The preparation of compound **4** was initiated by addition of 0.2 g (0.9 mmol) of PhIO[7] to a stirred solution of 1.3 g (1.2 mmol) of $[Mn_3O(O_2CC_6H_5)_6(py)_2(H_2O)]\cdot 0.5CH_3CN$[2d] in 100 mL of CH_3CN. After the reaction mixture was stirred for 12 h, the solvent was removed by rotary evaporation, leaving a brown glassy residue. This material was dissolved in ethyl acetate, and an equal volume of hexanes was carefully layered on top of the resulting solution. Large brown block-shaped crystals, suitable for elemental analysis[8] and X-ray diffraction studies,[9] deposited within 48 h (yield: ~20%).

The crystal structure of **4**, which is quite distinct from another nonanuclear manganese species,[10] is shown in Figure 1. While there are no symmetry elements crystallographically imposed on the molecule, a pseudo-2-fold rotation axis coincident with the Mn(1)-O(5) bond is discernable. This 2-fold axis relates the following atom pairs to one another: Mn(8), Mn(9); Mn(6), Mn(7); Mn(3), Mn(4); Mn(2), Mn(5). Thus, there are five distinct manganese coordination environments within **4**. Assuming that all carboxylate ligands are deprotonated and that all bridging O atoms are oxide groups (O^{2-}), it follows that all manganese atoms are in the +3 oxidation state. This conclusion is borne out by examination of the Mn-ligand distances and comparison to other Mn^{III}-oxo complexes.[11] All seven of the oxide groups are triply bridging. Of the thirteen benzoate groups, eleven are doubly bridging in a syn-syn configuration, while two (labeled b and c in Figure 1) are triply bridging. Triply bridging carboxylates have been observed for other manganese complexes, including **2**.[3,12] The base of the nonanuclear core (Figure 1) may be viewed as two "butterfly"-type Mn_4O_2 units[18] which share a central five-coordinate manganese atom, Mn(1). Another substructural type within **4** is the nearly planar $[Mn_3O]^{7+}$ unit, three of which occur, centered around μ_3-oxo groups O(5), O(6), and O(7). Atoms Mn(1), Mn(2), and Mn(5) are five-coordinate, and in all three cases the ligand geometry is best described as distorted square pyramidal with atoms O(5), O(e2), and O(d2), respectively, in apical positions. The unique manganese atom, Mn(1), has a rather interesting coordination environment consisting of five μ_3-oxo donors. Space-filling models indicate that the approach of a sixth ligand to Mn(1) is blocked by two benzoate phenyl rings and the two pyridine ligands.

Initial identification of **4** as a novel manganese-oxo-carboxylate "soluble phase" came from fast atom bombardment (FAB) mass spectral measurements. The FAB mass spectrum of **4**, using a nitrobenzyl alcohol matrix, reveals a characteristic pattern with peaks at 2181, 2060, 1939, and 1818 amu, corresponding to loss of 2py, (2py + $O_2CC_6H_5$), (2py + $2O_2CC_6H_5$), and (2py + $3O_2CC_6H_5$) from molecule **4**, respectively. An X-band EPR spectrum of **4** in frozen $CH_3CN/CH_3C_6H_5$ at 8 K revealed no intense absorptions. Nor is the compound electroactive in CH_3CN solution in the range ±1.0 V vs SSCE. However, current is passed at more negative potentials (<-1.5 V), and after doing so a new wave appears in the cyclic voltammogram ($E_{p,a} = 1.0$, $E_{p,c} = 0.75$ V vs SSCE). The infrared spectrum of **4** shows bands at 1600, 1557, 1415, and 716 cm^{-1} attributable to benzoate resonances and one at 498 cm^{-1}, which may be associated with a Mn-oxo core vibration.[13] At room temperature the magnetic moment of **4** is 13.2 μ_B. This indicates overall antiferromagnetic coupling between Mn atoms in **4** since the calculated value for 9 uncoupled high-spin Mn^{III} atoms is 14.7 μ_B.

In conclusion, by using an oxygen atom transfer agent, one is able to prepare a hitherto unknown polynuclear manganese-oxo-carboxylate species. The nonanuclear complex described above may be employed as a novel starting material in synthesis and may itself have interesting reactivity properties at the terminal coordination sites that are occupied by pyridine ligands. Attempts to isolate additional polynuclear species from reaction mixtures in which the Mn:O ratio has been varied are under way.

