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Structure and Properties of $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]$: A Novel Nonanuclear Manganese(III)–Oxo–Carboxylate Species Synthesized by Employing an Oxygen Atom Transfer Agent

Several higher nuclearity manganese–oxo–carboxylate complexes have been structurally characterized in recent years.[1] Included among these are $[Mn_3O(O_2CR)_6L_3]^{0/+}$ (**1**),[2] $[Mn_6O_2(O_2CR)_{10}L_4]$ (**2**),[3] and $[Mn_{12}O_{12}(O_2CR)_{16}L_4]$ (**3**),[4] where L is a neutral monodentate ligand such as H_2O, pyridine, or a carboxylic acid. Generally, these complexes are prepared by using dioxygen or MnO_4^- as oxidizing agents under ambient conditions and appear to be the most thermodynamically stable oxo–carboxylate species at their respective average manganese oxidation levels (**1**, +2.66/3.00; **2**, +2.33; **3**, +3.33). Our interest in polynuclear manganese–oxo–carboxylate species stems from a desire (i) to further characterize the rich fundamental coordination chemistry of this class of compounds, (ii) to prepare synthetic models for the manganese center in the oxygen-evolving complex of photosystem II,[1,5] and (iii) to investigate novel synthetic pathways to extended manganese–oxo materials.[6] In an attempt to gain a measure of control over, or at least to alter, the types of polynuclear complexes formed in solution, we decided to adjust the Mn:O ratio in a systematic fashion by allowing compound **1** (R = Ph) to react with varying quantities of the oxygen atom source PhIO. In this initial report, we demonstrate the success of this synthetic approach by describing the preparation and properties of a nonanuclear complex, $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]$ (**4**).

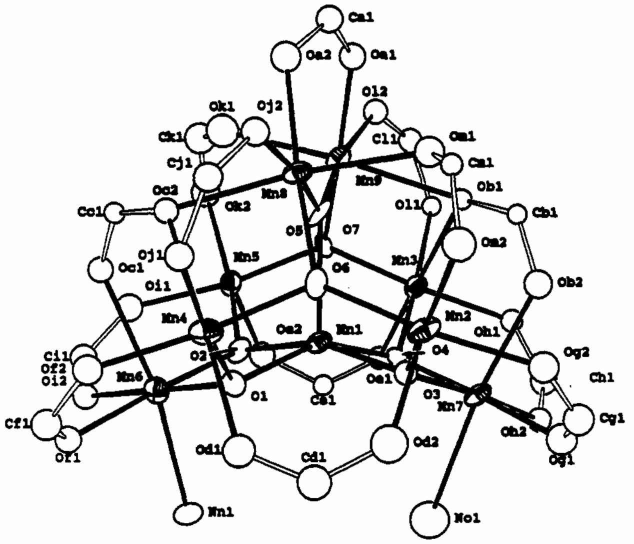

Figure 1. Structure of $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]$ (**1**) showing the 30% probability thermal ellipsoids and atom labeling scheme. Hydrogen atoms, benzoate phenyl rings, and pyridine carbon atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg) are as follows: Mn(1)–O(5), 2.19 (2); Mn(1)–O(1), 1.91 (2); Mn(1)–O(2), 1.92 (2); Mn(1)–O(3), 1.90 (2); Mn(1)–O(4), 1.91 (2); Mn(2)–O(3), 1.87 (2); Mn(2)–O(6), 1.83 (2); Mn(2)–O(m2), 1.99 (2); Mn(2)–(Og2), 1.95 (2); Mn(2)–O(d2), 2.09 (2); Mn(3)–O(7), 1.87 (2); Mn(3)–O(4), 1.89 (2); Mn(3)–O(e1), 2.14 (2); Mn(3)–O(h1), 1.94 (2); Mn(3)–O(l1), 1.99 (2); Mn(3)–O(b1), 2.26 (2); Mn(7)–O(3), 1.87 (2); Mn(7)–O(4), 1.86 (2); Mn(7)–O(g1), 1.97 (2); Mn(7)–O(h2), 2.00 (2); Mn(7)–O(b2), 2.16 (2); Mn(7)–N(o1), 2.30 (2); Mn(8)–O(5), 1.86 (2); Mn(8)–O(6), 1.92 (2); Mn(8)–O(j2), 1.99 (2); Mn(8)–O(m1), 2.22 (2); Mn(8)–O(c2), 2.20 (2); Mn(8)–O(a2), 1.93 (2); Mn(1)···Mn(7), 2.869 (6); Mn(1)···Mn(2), 3.306 (6); Mn(1)···Mn(3), 3.316 (6); Mn(1)···Mn(8), 3.411 (6); Mn(2)···Mn(3), 5.533 (6); Mn(2)···Mn(7), 3.379 (6); Mn(2)···Mn(8), 3.287 (6); Mn(3)···Mn(7), 3.259 (6); Mn(3)···Mn(9), 3.008 (6); Mn(8)···Mn(9), 3.307 (6); Mn(1)–O(5)–Mn(8), 114.2 (9); Mn(1)–O(5)–Mn(9), 117.4 (9); Mn(8)–O(5)–Mn(9), 128.4 (10); Mn(1)–O(3)–Mn(7), 99.2 (8); Mn(1)–O(3)–Mn(2), 122.7 (9); Mn(2)–O(3)–Mn(7), 129.7 (9); Mn(1)–O(4)–Mn(7), 98.9 (8); Mn(1)–O(4)–Mn(3), 121.7 (9); Mn(3)–O(4)–Mn(7), 120.7 (9); Mn(2)–O(6)–Mn(4), 132.3 (10); Mn(2)–O(6)–Mn(8), 122.3 (9); Mn(4)–O(6)–Mn(8), 104.3 (8).

