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Synthesis of a High-Valent, Four-Coordinate Manganese Cubane Cluster with a Pendant Mn Atom: Photosystem II-Inspired Manganese–Nitrogen Clusters

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Supporting Information

ABSTRACT: High-valent, four-coordinate manganese imido- and nitrido-bridged heterodicubane clusters have been prepared and characterized by single-crystal X-ray diffraction and spectroscopic techniques. The title compound, a corner-nitride-fused dicubane with the chemical formula $[Mn_5Li_3(\mu_6\text{-}N)(N)(\mu_3\text{-}N^tBu)_6(\mu\text{-}N^tBu)_3(N^tBu)]$ (**1**), has been prepared as an adduct with a nearly isostructural tetramanganese cluster with one Mn atom replaced by Li. An important feature of the reported chemistry is the formation of nitride from *tert*-butylamide, indicative of N–C bond cleavage facilitated by manganese.

Metalloclusters are used in biological systems as robust and versatile cofactors for redox reactions. For example, the iron–molybdenum cofactor (FeMoco) of nitrogenase effects the six-electron reduction of the N≡N triple bond,[1] and the tetramanganese oxygen-evolving complex (OEC) of photosystem II (PSII) performs the thermodynamically intensive water oxidation reaction in oxygenic photosynthesis[2] (Figure 1). Manganese is present in the active sites of several enzymes catalyzing redox reactions of oxygen species,[3] and thus high-oxidation-state metalloenzyme intermediates are of interest in the field of bioinorganic chemistry. Several groups have contributed much on the chemistry of high-oxidation-state species of manganese.[4]

Biophysical,[2] crystallographic,[5] and computational[6] analyses on the OEC of PSII have identified the active catalyst as a Mn_4Ca cluster. The recent crystal structure at 1.9 Å confirms the earlier formulation: a metal–oxo heterocubane with a dangler Mn atom attached to the outside of the cuboid via oxide bridges (Figure 1, left).[5] This model is further supported by computations. The cuboidal crystallographic model has generated interest in the synthesis of heterocubane-type manganese clusters, with notable contributions from the groups of Christou, Dismukes, and Agapie.[7]

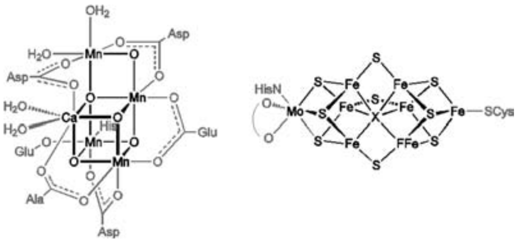

Figure 1. Crystallographic models of metallocluster enzyme active sites: OEC of PSII (left) and FeMoco of nitrogenase (right).

All of the currently available structurally characterized manganese oxo clusters with nuclearity greater than 3 are six-coordinate chelates,[8] a geometry that precludes terminal water binding for the vast majority; the few exceptions possessing aqua ligands[9] represent a remarkable scarcity among the hundreds of reported clusters. In contrast, the enzyme system contains a pendant manganese with only two protein-based coordinate covalent bonds and two water ligands.[5] Recent biophysical studies have additionally pointed to the possibility of OEC intermediates with coordination numbers less than 6.[2d] In an effort to generate labile, reactive systems, we are exploring the chemistry of unchelated manganese clusters with reduced coordination numbers by the use of bridging imide ligands as surrogates of oxide. The isolobal NR^{2-} ligand allows for control of the coordination environment of clusters using sterics rather than chelation. Only a few low-nuclearity examples of manganese imido clusters exist in the literature with high oxidation states.[10] A few examples of four-coordinate manganese amide clusters have been reported.[11] Monomeric, high-valent manganese(VII) imido complexes and clusters with pseudotetrahedral ligation have been reported by Danopoulos and Wilkinson,[10a,12] and manganese terminal imidos stabilized by corrole and corrolazine ligands have been isolated by Abu-Omar and Goldberg.[13] We report here the first four-coordinate, high-valent manganese cubane cluster.

