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The Highest-Nuclearity Manganese/Oximate Complex: An Unusual $\mathrm{Mn^{II/III}}_{15}$ Cluster with an S = 6 Ground State

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The synthesis, structure, and magnetochemical characterization of the largest manganese oxime cluster are reported. The $\mathrm{Mn_{15}}$/2-pyridinealdoxime compound is mixed-valence (II/III) and possesses an irregular structural motif with a novel Mn/O core. The oximato-bridged cluster exhibits an S = 6 ground state and a negative magnetoanisotropy.

The last 2 decades have witnessed a tremendous growth in interest in polynuclear manganese compounds (clusters) at moderate oxidation states with O- and N-based ligation.[1] This has been mainly due to their relevance to bioinorganic chemistry[2] and molecular magnetism,[3] as well as to the architectural beauty and aesthetically pleasing structures that they often possess.[1]

In the molecular magnetism area, Mn clusters containing at least some $\mathrm{Mn^{III}}$ ions have been found to often have large ground-state spin (S) values, which combined with a large and negative magnetoanisotropy (as reflected in a large and negative zero-field-splitting parameter, D) have led to some of these complexes being single-molecule magnets (SMMs).[3] SMMs are individual molecules or ions that behave as nanoscale magnets below a certain ("blocking") temperature and thus represent a molecular, "bottom-up" approach to nanomagnetism.

The chances of identifying new, high-spin $\mathrm{Mn^{III}}$-containing clusters and SMMs with unprecedented structural motifs will benefit from the development of new reaction systems with suitable organic ligands.[1,4] A popular such family of ligands are the 2-pyridyl oximes (Chart 1).[4d,5] These have recently attracted intense interest from synthetic inorganic chemists and magnetochemists because of the isolation of $[\mathrm{Mn^{III}}_3\mathrm{O(O_2CMe)_3(mpko)_3}](\mathrm{ClO_4})$, where mpko$^-$ is the anion of methyl 2-pyridyl ketone oxime (Chart 1), which is ferromagnetically coupled because of the distortion imposed on the triangular core by the *tridentate oximate ligand* and which is an SMM.[6]

A large number of polynuclear, homometallic Mn/2-pyridyl oximato complexes have been synthesized,[4d] but unfortunately only a few of them contain $\mathrm{Mn^{III}}$ ions and behave as SMMs.[6,7] In the present work, we report the highest-nuclearity Mn/oximato cluster to date from the use of the simplest 2-pyridyl oxime, namely, 2-pyridinealdoxime (paoH; Chart 1). This ligand previously gave exclusively $\mathrm{Mn^{II}}$ complexes of nuclearities 2,[8] 4[8] and 6,[9] and the interesting mixed-valence $[\mathrm{Mn^{II/III/IV}}_9\mathrm{O_6(O_2CMe)_4(pao)_8(paoH)_2}]$ cluster,[9a] which, however, was isolated in very small yields and thus its magnetic properties could not be studied.

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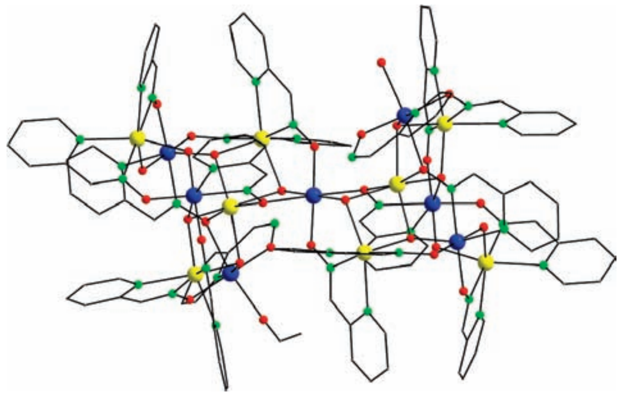
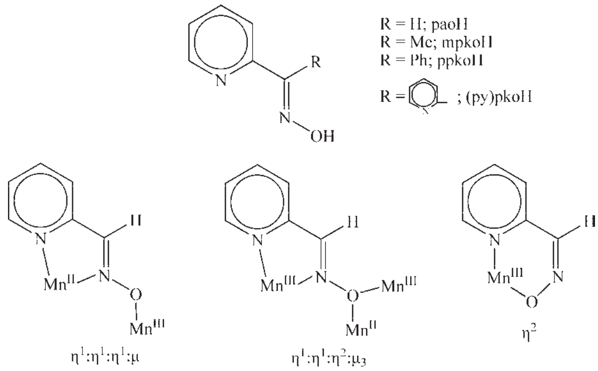


Figure 1. Molecular structure of the cation of complex **1**. H atoms have been omitted for clarity. Color scheme: Mn^{II}, yellow; Mn^{III}, blue; O, red; N, green; C, gray.

