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.

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(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 $[Na(12\text{-}MC_{Mn^{3+}N}\text{-}4)]NO_3$.

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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

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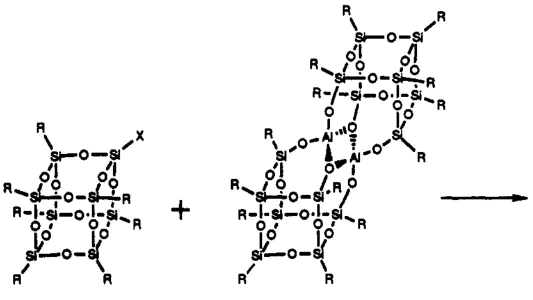
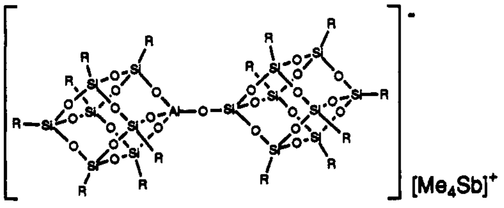
spherosilicates and silsesquioxanes as part of his research effort to elucidate mechanistic details of the sol–gel process. Agaskar[2] has developed an elegantly simple procedure for the synthesis of a wide variety of silylated spherosilicates, many of which offer interesting possibilities as precursors to organolithic macromolecular materials. Our interest in these compounds stems both from a general interest in using silsesquioxanes as models for silica and silica surfaces[3] and from our recent discovery that the reaction of **1c** with **2** gave high yields of **3**.[4] Tantalized by the prospect of being able to systematically construct truly immense aluminosilicate frameworks from aluminosilsesquioxanes and structurally well-defined polysilicate anions, we have been exploring routes to spherosilicates with labile functional groups. In this paper, we report syntheses of $[(Me_3SnO)_8(Si_8O_{12})]$ (**6**) and $[(Me_4SbO)_8(Si_8O_{12})]$ (**7**), two new cuboctameric spherosilicates that provide labile sources of anhydrous, aprotic $[(Si_8O_{20})^{8-}]$.



1a X = H
b OSnMe₃
c OSbMe₄

2

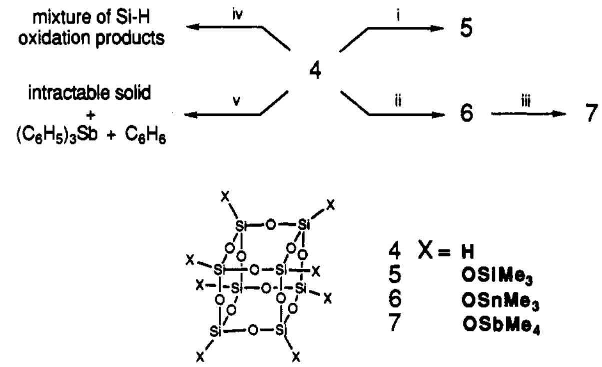


3 R = c-C_6H_{11}

Our first attempts to synthesize **6** and **7** sought to exploit the same highly efficient methodology that we previously used to prepare **1b–c** from **1a**.[4] Unfortunately, this methodology failed when attempted with $[H_8Si_8O_{12}]$[5] (**4**): unlike the reactions of **1a** with Me_3SnCl/Me_3NO and Me_4SbCl/Me_3NO, which afford quantitative (NMR) yields of **1b** and **1c**, respectively, the reactions of **4** under similar conditions produce complex mixtures of insoluble silica-like products. Even when deficiencies of Me_3NO are used in these reactions (<0.5 Me_3NO/molecule of **4**), the only solution species observable by ^1H NMR spectroscopy are unreacted starting materials. It was therefore necessary to develop alternative procedures for the oxidative stannylation and/or stibnation of **4**.

