

Controlled Assembly of Zero-, One-, Two-, and Three-Dimensional Metal Chalcogenide Structures

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A room-temperature solution route to the controlled synthesis of 0-, 1-, 2-, and 3-D assemblies of molecularly linked metal chalcogenide clusters using essentially identical building blocks is reported. The solvating, ligating, and reducing abilities of hydrazine at room temperature have been exploited to simultaneously dissolve metal chalcogenides and organize the resulting building blocks into frameworks of increasing dimensionalities. Control of the product dimensionality was achieved by varying the reactant ratios and the amount of hydrazine solvent employed in the reaction. The products have been characterized by single-crystal X-ray diffraction, Raman spectroscopy, and magnetic susceptibility.

The designed construction of ordered networks of inorganic clusters linked via organic molecules in the solid state is of great interest due to the materials properties that can be anticipated from such assemblies leading to potential applications in areas such as nanoscale electronics, photocatalysis, photovoltaics, and optoelectronics.¹ However, with some noteworthy exceptions,^{1c–d,2} the synthesis of these materials is often plagued by the lack of control during assembly leading to noncrystalline products.³ It is therefore highly desirable from a synthetic standpoint to design new routes that allow the directed synthesis of ordered materials. Herein, we report a room-temperature solution route to the controlled synthesis of 0-, 1-, 2-, and 3-D assembly of molecularly linked metal frameworks using metal chalcogenide building blocks.

Thus, we have employed the solvating, ligating, and reducing abilities of hydrazine at room temperature to simultaneously dissolve metal chalcogenides and organize the resulting building blocks into frameworks of increasing dimensionalities. The use of hydrazine as a solvent to prepare soluble metal chalcogenide precursors for semiconductor devices has been well documented by Mitzi et al.⁴ The structures synthesized consist of either isolated anionic metal chalcogenide units separated by hydrazinium cations and/or neutral hydrazine molecules,^{4a,b} 1-D metal chalcogenide chains attached to terminal hydrazines,^{4c} or 2-D metal chalcogenide slabs separated by a mixture of hydrazinium and hydrazine moieties.^{4d} All the structures described by Mitzi involve a single metal ion. In the present work, individual metal chalcogenide clusters are covalently linked to each other using hydrazine as a bridging ligand, and by fully employing the flexibility of hydrazine as either a monotopic or ditopic ligand, we demonstrate that we can *selectively* build structures of different dimensionalities (from 0-D to 3-D). The structures incorporate two different metals (Mn and Sn). The success of our procedure hinges on hydrazine serving several functions. First, it is reducing and thus converts the neutral chalcogenide species into the corresponding anion. Second, it is able to solvate the ionic species and prevent premature precipitation of materials. Finally, hydrazine can act as either a monotopic or a ditopic ligand toward metal ions. As described below, when hydrazine is in large excess, it acts primarily as a monotopic ligand, resulting in a solid of lower dimensionality. In lesser concentrations, hydrazine functions mainly as a ditopic ligand, linking up the building units to form higher-dimensional structures.⁵ To our knowledge, this critical combination of properties is unique to hydrazine.

All compounds were synthesized in hydrazine by dissolving solid mixtures of SnS₂ (or SnSe), S (or Se), and MnS

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- (5) This is an observed general trend with a seeming exception in the case of compound **4**. See the Supporting Information for the synthetic conditions for all four compounds.

under an inert atmosphere and stirring at room temperature. Single crystals were grown by diffusing 2-propanol into the filtered reaction mixtures over the time periods of 1–2 weeks. The same synthetic method applies to the preparations of compounds **1**–**4**, where control of the product dimensionality was achieved by varying the ratios of the reactants and, critically, the amount of hydrazine solvent employed in the reaction. Thus, using optimized reaction conditions, we were able to reproducibly obtain products of preferred dimensionality.⁶ Experimental details will be given for the synthesis of compound **1**; reaction conditions employed for the other compounds are available in the Supporting Information.

