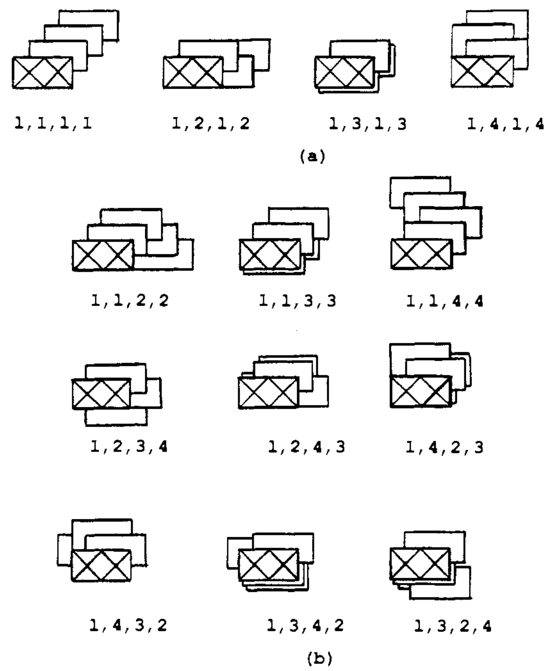

Figure 4. (a) Stable phases for nearest-neighbor stacking patterns. (b) Predicted stable competitive or next-nearest-neighbor phases.

the spins are restricted to lie in a plane, while the cubic anisotropy term further restricts the spin orientations toward the corners of a square in that plane. The following correspondences can be made

$$\vec{S} = (1, 0) \leftrightarrow \vec{t}_1$$
$$\vec{S} = (0, 1) \leftrightarrow \vec{t}_2$$
$$\vec{S} = (-1, 0) \leftrightarrow \vec{t}_3$$
$$\vec{S} = (0, -1) \leftrightarrow \vec{t}_4$$

where the components of the spin vectors refer to the coordinate system in Figure 3. The Hamiltonian for the isolated one-dimensional stacks is taken to be of the form

$$\mathcal{H} = K\sum_i \vec{S}_i\cdot\vec{S}_{i+1} + J\sum_i(\vec{S}_i\cdot\vec{S}_{i+1})^2 + D\sum_i(S_{i,x}S_{i+1,y} + S_{i,y}S_{i+1,x}) + K_2\sum_i \vec{S}_i\cdot\vec{S}_{i+2}$$

The three nearest-neighbor terms (K, J, D) describe the energy relations between consecutive pairs of translations. With K_2 small, four possible stable phases are predicted (at $T = 0$, since long-range order cannot exist at finite temperature for a 1d system), which are shown in Figure 4a. For convenience, the patterns are labeled by the subscripts of the sequence of $\vec{t}_k$ translation vectors defining the stacking arrangements. The ferrodistortive 1,1,1,1 and antiferrodistortive 1,3,1,3 phases are stable for $K \ll 0$ and $K \gg 0$, respectively, while the vertical 1,4,1,4 and horizontal 1,2,1,2 propagation patterns are found when $D \gg 0$ and $D \ll 0$, respectively. All four of these polytypes are now observed experimentally with the report of the $Cu_2X_4L^2$ structures.

The inclusion of the next-nearest-neighbor interaction leads to a very rich series of nine competition phases (analogous to the $\uparrow\uparrow\downarrow\downarrow$ phase of the next-nearest-neighbor spin $^1/_2$ Ising model), as shown in Figure 4b. The lower two rows contain three sets of degenerate entantiomorphic pairs of stacking patterns. The 1,1,2,2 pattern reported in this paper is the first of these competition phases to be observed experimentally.

The $T = 0$ phase diagram for this Hamiltonian is extremely rich, with regions of stability predicted for the four nearest-neighbor phases as well as for all nine competition patterns. This is illustrated in Figure 5 for a D, K section through the four-parameter space with $K_2 < 0$ and $J = 0.5\ K_2$. This particular section includes all four nearest-neighbor phases, as well as five regions where competition phases are predicted to be stable. The distribution of known phases (underlined in Figure 5) is such the currently unobserved phases lie in regions of parameter space intermediate between the areas occupied by the known phases. Thus, just as with the 1,1,2,2 phase, realization of other competition phases can be anticipated as design strategies are developed based upon interpretation of the factors that determine the values of the various energy parameters.