There were a number of possible strategies for effecting the oxidation of **4** without disrupting the silsesquioxane framework, but the observation by Klemperer and Millar[6] that **4** reacts with Me_3SnOMe to afford complex mixtures of incompletely trimethylstannylated spherosilicates (i.e., $[H_{8-n}(Me_3SnO)_nSi_8O_{12}]$) suggested that **6** and **7** might be available from the reactions of **4** with appropriately substituted ethers of heavier group 14 or 15 main-group elements. We therefore explored the reactivity of **4** toward a variety of readily available Si-, Sn-, and/or Sb-containing ethers.

Scheme I[a]



4 X = H
5 OSiMe₃
6 OSnMe₃
7 OSbMe₄

[a] Reaction conditions: (i) $Me_3SiOSbMe_4$, C_6D_6, 25 °C, 2 h; (ii) $Me_3SnOSnMe_3$, C_6D_6, 25 °C, 1 h; (iii) $Me_3COSbMe_4$ or $Me_3SiOSbMe_4$, C_6D_6, 25 °C, 8 h; (iv) $Me_3SiOSnMe_3$, C_6D_6, 80 °C, 10 h; (v) $Ph_4SbOSbPh_4$, C_6D_6, 80 °C, 10 h.

The results from the reactions of **4** with $Me_3SiOSnMe_3$,[7a] $Me_3SiOSbMe_4$,[7b] $Me_3SnOSnMe_3$,[7c] and $Ph_4SbOSbPh_4$[7d] are summarized in Scheme I. Like the reactions of hydridosilsesquioxanes with Me_3NO, the reactions of **4** with these main-group ethers occur much more rapidly than the corresponding reactions with **1a**. The reactions of **4** with $Me_3SiOSnMe_3$ and $Ph_4SbOSbPh_4$ produce complex mixtures of (inseparable) Si–H oxidation products,[8] but clean reaction chemistry is observed when $Me_3SiOSbMe_4$ and $Me_3SnOSnMe_3$ are used. The reaction[9] of **4** with $Me_3SiOSbMe_4$ affords a quantitative (NMR) yield of **5**,[2a,10] Me_3Sb, and methane. The last two products presumably result from the reductive elimination of methane from Me_4SbH.[11]

The addition of $Me_3SnOSnMe_3$ (66 mg) to a suspension of **4** (11 mg) in C_6D_6 (0.4 mL) quickly produces a homogeneous colorless solution. An ^1H NMR spectrum of the solution within 10 min of mixing exhibited resonances at δ 4.75 and 0.45 for Me_3SnH and a complete lack of resonances attributable to hydridosilsesquioxanes (δ 4.196 for **4**). The ^{13}C NMR spectrum exhibited resonances for Me_3SnH (δ −11.74) and unreacted $Me_3SnOSnMe_3$ (δ −2.47), as well as a large singlet at δ −2.91 for

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(8) (a) The reaction of **4** with $Me_3SiOSnMe_3$ (80 °C, C_6D_6, 10 h) gave a mixture of partially trimethylsilylated and trimethylstannylated spherosilicates. Similar results have been observed by Millar.[6] (b) The reaction of **4** with $Ph_4SbOSbPh_4$ (80 °C, C_6D_6, 10 h) does produce Ph_3Sb (^{13}C NMR), but the silsesquioxane product mixture is extremely complex.

(9) In a typical reaction, $Me_3SiOSbMe_4$ (52 mg, 190 μmol) was added to a suspension of **4** (10 mg, 24 μmol) in benzene. Methane evolution, which began immediately, ceased after 2 h. Evaporation of the solvent and volatiles (25 °C, 10^{-3} mTorr, 8 h) gave a quantitative yield of **5**, which was identical in all respects with a sample prepared by the reaction of **4** with Me_3NO/Me_3SiCl.[1a]

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(11) (a) Most attempts to prepare Me_4SbH and Ph_4SbH have afforded Me_3Sb and Ph_3Sb, respectively.[10b] In both cases there is some uncertainty about the mechanism(s) by which reduction occurs, but pentavalent antimony hydride complexes have been proposed as intermediates and most of the available data support these proposals. We are currently investigating the mechanism(s) of these reactions and will report the details in due course. (b) Doak, G. O.; Freedman, L. D. *Organometallic Compounds of Arsenic, Antimony, and Bismuth*; Wiley-Interscience: New York, 1970; p 339 and references cited therein.