Hydrazine (16 mL, 98%, anhydrous) was added to a solid mixture of SnSe (200 mg, 1.01 mmol), Se (377 mg, 4.77 mmol), and MnS (174 mg, 2 mmol). **Note!** Hydrazine is toxic and should be handled with care. Gas bubbles were observed upon the addition of hydrazine, and the mixture was allowed to stir at room temperature for 10 days, after which the reaction mixture was filtered through a 0.45 μm syringe filter and the dark green filtrate was evenly distributed into three test tubes. In each test tube, 3 mL of 2-propanol/hydrazine mixture (1:1 by volume) and 12 mL of pure 2-propanol were layered consecutively on top of the filtrate solution for crystal growth. Yellowish-green single crystals of **1** were obtained at the bottom and the wall of each test tube after 2 weeks.

The structures of the four compounds span from 0-D discrete molecules ($\text{SnSe}_4\text{Mn}_2(\text{N}_2\text{H}_4)_{10}$), **1**, to 1-D chains ($\text{SnS}_4\text{Mn}_2(\text{N}_2\text{H}_4)_6$), **2**, 2-D layers ($\text{SnSe}_4\text{Mn}_2(\text{N}_2\text{H}_4)_7$), **3**, and 3-D networks ($\text{SnS}_4\text{Mn}_2(\text{N}_2\text{H}_4)_5$), **4** (Figure 1). Hydrazine proves to be not only a solvent for the metal chalcogenides at room temperature but also a versatile molecular linker.

The coordination geometries in compounds **1**–**4** are tetrahedral for Sn and octahedral for Mn atoms. The Sn–Q (Q = S, Se), Q–Mn, and Mn–N bond lengths fall in the range of values observed for tetrahedral SnQ_4 and octahedral Mn(II).⁷ Compound **1** contains discrete molecular pieces of the composition $[\text{SnSe}_4\text{Mn}_2(\text{N}_2\text{H}_4)_8]$, which are segregated from each other by free hydrazine solvent molecules. As there are no coordination bonds between individual $[\text{SnSe}_4\text{Mn}_2(\text{N}_2\text{H}_4)_8]$ moieties, compound **1** is considered 0-D. The structure of compound **2** is comprised of parallel 1-D chains propagating in the *ac* plane via two types of alternating octahedral Mn(II) centers. Half of the Mn atoms are attached to the SnS_4 tetrahedra, whereas the other half are isolated metal centers which coordinate to six nitrogen atoms from the hydrazine molecules. Compound **3** forms a 2-D layered network featuring inorganic $[\text{SnSe}_4\text{Mn}_2]$ units bridged by hydrazine molecular linkers. Within each layer, $\text{Mn}_2(\text{N}_2\text{H}_4)_6$ dimers are linked through bridging hydrazine to form 1-D

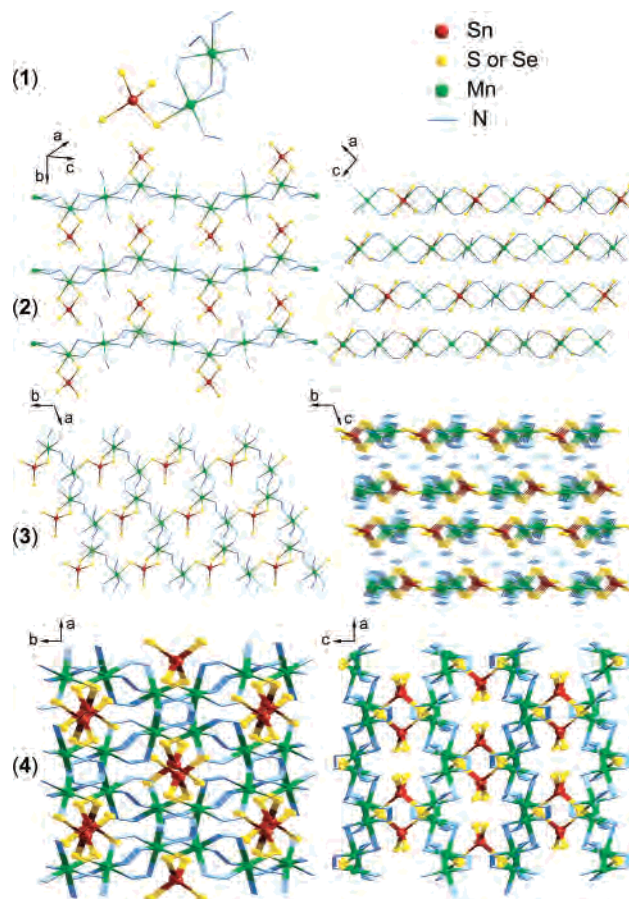


Figure 1. Crystal structures of compounds **1**–**4** showing how the metal chalcogenide building units are organized into zero, one, two, and three dimensions by the hydrazine linkers. All hydrogen atoms are omitted for clarity.