Acknowledgment. This work was supported by Grant No. GM 382751-01 from the National Institute of General Medical Sciences. W.H.A. was the recipient of a Presidential Young Investigator Award from the National Science Foundation (Grant CHE-8857455).

Supplementary Material Available: An ORTEP diagram with phenyl rings included and tables of atomic positional and thermal parameters and intramolecular distances and angles for compound **4** (16 pages). Ordering information is given on any current masthead page.

---

(7) Saltzman, H.; Sharefkin, J. G. *Org. Synth*. **1963**, *43*, 60-61.

(8) Anal. Calcd for $C_{101}H_{75}Mn_9N_2O_{33}$: C, 51.85; H, 3.23; N, 1.20. Found: C, 51.25; H, 3.13; N, 1.14.

(9) X-ray analysis for $[Mn_9O_7(O_2CC_6H_5)_{13}(py)_2]\cdot 3CH_3CN\cdot 7H_2O$: This complex crystallizes in the orthorhombic space group *Pbca*, with a = 26.206 (7) Å, b = 29.063 (8) Å, c = 31.618 (8) Å, V = 24,081 (12) $Å^3$, and $Z = 8$. Data collection at 130 K out to $2\theta = 44°$ yielded 4869 reflections with $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS86, G. Sheldrick) and refined by using 684 parameters to final R (R_w) values of 10% (12%) (SHELX76, G. Sheldrick).

(10) Christmas, C.; Vincent, J. B.; Chang, H.-R.; Huffman, J. C.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc*. **1988**, *110*, 823-830.

(11) (a) Hagen, K. S.; Armstrong, W. H.; Hope, H. *Inorg. Chem*. **1988**, *27*, 967-969. (b) Plaskin, P. M.; Stoufer, R. C.; Mathew, M.; Palenik, G. J. *J. Am. Chem. Soc*. **1972**, *94*, 2121-2122. (c) Stebler, M.; Ludi, A.; Burgi, H.-B. *Inorg. Chem*. **1986**, *25*, 4743-4750. (d) Collins, M. A.; Hodgson, D. J.; Michelsen, K.; Towle, D. K. *J. Chem. Soc., Chem. Commun*. **1987**, 1659-1660. (e) Towle, D. K.; Botsford, C. A.; Hodgson, D. J. *Inorg. Chim. Acta* **1988**, *141*, 167-168. (f) Suzuki, M.; Tokura, S.; Suhara, M.; Uehara, A. *Chem. Lett*. **1988**, 477-480. (g) Goodson, P. A.; Hodgson, D. J. *Inorg. Chem*. **1989**, *28*, 3606-3608. (h) Libby, E.; Webb, R. J.; Streib, W. E.; Folting, K.; Huffman, J. C.; Hendrickson, D. N.; Christou, G. *Inorg. Chem*. **1989**, *28*, 4037-4040. (i) Brewer, K. J.; Liegeois, A.; Otvos, J. W.; Calvin, M.; Spreer, L. O. *J. Chem. Soc., Chem. Commun*. **1988**, 1219-1220. (j) Suzuki, M.; Senda, H.; Kobayashi, Y.; Oshio, H.; Uehara, A. *Chem. Lett*. **1988**, 1763-1766. (k) Goodson, P. A.; Glerup, J.; Hodgson, D. J.; Michelsen, K.; Pedersen, E. *Inorg. Chem*. **1990**, *29*, 503-508.

(12) (a) Bertaut, E. F.; Duc, T. Q.; Burlet, P.; Thomas, M.; Moreau, J. M. *Acta Crystallogr*. **1974**, *B30*, 2234-2236. (b) Usubaliev, B. T.; Chiragov, F. M.; Musaev, F. N.; Amiraslanov, I. R.; Mamedov, Kh. S. *Zh. Strukt. Khim*. **1985**, *26*, 1990-1992.

(13) Johnson, M. K.; Powell, D. B.; Cannon, R. D. *Spectrochim. Acta* **1981**, *37A*, 995-1006.

