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Synthesis of Tetranuclear, Four-Coordinate Manganese Clusters with “Pinned Butterfly” Geometry Formed by Metal-Mediated N−N Bond Cleavage in Diphenylhydrazine

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Supporting Information

ABSTRACT: The preparation of four-coordinate tetramanganese−amide−hydrazide clusters is described. Reaction of $Mn(NR_2)_2$ (R = $SiMe_3$) with *N,N′*-diphenylhydrazine resulted in the formation of a black intermediary mixture that converted to a four-coordinate tetranuclear “pinned butterfly” cluster, $Mn_4(\mu_3\text{-}N_2Ph_2)_2(\mu\text{-}N_2Ph_2)(\mu\text{-}NHPh)_2(THF)_4$. This compound was isolated in ~90% yield and identified by single-crystal X-ray diffraction analysis. In pyridine, the THF ligands were replaced, giving the pyridyl complex $Mn_4(\mu_3\text{-}N_2Ph_2)_2(\mu\text{-}N_2Ph_2)(\mu\text{-}NHPh)_2(py)_4$. Charge counting considerations indicate that the clusters had gained two protons and two electrons in addition to the formative fragments. Isolation of the black mixture was achieved by extraction techniques from a reaction with a decreased loading of hydrazine run at low temperatures with decreased solvent polarity. The black mixture was characterized by FT-IR, UV−vis, and ^{1}H NMR spectroscopy. In addition, an isolable, colorless dimer, $Mn_2(\mu\text{-}NHPh)_2(NR_2)_2(THF)_2$, was present in the mixture and identified by single-crystal X-ray diffraction. These intermediates are discussed in light of possible mechanisms for formation of the tetranuclear cluster.

The oxidation of water to dioxygen represents a grand challenge for the development of catalytic water splitting systems that use electricity or sunlight to store energy in the bonds of H_2 and O_2.[1] In nature, a catalyst has evolved for the water oxidation reaction, which is ubiquitous in all oxygenic photosynthetic organisms. The oxygen-evolving complex (OEC) of photosystem II (PS II) is an oxo-bridged 4Mn−Ca cluster (Figure 1) that collects oxidizing equivalents from photo-oxidized chlorophyll, oxidizes H_2O to O_2 to return to its most reduced state, and pumps four water protons to the lumen.[2]

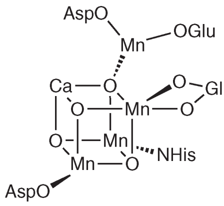

Figure 1. Crystallographic structural model of the OEC.

Chart 1. Pairs of (top row) PS II-Relevant Species and (bottom row) Their Nitrogen Analogues: (left to right) Water/Amine, Hydroxide/Amide, Oxide/Imide, Peroxide/Hydrazine, Dioxygen/Diazene

H_2O	OH^-	O^{2-}	HOOH	O=O
H_2NR	RNH^-	RN^{2-}	RNHNHR	RN=NR

Numerous examples of synthetic manganese−oxo clusters can be found in the literature and have been reviewed.[3] Almost exclusively, these synthetic clusters are six-coordinate with multidentate ligation. In the interest of generating biomimetic systems with accessible redox reactivity, we are exploring the chemistry of low-coordinate, unchelated manganese clusters by using imide as a surrogate of oxide. Isolobal, comparably sized, and equally charged, imides have been studied as oxide analogues in terminally bonded, monomeric transition-metal species.[4] Only a few reports of Mn−imido clusters exist, published by the groups of Wilkinson, Power, and Wright.[5] We seek to explore the cluster chemistry of manganese with nitrogen analogues of OEC-relevant substrates (Chart 1) using the R group to control the geometry and coordination number.

