COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A novel aggregate of $[Mn_2(\mu\text{-}O)_2]$ units: $[Mn_8O_{10}(O_2CMe)_6(H_2O)_2(bpy)_6]^{4+}$ with a serpentine core

Anastasios J. Tasiopoulos, Khalil A. Abboud and George Christou*
Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA.
E-mail: christou@chem.ufl.edu; Fax: +1 352-392-8757; Tel: +1 352-392-8314

Received (in Cambridge, UK) 19th November 2002, Accepted 9th January 2003
First published as an Advance Article on the web 29th January 2003

The synthesis, characterization and initial reactivity studies are reported of the mixed-valence ($Mn^{IV}{}_6Mn^{III}{}_2$) title compound, which possesses an unusual serpentine-like core and is the highest average oxidation state (+3.75) Mn_x (x > 4) cluster to date.

There is currently considerable interest in new high oxidation state Mn carboxylate clusters because of their relevance to many areas such as nanoscale magnetic materials,[1] bioinorganic chemistry,[2] and oxidation of organic compounds.[3] The materials area involves the ability of certain molecules, termed single-molecule magnets (SMMs), to retain their magnetization below a blocking temperature in the absence of an applied field. A large ground state spin (S) and a negative (easy axis) magnetoanisotropy are required for a molecule to be a SMM.[1] In the bioinorganic area, the water oxidation complex (WOC), which contains a tetranuclear Mn–oxo aggregate, is responsible for the photosynthetic oxidation of water to O_2.[2,4] A number of Mn_4 species containing Mn^{III} and/or Mn^{IV} have been prepared, but none of them exactly reproduces the properties of the WOC. Finally, Mn compounds with oxidation states III to VII have a long history as oxidising agents for a vast variety of organic compounds.[3] There is thus a continuing interest in new methodology to high oxidation state Mn clusters, and in the past this has led to a large number of polynuclear Mn_x clusters (x = 6–30).[5–10] We herein report a new reaction system and describe the initial product from its use, the novel $Mn^{IV}{}_6Mn^{III}{}_2$ cluster $[Mn_8O_{10}(O_2CMe)_6(H_2O)_2(bpy)_6]^{4+}$ with an unusual serpentine-like $[Mn_8O_{10}]^{10+}$ core. This compound is also the highest valent polynuclear Mn_x (x > 4) species discovered to date, with an average oxidation state of +3.75.

The synthesis involves a comproportionation between Mn^{II} and Mn^{VII} in H_2O–$MeCO_2H$ (10:3 v/v) in the presence of 2,2′-bipyridine (bpy). The $Mn^{II}:Mn^{VII}$ ratio (3:2) gives an average of Mn^{IV} (eqn. (1)). This reaction is a modification of the synthesis of $[Mn_{12}O_{12}(O_2CMe)_{16}(H_2O)_4]$, which employed more concentrated acetic acid (2:3), a $Mn^{II}:Mn^{VII}$ ratio giving an average of $Mn^{3.33+}$, and no bpy or other chelate.[11] Thus, a solution of $Mn(O_2CMe)_2{\cdot}4H_2O$ and one equiv. of bpy in aqueous $MeCO_2H$ was treated with $KMnO_4$ (0.66 equiv.) in the same solvent, followed by addition of $NaClO_4$. From the resulting dark brown solution were obtained X-ray quality, black crystals of $[Mn_8O_{10}(O_2CMe)_6(H_2O)_2(bpy)_6](ClO_4)_4$ (**1**) in 25% yield. With hydrated $Mn(NO_3)_2$ as the starting material, the mixed-anion salt $[Mn_8O_{10}(O_2CMe)_6(H_2O)_2(bpy)_6](NO_3)_2(ClO_4)_2$ (**2**) was obtained in comparable yield. The structures of both **1** and **2** have been obtained; however, the structure of **2** has disordered NO_3^- anions that complicate the refinement, and thus only the structure of **1** will be discussed here.