Department of Chemistry
University of California
Berkeley, California 94720

Donald W. Low
David M. Eichhorn
Alexandra Draganescu
William H. Armstrong*

Received August 21, 1990

A Functional Analogy between Crown Ethers and Metallacrowns

We have previously commented on the structural analogy of the crown ethers[1,2] to a new class of metal clusters called metallacrowns[3-6]. Both molecular classes contain core structures with 9- or 12-membered rings that include 3 or 4 formally neutral oxygen donors to which metal ions can be coordinated. The metallacrowns resemble lariat ethers[7] in that additional specificity is imparted by bridging anions, typically acetate, that span the position from ring to captured metal. The previous metallacrowns, whether vacant as in $[(VO)^{3+}(SHI)(CH_3OH)]_3$ (**1**, 9-$MC_{VO^{3+}N}$-3)[3,8] or with captured metals as in $Fe^{III}[Fe^{III}(SHI)(O-$

---

(1) Bajaj, A. V.; Poonia, N. S. *Coord. Chem. Rev*. **1988**, *87*, 55.

(2) Dietrich, B. *J. Chem. Educ*. **1985**, *62*, 954.

(3) Pecoraro, V. L. *Inorg. Chim. Acta* **1989**, *155*, 171.

(4) Lah, M. S.; Pecoraro, V. L. *J. Am. Chem. Soc*. **1989**, *111*, 7258.

(5) Lah, M. S.; Kirk, M. L.; Hatfield, W.; Pecoraro, V. L. *J. Chem. Soc., Chem. Commun*. **1989**, 1606.

(6) Lah, M. S.; Pecoraro, V. L. *Comments Inorg. Chem*., in press.

(7) Gokol, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc*. **1983**, *105*, 6786.

