

## Rare Oxidation-State Combinations and Unusual Structural Motifs in Hexanuclear Mn Complexes Using 2-Pyridyloximate Ligands

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The use of phenyl-2-pyridyl ketone oxime and di-2-pyridyl ketone oxime in Mn chemistry has led to hexanuclear clusters with unprecedented (Mn<sup>II</sup><sub>4</sub>Mn<sup>III</sup>Mn<sup>IV</sup>) or extremely rare (Mn<sup>II</sup>Mn<sup>III</sup><sub>5</sub> and Mn<sup>II</sup><sub>3</sub>Mn<sup>III</sup><sub>3</sub>) metal oxidation-state combinations and uncommon structural motifs.

Mixed valency in polynuclear (cluster) Mn chemistry currently attracts the intense interest of many groups around the world,<sup>1</sup> partly because Mn<sup>II</sup>/Mn<sup>III</sup>, Mn<sup>III</sup>/Mn<sup>IV</sup>, and Mn<sup>II</sup>/Mn<sup>III</sup>/Mn<sup>IV</sup> clusters are the main source of high-spin molecules<sup>2</sup> and single-molecule magnets (SMMs).<sup>3</sup> The majority of SMMs are Mn species because clusters of this metal often display large ground-state spin (*S*) values and large and negative magnetoanisotropies. Only a relatively few SMMs have contained Mn<sup>III</sup> exclusively;<sup>4</sup> most Mn SMMs have instead been mixed-valent, and such mixed-valence clusters containing Mn<sup>III</sup> are almost without exception valence-localized.<sup>1</sup> Another reason for the great current interest in Mn mixed valency is its relevance to the oxygen-evolving complex (OEC) in photosystem II (PSII).<sup>5</sup> Thus, it becomes apparent

why there is a continuing need for new synthetic methods that lead to mixed-valence Mn clusters.

Organic ligands play a key role in such efforts. Recently, we and others have been investigating a number of oxime-based ligands,<sup>6</sup> and one family of these has been the 2-pyridyl oximes<sup>7</sup> (Chart 1), which are key “players” in several areas of molecular magnetism, including SMMs<sup>8</sup> and single-chain magnets.<sup>9</sup> We have been seeking unprecedented or rare oxidation levels in mixed-valence Mn<sub>x</sub> complexes using anionic 2-pyridyl oximes, and herein we report the realization of our ambition for *x* = 6.

The reaction of MnBr<sub>2</sub>, phenyl 2-pyridyl ketone oxime (phpaoH), LiOH·H<sub>2</sub>O, and NaN<sub>3</sub> in a 1:1:1:1 molar ratio in EtOH (see the Supporting Information) led to a dark-green solution, which upon slow evaporation at room temperature gave black crystals of [Mn<sup>II</sup>Mn<sup>III</sup><sub>5</sub>O<sub>3</sub>(OEt)<sub>0.5</sub>(N<sub>3</sub>)<sub>3</sub>(phpao)<sub>6</sub>-Br(EtOH)<sub>1.5</sub>](Br)<sub>0.5</sub> (**1**) in 60% yield.

The cation of **1** (Figure 1)<sup>10</sup> contains one Mn<sup>II</sup> (Mn6) and five Mn<sup>III</sup> (Mn1–Mn5) atoms held together by three μ<sub>3</sub>-O<sup>2-</sup> groups (O7–O9), two η<sup>2</sup>:μ-N<sub>3</sub><sup>-</sup> groups (their donor atoms are N13 and N16), and six η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup>:μ-phpao<sup>-</sup> ligands.

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(9) For example, see: Miyasaka, H.; Julve, M.; Yamashita, M.; Clérac, R. *Inorg. Chem.* 2009, 48, 3420 (Forum Article).