$$3\ Mn^{II} + 2\ Mn^{VII} \rightarrow 5\ Mn^{IV} \qquad (1)$$

The centrosymmetric cation of **1** (Fig. 1)† consists of five $[Mn_2O_2]$ rhombs linked to give an unusual $[Mn_8O_{10}]$ core with a serpentine topology, emphasized in Fig. 2. The central $[Mn_4O_6]$ unit comprises three $[Mn_2O_2]$ units fused at Mn1 and Mn1′, and to each end of this is attached a $[Mn_2O_2]$ unit through bonds Mn3–O3 and Mn3′–O3′. The peripheral ligation is

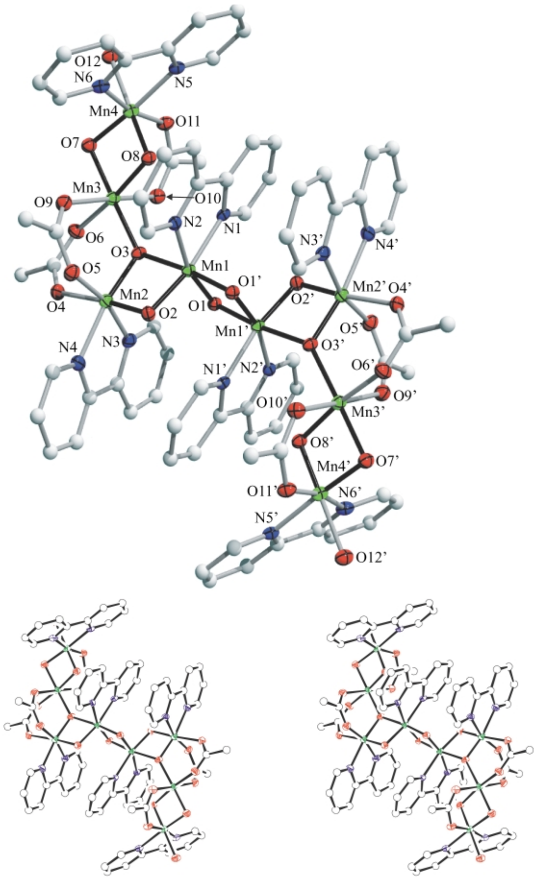

Fig. 1 Top: Labeled ORTEP plot in PovRay format of the cation of complex **1** (the thermal ellipsoids are set at 50% probability). Bottom: ORTEP stereoplot from the same viewpoint.

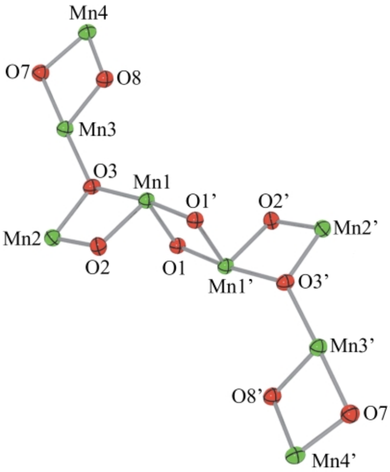

Fig. 2 The $[Mn_8O_{10}]^{10+}$ core of the cation of complex **1**, emphasizing its serpentine topology.

DOI: 10.1039/b211345g

provided by two terminal H_2O molecules, six chelating bpy groups, and six bridging acetate groups in their familiar *syn*,*syn* bridging modes. Charge considerations, inspection of metric parameters, bond valence sum calculations, and the presence of Mn^{III} Jahn–Teller elongation axes establish a trapped-valence $2Mn^{III},6Mn^{IV}$ situation with Mn3 and Mn3′ being the Mn^{III} ions; these are the only Mn ions not ligated by bpy groups. As expected, the Mn···Mn separations within the $[Mn_2O_2]$ units (2.675–2.790 Å) are significantly shorter than Mn2···Mn3 and Mn2′···Mn3′ (3.274 Å), which are each bridged by only one oxide ion. The anions and lattice solvent molecules participate in extensive O–H···O hydrogen-bonding interactions (~ 2.8 Å) amongst themselves and with the bound H_2O molecules.

