths are close to those reported for similar species.[10,21−23] The Mn−Cl bond length is relatively shorter in comparison to the reported values for chloromanganese-(III) species obtained with N$_4$ or N$_4$O ligands.[10,24,25]

Altogether, these results highlight the intricacies between the electrochemical properties and the chemical alterations
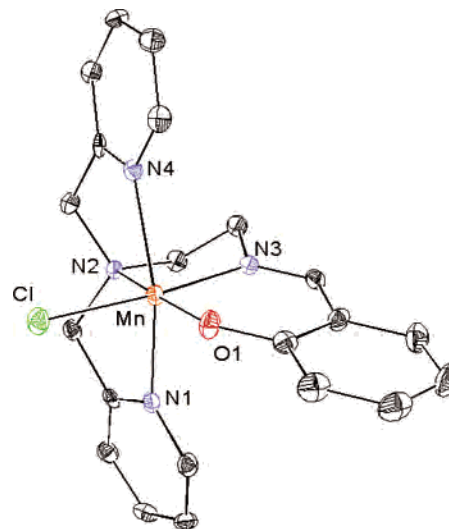

Figure 2. Molecular view of the cation [(L)Mn[III]Cl][+] (**3**). Displacement ellipsoids are drawn at the 50% probability level. Bond lengths (Å): Mn−O1 = 1.870(4), Mn−Cl = 2.266(2), Mn−N1 = 2.251(6), Mn−N2 = 2.133(6), Mn−N3 = 2.001(6), Mn−N4 = 2.254(6). Angles (deg): O1−Mn−N3 = 89.90(22), N2−Mn−N3 = 81.70(22), N2−Mn−Cl = 94.25(16), O1−Mn−Cl = 94.45(18), N1−Mn−N2 = 75.17 (22), N2−Mn−N4 = 77.81(22), N1−Mn−N4 = 152.90(22).

within the coordination sphere of the Mn ion, be it the Cl^{−} content or the protonic state of the phenol group of the ligand. This study stems from a classic metalation where the ligand was merely mixed with the metal source. The detailed electrochemical investigations in various conditions have permitted us to unravel an electron process coupled with chemical reactions (Cl^{−} expulsion and deprotonation). We believed that the understanding of such basic phenomena is important for Mn chemistry.

Supporting Information Available: X-ray crystallographic details of complex **3** in CIF format, experimental data, UV−visible spectra of complex **1** before and after bulk electrolysis at 1.0 V vs SCE (Figure S1), 9.4-GHz (X-band) EPR spectra of complex **1** in powder and in solution (Figure S2), and cyclic voltammograms of **1** in the presence of 1 equiv of 2,6-dimethylpyridine per Mn ion (Figure S3) and in the presence of 1 equiv of silver perchlorate per Mn ion (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The electronic transition characteristic of species **2** (ref 14) is not detected upon dissolution of **1** in acetonitrile. Furthermore, if an equilibrium between species **1** and **2** exists, the addition of silver perchlorate to a solution of complex **1** should lead to the displacement of the equilibrium toward the formation of species **2**. The cyclic voltammetry trace recorded on a solution of **1** after the addition of 1 equiv of silver perchlorate shows this it is not the case (Figure S4 in the Supporting Information).

(20) Rogez, G.; Marvilliers, A.; Sarr, P.; Parsons, S.; Teat, S. T.; Ricard, L.; Mallah, T. *J. Chem. Soc., Chem. Commun.* **2002**, 1460−1461.

(21) Horner, O.; Anxolabéhère-Mallart, E.; Charlot, M.-F.; Tchertanov, L.; Guilhem, J.; Mattioli, T. A.; Boussac, A.; Girerd, J.-J. *Inorg. Chem.* **1999**, *38*, 1222−1232.

(22) Neves, A.; Erthal, S. M. D.; Vencato, I.; Ceccato, A. S.; Mascarenhas, Y. P.; Nascimento, O. R.; Hörner, M.; Batista, A. A. *Inorg. Chem.* **1992**, *31*, 4749−4755.

(23) Sabater, L.; Guillot, R.; Aukauloo, A. *Tetrahedron Lett.* **2005**, *46*, 2923−2926.

(24) Triller, M. U.; Hsieh, W.-Y.; Pecoraro, V. L.; Rompel, A.; Krebs, B. *Inorg. Chem.* **2002**, *41*, 5544−5554.

(25) Shaikh, N.; Tanja, A.; Banerjee, P.; Kubiak, M.; Ciunik, Z.; Puchaleska, M.; Legendziewicz, J.; Vojpisek, P. *Inorg. Chim. Acta* **2004**, *357*, 25−35.