temperature. Short-range order effects play a much smaller role in the magnetic interactions of $[4\text{-Cl(py)H}]_3Fe_2Cl_9$ relative to those in $[4\text{-Br(py)H}]_3Fe_2Cl_9$.

The magnetic ordering temperature, 2.685 K, is lower than the value 2.73 K obtained by susceptibility measurements. This discrepancy is insignificant. The effects of the high pressure required for pelleting the sample are a likely source for the shift in the critical temperature.

The exchange constant J/k_B may be obtained from the tail of the heat capacity in the post transition region which follows the relation[7]

$$C_{p,ex}/R = 2[S(S+1)]^2zJ^2/3k_B{}^2T^2$$

where $S = {}^5/_2$ for iron(III) and z is the magnetic coordination number, assumed to be 6 for the present system. A plot of the excess heat capacity against T^{-2} should, therefore, be linear, and J/k_B may easily be obtained from its slope. Such a plot is indeed found to be linear between 2.9 and 4.5 K. The exchange constant, J/k_B, is found to be 0.110 K, in excellent agreement with the values of 0.110, 0.110, and 0.125 K obtained from magnetic susceptibility experiments.[2] The heat capacity is thus found to confirm the susceptibility results, and we conclude that long-range ordering dominates the magnetic interactions in this material.

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A Convenient Synthesis of Tricyclo[3.3.1.1^{3,7}]tetrasilathianes and Tricyclo[3.3.1.1^{3,7}]tetrasilaselenanes

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Introduction

There are only two reports describing the synthesis of adamantane-like structures composed of silicon and selenium, $(RSi)_4Se_6$, one which utilizes volatile H_2Se with a trichlorosilane[1] and the other requiring a reaction time of several days between trichlorosilane and hexamethyldisilathiane.[2] Of the few references for synthesizing the silicon–sulfur system, only one gives good yields deriving from $RSiCl_3$ and $(Me_3Si)_2S$.[3] The instability of the Si–S or Si–Se bond toward hydrolysis imposes the requirement of an anhydrous route to these compounds. Recently, we have reported convenient high-yield procedures for making anhydrous Na_2S[4] and Na_2Se[5,6] from sodium, sulfur, or selenium and a catalytic amount of naphthalene in THF as a useful step in preparing a variety of organic and organosilicon chalcogenides. In this note we describe a simple procedure for making silicon–chalcogenide adamantane cage systems on a preparative scale employing our sodium sulfide or sodium selenide that avoids the use of volatile selenides as well as meeting the requirement that the synthesis be anhydrous.

Experimental Section

Materials and General Procedures. Sodium sulfide and sodium selenide were prepared from sulfur or selenium powder, and sodium chips were prepared by cutting pellets. Commercially available trichlorosilanes (Petrarch) were distilled before use. Tetrahydrofuran was distilled from sodium benzophenone ketyl just prior to use. Hexane was stirred over H_2SO_4 and distilled. Benzene was dried by azeotropic removal of water and distilled into a storage bottle. All experiments were performed under a dry-nitrogen atmosphere and air-sensitive compounds were transferred in an argon-filled glovebox.

The ^{1}H (399.78 MHz), ^{13}C (100.52 MHz), ^{2}19Si (79.43 MHz), and ^{77}Se (76.22 MHz) NMR spectra were obtained on a JEOL GSX400 spectrometer. A 5-mm broad-band probe equipped with a variable-temperature accessory controlled the temperature at 25 ± 0.5 °C. Samples were prepared as 20–30% by volume solutions in $CDCl_3$ or C_6D_6. ^{1}H, ^{13}C, and ^{29}Si chemical shifts are reported in parts per million (ppm) with respect to Me_4Si (0 ppm) while ^{77}Se shifts are reported with respect to a 25% solution of Me_2Se in $CDCl_3$ (0 ppm). ^{29}Si NMR spectra were acquired by using a refocused INEPT pulse sequence. The ^{29}Si chemical shifts were measured from an external reference of 25% Me_4Si in $CDCl_3$. Infrared spectra were recorded on a Mattson Cygnus 25 FT-IR instrument. Elemental analysis was performed by Galbraith Laboratories in Knoxville, TN. Mass spectra were obtained on a MAT CH-5DF or CH7 mass spectrometer at 70 eV. Melting points were taken on a Thomas Hoover capillary melting point apparatus and are uncorrected.