The solid-state magnetic susceptibility (χ_M) of **1** was measured in the 5.00–300 K range in a 5 kG (0.5 T) magnetic field and plotted as $\chi_M T$ vs. T in Fig. 3. The $\chi_M T$ value decreases steadily from 7.28 cm^3 K mol^{-1} at 300 K to 0.37 cm^3 K mol^{-1} at 5.00 K. The $\chi_M T$ value for a cluster of two Mn^{III} and six Mn^{IV} non-interacting ions is 17.25 cm^3 K mol^{-1}, so the observed 300 K value indicates the presence of strong antiferromagnetic exchange interactions within the cation of **1**. The data in Fig. 3 indicate an $S = 0$ ground state for the cation, as expected from its structure; dinuclear $[Mn_2O_2]^{3+,4+}$ compounds are always antiferromagnetically coupled due to strong d_π–d_π overlap via the μ-O atoms in the Mn_2 edge-sharing bioctahedron. Although there is a strong likelihood in **1** of spin frustration within the triangular Mn1Mn2Mn3 unit, and its symmetry-related partner, the antiferromagnetic exchange at the central Mn1–Mn1′ pair will ensure an $S = 0$ ground state, whatever the spin of each half of the cation might be.

Complex **1** is the highest valent Mn_x ($x > 4$) cluster[12] and represents an unprecedented high level of aggregation of the otherwise common $[Mn_2O_2]^{3+,4+}$ unit. Even higher nuclearity species might be possible with the $[Mn_2O_2]$ unit as a building block. From a bioinorganic viewpoint, the octanuclearity is too high for modeling the WOC, but note that the structure can be described as a dimer of two $[Mn_4O_4]$ units bridged by the central two O^{2-} ions. This $[Mn_4O_4]$ unit ($Mn^{III},3Mn^{IV}$) is currently unknown in discrete form but would be particularly attractive as a potential model of the WOC. In particular, its $[Mn_3(\mu\text{-}O)(\mu_3\text{-}O)]$ unit defined by atoms Mn1Mn2Mn3O2O3 is unprecedented in any Mn/O^{2-} cluster of any nuclearity.

Complex **1** will almost certainly prove a valuable starting point to a number of other Mn_x complexes, given the results of preliminary reactivity studies. For example, the reaction of **1** with one equivalent of $[MnCl_3(bpy)(H_2O)]$ or an excess of 1 M $HClO_4$ in MeCN cleanly gave the dinuclear complexes $[Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Cl_2(bpy)_2](ClO_4)\cdot0.5MeCN$ (**3**) and asymmetric $[Mn_2(\mu\text{-}O)_2(\mu\text{-}O_2CMe)Cl(H_2O)(bpy)_2](ClO_4)_2\cdot H_2O$ (**4**), respectively, in pure, crystalline form. Both these complexes were only very recently obtained for the first time from a different procedure.[13] With an excess of 1 M HCl in MeCN, the product was polymeric $[MnCl_3(bpy)]_n$ (**5**).[14] In contrast, the reactions with $NaClO_4$ and $Mn(ClO_4)_2\cdot6H_2O$ gave products whose spectroscopic signatures do not correspond to those of known compounds, and which we are currently attempting to characterize, suggesting that **1** will also prove a source of new high oxidation state species not available by other methods.

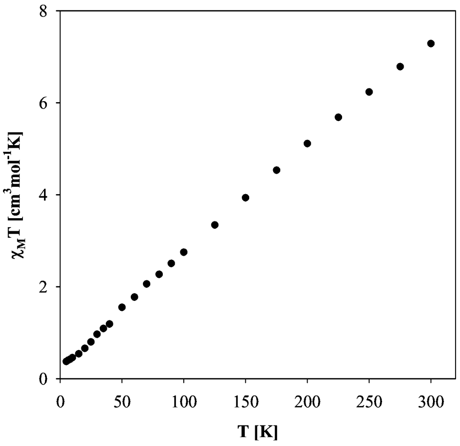

Fig. 3 Plot of $\chi_M T$ *vs.* T for complex **1**.

This work was supported by the University of Florida.

