Letter

Synthesis and characterization of a new kind of $Mn_2^{III,IV}$ μ-oxo complex: $[Mn_2O_2(terpy)_2(H_2O)_2](NO_3)_3 \cdot 6\ H_2O$, terpy = 2,2′:6′,2″-terpyridine

Marie-Noëlle Collomb,[*a] **Alain Deronzier,**[*a] **Aurélien Richardot**[a] **and Jacques Pécaut**[b]

[a] *Laboratoire d'Electrochimie Organique et de Photochimie Rédox (CNRS UMR 5630), Université Joseph Fourier, BP 53, 38041 Grenoble cedex 9, France*

[b] *Département de Recherche Fondamentale sur la Matière Condensée, Service de Chimie Inorganique et Biologique, Laboratoire de Chimie de Coordination (CNRS URA 1194), CEA/Grenoble, 38054 Grenoble cédex 9, France*

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A new kind of mixed-valence binuclear μ-oxo complex of manganese having two aqua ligands has been synthesized and structurally characterized.

Although the exact nature of the oxygen-evolving center in photosystem II remains ill-characterized, it is believed to contain a tetranuclear oxo-manganese cluster.[1] In order to mimic this natural active center much effort has been devoted during the last decade to designing molecules containing multinuclear μ-oxo-bridged manganese complexes. Among the numerous molecules synthesized for this purpose,[2] only the mixed-valence binuclear complex $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ (bpy = 2,2′-bipyridine) and the analogous 1,10-phenanthroline have been reported to be active for O_2 evolution from water oxidation under heterogeneous conditions.[3] However, this result remains questionable[4] and we reported recently[5] that the assumed active species $[Mn_2^{IV,IV}O_2(bpy)_4]^{4+}$ is unstable in water, leading to the stable tetranuclear species $[Mn_4^{IV}O_6(bpy)_6]^{4+}$, which is inactive as a homogeneous O_2 catalyst. Very recent work by Limburg *et al.*[6] reported that oxidation of some mononuclear complexes $[Mn(L)_2]^n$ with planar tridentate ligands L, like dpa (dpa = dipicolinate, $n = -1$) or terpy (terpy = 2,2′:6′,2″-terpyridine, $n = +2$), by oxone leads to O_2 evolution; the complex containing terpy appears to be the more stable. Although the mechanism involved is unknown, these authors observed the formation of a green intermediate dimer having a $Mn^{III}Mn^{IV}$ feature, as characterized by UV-visible and EPR spectroscopies. Furthermore, they suggested that the $Mn^{III}Mn^{IV}$ complex has a bis μ-oxo structure, the open coordination sites being occupied by the solvent (H_2O). The better activity of these kinds of complex *versus* bpy derivatives could result from the possible formation of higher oxidation states containing Mn=O species able to oxidize water by an inner-sphere mechanism. In this context, we report here the synthesis and the structural characterization of this new kind of mixed-valence complex $[Mn_2O_2(terpy)_2(H_2O)_2](NO_3)_3 \cdot 6H_2O$, **1**, containing terpy as a tridentate ligand, and a terminally bound water molecule on each Mn.

Reaction of 1.44 equiv. of terpyridine ligand with 1 equiv. of $Mn(NO_3)_2$, followed by subsequent addition of 0.42 equiv. of $KMnO_4$, affords a green solution that yields a green precipitate of **1** upon cooling.† Elemental analysis of **1** shows that it is the mixed-valence complex with the above formulation, which is confirmed by X-ray structure analysis.‡ The unit cell contains two distinct but very similar dimeric cations, six nitrate anions and twelve water molecules. The ORTEP diagram of the two cations, $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$, is represented in Fig. 1. Each cation possesses a crystallographically imposed center of symmetry implying that the two Mn ions (Mn^{III} and Mn^{IV}) for each dimer are crystallographically equivalent. To our knowledge, this unusual equivalence of the two Mn centers in a $Mn^{III}Mn^{IV}(\mu\text{-}O)_2$ dimeric structure has only been reported by Stebler *et al.*[7] in the case of the $[Mn_2^{III,IV}O_2(phen)_4](PF_6)_3 \cdot CH_3CN$ complex.[8]