6. The ^{119}Sn NMR spectrum[12] of a slightly larger scale reaction[13] exhibited singlet resonances for **6** (δ 118.42), $Me_3SnOSnMe_3$ (δ 114.03), and Me_3SnH (δ −102.33), and there was a single resonance at δ −101.55 in the ^{29}Si NMR spectrum. Except for **6**, all compounds in the reaction mixture are volatile and can be conveniently removed in vacuo (70 °C, 10^{-3} mTorr, 14 h) to afford a spectroscopically pure product. Fine colorless needles of **6** were obtained by recrystallization from hexane at −40 °C.

The reactions[14] of **6** with $Me_4SbOSiMe_3$ and $Me_4SbOCMe_3$ (C_6D_6, 25 °C) afford quantitative yields of **7** and the corresponding stannyl ethers (i.e., $Me_3SnOSiMe_3$ and $Me_3SnOCMe_3$). ^{13}C and ^{29}Si NMR spectra of the crude products obtained after evaporation of the volatiles (70 °C, 10^{-3} mTorr, 8 h) both consist of single resonances (^{13}C δ 11.44; ^{29}Si δ −104.33) and are clearly indicative of a spherosilicate with five-coordinate Me_4Sb groups.[4] A typical crude product is spectroscopically pure, but microcrystalline **7** can be obtained by recrystallization from hexane at −40 °C.

The facility with which heterosiloxane bonds can be heterolytically cleaved at the heteroatom (i.e., $Si{-}O{-}M \rightarrow [SiO^-] + [M^+]$)[15] provides a wealth of interesting chemical possibilities, ranging from our initial goal to synthesize supermolecular aluminosilsesquioxanes to the preparation of entirely new framework silicates under aprotic conditions. We have only begun to explore the chemistry of these new spherosilicates, but the observation that **7** reacts with Me_3SiCl and Me_3SnCl to afford **5** and **6**, respectively, is clearly consistent with our expectation that **7** would function as a labile, aprotic source of $[Si_8O_{20}]^{8-}$. Our efforts to use these spherosilicates to synthesize larger silsesquioxane and aluminosilsesquioxane frameworks will be presented in due course.

Acknowledgment. These studies were supported by the National Science Foundation (Grants CHE-8703016 and CHE-9011593) and an NSF-Presidential Young Investigator Award (Grant CHE-8657262). Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. F.J.F. gratefully acknowledges financial support from an Alfred P. Sloan Foundation Research Fellowship. We also thank Professor Walter G. Klemperer (University of Illinois) for helpful comments.

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(12) For an excellent review of ^{119}Sn NMR spectroscopy, including a large compilation of ^{119}Sn chemical shifts and coupling constants, see: Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73–186.

(13) In a typical reaction, $Me_3SnOSnMe_3$ (1.508 g, 4.39 mmol) was added to a suspension of **4** (230 mg, 0.542 mmol) in benzene. The mixture was stirred for 1 h at 25 °C; then the volatiles were removed in vacuo (70 °C, 10^{-3} mTorr, 14 h) to afford a quantitative yield of spectroscopically (^{1}H and ^{13}C NMR) pure **6**. Recrystallization from hexane (+25 to −40 °C) afforded fine white needles (54%). For **6**: ^{1}H NMR (500.13 MHz, C_6D_6, 23 °C) δ 0.362 (J_{Sn-H} = 58.2.1, 59.2 Hz); $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C) δ −2.91; $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 23 °C) δ −101.55; $^{119}Sn\{^1H\}$ NMR (37.3 MHz, C_6D_6, 23 °C) δ 118.42; mass spectrum (EI, 70 eV, 200 °C) *m/e* (relative intensity) 1840 (100%, $M^+ - CH_3$), 1662 (30%, $M^+ - CH_3 - Me_3Sn$), 165 (50%, Me_3Sn^+); mp 184–186 °C. Anal. Calcd (found) for $C_{24}H_{72}O_{20}Si_8Sn$: C, 15.54 (15.93); H, 3.91 (3.79).

