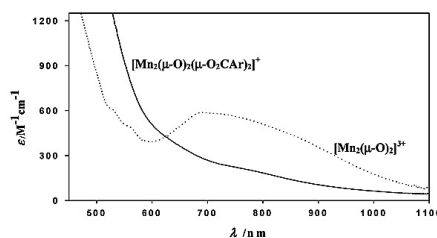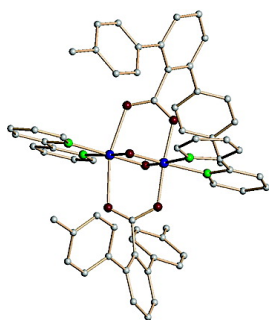Communication

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Multinuclear Oxo-Bridged Manganese Complexes with a Bulky Substituted Benzoate Ligand: Novel Species Obtained by Using Steric Control

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Dinuclear manganese centers are present in many enzyme active sites including catalase, rat liver arginase, aminopeptidase P (AMPP), and dinitrogen reductase-activating glycohydrolase (DRAG).[1] Arginase, AMPP, and DRAG are believed to contain carboxylate-bridged $Mn_2(II,II)$ active sites.[1] In contrast, the two-electron reduction of hydrogen peroxide is accompanied by an $Mn_2(II,II)$ to $Mn_2(III,III)$ core oxidation in Mn-catalase. Further oxidation of the $Mn_2(III,III)$ core leads to a formation of a catalytically inactive oxo-bridged $Mn_2(III,IV)$ core.[2] However, similar high-valent bimetallic $M_2(\mu\text{-O})_2$ "diamond-shaped" species are believed to be reactive intermediates capable of performing diverse organic functionalization in several iron- and copper-containing biological systems.[3] In addition, a bis-μ-oxo $Mn_2(III,IV)$ motif is considered to be a segment of the tetranuclear manganese cluster (Mn_4) in Photosystem II (PSII) water oxidase (WO) active site as postulated from EPR and EXAFS studies.[4] Manganese complexes containing $[Mn_2(\mu\text{-O})_2]^{2+/3+/4+}$, $[Mn_2(\mu\text{-O})_2(\mu\text{-carboxyl-ato})]^{2+/3+}$, and $[Mn_2(\mu\text{-O})(\mu\text{-carboxylato})_2]^{2+/3+}$ cores have been synthesized and studied extensively for many years.[5] The $[Fe_2(\mu\text{-O})_2]^{3+}$ and $[Cu_2(\mu\text{-O})_2]^{2+}$ complexes have also been prepared recently.[3] However, a synthetic dinuclear complex where the metal centers are bridged simultaneously by a pair of oxo groups and a pair of carboxylato groups is unknown in transition metal chemistry, even though the presence of such an intermediate in diiron or dimanganese enzyme active sites or as a structural fragment of PSII Mn_4 cluster cannot be ruled out.

Here, we report our recent achievement in obtaining such a complex, $[Mn^{III,IV}_2(\mu\text{-O})_2(bpy)_2(Ar^{tol}CO_2)_2](ClO_4)$ (**1**) (where bpy = 2,2′-bipyridine), with the aid of a sterically hindered carboxylate ligand, 2,6-di(p-tolyl)benzoate ($Ar^{tol}CO_2^-$). Such bulky carboxylates have also been used successfully by others in modeling the non-heme diiron enzyme active sites.[6] Complex **1** possesses very distinctive electronic properties as compared to those of other Mn_2-(III,IV) species. We also show that, when a methyl-substituted analogue of the bpy ligand was used as the chelating ligand, a novel high-valent hexanuclear species, $[Mn^{III}_2Mn^{IV}_4(\mu\text{-O})_4(\mu_3\text{-O})_4(dmb)_6\text{-}(Ar^{tol}CO_2)_2](OTf)_4$ (**2**) (where dmb = 4,4′-dimethyl-2,2′-bipyridine), resulted. Synthesis of high-nuclearity manganese clusters is also the subject of immense interest mainly due to the recent discovery of single-molecule magnets.[7]

Upon addition of 2 equiv of the sodium salt of $Ar^{tol}CO_2^-$ to 1 equiv of the $Mn_2(III,IV)$ complex, $[Mn_2(\mu\text{-O})_2(bpy)_4](ClO_4)_3$ (**3**), in acetonitrile, complex **1** was formed in high isolated yield (~87%). Two bpy ligands were replaced with two bulky carboxylates in the resulting compound. In contrast, when a similar ligand substitution reaction was attempted on $[Mn^{III,IV}_2(\mu\text{-O})_2(dmb)_4](OTf)_3$ (**4**), iso-structural to **3**, the poly-oxo-bridged hexanuclear manganese complex, **2**, was isolated in ~45% yield.