Synthesis of Tetramethyl-, Tetraethyl-, and Tetraphenyltricyclo-[3.3.1.1^{3,7}]tetrasilaselenane. The synthesis of $(EtSi)_4Se_6$ (**2**) described below is similar to that used for the methyl and phenyl analogues. A 500-mL reaction flask was equipped with a condenser, a 125-mL addition funnel and charged with sodium chips (2.76 g, 120 mmol), selenium powder (4.68 g, 60 mmol), naphthalene (1.5 g, 12 mmol), and 100 mL of THF. To insure complete consumption of sodium, the mixture was refluxed for 10 h, giving a white suspension of Na_2Se. (If a purple color persists at this point, small amounts of sodium can be added until the white endpoint is attained. For a green mixture, adding Se powder will eventually give the white suspension.) An additional 100 mL of THF was added and $EtSiCl_3$ (6.5 g, 40 mmol) dissolved in 50 mL of THF was placed in the addition funnel while the contents of the flask were cooled to 0 °C. The $EtSiCl_3$ solution was added dropwise over a 1 h period. The reaction mixture turned red after being stirred at room temperature for 12 h and then to tan after 1 day. THF was removed by vacuum, and the salts were removed by adding 100 mL of benzene followed by filtration through a coarse glass frit yielding a yellow liquid. The benzene was removed under reduced pressure, and the remaining light yellow solid was recrystallized in benzene/hexane to yield 2.1 g of **2** as white crystals. The filtrate was concentrated, and an additional 0.6 g was isolated after recrystallization (total yield of **2**: 2.7 g, 40%): mp 171–172 °C (lit.[1] 170–171 °C); ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H, CH_3), 1.65 (q, 2 H, CH_2); ^{13}C NMR ($CDCl_3$) δ 6.2, 18.9 (CH_2CH_3); ^{29}Si NMR ($CDCl_3$) δ 6.8; ^{77}Se NMR ($CDCl_3$) δ −110. MS: *m/e* 696 (M^+, 6.8%) with correct isotope distribution for six Se atoms.

The above procedure with $MeSiCl_3$ produced **1** as a white crystalline solid after recrystallization in two crops (total yield of **1**: 2.4 g, 37%): mp 280–283 °C (lit.[1] 283–284 °C). ^{1}H NMR ($CDCl_3$) δ 1.38 (s, CH_3); ^{13}C NMR ($CDCl_3$) δ 11.8; ^{29}Si NMR ($CDCl_3$) δ −0.8; ^{77}Se NMR ($CDCl_3$) δ −81. MS: *m/e* 640 (M^+, 3.9%) with correct isotope distribution for six Se atoms.

A similar procedure using $PhSiCl_3$ gave **3** as white crystals (total yield of **3**: 1.1 g, 12%): mp >270 °C; ^{1}H NMR (C_6D_6) δ 7.85 (d, 2 H, C_6H_5), 7.45 (m, 3 H, C_6H_5); ^{13}C NMR (C_6D_6) δ 134.8, 133.1, 131.2, 128.8 (C_6H_5); ^{29}Si NMR (C_6D_6) δ −6.1; ^{77}Se NMR (C_6H_6) δ −88. MS: *m/e* 894 (M^+, 3.7%) with correct isotopic distribution for six Se atoms. Anal. Calcd for $C_{24}H_{20}Si_4Se_6$: C, 32.22; H, 2.25. Found: C, 32.21; H, 2.30.

Synthesis of Tetramethyl- and Tetraethyltricyclo[3.3.1.1^{3,7}]tetrasilathiane. A 500-mL 3-necked round-bottomed flask fitted with a condenser/N_2 inlet and a 250-mL addition funnel was charged with sodium chips (5.50 g, 240 mmol), sulfur powder (3.80 g, 120 mmol), naphthalene (3.1 g, 24 mmol), and 200 mL of THF. A gray suspension of Na_2S resulted after 10 h at reflux. This mixture was cooled to 0 °C and treated by dropwise addition of $EtSiCl_3$ (13.1 g, 80 mmol) in 100 mL of THF over a 1-h period. Stirring at room temperature for 15 h gave a light tan mixture. Removal of solvent by vacuum followed by extraction and filtration with 50 mL of benzene gave a yellow solution. The benzene was removed under reduced pressure, naphthalene was removed by sublimation (50 °C, 0.1 Torr), and the remaining yellow solid was recrystallized in hexane to give 4.2 g (50% yield) of $(EtSi)_4S_6$ (**5**) as white crystals: mp 134–137 °C (lit.[7] 140 °C); ^{29}Si NMR ($CDCl_3$) δ 21.9 (lit.[7] δ 21.9).

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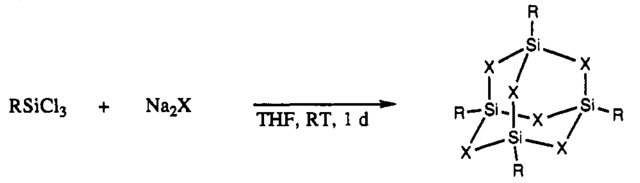
Scheme I



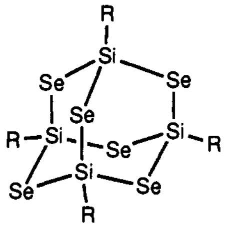
1 R = Me; X = Se (37%)
2 R = Et; X = Se (40%)
3 R = Ph; X = Se (12%)
4 R = Me; X = S (45%)
5 R = Et; X = S (50%)

$(MeSi)_4S_6$ (**4**) was synthesized in 45% yield using a procedure similar to that described for (**5**): mp 271–274 °C (lit.[3] 273–276 °C); ^{29}Si NMR ($CDCl_3$) δ 17.0 (lit.[3] δ 16.95).