Lee and co-workers achieved entry into low-coordinate iron−imido chemistry by the metal-mediated reductive cleavage of *N,N′*-diarylhydrazines.[6] In an attempt to mimic this entry for the manganese systems, we explored *N,N′*-diphenylhydrazine as an imide source. The reaction of a solution of colorless $Mn(NR_2)_2$[7] (R = $SiMe_3$) with a pale-yellow solution containing 1.25 equiv of PhNHNHPh in THF resulted in the formation of a black mixture (**1a**). Over the course of minutes, this black mixture turned orange, and in the presence of pentane, orange crystalline material precipitated over the course of 2 h. Single-crystal X-ray analysis identified this compound as the manganese−amide−hydrazide cluster $Mn_4(\mu_3\text{-}PhNNPh)_2(\mu\text{-}PhNNPh)(\mu\text{-}NHPh)_2(THF)_4$ (**2**), whose structure is shown in Figure 2. The terminal THF ligands were easily be replaced with pyridine by dissolution of **2** into pyridine, which led to precipitation of $Mn_4(\mu_3\text{-}PhNNPh)_2(\mu\text{-}PhNNPh)(\mu\text{-}NHPh)_2(py)_4$ (**2a**). These clusters (as well as cluster **1b**; see below) are remarkably air- and water-sensitive, turning instantly black and often smoldering upon exposure to air. **2** has a shelf life of weeks when stored at −30 °C in a well-maintained dry atmosphere box; **2a** is slightly more robust, lasting months at −30 °C under inert atmosphere.

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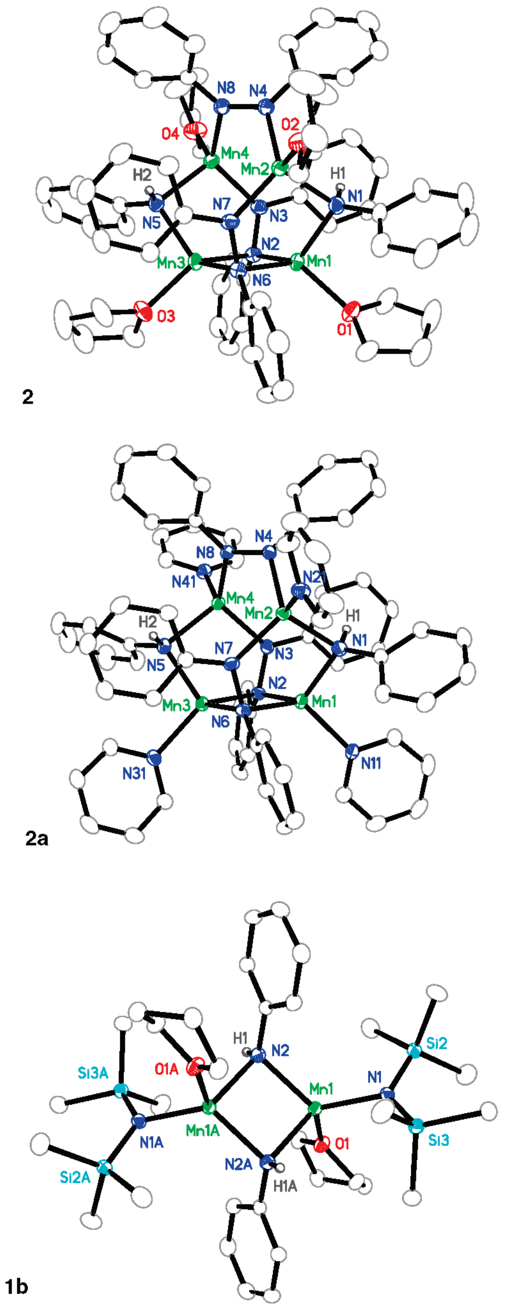

Figure 2. Thermal ellipsoid plots of compounds **2**, **2a**, and **1b**. Ellipsoids are set at 50% probability. N−H hydrogen atoms were located as Fourier difference peaks and refined, and they are shown as open circles. Carbon atoms are represented by open ellipses. C−H hydrogens have been omitted for clarity.