chains, and adjacent chains are interconnected to each other through SnSe_4 tetrahedra to give rise to the 2-D structure. These 2-D layers extend in the *ab* plane, while every two layers are separated by free hydrazine solvent molecules. Within a single $[\text{SnSe}_4\text{Mn}_2]$ unit, the coordination environments for the two Mn(II) atoms are slightly different, with one coordinating to four N atoms and two Se atoms, and the other to five N atoms and one Se atom. Single-crystal structural analysis on compound **4** reveals an extended framework built upon $[\text{SnS}_4\text{Mn}_2]$ structural units which are interconnected through ditopic hydrazine molecules in a 3-D arrangement. Two views of this 3-D structure along the crystallographic *c* and *b* axes, respectively, are illustrated in Figure 1 (4). Additional figures and more structural details of compounds **1**–**4** are available in the Supporting Information. Compounds **2** and **4** have no co-crystallized free solvent molecules, and each Sn atom is covalently bonded to two bridging S and two terminal S atoms in both structures. Compound **4** owes its 3-D structure to the efficient use of the hydrazine linkers: all the hydrazine molecules have entered the network structure as ditopic ligands in **4**, as opposed to in compounds **1**–**3** where a part of the hydrazine molecules acts as monotopic ligands. A summary of the crystallographic data of the four compounds is listed in Table 1.

(6) The use of reaction temperature to control the formation of products of different dimensions has been reported for other systems. See for example: Forster, P. M.; Burbank, A. R.; Livage, C.; Férey, G.; Cheetham, A. K. *Chem. Commun.* **2004**, 368–369.

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Table 1. Crystallographic Data for the Four Compounds (0-D to 3-D)^a

	chemical formula	space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	α (deg)	β (deg)	γ (deg)	R1
1	SnSe ₄ Mn ₂ (N ₂ H ₄) ₁₀	<i>P</i> 2 ₁ / <i>c</i>	10.304(4)	13.182(5)	18.270(7)	90	97.657(7)	90	3.35%
2	SnS ₄ Mn ₂ (N ₂ H ₄) ₆	<i>C</i> 2/ <i>c</i>	12.919(3)	8.934(2)	15.230(3)	90	106.992(4)	90	1.45%
3	SnSe ₄ Mn ₂ (N ₂ H ₄) ₇	<i>P</i> 1	8.103(2)	9.879(2)	13.021(3)	95.008(4)	94.423(4)	113.425(4)	4.93%
4	SnS ₄ Mn ₂ (N ₂ H ₄) ₅	<i>P</i> 2 ₁ / <i>n</i>	8.535(8)	13.300(12)	13.522(13)	90	90.588(16)	90	8.43%

^a X-ray data were collected on a Bruker SMART APEX CCD area detector system using Mo K α radiation at 115 K. The structures were solved using SHELXS and refined using the full matrix least-squares method on F_o^2 with SHELXL version 6.10. $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