Two possibilities, not distinguishable, have been suggested in order to explain the equivalence of the two Mn centers:[8,9] (1) the observed structure corresponds to a superposition of $Mn^{III}Mn^{IV}$ and $Mn^{IV}Mn^{III}$ complexes (class I in the classification of Robin and Day,[9] static disorder) and (2) the rate of the electron transfer $Mn^{III}Mn^{IV} \rightarrow Mn^{IV}Mn^{III}$, is faster than the measurement time scale, thus the two Mn ions appear to be identical (class II,[9] dynamic disorder). A third possiblity, in which the two manganese ions are chemically equivalent since the d electrons are totally delocalized over the two Mn centers (class III,[9] ordered structure), has been excluded after analysis of the thermal displacement parameters.[7] In our case, a 16-line EPR spectrum is observed for **1** (see further in the text), indicating that this dimer is probably a d electron localized species; thus only static disorder could explain the equivalence of the Mn ions.

Bond angles suggest (Fig. 1) that the geometry at each manganese center is approximately octahedral, the coordination spheres consisting of the three N atoms from a single terpy ligand, the two *cis*-bridging oxo ligands and the O atom of the coordinated water (noted O_{aqua}). The coordination in the equatorial plane is provided by the three O atoms and an N pyridine atom while the two axial positions are coordinated by the two other pyridine N atoms. The orientation of the two water molecules is *trans*. A *trans* geometry is also observed in the few manganese complexes, as yet isolated, containing a $Mn{-}O_{aqua}$ bond such as $[Mn_3^{IV}O_4(L)_4(H_2O)_2]^{4+}$ (L = bpy[10] and phen[11]), $[Mn_2^{III}O(O_2CCH_3)_2(bpy)_2(H_2O)_2]^{2+}$,[12] and $[Mn_2^{IV}O_2(O_2CCH_3)(bpy)_2(H_2O)_2]^{3+}$ [13] complexes.

In the following discussion, the average of the atom bond distances of the two dimeric cations present in the structure of **1** are used. The Mn—Mn bond distance of 2.7321(6) Å in **1** is at the high end of the range (2.588–2.741 Å) observed for other structurally characterized $Mn^{III}Mn^{IV}$ di-oxo-bridged complexes[14] and slightly longer than the values of 2.716 and 2.700 Å in the $[Mn_2^{III,IV}O_2(bpy)_4]^{3+}$ [15] and $[Mn_2^{III,IV}O_2(phen)_4]^{3+}$ [7] complexes. The Mn—O distances of 1.820(2) and 1.809(4) Å for the oxo bridges are consistent with the values of 1.820 and 1.808 Å observed by Stebler *et al.*[7] in the phen