Selected metrics for the clusters are given in Table 1. The cluster core of **2** can be described as a "pinned butterfly" geometry with C_2 point symmetry analogous to that described by Dismukes for OEC models.[8] The base is constructed from an Mn_2N_2 rhomb with each N belonging to one hydrazide nitrogen. This rhomb is nearly planar and slightly elongated along the N−N vector (see Table 1) with bond angles of ca. 91.5 and 88.5° for the Mn and N rhomb angles respectively. The base Mn atoms are further bridged to two "wing" Mn atoms through the hydrazide ligand and a bridging *N*-phenylamido ligand, forming a five-membered puckered metallacycle. The presence of the phenylamido ligands indicates that reductive cleavage of a hydrazine N−N bond has occurred. The two "wing" Mn atoms are further joined to one another by a third bridging diphenylhydrazide ligand that is roughly parallel to the Mn_2N_2 rhomb and forms a dihedral angle of 23.2° with respect to the $Mn(1)\cdots Mn(2)$ vector. All of the Mn atoms are terminally coordinated by THF. The metal−nitrogen contacts are longest (2.10−2.17 Å) for N(1), N(2), N(5), and N(6) because they are shared between two metal atoms, and the contacts for the remaining nitrogen atoms that ligate only one metal atom are a bit shorter (2.05−2.08 Å). The hydrazine N−N bonds are slightly elongated single bonds with distances between 1.45 and 1.47 Å, consistent with the assignment of deprotonated hydrazide.

The structural metrics of **2a** are quite similar to those of **2**. The Mn−N contacts in the Mn_2N_2 rhomb are slightly elongated because of the stronger σ-donation from the pyridine terminal ligands, though the rhomb angles are similar. The planarity of the base rhomb is slightly decreased, and the five-membered "wings" are slightly more puckered in **2a**, but there are no other major differences in the structures. Only a few examples of Mn clusters of primary amides have been reported.[9] Mn clusters with hydrazines are almost as rare and limited exclusively to acyl hydrazides.[10]

The solution behavior of **2** and **2a** is complex. Compound **2** showed no discernible ^1H NMR signature, which we attribute to a paramagnetic broadening by the high-spin Mn atoms and possibly speciation, resulting in extensive broadening. ^1H NMR analysis of compound **2a** was also uninformative.[11]

All of the NR_2^- ligands were removed via protolysis by the N−H protons of PhNHNHPh. Charge counting considerations on **2** and **2a** require the formal assignment of an all-Mn^{II} cluster. Thus, the cluster has two electrons and two protons more than expected on the basis of a simple 1:1 reaction stoichiometry. Therefore, the role of an additional (fifth) hydrazine molecule must be invoked to write the balanced chemical equation for the reaction:

$$4Mn(NR_2)_2 + 5PhNHNHPh + 4THF \rightarrow$$

$$\mathbf{2} + PhN{=}NPh + 8HNR_2$$

In this reaction, diphenylhydrazine plays several roles: the proton source for the protolysis of NR_2^- ligands, the ligand source for the formation of the hydrazide and amide ligands in **2** and **2a**, and the reductant, replacing the two electrons consumed in the N−N bond cleavage concomitant with formation of azobenzene. For example, the formation of an intermediate Mn(III)−imido species by reductive cleavage of the N−N bond followed by hydrogen atom transfer (HAT) from hydrazine to generate **2** and azobenzene is a plausible mechanism. Indeed, azobenzene and HNR_2 were observed in the soluble fraction of the reaction mixture by ^1H NMR spectroscopy. A similar mechanism has been proposed for hydrazine disproportionation by Zr complexes of redox-active ligands.[12a] The high yields of **2** and **2a** and the relatively low conversion (∼30%) to azobenzene all disfavor simple disproportionation mechanisms[13] for N−N bond cleavage, though more complex, metal-mediated radical disproportionations, such as those observed in iron chemistry, are also possible.[12b]

The reaction of $Mn(NR_2)_2$ with a decreased equivalency of PhNHNHPh (1.15:1 ratio) at low temperature and low dielectric constant (higher pentane concentration) resulted in a solution that maintained the black color. The use of pentane and low

