Isolation and Characterization of

[|MnIII|MnIII(salicylhydroximate)]4(acetate)2(DMF)3]6-

2DMF: An Inorganic Analogue of M2+(12-crown-4)

Myoung Soo Lah and Vincent L. Pecoraro*

Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109-1055

Received December 7, 1988

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 "metallocrown" ether type coordination using the mixed-valence complex [|MnIII|MnIII(salicylhydroximate)]4(acetate)2(DMF)3]6-2DMF (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 analysis5 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 trinionic 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 MnIII(SHI) units, with the Mn(III) ions bridged as Mn(III)-Mn(II)-Mn(III)-Mn(II)-Mn(III)-Mn(II). The remaining coordination positions occupied by DMF. Each of these remaining two ligands to the Mn(II) are acetates that bridge Mn(III) ions (Mn3 and Mn5) in the metallocrown scheme for 12-crown-4. The four oxygens of this 12-membered ring form the base of a nearly trigonal-prismatic capping Mn(II) ion (av Mn-Oring = 2.24 Å).

Figure 1. An ORTEP diagram of [MnIII|MnIII(salicylhydroximate)]4(acetate)2(DMF)3]6-2DMF with thermal ellipsoids at 30% probability showing numbering scheme for important atoms. Hydrogen atoms are omitted for clarity. Selected interatomic distances in Å and angles in deg reported as av (range) are as follows: Mn1-O3, 2.24 (2.18-2.26); Mn1-O2, 2.12 (2.11-2.13); Mn1-O2, 1.87 (1.83-1.88); Mn1-O8, 1.97 (1.95-1.97); Mn1-O9, 1.87 (1.85-1.88); Mn1-O3, 2.16 (2.14-2.18); Mn4-O1, 1.97 (1.93-1.99); Mn4-O2, 2.31 (2.20-2.45); N-OH, 1.40 (1.39-1.41); N-Cc, 1.30 (1.27-1.32); Cc-Cc, 1.33 (1.30-1.37); Mna-Mng, 4.64 (4.62-4.64); N-Mng-Mna, 88 (87-89); Mn4-O4, 119 (117-121); N-O5-Mn, 116 (114-117); cis-[O-O-Mn(II)-O], 74 (74-76); trans-[O-O-Mn(II)-O], 117 (112-121); cis-[O-O-Mn(II)-O], 82.1 (5). Abbreviations used are as follows: Oa = acetate oxygen; Cc = carbonyl carbon; Od = hydroxylimine oxygen; Oph = phenolate oxygen; Od = DMF oxygen; Cc = carbonyl carbon; Mn4 = Mn(III) in ring.

(6) X-ray parameters for [|MnIII|MnIII(salicylhydroximate)]4(acetate)2(DMF)3]6-2DMF: Mn-Ca-Cb 0.1578; P(C) 0.1514; a = 16.808 (6); b = 16.835 (6); c = 114.58 (3)°; ß = 96.55 (3)°; g = 65.75 (3)°; V = 3546 (2) Å3; Z = 2; µtotal = 1.478 g cm-3; µradial = 1.50 g cm-3; (Mo Kα) = 0.7107 Å, (Mo Kβ) = 0.818 cm-1; crystal dimensions 0.10 × 0.25 × 0.13 mm; largest residual 0.62 e Å3. The intensities of 6623 unique reflections were measured (0 < 2θ < 40°) at room temperature on a P2 diffractometer using Mo Kα radiation. The structure was solved by direct methods with MULTAN. Anisotropic thermal parameters were used for all heteroatoms except for the two DMF solvates which were refined isotropically. Calculations were carried out using the SHELX-76 program package. For 3881 data with F > 3σ(F), 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 \((-\text{Mn(III)}-\text{N}-\text{O})_4\) core with that of the crown ethers is interesting. The bite distance\(^5,7\) and cavity size\(^5,7\) for \(12\text{-crown}-4\) (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\(_{20}\)Mn\(_3\)N\(_4\) compared to 12-C\(_{20}\)-4 as a result of the increased Mn-N\((\text{av}=1.97\ \text{Å}; \ \text{range}=1.93-1.99)\) and Mn-O\((\text{av}=1.87\ \text{Å}; \ 1.83-1.88\ \text{Å})\) 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\(^5,7,10\), distances 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. This constant octahedra cavity size even though the Mn(III)-O and Mn(III)-N distances have been elongated. We have shown\(^11\) that SHI will form a stable trinuclear oxovanadium(V) cluster \(2\), [VO(salicylhydroximate)(CH\(_3\)OH)]\(_3\). The central core of this molecule is composed of \((-\text{M}-\text{N}-\text{G})_3\), linkages, making this compound analogous to 9-crown-3 (9-C\(_{22}\),3-). The cavity sizes of both 9-crown-3 and 9-C\(_{22}\),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 in ethanol. 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/cluster) is greater than the predicted spin only moment (1.14 µ/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 that has the capacity to form M-N-O-M linkages. This unique magnetic and spectroscopic properties.

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

Anna M. Oliver and Michael N. Paddon-Row*
Department of Organic Chemistry
University of New South Wales, P.O. Box 1
Kensington, New South Wales 2033, Australia

Martyn C. R. Symons*
Department of Chemistry, University of Leicester
Leicester, LE1 7RH, England
Received March 15, 1989

Recent photoelectron spectroscopic (pes) studies on the dienes \(1\a\) and \(2\a\) and their dibenzo analogues\(^1\) revealed the presence of unusually large \(\pi,\pi\) splittings which were attributed to a novel variant of through-bond interactions,\(^2\) called latelic hyperconjugation.\(^1b,4\) In this model, interactions occur through the mixing of the \(\sigma\) orbitals of \(1\a\) and \(2\a\) with the pseudo-\(\pi\) orbital(s) of the central CH\(_2\) group(s), the overall interacting ribbon topology resembling the Goldstein-Hoffmann latelic array.\(^3\) Thus, for \(1\a\), such mixing causes the \(b_1,\pi,\pi\) combination of \(\sigma\) orbitals to be raised in energy, relative to the \(a_1,\pi,\pi\) combination which, by dint of symmetry, cannot mix with the pseudo-\(\pi\) orbital of the CH\(_2\) group and whose energy, therefore, remains unchanged. The large degree of \(\pi,\pi\) mixing can be seen from inspection of the atomic orbital coefficients in the (STO-3G) HOMO of the model ethene—CH\(_4\)—ethene "complex"\(^4\), whose geometry mimics the orientation of the interacting components of \(1\a\).\(^3\)

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 \(\pi,\pi\) splitting energy,\(^3d\) the very large \(\pi,\pi\) splitting found for \(1\a\) (0.52 eV\(\pi,\pi\)) suggests that the rate of hole transfer between the two double bonds in the cation radical \(1\a^{+}\) could so fast (\(>10^{14}\))