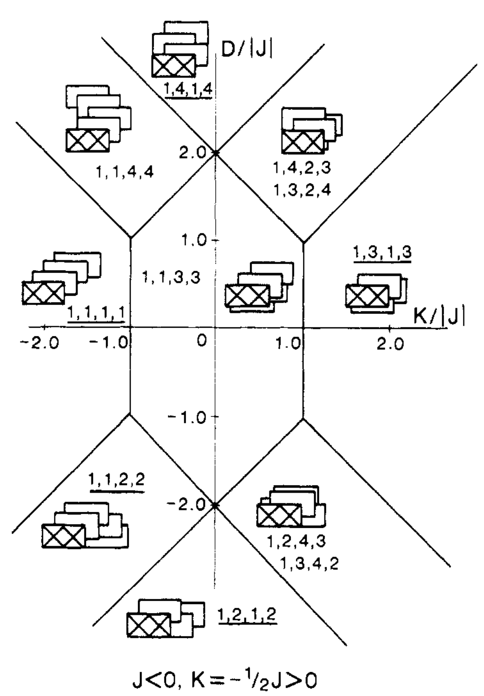

Figure 5. Section of the predicted phase diagram in the D, K plane for $K_2 < 0$ and $J/|K| = 0.5$. Underlined phases have been observed experimentally. Only one envelope diagram has been included for the two regions containing degenerate enantiomorphic pairs.

Acknowledgment. The support of NSF Grant DMR-8803382 is gratefully acknowledged.

Registry No. (4-methylpyridinium)$_2$Cu$_3$Cl$_8$, 116155-35-2; (4-methylpyridinium)$_2$Cu$_3$Br$_8$, 129029-38-5; Cu$_2$Cl$_4$(4,4′-dimethyl-2,2′-bipyridine), 128900-79-8; Cu$_2$Br$_4$(4,4′-dimethyl-2,2′-bipyridine), 128900-80-1.

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A Simple Synthesis of 3-Bromo-*o*-carborane[1]

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Received March 7, 1990

Although more than one synthesis of 3-bromo-*o*-carborane (**1**) appears in the literature, no current route makes this potentially useful compound easily available. We report here a simple modification of one synthesis of **1** that provides this molecule in good yield and high purity.

One multistep source of **1** is the Sandmeyer reaction of 3-amino-*o*-carborane (**2**), itself available in nearly quantitative yield from $(B_{10}C_2H_{12})^{2-}$.[2,3] The yield of **1** from this procedure seems not to be reported, but that of the related 3-chloro-*o*-carborane is 47.5%.

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[1] Support for this work by the National Science Foundation through Grant CHE 8800448 is gratefully acknowledged.

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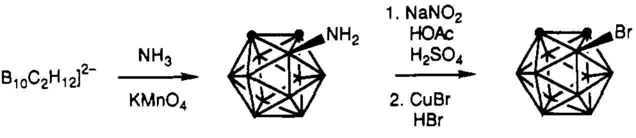
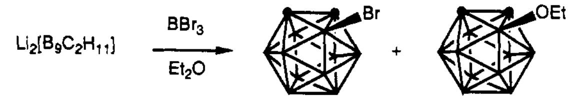


2 1

The easiest current route to **1** is that of Roscoe, Kongpricha, and Papetti,[4] which involves the treatment of $Li_2[B_9C_2H_{11}]$ with boron tribromide. Two bromides are displaced, and the residual B–Br is incorporated into the icosahedral cage at the 3-position. Although the reaction as described is not difficult to carry out, the yield reported is only 26% and we have found that complications are introduced by the necessity of separating an unreported side product formed in approximately the same yield as **1**. We have identified this compound as 3-ethoxy-*o*-carborane (3).[5]

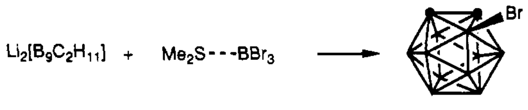


1 3

A mechanistic analysis of the Roscoe procedure points out a probable source of 3 and suggests an effective modification. Boron tribromide is a well-known reagent used for ether cleavage reactions.[6] Complex formation is followed by displacement by bromide with formation of ethoxydibromoborane, doubtless the active ingredient in the formation of 3 in the Roscoe procedure.

$$Et_2O + BBr_3 \longrightarrow EtOBBr_2 \xrightarrow{Li_2[B_9C_2H_{11}]} 3$$

In order to avoid this simple, but seriously offending side reaction, we need only thwart the ether cleavage reaction. The boron tribomide–methyl sulfide complex is commercially available[7] and serves to convert $Li_2[B_9C_2H_{11}]$ into **1** without complicating side products. Pure material can be obtained in >65% yield after recrystallization from chloroform/hexanes.