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[1] In order to limit the scope of this discussion, we will consider only "pure" manganese–oxo–carboxylate aggregates, in which terminal sites are often occupied by solvent molecules. In recent years, many other polynuclear species that contain polydentate ligands have been reported. Naturally, these polydentate ligands can have a considerable influence on the polynuclear structures that form. See for example: (a) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 9121–9122. (b) Chan, M. K.; Armstrong, W. H. *J. Am. Chem. Soc.* **1990**, *112*, 4985–4986. (c) Chan, M. K.; Armstrong, W. H. Submitted for publication. (d) Pal, S.; Chan, M. K.; Armstrong, W. H. Submitted for publication. (e) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153–1172. (f) Pecoraro, V. L. *Photochem. Photobiol.* **1988**, *48*, 249–264. (g) Christou, G. *Acc. Chem. Res.* **1989**, *22*, 328–335. (h) Brudvig, G. W.; Crabtree, R. H. *Prog. Inorg. Chem.* **1989**, *37*, 99–142. (i) Armstrong, W. H. In *Manganese Redox Enzymes*; Pecoraro, V. L., Ed.; VCH: New York, to be submitted.

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The preparation of compound **4** was initiated by addition of 0.2 g (0.9 mmol) of PhIO[7] to a stirred solution of 1.3 g (1.2 mmol) of $[Mn_3O(O_2CC_6H_5)_6(py)_2(H_2O)]\cdot 0.5CH_3CN$[2d] in 100 mL of CH_3CN. After the reaction mixture was stirred for 12 h, the solvent was removed by rotary evaporation, leaving a brown glassy residue. This material was dissolved in ethyl acetate, and an equal volume of hexanes was carefully layered on top of the resulting solution. Large brown block-shaped crystals, suitable for elemental analysis[8] and X-ray diffraction studies,[9] deposited within 48 h (yield: ~20%).

The crystal structure of **4**, which is quite distinct from another nonanuclear manganese species,[10] is shown in Figure 1. While there are no symmetry elements crystallographically imposed on the molecule, a pseudo-2-fold rotation axis coincident with the Mn(1)–O(5) bond is discernable. This 2-fold axis relates the following atom pairs to one another: Mn(8), Mn(9); Mn(6), Mn(7); Mn(3), Mn(4); Mn(2), Mn(5). Thus, there are five distinct manganese coordination environments within **4**. Assuming that all carboxylate ligands are deprotonated and that all bridging O atoms are oxide groups (O^{2-}), it follows that all manganese atoms are in the +3 oxidation state. This conclusion is borne out by examination of the Mn–ligand distances and comparison to other Mn^{III}–oxo complexes.[11] All seven of the oxide groups are triply bridging. Of the thirteen benzoate groups, eleven are doubly bridging in a syn–syn configuration, while two (labeled b and c in Figure 1) are triply bridging. Triply bridging carboxylates have been observed for other manganese complexes, including **2**.[3,12] The base of the nonanuclear core (Figure 1) may be viewed as two "butterfly"-type Mn_4O_2 units[1g] which share a central five-coordinate manganese atom, Mn(1). Another substructural type within **4** is the nearly planar $[Mn_3O]^{7+}$ unit, three of which occur, centered around μ_3-oxo groups O(5), O(6), and O(7). Atoms Mn(1), Mn(2), and Mn(5) are five-coordinate, and in all three cases the ligand geometry is best described as distorted square pyramidal with atoms O(5), O(e2), and O(d2), respectively, in apical positions. The unique manganese atom, Mn(1), has a rather interesting coordination environment consisting of five μ_3-oxo donors. Space-filling models indicate that the approach of a sixth ligand to Mn(1) is blocked by two benzoate phenyl rings and the two pyridine ligands.