(10) Crystal structure data for **1**: C<sub>152</sub>H<sub>131</sub>Mn<sub>12</sub>N<sub>42</sub>O<sub>22</sub>Br<sub>3</sub>, *M<sub>w</sub>* = 3797.00, monoclinic, space group *P*2<sub>1</sub>/*c* with *a* = 12.364(2) Å, *b* = 31.637(4) Å, *c* = 22.786(3) Å, β = 94.968(2)°, *V* = 8879(2) Å<sup>3</sup>, *T* = 150(2) K, *Z* = 2, R1 [*I* > 2σ(*I*)] = 0.0596, wR2 (*F*<sup>2</sup>, all data) = 0.1778. Crystal structure data for 2·3CH<sub>2</sub>Cl<sub>2</sub>: C<sub>93</sub>H<sub>72</sub>Mn<sub>6</sub>N<sub>8</sub>O<sub>18</sub>Cl<sub>6</sub>, *M<sub>w</sub>* = 2512.63, triclinic, space group *P*1 with *a* = 14.9607(7) Å, *b* = 18.1375(7) Å, *c* = 21.3836(8) Å, α = 100.943(3)°, β = 107.534(3)°, γ = 112.724(4)°, *V* = 4784.7(3) Å<sup>3</sup>, *T* = 100(2) K, *Z* = 2, R1 [*I* > 2σ(*I*)] = 0.0714, wR2 (*F*<sup>2</sup>, all data) = 0.1987. Crystal structure data for 3·1.5H<sub>2</sub>O: C<sub>172</sub>H<sub>134</sub>Mn<sub>12</sub>N<sub>20</sub>O<sub>51</sub>Cl<sub>2</sub>, *M<sub>w</sub>* = 4027.17, monoclinic, space group *P*2<sub>1</sub>/*c* with *a* = 20.935(2) Å, *b* = 17.042(2) Å, *c* = 25.320(3) Å, β = 108.530(2)°, *V* = 8564.7(16) Å<sup>3</sup>, *T* = 150(2) K, *Z* = 2, R1 [*I* > 2σ(*I*)] = 0.0383, wR2 (*F*<sup>2</sup>, all data) = 0.1099.

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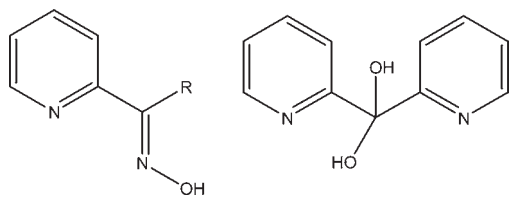
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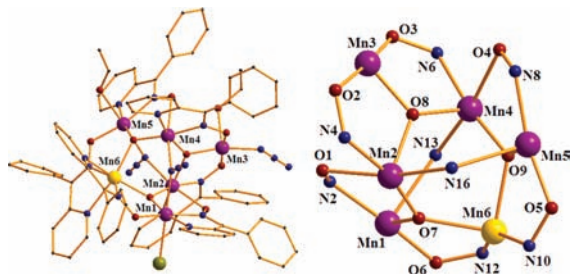
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Chart 1. Ligands Discussed in the Text<sup>a</sup>

<sup>a</sup>Note that  $\text{dpk}\cdot\text{H}_2\text{O}$  and its anions do not exist as free species but exist only in their respective metal complexes. R = Ph,  $\text{phpaoH}$ ; R = 2-pyridyl,  $\text{pypaOH}$ .

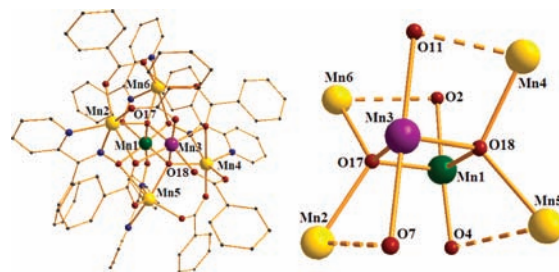


**Figure 1.** Metal-labeled representation of the cation of **1** (left) and its core (right). The latter has been drawn to include the six diatomic oximate groups. Color scheme:  $\text{Mn}^{\text{II}}$ , yellow;  $\text{Mn}^{\text{III}}$ , purple; O, red; N, blue; C, dark gray.