1, 65.4%

Experimental Section

3-Bromo-*o*-carborane (1). $[Me_3NH][B_9C_2H_{12}]$[8] (1.25 g, 6.5 mmol) was placed in 30 mL of methyl sulfide in a 250-mL, three-necked flask equipped with a magnetic stirrer, reflux condenser, and a gas inlet and outlet. The system was flushed slowly with argon while the reaction was in progress. A solution of 2.5 M *n*-butyllithium in hexane (5.2 mL, 13 mmol) was slowly added with a syringe to the mixture with stirring at room temperature. After the addition was completed, the reaction mixture was stirred at room temperature for an additional 2 h and then heated to reflux for 4 h. After the reaction mixture cooled to room temperature, the boron tribromide–methyl sulfide complex (2.5 g, 7.9 mmol) was added slowly, with vigorous stirring. The stirring was continued for another 2 h after the addition was completed. The reaction mixture was then hydrolyzed with 2 mL of water to remove the excess boron tribromide. The organic layer was separated out and then evaporated to dryness under vacuum. The resulting solid was purified by recrystallization from chloroform/hexanes to give 3-bromo-*o*-carborane (950 mg, 65.4% yield). Mp: 118–120 °C (lit. 118.5–119,[3] 121–122 °C[4]). ^1H NMR (δ, $CDCl_3$): 3.82 (s, 2 H), 3.55–1.12 (m, 9 H). MS [*m/e* (assignment, % relative intensity)]: 225 (M + 2, 26), 224 (M + 1, 52), 223 (M, 83), 222 (M – 1, 100), 221 (M – 2, 98), 220 (M – 3, 75), 199 (M – 4, 52), 142 (12).

3-Ethoxy-*o*-carborane (3). This material was produced by using the procedure of Roscoe et al.[4] Mp: 40–41 °C (lit.[5] 38 °C). ^1H NMR (δ, $CDCl_3$): 3.94 (q, 2 H), 3.53 (s, 2 H), 3.45–1.32 (m, 9 H), 1.27 (t, 3 H). MS [*m/e* (assignment, % relative intensity)]: 190 (M + 2, 5), 189 (M + 1, 13), 188 (M, 16), 187 (M – 1, 13), 173 (M – 15, 100), 159 (M – 29, 18).

Registry No. **1**, 22258-25-9; **3**, 52138-59-7; $[Me_3NH][B_9C_2H_{12}]$, 12543-22-5; $Li_2[B_9C_2H_{11}]$, 62601-97-2.

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Models for Structural Environments in Silicon Chalcogenide Glasses. Synthesis, Characterization, and Single-Crystal X-ray Structures of $Si(SC_6H_5)_4$ and $Si(SeC_6H_5)_4$

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Received January 11, 1990

Introduction

Non-oxide chalcogenide glasses, which are formed by the sulfides, selenides, and tellurides of many main-group elements are important materials with promising applications in infrared optics and semiconductor technology. The development of materials with improved properties for device applications remains an important goal in this area of study, which requires a detailed structural description of the glassy state and its relationship to the physicochemical properties. These objectives necessitate the use of suitable techniques, such as solid-state NMR, which can probe the short-range order present in these systems.

To appropriately interpret NMR spectra of glasses, corresponding benchmark data on compounds with crystallographically well-characterized local environments are required. Therefore, in our continuing effort to understand the structural organization of silicon chalcogenide glasses, we report here the preparation, characterization, and single-crystal X-ray structures of two compounds with the anticipated $SiCh_{4/2}$ (Ch = S, Se) connectivity, namely $Si(SC_6H_5)_4$ and $Si(SeC_6H_5)_4$.

Experimental Section

Sample Preparation and Characterization. Chemicals. Thiophenol (Aldrich, 97%) was dried over P_2O_5 and then vacuum distilled. Benzene (Fisher) was dried over P_2O_5 and then distilled under N_2. Sodium (Fisher), phenylselenol (Alfa), silicon tetrachloride (Aldrich), and anhydrous ethyl ether (Fisher) were used without further purification. The synthetic procedures follow those published previously for these compounds.[1,2]

Preparation of $Si(SC_6H_5)_4$. Excess thiophenol (70 mL, 684 mmol) was added to 2 g (87.0 mmol) of sodium under N_2. This, at times vigorous, reaction was allowed to continue overnight at room temperature with intermittent stirring to yield a suspension of white $NaSC_6H_5$ in thiophenol. To this suspension was slowly added silicon tetrachloride (0.90 mL, 7.9 mmol) with swirling. After the initial reaction subsided, the mixture was heated at 90 °C for 15 min. NaCl and excess $NaSC_6H_5$ were filtered off, and the crude $Si(SC_6H_5)_4$ was then isolated from the solution. Recrystallization of $Si(SC_6H_5)_4$ from an anhydrous ethyl ether–thiophenol solution (30:1) by the slow evaporation of ether resulted in colorless crystals, yield 1.24 g (34%). Mp: 115.0 °C (lit.[2] mp: 114.5 °C). Mass spectrum: parent peak at 464 g/mol.

Preparation of $Si(SeC_6H_5)_4$. A suspension of white $NaSeC_6H_5$ was synthesized by the reaction of sodium (0.698 g, 30.4 mmol) and benzeneselenol (5 g, 32 mmol) in 50 mL of benzene. To this suspension was added silicon tetrachloride (0.670 mL, 5.85 mmol) at room temperature. After 1 week at room temperature, the mixture was warmed to 45 °C for 15 min and subsequently cooled. Excess $NaSeC_6H_5$ and NaCl were filtered out and the crude $Si(SeC_6H_5)_4$ was isolated. The product was recrystallized in an ethyl ether–benzeneselenol solution (30:1) and then washed with a minimum of ethyl ether to give colorless crystals, yield

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