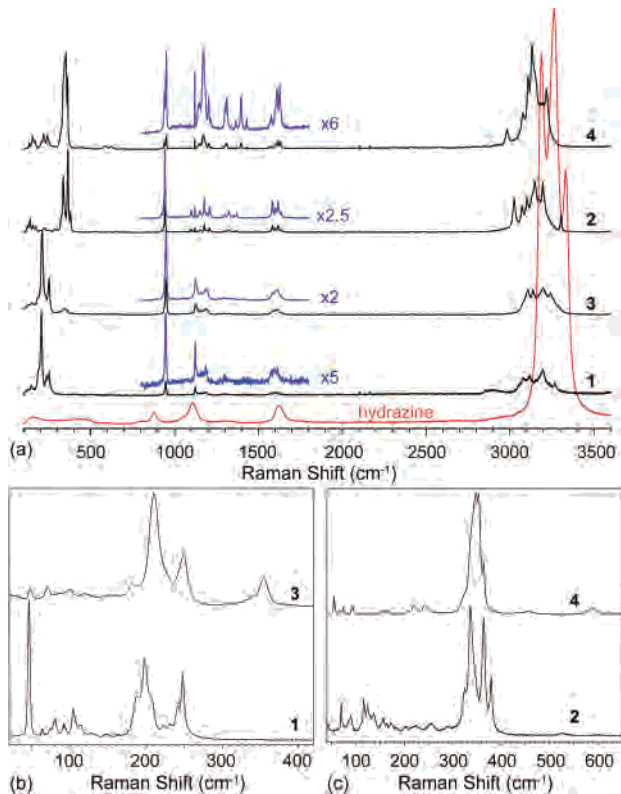


Figure 2. (a) Raman spectra of pure solid compounds **1–4** compared to that of pure hydrazine and (b and c) comparisons of low-frequency Raman spectra between compounds with similar building blocks. Spectra in (a) were taken on a Renishaw Invia Raman spectrometer, and the low-frequency spectra were taken on a Dilor XY spectrometer, both with 514 nm excitation.

Raman spectra of single crystals of compounds **1–4** (Figure 2) exhibit peaks due to hydrazine vibrations in the region above 800 cm⁻¹, as evidenced by comparison with the Raman spectrum of pure hydrazine (Figure 2a). Six peaks are observed in the spectrum of hydrazine: three located near 3000 cm⁻¹ (3335, 3263, and 3186 cm⁻¹), corresponding to the internal NH₂ stretching; one at 1627 cm⁻¹ attributed to NH₂ deformation and two at 1110 and 875 cm⁻¹ assigned to N–N stretching and NH₂ rocking, respectively.⁸ The modes in the solid-state compounds are shifted, narrowed, and/or split compared with the liquid modes, indicating the complex, yet highly ordered, environments for hydrazine in these compounds (either as monotopic ligand, ditopic ligand, and/or free solvent). The low-frequency Raman spectra (Figure 2b,c), on the other hand, reflect mainly inorganic

building-block-related features. The strong peaks located near 200 and 250 cm⁻¹ in the Se compounds are assigned to the symmetric and asymmetric Sn–Se stretch of SnSe₄ tetrahedra, respectively.^{9a} The stretching frequencies increase from SnSe₄ to SnS₄, leading to peaks between 300 and 400 cm⁻¹ in the S compounds.⁹ The small peaks near 250 cm⁻¹ in the S compounds are attributed to Mn–S stretching.¹⁰ Knowledge of all of these Raman modes will be valuable in spectroscopically probing the assembly of **1–4** in solution.

DC magnetic susceptibility measurements were performed on compound **3** (Quantum Design SQUID magnetometer; 1.8–350 K; $H = 0.01, 0.1, \text{ and } 1 \text{ T}$). The effective moment of 5.9 $\mu_B/\text{mol}_{\text{Mn}}$ determined from a Curie–Weiss fit over a temperature range of $T = 20\text{--}350 \text{ K}$, at all three fields, indicates a Mn²⁺ oxidation state (spin state 5/2). The same fit found the sample to be weakly anti-ferromagnetic, with a $|\theta_W|$ of <10 K. Experimental details of the magnetic measurements are presented in the Supporting Information.

In summary, the work presented here demonstrates the rich structural chemistry that can be derived from relatively simple building blocks under appropriate conditions, as well as the special role that hydrazine can play in the construction of 0-, 1-, 2-, and 3-D chalcogenide structures. The extension of this work to other inorganic systems is currently underway, as is the substitution of hydrazine with other ligands (such as those that support electronic communication) to produce new functional materials.

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Supporting Information Available: X-ray crystallographic files (CIF) for compounds **1–4**. Additional synthetic details and structural descriptions of compounds **1–4** along with more crystallographic figures (including thermal ellipsoid drawings); experimental details of the magnetic measurements performed on compound **3**; and Raman spectra of compounds **1** and **3** collected on a large quantity of crystals to check phase purity. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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