Notes and references

† *Crystal structure data* for $\mathbf{1}\cdot3MeCO_2H\cdot2H_2O$: $C_{78}H_{86}Cl_4Mn_8N_{12}O_{48}$, M_r = 2540.91, triclinic, space group $P\bar{1}$, a = 13.1494(7), b = 13.7254(7), c = 15.8387(8) Å, α = 65.623(2), β = 79.268(2), γ = 73.316(2)°, V = 2486.6(2) Å^3, T = 133 K, Z = 1, 22247 reflections collected, 11071 unique (R_{int} = 0.0520), $R1$ = 0.0399 for 6093 reflections with $I > 2\sigma(I)$, and $wR2$ = 0.0824 using all 11071 reflections). In addition to the Mn_8 cation and four ClO_4^- anions, the unit cell contains two ordered H_2O molecules and an area of disordered solvents. This area was interpreted as three acetic acid molecules and a number of additional peaks, probably water molecules. The contribution of the disordered area to the overall intensity data was removed using program SQUEEZE.[15] Five elemental analyses on samples from five different preparations all gave a formulation of $\mathbf{1}\cdot3MeCO_2H\cdot8H_2O$: $C_{78}H_{98}Cl_4Mn_8N_{12}O_{54}$, M_r = 2649.0. CCDC 192829. See http://www.rsc.org/suppdata/cc/b2/b211345g/ for crystallographic data in CIF or other electronic format.

1 G. Christou, D. Gatteschi, D. N. Hendrickson and R. Sessoli, *MRS Bull.*, 2000, **25**, 66; R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804; R. Sessoli, D. Gatteschi, A. Ganeschi and M. A. Novak, *Nature*, 1993, **365**, 141.

2 *Manganese Redox Enzymes*, ed. V. L. Pecoraro, VCH Publishers, New York, 1992.

3 D. Arndt, in *Manganese Compounds as Oxidizing Agents in Organic Chemistry*, Open Court Publishing Company, Illinois, USA, 1981; A. S. Larsen, K. Wang, M. A. Lockwood, G. L. Rice, T.-J. Won, S. Lovell, M. Sadilek, F. Turecek and J. M. Mayer, *J. Am. Chem. Soc.*, 2002, **124**, 10112.

4 V. K. Yachandra, K. Sauer and M. P. Klein, *Chem. Rev.*, 1996, **96**, 2927.

5 M. Soler, E. Rumberger, K. Folting, D. N. Hendrickson and G. Christou, *Polyhedron*, 2001, **20**, 1365; E. K. Brechin, M. Soler, J. Davidson, D. N. Hendrickson, S. Parsons and G. Christou, *Chem. Commun.*, 2002, 2252; S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1996, **118**, 7746.

6 D. J. Price, S. R. Batten, B. Moubaraki and K. S. Murray, *Chem. Commun.*, 2002, 762.

7 C. Canada-Vivalta, J. C. Huffman, W. E. Streib, E. R. Davidson and G. Christou, *Polyhedron*, 2001, **20**, 1375.

8 J. T. Brockman, J. C. Huffman and G. Christou, *Angew. Chem., Int. Ed.*, 2002, **41**, 2506.

9 C. Boskovic, J. C. Huffman and G. Christou, *Chem. Commun.*, 2002, 2502; E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. Sanudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson and G. Christou, *J. Am. Chem. Soc.*, 2002, **124**, 9710.

10 G. Aromi, A. Bell, S. J. Teat, A. G. Whittaker and R. E. P. Winpenny, *Chem. Commun.*, 2002, 1896.

11 T. Lis, *Acta Crystallogr., Sect. B*, 1980, **36**, 2042.

12 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; C. E. Dube, D. W. Wright, S. Pal, P. J. Bonitatebus and W. H. Armstrong, *J. Am. Chem. Soc.*, 1998, **120**, 3704; C. Philouze, G. Blondin, J.-J. Girerd, J. Guilhem, C. Pascard and D. Lexa, *J. Am. Chem. Soc.*, 1994, **116**, 8557; S. Mukhopadhyay, R. J. Staples and W. H. Armstrong, *Chem. Commun.*, 2002, 864; S. Pal and W. H. Armstrong, *Inorg. Chem.*, 1992, **31**, 5417; S. Bhaduri, M. Pink and G. Christou, *Chem. Commun.*, 2002, 2352.

13 S. Bhaduri, A. J. Tasiopoulos, M. A. Bolcar, K. A. Abboud, W. E. Streib and G. Christou, *Inorg. Chem,* in press.

14 S. P. Perlepes, A. G. Blackman, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1991, **30**, 1665.

15 PLATON: L. Spek, *Acta Crystallogr., Sect. A*, 1990, **46**, 1–34.