(14) In a typical reaction, a benzene solution of **6** (400 mg, 0.216 mmol) and $Me_3COSbMe_4$ or $Me_3SiOSbMe_4$ (1.94 mmol) were stirred overnight at 25 °C. Evaporation of the solvent and volatiles (70 °C, 10^{-3} mTorr, 8 h) afforded a quantitative yield of spectroscopically (^{1}H and ^{13}C NMR) pure **7**. Fine microcrystals of **7** were obtained in 60% yield by recrystallization from hexane (+25 to −40 °C). For **7**: ^{1}H NMR (500.13 MHz, C_6D_6, 23 °C) δ 1.083 ($w_{1/2}$ = 23 Hz); $^{13}C\{^1H\}$ NMR (125.03 MHz, C_6D_6, 23 °C) δ 11.44; $^{29}Si\{^1H\}$ NMR (99.4 MHz, C_6D_6, 23 °C) δ −104.33; mass spectrum (EI, 70 eV, 200 °C) *m/e* (relative intensity) 180 (50%, Me_4Sb^+), 165 (80%, Me_3Sb^+), 151 (100%, Me_2Sb^+); mp >400 °C. Anal. Calcd (found) for $C_{32}H_{96}O_{20}Si_8Sb$: C, 21.05 (17.63); H, 5.40 (5.05). The combustion analysis of **7** consistently gives carbon and hydrogen contents that are lower than expected. This is presumably because the oxidation of these highly siliceous compounds is often incomplete. (To facilitate combustion, our samples are usually mixed with WO_3 in tin capsules and allowed an extended combustion time (Desert Analytics)). Considering the source of **7** and its reactions with (TMS)Cl and Me_3SnCl, which give quantitative yields of **5** and **6**, we are confident of our structural assignment.

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Electron Transfer in Inorganic Nitrogen Fixation[1]

The biological reduction of dinitrogen involves a series of concomitant electron- and proton-transfer steps. Within this context, dinitrogen complexes of molybdenum(0) and tungsten(0) react with strong acids to produce ammonia, or hydrazine and ammonia.[2-6] The initial phase of the reaction, which encompasses protonation and intramolecular electron reorganization, leads to the rapid formation of a hydrazido(2−) complex;[1,5,7-10] e.g. eq 1,

$$\textit{trans}\text{-}[Mo(N_2)_2(dpepp)(PPh_3)] + 2HBr \rightarrow [MoBr(NNH_2)(dpepp)(PPh_3)]Br + N_2 \quad (1)$$

$$2\{Mo^{IV}(NNH_2)\} \xrightarrow{4H^+} 2\{Mo^{III}\} + 2NH_4^+ + N_2 \quad (2)$$

where dpepp = $PhP(CH_2CH_2PPh_2)_2$. The final phase, in THF solution, involves disproportionation[11] (intermolecular electron transfer) of the hydrazido(2−) complex to yield about 1 mol of ammonia/mol of Mo and 0.5 mol of N_2/mol of Mo (eq 2).[5] In CH_2Cl_2 solution, hydrazine is formed in addition to ammonia and N_2. In order to achieve the goal of developing a catalytic cycle for dinitrogen reduction, coupling of a reducing agent and a proton source is required. We wish to report the discovery of simple two-electron-reducing agents that fulfill the role of reducing the hydrazido(2−) ligand to ammonia, thus circumventing disproportionation (see Table I).

Reaction of *trans*-$[Mo(N_2)_2(dppe)(PPh_2Me)_2]$ (**1**), where dppe = $Ph_2PCH_2CH_2PPh_2$, with HBr (20 mol) in CH_2Cl_2 (48 h) produced ammonia, hydrazine, and N_2 in yields of 0.39, 0.44, and 1.39 mol/mol of **1**, respectively, for a 100% nitrogen atom balance.[11] Addition of $SnCl_2$ (4 mol) to a similar reaction mixture caused significant changes in the yields of reduction products: 1.18, 0.25, and 1.19 mol/mol of **1**, respectively, for a 100% nitrogen atom balance and ca. 300% increase in the yield of ammonia.[12,13]

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