The heating of MnF_3 with $LiNH^tBu$[14] in a 1:1 mixture of benzene and tetrahydrofuran (THF) in a pressure flask at 120 °C under anaerobic conditions gives a dark-brown solution after 22 h. The compound is purified by extraction of the dried mixture into pentane, from which black crystalline material precipitates. Single-crystal X-ray analysis on this material identifies the material as a cocrystallized mixture of two clusters. The first, shown in Figure 2, is a corner-fused dicubane cluster, $[Mn_5Li_3(\mu_6\text{-}N)(N)(\mu_3\text{-}N^tBu)_6(\mu\text{-}N^tBu)_3(N^tBu)]$ (**1**). This cluster is composed of a $Mn_4(N^tBu)_3N$ heterocubane, corner-fused through the nitride to a $MnLi_3(N^tBu)_3$ heterocubane. The two cubanes are further bridged by three μ_2-*tert*-butylimide ligands. The two ends are terminally ligated by *tert*-butylimide on the Mn_4 cubane side and nitride on the "pendant" Mn atom. FTIR analysis indicates the absence of N–

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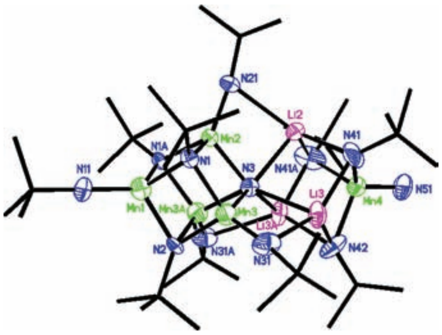

Figure 2. Crystal structure of **1**. Ellipses are set at the 50% probability level. Carbon atoms are displayed as stick models, and hydrogens are omitted for clarity.

H protons in compound **1** (Supporting Information), consistent with the crystallographic assignment of nitride and imide ligands as opposed to protonated amides. This cluster geometry is, coincidentally, a manganese–lithium analogue of the FeMoco cluster geometry (Figure 1). An iron imido cubane cluster with similar terminal imido ligation has been reported by Lee and co-workers.[15] A few examples of low-valent manganese–nitrogen cubanes have been reported with monoanionic phosphinimide bridging ligands.[16] An iron sulfide–thiolate cluster with geometry analogous to that of **1** was reported by the group of Tatsumi,[17] and a cobalt imido cluster with an analogous geometry (minus the central nitride) was reported by Link and Fenske.[18] The corner-fused dicubane geometry is the proposed active structure in the cobalt oxo water oxidation catalyst of Nocera et al. but with the corner fusion at a metal atom.[19]

Selected metrics from X-ray diffraction data are shown in Table 1. The terminal imido group on the Mn_4N_4 cube (left half, Figure 2) has a bond length of 1.66 Å, consistent with a multiply bonded terminal imido ligand, and is comparable to known Mn-terminal imidos.[10,12,13] The Mn–N bonds between the metal and the μ_3-imides and μ_6-nitride are in the range of 1.88–1.92 Å (single bonds). The μ_2-imido bridges between the Mn_4N_4 and the $MnLi_3N_4$ moieties show metrics indicating that the nitrogen atoms are more closely associated with—and multiply bonded to—the manganese atoms, (1.68–1.69 Å). The presence of multiple bonding in cluster **1** is worth noting, as π-bonding may has been proposed to have implications in the mechanism of the OEC,[19] but is underrepresented in synthetic Mn cluster chemistry.

The oxidation of Mn^{III} to higher oxidation states is achieved via disproportionation of Mn^{III}, a phenomenon that is mediated by the strongly π-donating imido ligands and has been previously seen in manganese imide chemistry.[12] Manganese-mediated cleavage of N–C(^{t}Bu) bonds to form nitrides has been observed previously by Danopoulos and Wilkinson. In the formation of the tetrahedral $[Mn^{VII}(N^tBu)_3N]^{2-}$ complex from the reaction of $Mn^{VII}(N^tBu)_3Cl$ with $[NH^tBu]^-$, the N–C(^{t}Bu) bond is proposed to be broken via deprotonation of a methyl proton and elimination of isobutylene.[10a] Thus, the formation of **1** can be expressed by the following balanced chemical equation:

Table 1. Selected Metrics[a] in 1 (Å)

Mn(1/4)–N(11/51)	1.660(10)/1.555(19)
Mn(1/1/4/4)–N(1/2/41/42)	1.918(6)/1.905(8)/1.959(8)/1.940(10)
Mn(2)–N(1/3/21)	1.900(6)/1.875(8)/1.677(9)
Mn(3)–N(1/2/3/31)	1.910(6)/1.898(6)/1.893(6)/1.678(7)
Li(2)–N(3/21/41)	2.176(19)/2.452(19)/2.043(13)
Li(3)–N(3/31/41/42)	2.212(14)/2.449(15)/2.006(15)/ 2.070(14)
Mn(1/1/2/3)···Mn(2/3/3/3A)	2.531(2)/2.555(2)/2.5150(18)/2.526(3)