0020-1669/91/1330-0878$02.50/0

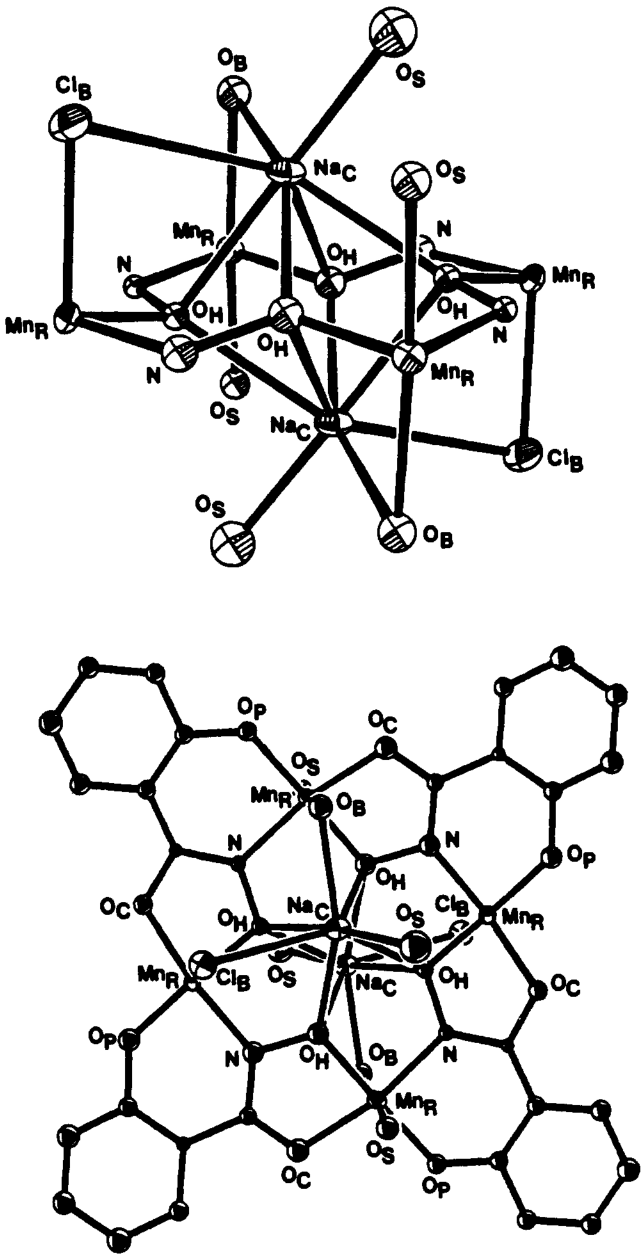

Figure 1. ORTEP diagrams of $\{Na_2[Mn^{III}(SHI)(Cl)_{0.5}(DMF)_1]_4{\cdot}3DMF\}$ (**4**): (top) $(NaCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$ core, showing the displacement of Na(I) ions above and below the plane of oxygen atoms; (bottom) complete structure of **4**, illustrating the interaction between sodium and chloride ions. Selected averaged separations (Å) and angles (deg): M_R–M_R = 4.59; M_R–M_C = 3.42; M_R–O_H = 1.88; M_R–O_C = 1.94; M_R–O_P = 1.85; M_R–N = 1.98; M_R–O_B = 2.43; M_R–Cl_B = 2.43; M_R–O_S = 2.23; M_C–O_H = 2.44; M_C–O_B = 2.47; M_C–Cl_B = 3.00; M_C–O_{OOP} = 1.66; CS = 0.56; BD = 2.62; N–M_R–O_H = 88; M_R–O_H–N = 112; O_H–N–M_R = 114. Abbreviations used: M_R = ring metal; M_C = encapsulated metal; O_H = hydroximate oxygen; O_C = hydroximate carbonyl oxygen; O_P = phenolate oxygen; O_S = solvent oxygen; O_B = bridging DMF; Cl_B = bridging chloride; M_C–O_{OOP} = out of plane distance for encapsulated metal based on best least-squares plane for O_H atoms; CS = cavity radius; BD = bite distance.

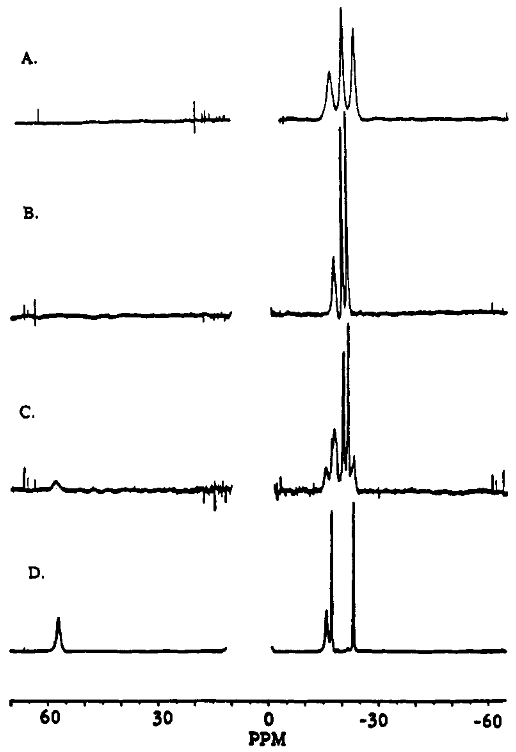

Figure 2. ^1H NMR spectra of compounds **3**, **4**, and **6** in DMF-d_7/acetonitrile-d_3 (1:3): (A) **6**; (B) **4**; (C) **4** plus 0.7 equiv of manganese(II) acetate; (D) **3**.

Ac)$(CH_3OH)]_3$ [**2**, $Fe^{III}(OAc)_3(9\text{-}MC_{Fe^{3+}N}\text{-}3)$]^{5,8} and Mn^{II}-$[Mn^{III}(SHI)(OAc)_{0.5}(DMF)_{1.5}]_4$ [**3**, $Mn^{II}(OAc)_2(12\text{-}MC_{Mn^{3+}N}\text{-}4)$],^{4,8} are homometallic, with the latter exhibiting mixed valency. Two important properties needed to complete the metallacrown analogy were the generation of mixed metallacrowns where the captured ion differed from the ring metal and the solution conversion of one metallacrown $M(12\text{-}MC_{M^{3+}N}\text{-}4)$ to a new form $M'(12\text{-}MC_{M^{3+}N}\text{-}4)$. Herein we accomplish both objectives by presenting the X-ray structure[9] of $\{Na_2[Mn^{III}(SHI)(Cl)_{0.5}(DMF)]_4(DMF)_2{\cdot}3DMF\}$ (**4**, $(NaCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$) and by following the conversion of **4** to **3** using ^1H NMR spectroscopy.

