

Communications to the Editor

Isolation and Characterization of $\{Mn^{II}[Mn^{III}(\text{salicylhydroximate})_4(\text{acetate})_2(\text{DMF})_6]\}_6 \cdot 2\text{DMF}$: An Inorganic Analogue of $M^{2+}(\text{12-crown-4})$

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The binding of monovalent and divalent ions by crown ethers has long been appreciated.¹⁻³ The etheral oxygen atoms are well suited for sequestration of the hard alkaline earths and alkali metals. Selectivity is introduced by varying the ring size and the number of oxygen donors. This results in a central pocket designed for specific ions.^{4,5} Although ligands of the type 12-crown-4 have been known for many years, there are no reports of a comparable ring system composed solely of transition metals and other heteroatoms that can bind divalent metals. Such materials are of interest since the basicity of the oxygen donors is different from the carbon analogues, and the transition-metal bond distances and angles should lead to ligands of different cavity sizes relative to the corresponding 12-crown-4. In this report, we provide structural evidence for the first "metalloccrown" ether type coordination using the mixed-valence complex $\{Mn^{II}[Mn^{III}(\text{salicylhydroximate})_4(\text{acetate})_2(\text{DMF})_6]\}_6 \cdot 2\text{DMF}$ (**1**).

The title complex may be prepared by the reaction of manganese(II) acetate with 1 equiv of salicylhydroxamic acid in DMF. Crystals of **1** were obtained by allowing the solution to stand in a fume hood for a week. X-ray analysis⁶ provided a model ($R = 0.077$) with a highly asymmetric cluster of five manganese atoms illustrated as Figure 1. The salicylhydroxamic acid is triply deprotonated; therefore, this trianionic ligand is coordinated as a salicylhydroximate (SHI) rather than the doubly deprotonated salicylhydroxamate. The hydroxylimine nitrogen and phenolate oxygen are bound to one metal, while the hydroxylimino and carbonyl oxygens are bound to a second Mn(III). The molecular core is composed of four interlinking $Mn^{III}(\text{SHI})$ units, with the Mn(III) ions bridged as $\{Mn-N-O-Mn-N-O-Mn-N-O-Mn-N-O\}$ through the hydroxylimino nitrogen and oxygen atoms, generating a structure that is very similar to 12-crown-4. The four oxygens of this 12-membered ring form the base of a nearly trigonal-prismatic capping Mn(II) ion ($\text{av } Mn1-O_{\text{ring}} = 2.24 \text{ \AA}$