Chart 1. (top) 2-Pyridyl Oxime Ligands Discussed in the Text and (bottom) Crystallographically Established Coordination Modes of pao^- in Complex **1**



We have now discovered a simple synthetic route into significantly higher-nuclearity Mn/2-pyridyl oximato species, which also possess interesting magnetic properties. In particular, the compound reported herein is a new example of a mixed-valence, $Mn^{II/III}$ noncarboxylate species with an unprecedented structural motif and a rare nuclearity, which additionally exhibits an appreciable ground-state spin value. We believe this work presages a rich new area of higher-nuclearity Mn^{III}/oxime products than is currently known.

The reaction of $Mn(ClO_4)_2 \cdot 6H_2O$, paoH, and NEt_3 in a 1:1:1 molar ratio in MeCN gave a dark-brown solution that upon layering with Et_2O/hexanes (1:1, v/v) gave brown crystals of $[Mn_{15}O_{0.5}(OH)_{11.5}(pao)_{18}(EtOH)(H_2O)](ClO_4)_{6.5} \cdot 5MeCN \cdot 6H_2O$ ($\mathbf{1} \cdot 5MeCN \cdot 6H_2O$) in 45% yield.[10] The cation of **1** (Figure 1) consists of 15 distorted octahedral Mn atoms held together by eight μ_3-OH^- (one of which is disordered with an O^{2-} ion in a 1:1 ratio) and 4 μ-OH^- ions and 12 η^1:η^1:η^1:μ and four η^1:η^1:η^2:μ_3 pao^- groups (Chart 1). In addition, there are two N,O-chelating (η^2) pao^- groups on Mn6 and Mn13 and terminal EtOH and H_2O ligands on the same metal atoms, respectively; the η^2 N,O-binding mode for pao^- has not been seen before.[4d] The coordinated EtOH group likely comes from a metal-assisted oxidative degradation of Et_2O. The novel $[Mn_{15}(\mu_3\text{-}O)_{0.5}(\mu_3\text{-}OH)_{7.5}(\mu\text{-}OH)_4]^{24.5+}$ core of **1** (Figure 2, top) can be conveniently described as consisting of a series of edge- and vertex-sharing Mn_3 triangles[11] linked through the μ_3-OH^-/O^{2-} ions; the two extrinsic Mn atoms (Mn8 and Mn15) are linked to the central $[Mn_{13}(\mu_3\text{-}O)_{0.5}(\mu_3\text{-}OH)_{7.5}]^{20.5+}$ "triangle"-based subcore by the four μ-OH^- ions. If we consider the bridging diatomic oximate groups as part of the core, then the latter becomes $[Mn_{15}(\mu_3\text{-}O)_{0.5}(\mu_3\text{-}OH)_{7.5}(\mu\text{-}OH)_4(\mu_3\text{-}ON)_4(\mu\text{-}ON)_{12}]^{8.5+}$ (Figure 2, bottom). The Mn oxidation states of **1** are obvious from the metric parameters, the bond valence sum (BVS) calculations,[11,12] and the clear presence of Jahn–Teller axial elongations at Mn(1,4,6,7,11,13,14).[11] Thus, the latter atoms are Mn^{III} and the remaining ones are Mn^{II}, giving an overall $Mn^{II}_8Mn^{III}_7$ description. The protonation level of OH^- and OR^- [R = (py)C(H)N−] groups was also confirmed by O-atom BVS calculations.[11] It should be noted that, because of the large number of strong intramolecular hydrogen bonds among bridging OH^- groups and between them and oximate O atoms, it is almost impossible to detect the exact position of the O^{2-}/OH^- ion.[11]