The crystal structure reveals that **1** contains the $[Mn_2(\mu\text{-O})_2\text{-}(bpy)_2]^{3+}$ unit with all atoms approximately coplanar (Figure 1a)
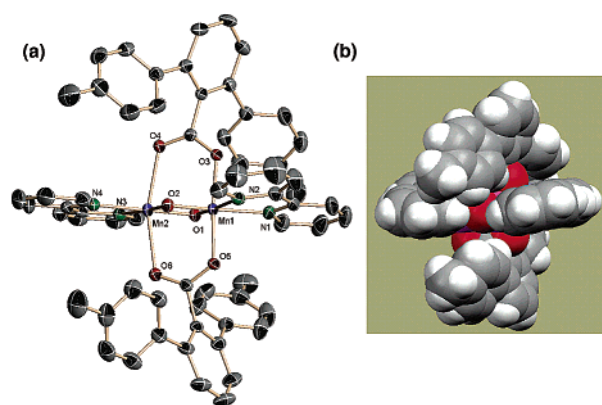

Figure 1. The cation of complex **1**: (a) an ORTEP view showing 50% probability thermal ellipsoids (H atoms are omitted for clarity); (b) a space-filling view.
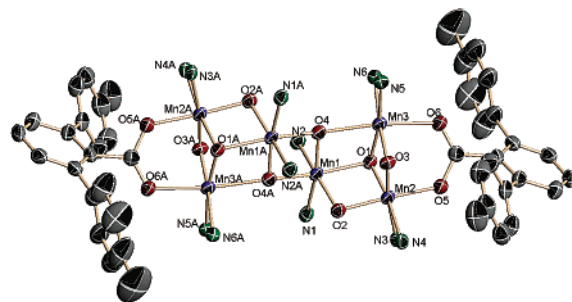
Figure 2. An ORTEP view of the cation of **2** showing 50% probability thermal ellipsoids (H atoms and the dmb ligands are omitted for clarity).

while two carboxylate ligands bridge between Mn centers on either side of this plane. The closest analogues are the diiron and dicobalt species with a $[M_2(\mu\text{-OH})_2(\mu\text{-carboxylato})_2]$ core synthesized with the same bulky carboxylate ligand.[6a,c] It is clearly evident from the Mn−O(carboxylate) bond lengths that the Mn centers are valence-trapped in **1**. Mn(2)−O(4) and Mn(2)−O(6) bonds (av 2.317 Å) are markedly longer than Mn(1)−O(3) and Mn(1)−O(5) bonds (av 1.943 Å), which suggests that Mn(1) is formally +4 and Mn(2) is in the +3 oxidation state. The Mn−O(carboxylate) bonds are along the Jahn−Teller axis of elongation for the Mn^{III} center. The complex has an Mn···Mn distance of 2.505(1) Å and Mn−O−Mn angles averaging 88.3°, which, to our knowledge, are the shortest distance and smallest angles reported for any $[Mn_2(\mu\text{-O})_2]$ species. Most likely, the presence of the fourth bridging carboxylate group between Mn centers is responsible for shortening of the Mn···Mn distance and diminishment of the Mn−O−Mn angles.

The crystal structure of **2** consists of a unique hexanuclear motif (Mn_6) (Figure 2) where two cuboidal $[Mn_3O_4]$ units are fused together through a pair of "T-shaped" μ_3-oxo groups. This trinuclear unit as well as the tetranuclear moiety formed by Mn(1A), Mn(1),
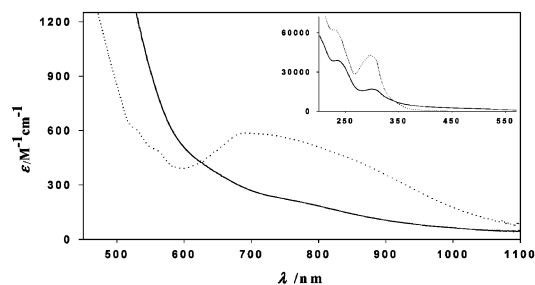
Figure 3. Electronic spectra of **1** (−) and **3** (· · ·) in acetonitrile.