The reaction of H_3SHI[8]/$MnCl_2$/sodium trichloroacetate (NaTCA) (1:1:2) in DMF leads to isolation of **4**. However, if the same reaction is completed with sodium acetate, which is more basic than trichloroacetate, **3** is recovered. We have also prepared[10] the isostructural $(LiCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$ using LiTCA as the base. Thus, the captured metal is related to the type and basicity of the bridging ligands. An ORTEP diagram of **4** is shown in Figure 1 with the $(NaCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$ core emphasized. The metallacrown core of **4** is similar to that in **3** with the ring Mn(III) separations of 4.6 Å. The cavity radii (**3**, 0.57 Å; **4**, 0.6

---

(8) H_3SHI is salicylhydroxamic acid. Our nomenclature is M'A[X-$MC_{M^{n+}H}$-Y], where X and Y indicate ring size and number of oxygen donor atoms, MC specifies a metallacrown, M and *n* are the metal and its oxidation state, and H is the identity of the remaining heteroatom bridge. Thus, $12\text{-}MC_{Mn^{3+}N}\text{-}4$ 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 VO^{3+} analogue $9\text{-}C_{VO^{3+}N}\text{-}3$. The captured metal (M') and bridging anion (A) are given preceding the ring designation.

(9) X-ray parameters for $\{Na_2[Mn^{III}(SHI)(Cl)_{0.5}(DMF)]_4(DMF)_2{\cdot}3DMF\}$ (**4**): $Na_2Mn_4C_{55}H_{79}N_{13}O_{21}Cl_2$, 1595 g/mol, $P\bar{1}$; a = 11.920 (5), b = 12.892 (6), c = 13.107 (4) Å; α = 97.68 (3), β = 98.16 (3), γ = 113.53 (3)°; V = 1816 (1) Å^3; Z = 1; ρ_{calcd} = 1.482, ρ_{obs} = 1.48 g/cm^3; λ(Mo Kα) = 0.7107 Å; μ(Mo Kα) = 8.2 cm^{-1}; crystal dimensions 0.15 × 0.25 × 0.5 mm; largest residual 0.60 e/Å^3. The intensities of 3342 unique reflections were measured by the Wychoff method ($0 < 2\theta < 40°$) at room temperature on an R$\bar{3}$ diffractometer using Mo Kα radiation. The structure was solved by direct methods with SHELXTL-PLUS. Anisotropic thermal parameters were used for all manganese, sodium, and chloride atoms. All other atoms of the ligands and DMF solvates were refined isotropically. Phenyl rings were refined as rigid groups. Calculations were carried out by using the SHELXTL-PLUS program package. For 1205 data with $I > 3\sigma(I)$, the final R = 0.089 and R_w = 0.092. Anal. Calcd for **4**: C, 41.41; H, 4.99; N, 11.40; Na, 2.88; Cl, 4.44; Mn, 13.78. Found: C, 40.90; H, 4.74; N, 11.08; Na, 2.90; Cl, 4.55; Mn, 14.30.

(10) Anal. Calcd for $Li_2[Mn^{III}(SHI)(Cl)_{0.5}(DMF)]_4{\cdot}5H_2O$ (**6**): C, 37.31; H, 4.23; N, 8.71; Li, 1.08; Cl, 5.51; Mn, 17.07. Found: C, 36.82; H, 4.31; N, 8.19; Li, 0.83; Cl, 5.23; Mn, 17.34. Important IR bands for **4** (**6**) (cm^{-1}): 1599 (1598), 1567 (1568), 1513 (1516), 1470 (1470), 1432 (1433), 1391 (1387), 1317 (1315), 1257 (1257), 1247 (1245), 1155 (1156), 1099 (1099), 1034 (1037), 936 (940), 865 (863), 752 (755), 688 (688), 680 (682), 650 (652), 610 (623), 586 (587). UV–vis (acetonitrile) [λ, nm (ε)]: **3**, 339 (21 000), 440 (5400); **4**, 339 (18 000); **6**, 339 (21 000).