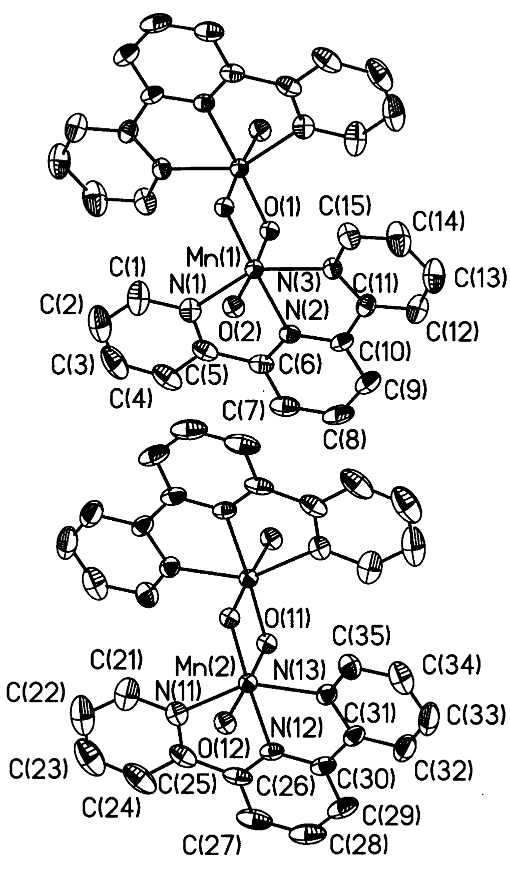

Fig. 1 X-ray structure of $[Mn_2^{III,IV}O_2(terpy)_2(H_2O)_2]^{3+}$ (ORTEP representation of the two similar dimeric cations present in an unit cell). Selected bond distances (Å) and angles (°): Mn(1)—Mn(1)$^{\#1}$ 2.7315(12), Mn(1)—O(1) 1.818(3), Mn(1)—O(1)$^{\#1}$ 1.812(3), Mn(1)—O(2) 2.009(3), Mn(1)—N(1) 2.132(4), Mn(l)—N(2) 2.044(3), Mn(l)—N(3) 2.131(3), Mn(1)—O(1)—Mn(1)$^{\#1}$ 97.61(12), O(1)—Mn(1)—O(1)$^{\#1}$ 82.39(12), N(1)—Mn(1)—O(1) 94.09(12), O(2)—Mn(1)—O(1) 175.40(11), N(2)—Mn(1)—O(1) 90.24(12), N(3)—Mn(1)—O(1) 96.75(12). Mn(2)—Mn(2)$^{\#2}$ 2.7327(12), Mn(2)—O(11) 1.821(2), Mn(2)—O(11)$^{\#2}$ 1.805(3), Mn(2)—O(12) 2.012(3), Mn(2)—N(11) 2.125(4), Mn(2)—N(12) 2.037(3), Mn(2)—N(13) 2.125(3), Mn(2)—O(11)—Mn(2)$^{\#2}$ 97.83(12), O(11)—Mn(2)—O(11)$^{\#2}$ 82.17(12), N(11)—Mn(2)—O(11) 95.22(12), O(12)—Mn(2)—O(11) 176.54(11), N(12)—Mn(2)—O(11) 90.37(12), N(13)—Mn(2)—O(11) 95.64 (12).

complex and are in good agreement with those of other similar $Mn^{III}Mn^{IV}(\mu\text{-}O)_2$ complexes cited in the literature.[14] Moreover, the Mn—O distance is comparable to the Ru—O distance in the homogeneous water oxidation catalyst $[Ru_2^{III}O(bpy)_4(H_2O)_2]^{3+}$ (1.869 Å).[16]

The $Mn—O_{aqua}$ bond length [2.011(2) Å] distance compares well with those observed in the trinuclear bpy[10] and phen[11] complexes (average 2.045 and 2.009 Å, respectively) and in the $[Mn_2^{IV}O_2(O_2CCH_3)(bpy)_2(H_2O)_2]^{3+}$ complex[13] (average 1.991 Å). On the other hand, it is shorter than the $Ru^{III}—O_{aqua}$ bond in $[Ru_2^{III}O(bpy)_4(H_2O)_2]^{3+}$ (average 2.136 Å)[16] and the $Mn^{III}—O_{aqua}$ bond in $[Mn_2^{III}O(O_2CCH_3)_2(bpy)_2(H_2O)_2]^{2+}$ (average 2.312 Å).[12] The $Mn—O_{aqua}$ distance in **1** is also significantly longer than the $Mn^{IV}—OH$ bond distance of 1.881 Å reported by Wieghardt *et al.*,[17] confirming that the bound species is an aqua group.