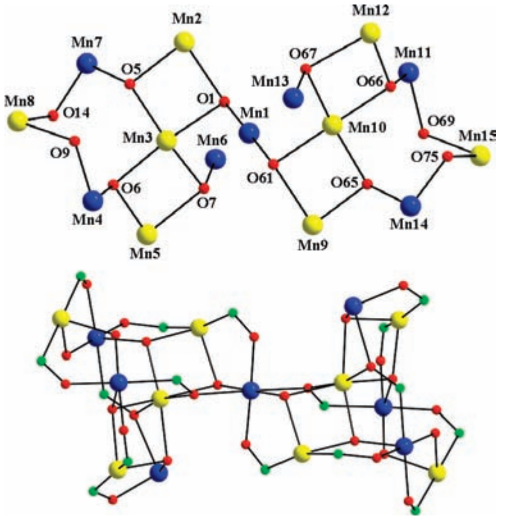


Figure 2. Partially labeled PovRay representations of (top) the $[Mn_{15}O_{0.5}(OH)_{11.5}]^{24.5+}$ core of **1** and (bottom) its complete $[Mn_{15}(\mu_3\text{-}O)_{0.5}(\mu_3\text{-}OH)_{7.5}(\mu\text{-}OH)_4(\mu_3\text{-}ON)_4(\mu\text{-}ON)_{12}]^{8.5+}$ core. Color scheme: same as in Figure 1.

While the number of polynuclear complexes of 3d metals at intermediate oxidation states continues to grow rapidly, some nuclearities remain rare. Pentadecanuclear, nonorganometallic 3d metal complexes are particularly rare;[13] **1** is only the fourth Mn_{15} cluster ever reported[13c−e] and the first with such a closed-like structural topology and a $Mn^{II}_8Mn^{III}_7$ oxidation level.

Solid-state direct-current (dc) magnetic susceptibility (χ_M) data for complex $\mathbf{1} \cdot 6H_2O$ were collected in the temperature range 5.0−300 K in an applied field of 1 kG (0.1 T). The data

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(10) Anal. Calcd (found) for $\mathbf{1} \cdot 6H_2O$: C, 33.12 (32.70); H, 3.44 (2.99); N 12.99 (12.67). Crystal structure data for $\mathbf{1} \cdot 5MeCN \cdot 6H_2O$: $C_{120}H_{134.5}Mn_{15}N_{41}O_{64}Cl_{6.5}$, M_w = 4229.71, monoclinic, space group $P2_1/c$ with a = 34.191(4) Å, b = 15.257(2) Å, c = 34.144(4) Å, β = 106.328(2)°, V = 17093(4) Å^3, T = 100(2) K, Z = 2, R1 [$I > 2\sigma(I)$] = 0.0902, and wR2 = 0.1866 (F^2, all data).

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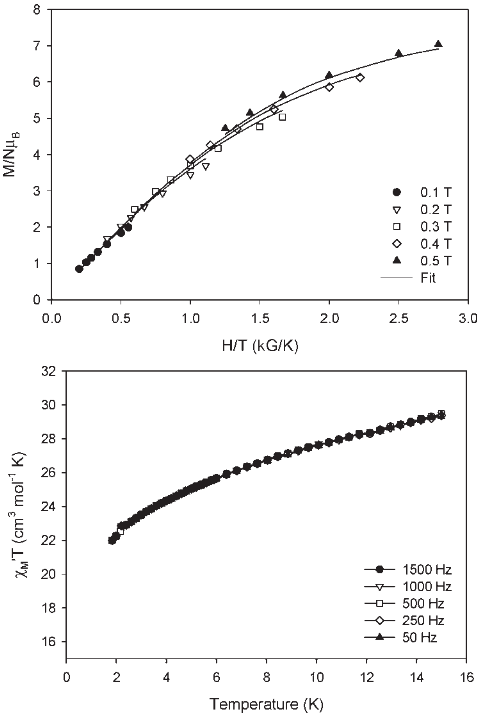

Figure 3. (top) Plot of $M/N\mu_B$ vs H/T for complex $\mathbf{1}\cdot 6H_2O$ at the indicated applied fields. The solid lines are the fit of the data; see the text for the fit parameters. (bottom) Plot of the in-phase (χ'_M) (as $\chi'_M T$) ac susceptibility signals for $\mathbf{1}\cdot 6H_2O$, measured in a 3.5 G field oscillating at the indicated frequencies.