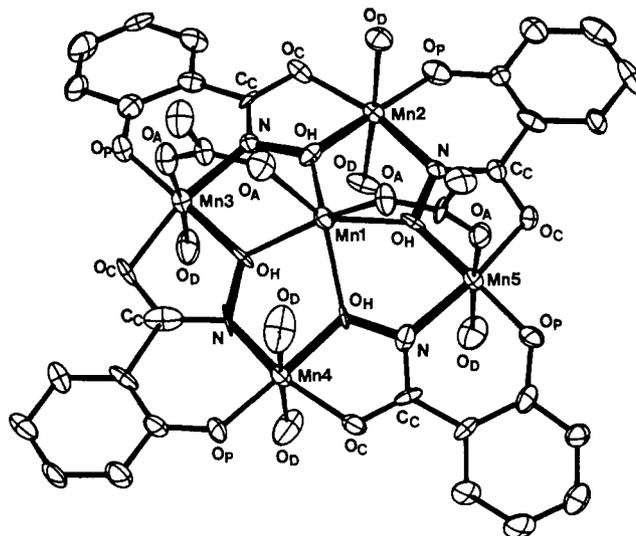


Figure 1. An ORTEP diagram of $\{Mn^{II}[Mn^{III}(\text{salicylhydroximate})_4(\text{acetate})_2(\text{DMF})_6]\}_6 \cdot 2\text{DMF}$ with thermal ellipsoids at 30% probability showing numbering scheme for important atoms. Hydrogen atoms are omitted for clarity. Selected interatomic distances in \AA and angles in deg reported as $\text{av}(\text{range})$ are as follows: $Mn1-O_H$, 2.24 (2.18-2.26); $Mn1-O_A$, 2.12 (2.11-2.13); $Mn(III)-O_H$, 1.87 (1.83-1.88); $Mn(III)-O_C$, 1.97 (1.95-1.97); $Mn(III)-O_P$, 1.87 (1.85-1.88); $Mn(III)-O_A$, 2.16 (2.14-2.18); $Mn(III)-N$, 1.97 (1.93-1.99); $Mn(III)-O_D$, 2.31 (2.20-2.45); $N-O_H$, 1.40 (1.39-1.41); $N-C_C$, 1.30 (1.27-1.32); C_C-O_C , 1.33 (1.30-1.37); Mn_R-Mn_R , 4.64 (4.62-4.64); $N-Mn(III)-O_H$, 88 (87-89); $Mn(III)-N-O_H$, 119 (117-121); $N-O_H-Mn(III)$, 116 (114-117); $cis-[O_H-Mn(II)-O_H]$, 74 (74-76); $trans-[O_H-Mn(II)-O_H]$, 117 (112-121); $cis-[O_C-Mn(II)-O_C]$, 82.1 (5). Abbreviations used are as follows: O_A = acetate oxygen; O_C = carbonyl oxygen; O_H = hydroxylimino oxygen; O_P = phenolate oxygen; O_D = DMF oxygen; C_C = carbonyl carbon; Mn_R = Mn(III) in ring.

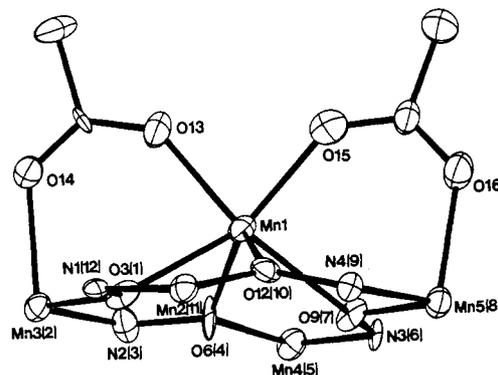


Figure 2. An ORTEP diagram of the $Mn^{II}(-Mn^{III}-N-O)_4(OAc)_2$ core illustrating the similarity of the coordination environment to $M^{2+}(\text{12-crown-4})$. Numbers in brackets represent corresponding numbering scheme for 12-crown-4.

(range = 2.18-2.26); $Mn1-O_{\text{acetate}} = 2.12 \text{ \AA}$ (2.11-2.13); the twist angle is 10.5° with $Mn1$ displaced out of the best least-squares plane defined by $O3, O6, O9,$ and $O12$ by 1.20 \AA as shown in Figure 2. The remaining two ligands to the Mn(II) are acetates that bridge Mn(III) ions ($Mn3$ and $Mn5$) in the metalloccrown structure. The ring Mn(III) ions are six coordinate with the remaining coordination positions occupied by DMF. Each of these ions exhibits a typical axial Jahn-Teller distortion. The average ring manganese separation is 4.64 \AA , and the average $Mn(III)-Mn(II)$ separation is 3.54 \AA .

