A novel aggregate of [Mn₂(μ-O)₂] units: [Mn₈O₁₀(O₂CMe)₆(H₂O)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 IV₆MnIII₂) title compound, which possesses an unusual serpentine-like core and is the highest average oxidation state (+3.75) Mnₓ (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, bioinorganic chemistry, and oxidation of organic compounds. 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. 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 O₂. A number of Mn₄ species containing MnIII and/or MnIV have been prepared, but none of them exactly reproduces the properties of the WOC. Finally, Mn compounds with oxidation states in to vii have a long history as oxidising agents for a vast variety of organic compounds.

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 [Mn₆O₉]⁴⁺ core of the cation of complex 1, emphasizing its serpentine topology.
provided by two terminal H2O molecules, six chelating bpy groups, and six bridging acetate groups in their familiar syn-syn bridging mode. Charge considerations, inspection of metric parameters, bond valence sum calculations, and the presence of MnIII–Jahn–Teller elongation axes establish a trapped-valence 2MnIII.6MnIV situation with Mn3 and Mn3’ being the MnIII ions; these are the only Mn ions not ligated by bpy groups. As expected, the Mn–Mn separations within the [Mn3O2·3H2O] 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 H2O molecules.

The solid-state magnetic susceptibility (χsp) of I was measured in the 5.00–300 K range in a 5 kG (0.5 T) magnetic field and plotted as χspT vs. T in Fig. 3. The χspT value decreases steadily from 7.28 cm3 K mol−1 at 300 K to 0.37 cm3 K mol−1 at 5.00 K. The χspT value for a cluster of two MnIII and six MnIV non-interacting ions is 17.25 cm3 K mol−1, so the observed 300 K value indicates the presence of strong antiferromagnetic exchange interactions within the cation of I. The data in Fig. 3 indicate an S = 0 ground state for the cation, as expected from its structure; dinuclear [Mn2O2]+,4+ compounds are always antiferromagnetically coupled due to strong d4–d4 overlap via the μ-O atoms in the Mn-edge-sharing biotahedron. Although there is a strong likelihood in I 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 of the cation might be.

Complex I is the highest valent Mn (x > 4) cluster12 and represents an unprecedented high level of aggregation of the otherwise common [Mn2O2]15,46 unit. Even higher nuclearity species might be possible with the [Mn2O2] 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 [Mn2O2] units bridged by the central two O2– ions. This [Mn2O2] unit (MnIII,MnIV) is currently unknown in discrete form but would be particularly attractive as a potential model of the WOC. In particular, its [Mn2(μ-O)(μ1-O)] unit defined by atoms Mn1Mn2Mn3O2O3 is unprecedented in any MnIII–O2− cluster of any nuclearity. Complex I will almost certainly prove a valuable starting point to a number of other MnIII complexes, given the results of preliminary reactivity studies. For example, the reaction of I with one equivalent of [MnCl2(bpy)(H2O)] or an excess of 1 M HClO4 in MeCN cleanly gave the dinuclear complexes [Mn2(μ-O)(μ1-O2CMe2Cl)]ClO4·0.5MeCN (3) and asymmetric [Mn2(μ-O)(μ1-O2CMe4Cl2H4O(bpy)]ClO4·H2O (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 [MnCl2(bpy)]n (5).14 In contrast, the reactions with NaClO4 and Mn(ClO4)2·6H2O gave products whose spectroscopic signatures do not correspond to those of known compounds, and which we are currently attempting to characterize, suggesting that I will also prove a source of new high oxidation state species not available by other methods.

This work was supported by the University of Florida.

Notes and references

† Crystal structure data for I: 3MeCO2H·2H2O: C78H98Cl4Mn8N12O54, Mn = 2540.91, triclinic, space group P1, a = 13.1494(7), b = 13.7254(7), c = 15.8387(6) Å, α = 65.628(2), β = 79.268(2), γ = 73.316(2)°, V = 2466.6(2) Å3, T = 133 K, Z = 1, 22237 reflections collected, 11071 unique (Rint = 0.0520), R1 = 0.0399 for 6093 reflections with I > 2σ(I), and wR2 = 0.0824 using all 11071 reflections. In addition to the MnII cation and four ClO4− ions, the unit cell contains two ordered H2O 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 3MeCO2H·2H2O: C78H98Cl4Mn8N12O54, Mn = 2649.0. CCDC 192829. See http://www.rcsb.org/sup/pdb/5b2/t2l1345g for crystallographic data in CIF or other electronic format.