Å) and bite distances (**3**, 2.67 Å; **4**, 2.6 Å) are also essentially identical. The obvious structural differences are the substitution of Na(I) for Mn(II) and chloride for acetate and the slight distortion of the metallacrown ring from planarity in **4**. In addition, two Mn(III) ions, those bound to chloride, are five-coordinate in **4**, while all of the Mn(III) ions are six-coordinate in **3**. The displacement of sodium toward chloride to form a short Na–Cl distance (3.0 Å vs 2.81 Å in NaCl[11]) leads to a distortion of the metallacrown ring, since the chloride forms a single atom bridge between the Mn(III) and Na(I). The sodium ions are located 1.7 Å above and below the best least-squares plane of oxygen atoms, while one Mn(II) is bound in **3** and is displaced from the ring by 1.2 Å.

Paramagnetically shifted proton resonances of Mn(III) complexes containing phenolates and acetates can be useful probes of manganese cluster structure and reactivity.[12-14] The ^{1}H NMR spectra (Figure 2A,B) illustrate that $(LiCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$ and $(NaCl)_2[12\text{-}MC_{Mn^{3+}N}\text{-}4]$ have similar, but nonidentical spectra, consistent with the retention of the monovalent cations on the metallacrown rings. A significant portion of the species obtained when **4** is dissolved in DMF/acetonitrile can be converted directly to **3** (Figure 2C,D) by the addition of 0.7 equiv of manganese(II) acetate. The three phenolate resonances at −15.5, −18.6, and −20.1 ppm are lost to intensity for **3** at −14.1, −15.5, and −23.0 ppm as the Mn(II) salt is added. Furthermore, the broad resonance for coordinated acetate appears (+56 ppm, confirmed by using the acetate-d_3 analogue of **3**).[15] Because of the relative insensitivity of NMR spectroscopy, we cannot prove at this time that <5% of the metallacrown does not dissociate, presumably as the demetalated form, and that **3** is isolated by re-forming the cluster. However, all resonances are assigned for the detectable species in these conversion experiments. Furthermore, the related $9\text{-}MC_{VO^{3+}N}\text{-}3$ (**1**),[3,8] which does not have a captured metal, is stable in acetonitrile, suggesting that the $12\text{-}MC_{M^{3+}N}\text{-}4$ cores would also be stable when demetalated.

These data show we can change one metallacrown to another while still in solution. Therefore, the conversion of **4** to **3** is not a result of either selective crystallization of **3** or the templating of a new cluster around Mn(II) as it crystallizes. Thus, by showing that through the simple expedient of adding a new metal salt one can convert one metallacrown to another, we have established a functional analogy to the organic parents that can now be exploited to prepare a wide variety of bimetallic metallacrowns.

In addition to these direct solution probes, the qualitative metal/anion preference for the $12\text{-}MC_{Mn^{3+}N}\text{-}4$ core can be assessed by product analysis of synthetic reactions. When 1 equiv of Mg(II) acetate is added to **3** in DMF and allowed to crystallize (3 days, ≈90% recovered), a 7:3 mixture of **3** and **5** results. This is not a kinetically controlled ratio, as we have followed the increase in the +56 ppm resonance as acetate is added to the acetate-d_3 form of **3** and conclude that anion exchange is complete in a few hours. Also when the reactions are monitored with NMR spectroscopy, the conversion of **3** to **5** is complete in 24 h. Addition of manganese(II) acetate to **4** gives **3**; however, adding NaCl or sodium acetate to **3** does not cause a conversion to **4**. Once again, we do not believe this is a kinetic phenomenom, as the chloride of **4** is rapidly displaced in DMF (<1 min) when $AgNO_3$ is added.[16]

It is clear from these data that when one discusses cation binding by metallacrowns, it is critical to define the anion(s) present. We are attempting to gather stability constants for metals and anions with metallacrowns in order to assess the feasibility of using these compounds as the basis for cation and anion selective sensors. This task is complicated, since the measured equilibrium constant for cation (or anion) binding is dependent on the types of anions (or cations) present and the affinity of these anions (or cations) with the chosen cation (or anion) for the metallacrown. However, we can qualitatively define relative cation preferences in the presence or absence of acetate on the basis of the data above for $12\text{-}MC_{Mn^{3+}N}\text{-}4$. At stoichiometric levels of acetate the relative cation affinity is Mn(II) > Mg(II) ≫ Na(I). Tentatively, it appears that sodium is prefered over Mn(II) and Mg(II) when acetate is absent and chloride is present. Finally, **3** or **5** is recovered exclusively (and in greater than 90% yield) when Na(I), M(II) [Mn(II) or Mg(II)], acetate, and chloride are mixed under synthetic conditions, suggesting that $Mn^{II}(OAc)_2 > Mg^{II}(OAc)_2 >$ NaCl for $12\text{-}MC_{Mn^{3+}N}\text{-}4$.