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- (6) X-ray parameters for $\{Mn^{II}[Mn^{III}(\text{salicylhydroximate})_4(\text{acetate})_2(\text{DMF})_6]\}_6 \cdot 2\text{DMF}$: $Mn_4C_{56}H_{78}N_{12}O_{24}$, 1578 g/mol, triclinic, $P1$; $a = 15.148(6) \text{ \AA}$; $b = 16.808(6) \text{ \AA}$; $c = 16.835(6) \text{ \AA}$; $\alpha = 114.58(3)^\circ$; $\beta = 96.55(3)^\circ$; $\gamma = 65.76(3)^\circ$; $V = 3546(2) \text{ \AA}^3$; $Z = 2$; $\rho_{\text{calcd}} = 1.478 \text{ g cm}^{-3}$; $\rho_{\text{obsd}} = 1.50 \text{ g cm}^{-3}$; $\lambda(\text{Mo K}\alpha) = 0.7107 \text{ \AA}$, $\mu(\text{Mo K}\alpha) = 8.81 \text{ cm}^{-1}$; crystal dimensions $0.32 \times 0.28 \times 0.13 \text{ mm}$; largest residual 0.62 e/\AA^3 . The intensities of 6623 unique reflections were measured ($0 < 2\theta < 40^\circ$) at room temperature on a P_2 diffractometer using $\text{Mo K}\alpha$ radiation. The structure was solved by direct methods with MULTAN78. Anisotropic thermal parameters were used for all heteroatoms except for the two DMF solvates which were refined isotropically. Calculations were carried out by using the SHELX-76 program package. For 3831 data with $I > 3\sigma(I)$, the final $R = 0.077$. Elemental Anal. for **1** calcd: C, 42.59; H, 4.94; N, 10.65; Mn, 17.41. Found: C, 42.02; H, 4.67; N, 10.21; Mn, 17.83.

A comparison of the $(-Mn(III)-N-O)_4$ core with that of the crown ethers is interesting. The bite distance^{5,7} and cavity size^{5,7} for 12-crown-4 (2.79 and 0.6 Å) is similar to **1** where the average bite distance is 2.67 Å and the cavity size is 0.5 Å. One might expect an expansion of the cavity of the 12- $C_{Mn^{3+}N}^{-4}$ compared to 12-crown-4 as a result of the increased Mn-N ($av_{ring} = 1.97$ Å; range = 1.93-1.99) and Mn-O ($av_{ring} = 1.87$ Å; (1.83-1.88 Å)) distances relative to the corresponding C-C (1.50 Å) and C-O (1.42 Å) distances. However, this bond distance increase is compensated by the bond angles about the Mn(III) ion. In the crown complexes^{1-5,7,9,10} angles between 108° and 113° are commonplace, while the average O-Mn-N, Mn-N-O, and N-O-Mn angles are 88° (87-89), 119° (117-121), and 116° (114-117), respectively. Thus, the octahedral angle decreases the cavity size even though the Mn(III)-O and Mn(III)-N distances have been elongated. We have shown¹¹ that SHI will form a stable trinuclear oxovanadium(V) cluster **2**, $[VO(salicylhydroximate)(CH_3OH)]_3$. The central core of this molecule is composed of $(-M-N-O)_3$ linkages, making this compound analogous to 9-crown-3 (9- $C_{V^{5+}N}^{-3}$). The cavity sizes of both 9-crown-3 and 9- $C_{V^{5+}N}^{-3}$ are too small to accommodate other ions. Therefore, unlike **1**, the hydroxylimino oxygens of **2** were coordinated solely to the vanadium(V).

On the basis of solution conductivity, ¹H NMR, and EPR measurements,¹² the cluster **1** completely dissociates when dissolved in methanol. Although poorly soluble, the complex appears to retain its integrity as a pentanuclear cluster in acetonitrile. An intermediate behavior is observed in DMF where 20% of the Mn(II) dissociates from the cluster; however, the $[Mn(SHI)]_4$ core remains intact.¹² This solution chemistry is similar to that reported for **2** which is very stable in acetonitrile but dissociates in methanol. The room temperature, solid-state susceptibility of **1** (13.8 μ_B /cluster) is greater than the predicted spin only moment (11.4 μ_B /cluster) indicating that the compound is weakly ferromagnetic. Variable temperature measurements are in progress to ascertain the magnitude of the exchange coupling in this material.

In conclusion, the first example of a crown ether type coordination mode using a ring system composed partially of transition-metal ions and entirely of heteroatoms has been achieved by stabilizing a cluster of manganese with a high denticity ligand that has the capacity to form M-N-O-M linkages. This unique example of metal ion recognition illustrates a possible direction for designing moderate nuclearity clusters which, through the judicious choice of the capping metal ion, may have interesting magnetic and spectroscopic properties.