Peripheral ligation is provided by one terminal azido group and terminal  $\text{Br}^-$  and  $\text{EtOH}$  ligands. The structure consists of three  $\{\text{Mn}_3(\mu_3\text{-O})\}$  triangular units, two homovalent and one valence-trapped, mixed-valent. Each unit is sharing one vertex with each neighboring unit, resulting in the formation of a fused-triangle topology. An inner isosceles  $\{\text{Mn}_2\text{Mn}_4\text{Mn}_6\}$  triangle and an outer scalene  $\{\text{Mn}_1\text{Mn}_3\text{Mn}_5\}$  triangle form. Each edge of the inner  $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2\}$  triangle is bridged by an  $\text{O}^{2-}$  group, and the  $\{\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_2(\mu\text{-O})_3\}$  hexagon has a chair conformation. The two triangles are communicating through the oxo ligands that become  $\mu_3$ , the six oximate groups, and the two end-on azido ligands, each bridging two  $\text{Mn}^{\text{III}}$  atoms. The angle between the planes of the two triangles is  $72.5^\circ$ . This structural motif is unusual in Mn chemistry.<sup>12</sup> The  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_5$  oxidation level in a discrete  $\text{Mn}_6$  cluster has been observed only in a small number of complexes.<sup>11,12</sup>

The reaction of  $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{PhCO}_2\text{H}$ ,  $\text{phpaoH}$ ,  $\text{Et}_3\text{N}$ , and  $\text{I}_2$  in a 1.5:1.5:1:2.5:1.5 molar ratio in  $\text{CH}_2\text{Cl}_2$  gave a dark green/black solution that upon layering with hexanes gave black crystals of  $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_2(\text{O}_2\text{CPh})_6(\text{phpao})_4](\text{I}_3)\cdot 3\text{CH}_2\text{Cl}_2$  ( $2\cdot 3\text{CH}_2\text{Cl}_2$ ) in 60% yield.

The cation of **2** (Figure 2)<sup>10</sup> consists of one  $\text{Mn}^{\text{IV}}$  (Mn1), one  $\text{Mn}^{\text{III}}$  (Mn3), and four  $\text{Mn}^{\text{II}}$  (Mn2, Mn4, Mn5, and Mn6) atoms arranged as two edge-sharing tetrahedra; the common edge is Mn1–Mn3. At the center of each tetrahedron lies a



**Figure 2.** Metal- and oxide-labeled representation of the cation of **2** (left) and its core (right). The dashed lines represent weakly bonding interactions. The color scheme is the same as that in Figure 1 plus the following:  $\text{Mn}^{\text{IV}}$ , green.

$\mu_4\text{-O}^{2-}$  group. Peripheral ligation is provided by six  $\text{PhCO}_2^-$  and four  $\text{phpao}^-$  ligands. Each Mn center is six-coordinate and possesses distorted octahedral geometry. The  $\text{PhCO}_2^-$  groups separate into two classes. Four are  $\eta^1:\eta^1:\mu$  and the other two are  $\eta^1:\eta^2:\mu_3$ . Two  $\text{phpao}^-$  groups are  $\eta^1:\eta^1:\eta^1:\mu$ , with the N atoms forming a five-membered chelating ring with a  $\text{Mn}^{\text{II}}$  atom and the oximate O atom terminally ligated to the  $\text{Mn}^{\text{IV}}$  center. The other two  $\text{phpao}^-$  ligands are  $\eta^1:\eta^1:\eta^2:\mu_3$ , each bridging two  $\text{Mn}^{\text{II}}$  atoms and the  $\text{Mn}^{\text{IV}}$  center. Of interest is the preference of the four oximate O atoms to bind to the  $\text{Mn}^{\text{IV}}$  atom. Considering only the monatomic bridges, the core is  $\{\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}(\mu_4\text{-O})_2(\mu\text{-OR}')_2(\mu\text{-OR}'')_2\}^{7+}$ , where  $\text{R}' = \text{PhCO}-$  and  $\text{R}''\text{O}^- = \text{phpao}^-$  (Figure 2, right). Complex **2** is the first hexanuclear Mn cluster with the  $\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$  oxidation-state level. Complex **2** has a structural relationship with the very stable members of the  $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2(\mu_4\text{-O})_2(\eta^1:\eta^1:\mu\text{-O}_2\text{CR}')_6(\eta^1:\eta^2:\mu_3\text{-O}_2\text{CR}'')_4(\text{L})_4]$  family of clusters (L = monodentate ligand).<sup>13</sup> 2-Pyridyloximate ligands have been recently shown to be capable of substituting one carboxylate and one neutral ligand.<sup>8</sup> This is also the case here, where four of the  $\text{PhCO}_2^-$  ligands (two  $\eta^1:\eta^1:\mu$  and two  $\eta^1:\eta^2:\mu_3$ ) and all of the L ligands have been replaced by two  $\mu$  and two  $\mu_3$ - $\text{phpao}^-$  groups.