The IR spectrum of **1** exhibits in the 670–770 cm^{-1} region only an intense band at 706 cm^{-1} assigned to a stretching mode of the di-μ-oxo bridge,[18] while vibrations at 1384(vs) and 830 cm^{-1} confirm the presence of NO_3^- as counter ions. Several spectroscopic measurements carried out in stabilized§ aqueous solutions confirm the mixed-valence nature of complex **1**. In contrast to the bpy and phen di-μ-oxo complexes,[4,5,18] **1** is insoluble in usual organic solvents like CH_3CN and CH_2Cl_2 but soluble and stable for several hours in unbuffered pure water solution at pH 4.5. Obviously, aqueous solutions of **1** are also stable in the presence of terpyridyl buffer at pH 4 (for pH > 4, the terpy ligand precipitates in solution). The addition of electrolyte like 0.1 M $NaNO_3$ or Na_2SO_4 does not affect this stability. The UV-visible absorption spectrum of a green solution of **1** measured in distilled water at pH 4.5 is reminiscent of that of $[Mn_2O_2(bpy)_4]^{3+}$ in a bpy/bpyH$^+$ buffer (Fig. 2).[5] The band at 553 nm (ε = 678 l mol^{-1} cm^{-1}) is possibly ascribable to a d–d transition band, while that at 654 nm (ε = 585 l mol^{-1} cm^{-1}) is due to a ligand (O)-to-metal charge transfer.[18]

As expected, EPR spectroscopic measurements of a solution of **1** in H_2O (pH 4.5) containing 20% CH_3CN at 100 K give a 16-line signal, centered at $g = 2$.[18] **1** can be also characterized by electrospray ionization mass spectroscopy (ES). As previously observed for some dinuclear oxo-iron complexes containing aqua ligands,[19] these ligands are too labile to remain coordinated to metal atoms under ES conditions. The most abundant peak at *m*/*z* 732 in the spectrum is due to the $[Mn_2O_2(terpy)_2](NO_3)_2^+$ cation.

The cyclic voltammogram (CV) at a vitreous carbon electrode of **1** in water containing 0.1 M $NaNO_3$ (pH 4.5) has been compared to that obtained in an aqueous bpy buffer for the $[Mn_2O_2(bpy)_4]^{3+}$ complex. It should be recalled that the latter complex is stable in aqueous solution only in this specific medium.[4,18a] For the bpy complex, the quasi-reversible oxidation wave leading to the $Mn^{IV}Mn^{IV}$ species appears at $E_{1/2} = 1.16$ V *vs.* Ag/AgCl while the irreversible reduction wave producing the mononuclear complex $[Mn(bpy)_3]^{2+}$ as final product is seen [Fig. 3(*A*)] at $Ep_c = 0.40$ V.[5] For the terpy complex, potentials are strongly shifted to more positive values with regard to those of the bpy one, in accordance with the smaller electron-donating effect of the aqua ligand than that of pyridine. As a consequence, the irreversible reduction peak, leading to the mononuclear complex $[Mn(terpy)_3]^{2+}$, is now located at $Ep_c = 0.56$ V [Fig. 3(*B*)]. Upon oxidation, no reversible redox system corresponding to formation of the $Mn^{IV}Mn^{IV}$ species is observed. On the CV curve a large continuous increase of the anodic current with a shoulder at 1.00 V is observed by scanning the potential up to 1.40 V. On the reverse scan only a small irreversible peak at 0.86 V is seen. In order to explain the shape of the oxidation system of this complex, two possibilities can be proposed: (1) the oxidation potential of the $Mn^{III}M^{IV}/Mn^{IV}Mn^{IV}$ system is located outside the electroactivity range of the solvent or (2) the irreversibility of the system is due to a catalytic effect toward the oxidation of water. We are currently undertaking a careful bulk electrolysis study in order to try to solve these questions.