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(8) Our proposed nomenclature is $X-C_{M^n+H}^{-Y}$ where X and Y indicate ring size and oxygen donor atoms, M and n are the metal and its oxidation state, and H is the identity of the remaining heteroatom bridge. Thus, 12- $C_{Mn^{3+}N}^{-4}$ indicates the basic core structure of 12-crown-4 with the carbon atoms replaced by Mn(III) and N atoms throughout the ring. A similar situation is described by the vanadium(V) analogue 9- $C_{V^{5+}N}^{-3}$.

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(12) The X-band EPR spectrum of **1** in methanol at 110 K shows a very strong six-line component that is the hallmark of uncomplexed Mn(II). In DMF, a six-line signal is also observed; however, a standard curve indicates that this signal arises from 20 ± 10% of the Mn(II) in the sample. Addition of methanol to this DMF solution causes a dramatic increase in the six-line signal. In contrast, acetonitrile solutions of **1** contain an additional broad derivative shaped resonance centered at $g = 2$ that underlies a very weak six-line signal. The intensity of this broad feature is slightly greater at 4 K than at 110 K suggesting that it arises from the electronic ground state. Thus, we believe that this poorly resolved signal is associated with the intact cluster, while the small amount of six-line signal corresponds to less than 5% of the overall spin. These conclusions are supported by the ¹H NMR of **1** in different solvents. No paramagnetically shifted resonances are seen in methanol-*d*₄ showing that the entire complex has dissociated. In DMF-*d*₆, coordinated acetate resonances are observed at +56.1 ppm, and resonances from the phenolate ring protons are at -14.1, -15.5, -22.4, and -23.0 ppm. The same peaks are observed at -16.4, -17.6, -21.4 and -22.0 ppm (phenolate) and +60.6 ppm (acetate) in acetonitrile-*d*₃. The acetate resonances were confirmed by obtaining spectra of **1** prepared using acetate-*d*₃.

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Supplementary Material Available: Table I, fractional atomic coordinates for all atoms; Table II, thermal parameters for all atoms; Table III, bond distances for all atoms; Table IV, bond angles for all atoms; and Figure 3, $[Mn^{II}[Mn^{III}(salicylhydroximate)]_4(acetate)_2(DMF)_6] \cdot 2DMF$, showing the complete atom numbering scheme (25 pages); Table V, observed and calculated structures factors (16 pages). Ordering information is given on any current masthead page.

Evidence for Positive Hole Delocalization over Two Double Bonds Separated by 6 Å in the Cation Radical of a Nonconjugated Diene: A Consequence of Laticyclic Hyperconjugation

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Recent photoelectron spectroscopic (pes) studies on the dienes **1a**¹ and **2**² and their dibenzo analogues² revealed the presence of unusually large π, π splittings which were attributed to a novel variant of through-bond interactions,³ called laticyclic hyperconjugation.^{1b,4} In this model, interactions occur through the mixing of the π orbitals of **1a** and **2** with the pseudo- π orbital(s) of the central CH_2 group(s), the overall interacting ribbon topology resembling the Goldstein-Hoffmann laticyclic array.⁵ Thus, for **1a**, such mixing causes the $b_1 \pi_- (= \pi - \pi)$ combination of π orbitals to be raised in energy, relative to the $a_1 \pi_+ (= \pi + \pi)$ combination which, by dint of symmetry, cannot mix with the pseudo- π orbital of the CH_2 group and whose energy, therefore, remains unchanged. The large degree of $\pi, pseudo-\pi$ mixing can be seen from inspection of the atomic orbital coefficients in the (STO-3G) HOMO of the model ethene- $\cdots CH_2 \cdots$ ethene "complex" **4**, whose geometry mimics the orientation of the interacting components of **1a**.³

In view of the nexus between the rate of positive hole transfer in the ground-state cation radical of, say, a diene and the observed π, π splitting energy,^{3d,6} the very large π, π splitting found for **1a** (0.52 eV^{1a,b}) suggests that the rate of hole transfer between the two double bonds in the cation radical **1a**⁺ could so fast ($> 10^{14}$

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