Table 1. Selected Bond Distances (Å) and Angles (deg)[a] for $Mn_4(\mu_3\text{-PhNNPh})_2(\mu\text{-PhNNPh})(\mu\text{-NHPh})_2(THF)_4$ (2) and $Mn_4(\mu_3\text{-PhNNPh})_2(\mu\text{-PhNNPh})(\mu\text{-NHPh})_2(py)_4$ (2a)

	2[b]	2a
Mn(1)−N(1/2/6)	2.1054(14)/2.0957(13)/2.1719(15)	2.119(2)/2.140(2)/2.1699(18)
Mn(2)−N(1/4/7)	2.1483(14)/2.0448(14)/2.0673(14)	2.155(2)/2.050(2)/2.058(2)
Mn(1)···Mn(2/3/4)	3.1861(9)/2.9760(10)/4.1187(9)	3.2405(6)/2.9777(5)/4.0346(6)
N(2/4)−N(3/8)	1.4661(18)/1.453(2)	1.470(3)/1.444(2)
N2···N6	3.059(3)	3.089(2)
N(2/6/6)−Mn(1)−N(1/1/2)	121.57(5)/105.57(5)/91.59(5)	126.11(8)/101.84(7)/91.58(7)
N(1/1/7)−Mn(2)−N(7/4/4)	101.94(6)/111.20(6)/124.18(5)	102.01(7)/110.23(8)/117.13(7)
Mn(1)−N(1/2)−Mn(2/3)	97.01(6)/88.41(5)	98.63(8)/87.61(7)
Mn(1/3/4)−N(2/2/3)−N(3/3/2)	96.63(8)/105.19(9)/122.20(10)	88.68(11)/105.65(11)/119.46(13)

[a] Divided entries refer to separate, related atoms and their associated metrics in the order given, e.g., N(2/6/6)−Mn(1)−N(1/1/2) denotes the three angles N(2)−Mn(1)−N(1), N(6)−Mn(1)−N(1), and N(6)−Mn(1)−N(2). [b] For **2**, atoms Mn(3), Mn(4), N(5), N(6), N(7), and N(8) are symmetry equivalents of Mn(1), Mn(2), N(1), N(2), N(3), and N(4), respectively. The naming scheme has been changed for consistency with **2a**.

temperatures lowers the solubility of hydrazine and thus its rate of reactivity with **1a**. The maintenance of **1a** by decreased hydrazine availability supports the hypothesis that **1a** reacts with PhNHNHPh to form **2**. Extraction techniques allowed the identification of at least three compounds in the reaction mixture. The residue after filtration of the reaction mixture was identified by FT-IR as **2**. The black intermediary mixture **1a** was isolated by extraction of the dried filtrate into pentane. This substance is hypersoluble in organic solvents and has eluded structural characterization to date. The electronic absorption spectrum of this extracted mixture was identical to that of **1a** generated in situ. FT-IR analysis of **1a** indicated the presence of aliphatic C−H stretches belonging to Me_3Si and aryl C−H stretches but no THF stretches[14] or N−H stretches. The ^1H NMR spectrum of **1a** exhibited broad, paramagnetically shifted signals (see the Supporting Information).

After removal of **1a** by extraction, crystals of the dimeric compound $Mn_2(\mu\text{-NHPh})_2(NR_2)_2(THF)_2$ (**1b**) were isolated from the residue and identified by single-crystal X-ray diffraction (Figure 2). This compound may be an intermediate en route to **2** that is isolable only under conditions of limiting PhNHNHPh, precluding aggregation to form **2**. Alternatively, **1b** may be a second product that does not form in large amounts in the 4:5 ratio reaction but becomes favored under reduced hydrazine loading. **1b** can be prepared directly from $Mn(NR_2)_2$ and aniline in good yield (82%).

We have reported here the preparation of a four-coordinate tetramanganese "pinned butterfly" that forms from as yet unidentified intermediates (**1a**). Detailed mechanistic investigations into the formation of these species, the intermediacy of **1b**, and the involvement of HAT will be the subject of subsequent study.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystal data tables; experimental procedures; FT-IR and absorption spectra of **1a**, **1b**, **2**, and **2a**; ^1H NMR spectra of **1a**, **1b**, and **2b**; and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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