Initial identification of **4** as a novel manganese–oxo–carboxylate "soluble phase" came from fast atom bombardment (FAB) mass spectral measurements. The FAB mass spectrum of **4**, using a nitrobenzyl alcohol matrix, reveals a characteristic pattern with peaks at 2181, 2060, 1939, and 1818 amu, corresponding to loss of 2py, (2py + $O_2CC_6H_5$), (2py + $2O_2CC_6H_5$), and (2py + $3O_2CC_6H_5$) from molecule **4**, respectively. An X-band EPR spectrum of **4** in frozen $CH_3CN/CH_3C_6H_5$ at 8 K revealed no intense absorptions. Nor is the compound electroactive in CH_3CN solution in the range ±1.0 V vs SSCE. However, current is passed at more negative potentials (<–1.5 V), and after doing so a new wave appears in the cyclic voltammogram ($E_{p,a} = 1.0$, $E_{p,c} = 0.75$ V vs SSCE). The infrared spectrum of **4** shows bands at 1600, 1557, 1415, and 716 cm^{-1} attributable to benzoate resonances and one at 498 cm^{-1}, which may be associated with a Mn–oxo core vibration.[13] At room temperature the magnetic moment of **4** is 13.2 μ_B. This indicates overall antiferromagnetic coupling between Mn atoms in **4** since the calculated value for 9 uncoupled high-spin Mn^{III} atoms is 14.7 μ_B.

In conclusion, by using an oxygen atom transfer agent, one is able to prepare a hitherto unknown polynuclear manganese–oxo–carboxylate species. The nonanuclear complex described above may be employed as a novel starting material in synthesis and may itself have interesting reactivity properties at the terminal coordination sites that are occupied by pyridine ligands. Attempts to isolate additional polynuclear species from reaction mixtures in which the Mn:O ratio has been varied are under way.

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Supplementary Material Available: An ORTEP diagram with phenyl rings included and tables of atomic positional and thermal parameters and intramolecular distances and angles for compound **4** (16 pages). Ordering information is given on any current masthead page.

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(8) Anal. Calcd for $C_{101}H_{75}Mn_9N_2O_{33}$: C, 51.85; H, 3.23; N, 1.20. Found: C, 51.25; H, 3.13; N, 1.14.

(9) X-ray analysis for $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]\cdot 3CH_3CN\cdot 7H_2O$: This complex crystallizes in the orthorhombic space group *Pbca*, with $a = 26.206$ (7) Å, $b = 29.063$ (8) Å, $c = 31.618$ (8) Å, $V = 24{,}081$ (12) Å^3, and $Z = 8$. Data collection at 130 K out to $2\theta = 44°$ yielded 4869 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS86, G. Sheldrick) and refined by using 684 parameters to final R (R_w) values of 10% (12%) (SHELX76, G. Sheldrick).

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Department of Chemistry
University of California
Berkeley, California 94720

Donald W. Low
David M. Eichhorn
Alexandra Draganescu
William H. Armstrong*

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A Functional Analogy between Crown Ethers and Metallacrowns

We have previously commented on the structural analogy of the crown ethers[1,2] to a new class of metal clusters called metallacrowns[3-6]. Both molecular classes contain core structures with 9- or 12-membered rings that include 3 or 4 formally neutral oxygen donors to which metal ions can be coordinated. The metallacrowns resemble lariat ethers[7] in that additional specificity is imparted by bridging anions, typically acetate, that span the position from ring to captured metal. The previous metallacrowns, whether vacant as in $[(VO)^{3+}(SHI)(CH_3OH)]_3$ (**1**, 9-$MC_{VO^{3+}N}$-3)[3,8] or with captured metals as in $Fe^{III}[Fe^{III}(SHI)(O$-

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