In conclusion, this structural study validates the proposal of Limburg *et al.*[6] about the formation of a binuclear μ-oxo

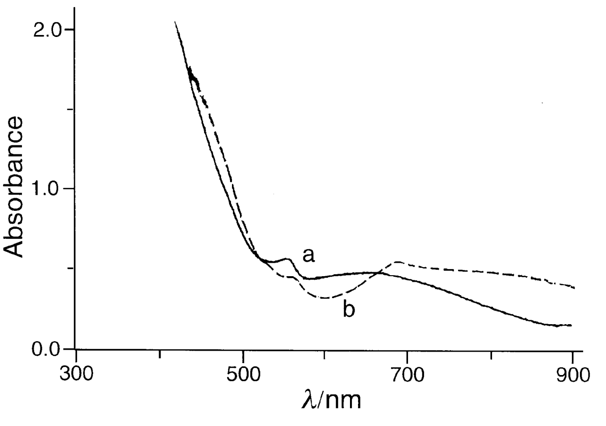

Fig. 2 Visible spectra in an aqueous solution containing 0.1 M $NaNO_3$ at pH 4.5 of (*a*) **1** (0.9 mM) and (*b*) $[Mn_2O_2(bpy)_4]^{3+}$ (1 mM) in 0.05 M bpy/bpyH$^+$ buffer.

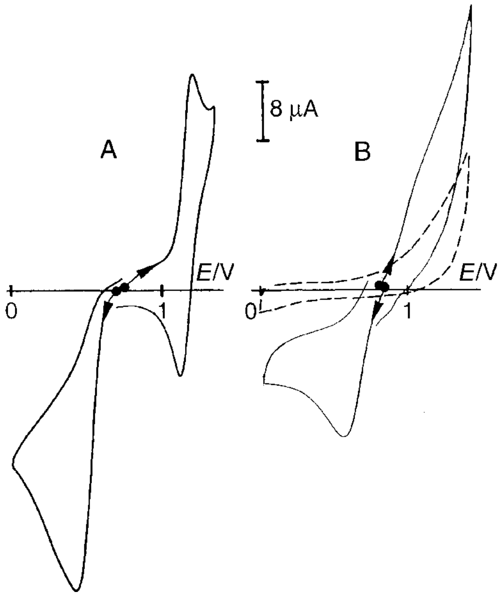

Fig. 3 Cyclic voltammograms in aqueous solutions (pH = 4.5) at a carbon working electrode (diam. 0.5 cm) (scan rate 20 mV s^{-1}) of (*A*) $[Mn_2O_2(bpy)_4]^{3+}$ (2 mM) in 0.05 M bpy/bpyH$^+$ buffer containing 0.1 M $NaBF_4$ and (*B*) **1** (1 mM) containing 0.1 M $NaNO_3$. Dashed line curve is of the pure electrolyte. Potentials are referenced to an Ag/AgCl reference electrode.

complex of manganese having two aqua ligands, during the operation of their catalytic water oxidation system.

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Notes and references

† Selected data for $[Mn_2O_2(terpy)_2(H_2O)_2](NO_3)_3 \cdot 6H_2O$: elemental analysis calculated for $C_{30}H_{38}Mn_2N_9O_{19}$: C 38.39, H 4.08, N 13.43, Mn 11.71; found: C 38.17, H 3.87, N 13.71, Mn 11.63; ES-MS (4.5 eV) *m*/*z*: 732.0 $[Mn_2^{III,IV}O_2(terpy)_2](NO_3)_2^+$, 687.0 $[Mn_2^{IV,IV}O_2(terpy)_2(OH)](NO_3)^+$, 670.0 $[Mn_2^{III,IV}O_2(terpy)_2](NO_3)^+$, 625.0 $[Mn_2^{III,IV}O_2(terpy)_2(OH)]^+$, 454.0 $[Mn_2^{IV,IV}O_2(terpy)(OH)](NO_3)^+$, 437.0 $[Mn_2^{III,IV}O_2(terpy)](NO_3)^+$; IR (KBr) cm^{-1}: 3390(m, br), 1600(s), 1573(m), 1477(s), 1451(s), 1384(vs), 1247(w), 1166(w), 1025(m), 1015(m), 830(w), 777(s), 706(m).