The use of di-2-pyridyl ketone oxime ( $\text{pypaOH}$ ; Chart 1) in manganese benzoate chemistry led to a  $\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3$  cluster. The reaction of  $\text{Mn}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ ,  $\text{PhCO}_2\text{H}$ ,  $\text{NBu}^n_4\text{MnO}_4$ , and  $\text{pypaOH}$  in a 4:5:1:5 molar ratio in  $\text{CH}_2\text{Cl}_2$  gave a black solution, from which was obtained  $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3\text{O}_2(\text{O}_2\text{CPh})_6(\text{pypaO})_2(\text{dpk}\cdot\text{OH})_2](\text{ClO}_4)\cdot 1.5\text{H}_2\text{O}$  ( $3\cdot 1.5\text{H}_2\text{O}$ ) upon layering with hexanes in 65% yield (see the Supporting Information). The  $\text{dpk}\cdot\text{OH}^-$  ligand is the monoanion of the *gem*-diol form of di-2-pyridyl ketone ( $\text{dpk}\cdot\text{H}_2\text{O}$ ; Chart 1) produced in situ from the metal-assisted hydrolytic deoximation and nucleophilic attack of  $\text{H}_2\text{O}$  to the ketone group that forms, followed by single deprotonation, as has already been observed in Mn chemistry.<sup>14</sup>

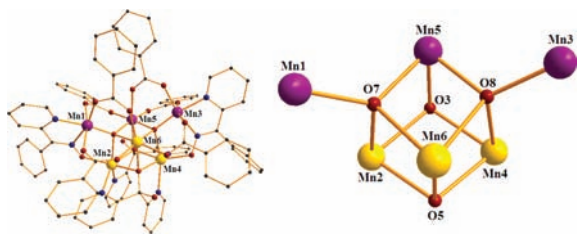
The cation of **3** (Figure 3)<sup>10</sup> contains three  $\text{Mn}^{\text{II}}$  (Mn2, Mn4, and Mn6) and three  $\text{Mn}^{\text{III}}$  (Mn1, Mn3, and Mn5) atoms; it is held together by six  $\eta^1:\eta^1:\mu\text{-PhCO}_2^-$ , two  $\eta^1:\eta^1:\eta^1:\mu\text{-pypaO}^-$  (the second 2-pyridyl N atom of each  $\text{pypaO}^-$  is unbound), and two  $\eta^1:\eta^3:\eta^1:\mu_3\text{-dpk}\cdot\text{OH}^-$  ligands. The core of the complex is  $\{\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3(\mu_3\text{-O})_2(\mu_3\text{-OR}''''')_2\}^{9+}$ , where  $\text{R}'''''\text{O}^- = \text{dpk}\cdot\text{OH}^-$ . It consists of a central  $\{\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}(\mu_3\text{-O})_2(\mu_3\text{-OR}''''')_2\}^{3+}$  cubane subcore, with the remaining

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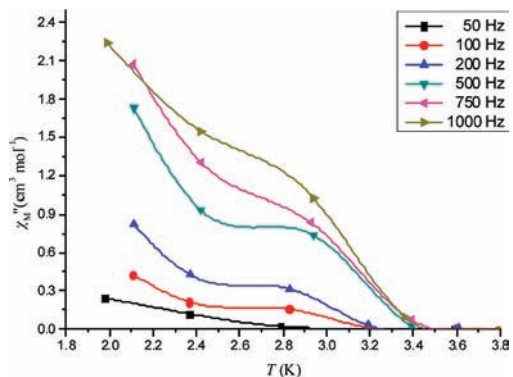


**Figure 3.** Metal-labeled representation of the cation of **3** (left) and its core (right). The color scheme is the same as that in Figure 1. O7 and O8 are the two oxo groups, and O3 and O5 are the triply bridging O atoms of the  $\text{dpk}\cdot\text{OH}^-$  ligands.