The preference of $12\text{-}MC_{Mn^{3+}N}\text{-}4$ for Mn(II) over Na(I) is a result of three factors: the smaller ionic radius (Mn(II), 0.83 Å; Na(I), 1.12 Å), the increased charge, and the stronger anion bridge (acetate vs chloride). The slight preference for Mn(II) relative to Mg(II) (0.72 Å) shows that ionic radius is not the only arbiter in metallacrown specificity. In this case the bridging ligand imparts an additional level of selectivity for metal sequestration. The ease of displacement of sodium from **4** makes it a useful precursor to metallacrowns that may find utility in anion and cation sensors, in catalysis, or as precursors to new polymer materials.

Acknowledgment. This work was supported by the Alfred P. Sloan Foundation.

Supplementary Material Available: For **4**, Tables 1–4, listing fractional atomic positions for all atoms, anisotropic thermal parameters of all non-hydrogen atoms, a complete set of bond distances, and a complete set of bond angles, respectively, and Figure 3, showing a complete numbering scheme for all atoms (6 pages); Table 5, listing observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Willard H. Dow Chemical Laboratories
University of Michigan
Ann Arbor, Michigan 48109-1055

Myoung Soo Lah
Vincent L. Pecoraro*

Received May 4, 1990

---

(11) Wells, A. F. *Structural Inorganic Chemistry*, 3rd ed.; Clarendon Press: Oxford, England, 1962.

(12) Bonadies, J. A.; Maroney, M. L.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 2044.

(13) Li, X.; Pecoraro, V. L. *Inorg. Chem.* **1989**, *28*, 3403.

(14) Larson, E. J.; Pecoraro, V. L. *J. Am. Chem. Soc.*, in press.

(15) Similar chemistry is seen by addition of 0.7 equiv of magnesium(II) acetate to form $Mg^{II}[Mn^{III}(SHI)(OAc)_{0.5}(DMF)_{1.5}]_4$ (**5**) with the bound acetate resonance appearing at +33 ppm. When more than 0.7 equiv of manganese(II) or magnesium(II) acetate is added to the NMR tube, another reaction occurs that keeps the metallacrown ring intact but generates additional acetate peaks at +28 ppm. This new material, which we are attempting to characterize, can be generated by addition of sodium acetate. Since its production is independent of the acetate salt used, it is most likely a structure with additional coordinated acetates.

(16) Silver chloride and a new metallacrown are generated. Although we have not structurally characterized this compound, we believe it to be $[Na(12\text{-}MC_{Mn^{3+}N}\text{-}4)]NO_3$.

(17) Lah, M. S.; Pecoraro, V. L.; Kirk, M. L.; Hatfield, W. In *Biosensors*; Buck, R., Bowden, E., Umana, M. Eds.; Marcel Dekker: New York, 1990; p 201.

Synthesis and Characterization of Labile Spherosilicates: $[(Me_3SnO)_8Si_8O_{12}]$ and $[(Me_4SbO)_8Si_8O_{12}]$

Structurally well-defined silsesquioxanes and silicate clusters have recently attracted interest as "building blocks" for the preparation of highly siliceous materials. Klemperer,[1] for example, has developed efficient syntheses of several highly functionalized

---

(1) (a) Agaskar, P. A.; Day, V. W.; Klemperer, W. G. *J. Am. Chem. Soc.* **1987**, *109*, 5554–6. (b) Day, V. W.; Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 8262–4. (c) Klemperer, W. G.; Mainz, V. V.; Millar, D. M. *Mater. Res. Soc. Symp. Proc.* **1986**, *73*, 3–13.

0020-1669/91/1330-0880$02.50/0