‡ Green-black, air-stable crystals of **1** suitable for X-ray diffraction analysis can be obtained by evaporating the green solution of **1** at 0 °C for 6 h. Crystal data for **1**. $C_{30}H_{38}Mn_2N_9O_{19}$, $M = 938.57$, triclinic, space group $P\bar{1}$ (no 2); $R = 0.0617$, $wR = 0.1673$; $a = 7.7480(9)$, $b = 13.775(2)$, $c = 19.596(2)$ Å, $\alpha = 74.470(2)$, $\beta = 88.066(2)$, $\gamma = 79.844(2)°$; $U = 1983.3(4)$ Å^3; $\mu = 7.26$ cm^{-1} $T = 293$ K; $Z = 2$; 12930 measured reflections, 9085 were independent and 4292 were observed with $I > 2\sigma(I)$. CCDC reference number 440/102.

§ The stability of **1** in aqueous solutions was evaluated by the persistence of the green color of solutions and by the fact that no change in the absorption spectrum appears after several hours.

1 V. K. Yachandra, K. Sauer and M. P. Klein, *Chem. Rev.*, 1996, **96**, 2927 and references therein.
2 See, for instance: R. Manchanda, G. W. Brudvig and R. H. Crabtree, *Coord. Chem. Rev.*, 1995, **144**, 1 and references therein.
3 (*a*) R. Ramaraj, A. Kira and M. Kaneko, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 825 and *Chem. Lett.*, 1987, 261. (*b*) G. J. Yao, A. Kira and M. Kaneko, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 4451.
4 M. G. Ghost, J. W. Reed, R. N. Bose and E. S. Gould, *Inorg. Chem.*, 1994, **33**, 73.
5 (*a*) M.-N. Collomb Dunand-Sauthier, A. Deronzier, X. Pradon, S. Ménage and C. Philouze, *J. Am. Chem. Soc.*, 1997, **119**, 3173. (*b*) M.-N. Collomb Dunand-Sauthier, A. Deronzier, A. Piron, X. Pradon and S. Ménage, *J. Am. Chem. Soc.*, 1998, **120**, 5373.
6 J. Limburg, G. W. Brudvig and R. H. Crabtree, *J. Am. Chem. Soc.*, 1997, **119**, 2761.
7 M. Stebler, A. Ludi and H.-B. Bürgi, *Inorg. Chem.*, 1986, **25**, 4743.
8 R. Manchanda, G. W. Brudvig, S. De Gala and R. H. Crabtree, *Inorg. Chem.*, 1994, **33**, 5157.
9 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
10 J. E. Sarneski, H. H. Thorp, G. W. Brudvig, R. H. Crabtree and G. K. Schulte, *J. Am. Chem. Soc.*, 1990, **112**, 7255.
11 K. R. Reddy, M. V. Rajasekharan, N. Arulsamy and D. J. Hodgson, *Inorg. Chem.*, 1996, **35**, 2283.
12 S. Ménage, J.-C. Girerd and A. Gleizes, *J. Chem. Soc., Chem. Commun.*, 1988, 431.
13 B. C. Dave, R. S. Czernuszewicz, M. R. Bond and C. J. Carrano, *Inorg. Chem.*, 1993, **32**, 3593.
14 S. Pal, M. M. Olmstead and W. H. Armstrong, *Inorg. Chem.*, 1995, **34**, 4708 and references therein.
15 P. M. Plaskin, R. C. Stoufer, M. Mathew and G. J. Palenik, *J. Am. Chem. Soc.*, 1972, **94**, 2121.
16 J. A. Gilbert, D. S. Eggleston, W. R. Murphy, Jr., D. A. Geselowitz, S. W. Gersten, D. J. Hodgson and T. J. Meyer, *J. Am. Chem. Soc.*, 1985, **107**, 3855.
17 K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols and J.-J. Girerd, *J. Am. Chem. Soc.*, 1988, **110**, 7398.
18 (*a*) S. R. Cooper and M. Calvin, *J. Am. Chem. Soc.*, 1977, **99**, 6623. (*b*) S. R. Cooper, G. C. Dismukes, M. P. Klein and M. Calvin, *J. Am. Chem. Soc.*, 1978, **100**, 7248.
19 U. N. Anderson, C. T. McKenzie and G. Bojesen, *Inorg. Chem.*, 1995, **34**, 1435.

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