two  $\text{Mn}^{\text{III}}$  atoms attached to the two vertices of the cube that are occupied by the  $\text{O}^{2-}$  groups, the latter becoming  $\mu_4$  as a result (Figure 3, right). Complex **3** is the fourth structurally characterized  $\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3$  cluster,<sup>15</sup> but its metal topology and core are both novel.<sup>15a</sup>

In all of the above structural descriptions, the Mn oxidation states were obtained from metric parameters, bond valence sum (BVS) calculations (Table S1 in the Supporting Information),<sup>16</sup> and the clear Jahn–Teller axial elongation at the near-octahedral  $\text{Mn}^{\text{III}}$  atoms. The nature of both the oxidizing agent used ( $\text{O}_2$ ,  $\text{I}_2$ , and  $\text{MnO}_4^-$ ) and the inorganic anion present ( $\text{Br}^-/\text{N}_3^-$  and  $\text{ClO}_4^-$ ) seem to affect the final product.

Solid-state direct-current magnetic susceptibility ( $\chi_M$ ) data on dried **1–3** were collected under a 0.1 T field in the 5.0–300 K range (Figure S1 in the Supporting Information). In each case, the 300 K value of  $\chi_M T$  is below the spin-only value expected for uncoupled  $[\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_5]$ ,  $[\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}]$ , and  $[\text{Mn}^{\text{II}}_3\text{Mn}^{\text{III}}_3]$  units, indicating moderate (**2** and **3**) or strong (**1**) intramolecular antiferromagnetic interactions.<sup>17</sup> The  $\chi_M T$  product for **1** and **2** constantly decreases with decreasing  $T$ , with the low-temperature values suggesting  $S = 5/2 \pm 1$  ground states for both. The rise of the  $\chi_M T$  product as  $T$  decreases for **3** indicates ferrimagnetic coupling with the maximum suggestive of  $S = 15/2 \pm 1$ . Magnetization data for **3** (Figure S4 in the Supporting Information) were fit by a matrix diagonalization method employing the Hamiltonian  $\hat{H} = D[\hat{S}_z^2 - S(S+1)/3] + \mu_B g H \hat{S}_z$ , giving the parameters  $S = 15/2$ ,  $g = 2.07$ , and  $D = -0.317 \text{ cm}^{-1}$ . The slightly anomalous  $g$  value likely results from the simplified fitting model (giant-spin approximation), and we stress the numbers quoted should be taken only as a guide. Out-of-phase alternating-current (ac) susceptibility studies (Figure 4) suggest **3** to be an SMM, with the tails of the



**Figure 4.** Out-of-phase ( $\chi_M''$ ) vs  $T$  ac susceptibility signals for **3** in a 3.5 G field oscillating at the indicated frequencies.

signals (but no peaks) appearing below 4 K in the 1000–50 Hz frequency range.<sup>17</sup>

In conclusion, the synthesis of mixed-valence  $\text{Mn}_6$  clusters with unprecedented or rare metal oxidation-state combinations and structural motifs has been achieved via the use of 2-pyridyloximate ligands. Although the nuclearity and metal topology of the OEC in PSII<sup>5</sup> are different compared to those in **2**, attaining a system with three different Mn oxidation states is a goal for many biomimetic chemists working on finding ways of modeling PSII. There are strong pieces of evidence supporting the  $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}_2$  assignment of the  $S_0$  state (the product state of the biological catalyst) of the OEC.<sup>5</sup> Compound **2** demonstrates that  $\text{Mn}^{\text{II}}$  and  $\text{Mn}^{\text{IV}}$  can be stable to comproportionation within the same molecule, suggesting that the OEC would be capable of stabilizing three Mn oxidation states and supporting the oxidation-state assignment for its lowest  $S$  state. On the basis of our ongoing studies and the results arising from them, our belief is that we have seen only the tip of the iceberg in the area of mixed-valence  $\text{Mn}_x$  ( $x > 6$ ) cluster chemistry with this class of ligands and that many interesting molecules await discovery.

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(17) Details will be reported in a forthcoming full paper.

**Supporting Information Available:** Crystallographic data in CIF format, BVS calculations (Table S1), and synthetic procedures, magnetic susceptibility, and magnetization data for **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.