[a] Divided entries refer to separate, related atoms and their associated metrics in the order given; e.g., Mn(2)–N(1/3/21) denotes three bond lengths, Mn(2)–N(1), Mn(2)–N(3), and Mn(2)–N(21).

$$\begin{aligned}&13MnF_3 + 26LiNH^tBu \rightarrow \mathbf{1} + 14^tBuNH_2 + 23LiF\\&\quad + 2(CH_3)_2C{=}CH_2 + 8MnF_2 \qquad (1)\end{aligned}$$

The terminal Mn≡N multiple bond is short, 1.56 Å, consistent with a multiply bonded nitride. The ^{1}H NMR spectrum shows a number of broad, poorly resolved signals in the diamagnetic region, belonging to the *tert*-butyl groups. The Mn–N cubane fragment has been detected by mass spectrometry (MS) in acetonitrile solution. The loss of the lithium cube in the MS experiment suggests that the Li–N contacts may be labile in the solution phase. The compound decomposes in air over the course of several minutes.

Crystallographic modeling of pure **1** in the X-ray crystal structure is unsatisfactory because the occupancy of the pendant manganese nitride moiety refines to less than 1 (ca. 0.5). The product is better described as a compositionally disordered cocrystal of **1** and a nearly isostructural cluster without the pendant Mn atom. Three clusters have been examined as models for the second cluster species in crystal structure refinement, and $[Mn_4Li_4(\mu_6\text{-}N)(\mu_3\text{-}N^tBu)_6(\mu\text{-}N^tBu)_3(N^tBu)]$ (**1a**; Figure 3) is supported as the second component by additional crystallographic analyses and IR spectroscopy (see Supporting Information).

In addition to **1** and **1a**, a contaminant cluster, comprising a very small component of the reaction mixture, has been identified by X-ray diffraction. Reduced temperature and stirring time result in the obtainment of two polymorphs of green crystals identified as a THF variant of the $Li_2[Mn^{VII}(N^tBu)_3N]^{2-}\cdot LiCl$ complex of Danopoulos and Wilkinson (see Supporting Information).[10a] It should be noted that chloride was not provided as a reagent in this reaction, indicating that this cluster arises as a result of chloride contamination in one of the two starting materials. This compound tcan be reproducibly prepared from different MnF_3 reagent bottles from different vendors (Aldrich and Strem) and from different preparations of LiNH^{t}Bu.[14] Isolation of this material only at low temperatures may suggest that the formation of tris(imido)nitridomanganese(VII) is facile, and additional heating may be required to dissolve additional MnF_3 and/or drive its comproportionation with Mn^{VII} to give the $Mn^{IV/V}$ cluster species, although this mechanism is speculative.

The clusters **1** and **1a** are a mixture of Mn^{IV} and Mn^V ions based on bond-valence-summation (BVS) calculations.[21] This

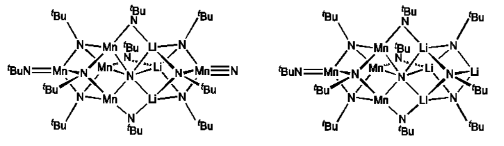
1 **1a**

Figure 3. Lewis structures of the two components in cocrystalline **1** and **1a**.

assignment is supported by X-ray photoelectron spectroscopy (XPS). The energy of the $2p_{3/2}$ band is 642−643 eV, in the expected range for Mn^{IV}, with a shoulder in the direction of the region of Mn^{V} at 645 eV (Supporting Information).[22] It is worthwhile to note that the 4+ and 5+ oxidation states are those believed to be present in the water-oxidizing S_4 state of PSII.[2]

In summary, we have prepared a high oxidation-state, four-coordinate manganese heterocubane cluster with a pendant manganese and s-block metal atoms (Li), the first compound to have all of these features. The multiple bonding in these systems represents a departure from traditional synthetic manganese−oxygen clusters and is worth noting in the context of a proposed S_4 state description[20] of the OEC, where π donation from a terminal oxo into the pendant manganese may be crucial to make the manganese-bound oxygen electrophilic enough to react with the hydroxide ion and thus favor the reduction of the pendant Mn atom concomitant with O−O bond formation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystalllographic data in CIF format, full experimental protocols, full tables of X-ray metrics, additional crystallographic discussion, MS spectra, ^1H NMR, FT-IR, UV−Vis, XPS, and BVS calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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