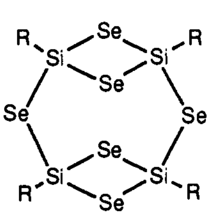
Results and Discussion

When $RSiCl_3$ (R = Me, Et, Ph) is added to sodium selenide, made in situ from sodium, selenium, and a catalytic amount of naphthalene, the corresponding tricyclo[3.3.1.1^{3,7}]tetrasilaselenane is produced (Scheme I). Likewise if $RSiCl_3$ (R = Me, Et) is added to similarly generated Na_2S, the silicon–sulfur cage systems can be made. All compounds are white, crystalline solids, which decompose over the course of hours if left in air. Decomposition of the selenium-containing molecules produces a reddish solid, presumably including amorphous elemental selenium.

The silicon–sulfur system is well characterized and possesses an adamantane-like structure as determined by X-ray crystal structure analysis.[2] There are two possible structures for a $(RSi)_4Se_6$ cage system given below as A and B. ^{1}H, ^{13}C, and ^{29}Si NMR data will be nearly identical for the two structures except for slight differences in chemical shifts. However, ^{77}Se NMR will discriminate between structures. For A, the ^{77}Se NMR spectra should exhibit one absorption. In B, the ^{77}Se NMR spectra should show two peaks, one signal for the Se atoms in the four-membered rings and another for the Se atoms bridging the two four-membered rings. We observed only one peak in the ^{77}Se spectrum confirming A as the structure.



A



B

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Synthesis, Structure, and Properties of a Complex That Consists of an $\{Mn_2O_2(O_2CCH_3)\}^{2+}$ Core and a Spanning Hexadentate Ligand

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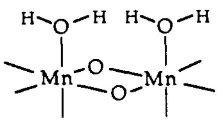
Much of the current interest in higher valent polynuclear manganese complexes stems from the fact that such a species is thought to catalyze water oxidation in the photosystem II (PSII) oxygen-evolving complex (OEC).[1] The PSII OEC manganese aggregate has been shown by EXAFS[2] studies to have short (~2.7 Å) Mn⋯Mn distances[3] and a multiline EPR signal[4] at $g \sim 2$. Binuclear complexes containing the $\{Mn_2O_2\}^{3+}$ core may be thought of as simple models for the water oxidation active site because they possess short Mn⋯Mn distances and EPR spectra which consist of 16 principal hyperfine lines centered at $g \sim 2$. In the last few years many $\{Mn^{III}Mn^{IV}O_2\}^{3+}$ species have been reported.[5-8] On the other hand, relatively few examples of the $\{Mn^{III}Mn^{IV}O_2(O_2CCH_3)\}^{2+}$ core exist.[9]

One important objective of ours has been to shield one side of an $\{Mn_2O_2\}^{3+}$ core with a hexadentate ligand in order to ensure that the remaining two manganese coordination sites are oriented syn with respect to each other, as shown in I. This structural type is desirable for at least two reasons: (i) It is possible that the critical step in photosynthetic water oxidation involves O–O bond formation between two terminally ligated O^{2-} or perhaps OH^- groups across the face of an Mn_2O_2 substructure of the active-site manganese complex. Synthetic complexes of the type shown above would allow us to test this hypothesis. (ii) One important structural candidate for the PSII OEC is a dimer of bis(oxo)-bridged dimers.[10] One can easily see that syn-coordinated complexes as depicted above could act as precursors to "dimer-of-dimers" structures. For instance, under basic conditions one might obtain two bis(μ-oxo) dimers bridged together by two



I

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(2) Abbreviations used: PSII, photosystem II; OEC, oxygen-evolving complex; EXAFS, extended X-ray absorption fine structure; EPR, electron paramagnetic resonance; IR, infrared; tppn, *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-1,3-propanediamine; tpen, *N*,*N*,*N'*,*N'*-tetrakis(2-pyridylmethyl)-1,2-ethanediamine; bpy, 2,2'-bipyridine; phen, 1,10-phenanthroline; tren, $N(CH_2CH_2NH_2)_3$; tacn, 1,4,7-triazacyclononane; cyclam, 1,4,8,11-tetraazacyclotetradecane; DMEPA, ((6-methyl-2-pyridyl)methyl)(2-(2-pyridyl)ethyl)(2-pyridylmethyl)amine; Fc, ferrocene.

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