Mn(2), and Mn(3) are found in several proposed structures for the PSII active site.[4] The average oxidation state for the Mn ions in **2** is +3.6, which is the highest for any Mn$_6$ complex discovered to date. The trinuclear moiety contains one Mn^{III} and two Mn^{IV} ions. On the basis of the ligand environments and metal−ligand bond distances, Mn(3) is assigned as the +3 ion and Mn(2) as a +4 ion. Mn(3) is bonded to two μ_3-oxo groups and has two Jahn−Teller elongated Mn−oxygen bonds (Mn(3)−O(4) = 2.185(3) Å and Mn-(3)−O(6) = 2.182(4) Å). In contrast, Mn(2) is connected to only one μ_3-oxo group, and the Mn−oxygen bonds are generally much shorter (Mn(3)−O(1) = 1.948(4) Å vs Mn(2)−O(1) = 1.860(4) Å, Mn(3)−O(3) = 1.812(4) Å vs Mn(2)−O(3) = 1.797(4) Å, Mn-(2)−O(2) = 1.826(3) Å, and Mn(2)−O(5) = 1.954(3) Å). These two terminal Mn centers are also linked by a bridging bulky benzoate ligand. Mn(1) is in +4 oxidation state as it is stabilized by four hard oxide (O^{2-}) ligands. Each of the Mn ions has a single chelating dmb ligand coordinated to it.

We suggest that the electronic and especially steric properties of this sterically encumbering aryl carboxylate ligand play a dominant role in forming such unprecedented complexes. An oxygen-rich environment for the Mn centers in **1**, similar to that observed in the PSII active site, has been made possible with the aid of this bulky carboxylate ligand. The bridging mode of the carboxylates as well as the steric clash between the bipyridine rings and the tolyl groups on the benzoate ligands force the bpy ligands to be coplanar with the [Mn$_2$O$_2$]$^{3+}$ moiety in **1** in contrast to **3**. Also, in **1**, the plane containing the tolyl rings is staggered with respect to that of pyridine rings to minimize steric strain. A space-filling model of **1**, shown in Figure 1b, clearly shows that there is no room to fit substituents on the pyridine rings without encountering severe steric interactions. Apparently, the ligand substitution attempt on **4** initiates a dramatic aggregation process, forming a hexanuclear cluster to minimize steric strain between the ligands. Furthermore, two tolyl groups on the phenyl ring enhance the electron-donating power of this carboxylate ligand and make it a harder donor as compared to benzoate. As a result, this ligand stabilizes higher oxidation states of Mn centers. All of our efforts to date in synthesizing isostructural compounds with acetate and benzoate ligands have been unsuccessful.

The electronic spectrum of **1** in the visible region, shown in Figure 3, is remarkably different from that of any other [Mn^{III,IV}$_2$-(μ-O)$_2$]$^{3+}$ complex,[8] highlighting its unusual electronic properties. The low energy band at 684 nm and shoulders at 525 and 555 nm in the spectrum of **3** are absent in that of **1**. Only a broad less intense shoulder at 760 nm appears in the case of **1**. The bands in the UV region have similar energies, although the absorptivities are quite different. The electronic spectrum of the "superoxidized" form of catalase is very distinct as well as compared to that of the reported Mn$_2$(III,IV) model complexes.[8b] The NMR spectrum of **1** in CD$_3$CN supports a dinuclear structure in solution containing

valence-trapped Mn^{III} and Mn^{IV} centers. Unusual electronic properties for **1** are also evident when this spectrum is compared to other [Mn^{III,IV}$_2$(μ-O)$_2$]$^{3+}$ species, which exhibit valence delocalization as measured by NMR at room temperature. All 16 proton resonances arising from two bpy ligands due to the lack of symmetry in **1** are clearly observed in the spectrum, among which four peaks for 6,6′ protons are broadened because of their close proximity to the Mn centers. A frozen dichloromethane solution of **1** at 4.0 K displays a 16-line EPR signal centered at $g \approx 2$, analogous to that observed for all other [Mn^{III,IV}$_2$(μ-O)$_2$] species.[9] This result suggests an $S = ^1/_2$ ground state for **1**, implying antiferromagnetic coupling between two high-spin Mn^{III} and Mn^{IV} ions. Variable-temperature magnetic susceptibility experiments on both complexes **1** and **2** suggest that the manganese centers are overall antiferromagnetically coupled. Detailed analyses of the solid-state EPR, bulk magnetic properties, and DFT calculations of these complexes are presently underway.

This work addresses for the first time the synthesis of a bis-μ-oxo, bis-μ-carboxylato Mn$_2$(III,IV) complex supported by a sterically hindered carboxylate ligand. Compound **1** has extraordinary electronic properties, judging by its NMR, UV−vis, and electrochemical (see Supporting Information) behavior. Placing methyl groups at the 4,4′ positions of the bpy ligand causes a severe steric perturbation, primarily at the Mn^{IV} center. This results in destabilization of the dinuclear core, causing it to convert to an Mn$_6$ species, **2**. Our current focus is directed toward the detailed analysis of the magnetic and spectroscopic properties of these complexes. Finally, we are modulating and optimizing the size of the substituents on both the N-donor and the carboxylate ligands to synthesize additional oxo-bridged polynuclear manganese species, especially desired tetranuclear complexes, as structural and functional models for WO active site.

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