are plotted as $\chi_M T$ vs T in Figure S5 in the Supporting Information and clearly indicate an appreciable ground-state spin (S) value. $\chi_M T$ for $\mathbf{1}\cdot 6H_2O$ steadily decreases from 47.46 cm^3 K mol^{-1} at 300 K to 23.69 cm^3 K mol^{-1} at 5.0 K. The overall shape of the $\chi_M T$ vs T curve and the fact that the 300 K $\chi_M T$ value is much less than the spin-only (g = 2) value of 56 cm^3 K mol^{-1} for eight Mn^{II} and seven Mn^{III} noninteracting ions are both indicative of predominant antiferromagnetic exchange interactions within **1**. The 5.0 K value is suggestive of an $S = 6$ or 7 ground state; their spin-only values are 21 and 28 cm^3 K mol^{-1}, respectively.

In order to confirm the ground state of $\mathbf{1}\cdot 6H_2O$, magnetization (M) data were collected in the 0.1−0.5 T and 1.8−5.0 K ranges, and these are plotted as $M/N\mu_B$ vs H/T in Figure 3 (top). We used only low field data (< 1.0 T) to avoid problems from low-lying excited states, expected for high-nuclearity clusters with a high density of spin states and/or when Mn^{II} ions are present, with the latter giving weak exchange interactions. The data were fit by matrix diagonalization to a model that assumes that only the ground state is populated, includes axial zero-field splitting ($D\hat{S}_z^2$) and the Zeeman interaction, and carries out a full powder average. The best fit (solid lines in Figure 3, top) gave $S = 6$, $g = 1.99$, and $D = -0.20$ cm^{-1}; alternative fits with $S = 5$ or 7 were rejected because they give unreasonable values of g and D.

Alternating-current (ac) susceptibility studies are also a powerful complement to dc studies for determining the ground state of a system because they preclude any complications arising from the presence of a dc field and/or low-lying excited states. For $\mathbf{1}\cdot 6H_2O$, the in-phase (χ_M') ac signal, shown as $\chi_M'T$ in Figure 3 (bottom), is almost linearly decreasing with decreasing temperature in the 4−15 K region, indicating depopulation of a high density of excited states with spin S greater than that of the ground state. Extrapolation of the data above 4 K (to avoid the effects of intermolecular interactions and magnetization relaxation phenomena at lower temperatures) down to 0 K gives ~21 cm^3 K mol^{-1}, indicating an $S = 6$ ground state with $g \sim 2$, in good agreement with the dc magnetization fits.

The $S = 6$ ground state and the negative D value suggested that **1** might be a SMM. The upper limit to the barrier is $U = S^2|D| = 7.16$ cm^{-1} = 10.31 K, but the true, effective barrier (U_{eff}) will be significantly less because of the quantum tunneling mechanism.[3] At temperatures < 2.0 K, very weak frequency-dependent tails of out-of-phase (χ_M'') ac susceptibility signals for $\mathbf{1}\cdot 6H_2O$ were observed whose maxima lie below the operating minimum temperature of our SQUID instrument.[11] This behavior is indicative of slow magnetization relaxation, suggesting **1** to possibly be a new SMM but one with a small relaxation barrier. Further confirmation of the SMM behavior would require single-crystal studies on a micro-SQUID down to 40 mK,[14] but this was not pursued because there are now many SMMs with such small relaxation barriers.

In summary, the employment of the versatile paoH group, the most flexible of all of the 2-pyridyl oximes, in Mn chemistry has led to the highest-nuclearity Mn/oxime cluster to date at any oxidation state level, showing that tridentate oximes can indeed support large nuclearities without requiring the copresence of ancillary groups such as carboxylates. The obtained product is new in multiple ways, as described, but it also provides the opportunity for a study of its chemical reactivity and its magnetostructural properties. In particular, we are currently trying to (i) raise the value of S in **1** and, thus, "switch on" its SMM properties by controllable routes such as replacement of the μ- and μ_3-OH$^-$ ions with end-on bridging pseudohalides (N$_3^-$, OCN$^-$, etc.) and (ii) prepare either analogues of **1** or new Mn clusters with bulky 2-pyridyl oximes (see Chart 1). Finally, the present work seems to answer positively the question concerning the ability or not of oximes to combine *both* very high-nuclearity molecules and magnetically interesting species.

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Supporting Information Available: Crystallographic data for $\mathbf{1}\cdot 5MeCN\cdot 6H_2O$ in CIF format and various structural and magnetism figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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