Ion Exchange

$\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$: A Robust Open Framework Based on Metal-Linked Penta-Supertetrahedral $[Zn_4Sn_4S_{17}]^{10-}$ Clusters with Ion-Exchange Properties**

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The huge diversity in structure and pore size encountered in open-framework aluminosilicate zeolite materials is not yet reflected in sulfide and chalcogenide compounds. Interest in chalcogenides with open frameworks, however, is growing, and progress towards developing this important class of materials has been steady in the past decade.[1–3] Because of the wider chemical and bonding flexibility, in principle, chalcogenides can be even more diverse in composition and structure than zeolites. In addition, they can uniquely combine properties of zeolitic micropores—exploited in solid-acid, ion-exchange, and absorption materials—with properties of semiconductors that provide the basis of electronic, optical, and photonic applications.

Some chalcogenides with open frameworks are based on so-called supertetrahedral clusters, denoted as T*n* (*n* is the number of metal layers).[2c] Other frameworks are based on different units that range from simple tetrahedra to so-called penta-supertetrahedral clusters denoted as P*n*.[1a,2a,2b] Recently the family of compounds featuring $A_{10}[M_4M'_4S_{17}]$ (A = K, Cs; M = Zn, Cd, Fe, Co; M′ = Sn, Ge)[4] and $A'[Sn_4M^{II}_4Se_{17}]$ ($A' = [K_{10}(H_2O)_{16}(CH_3OH)_{0.5}]$, $[K_{22}(H_2O)_7(CH_3OH)_{18}](SnSe_4)_3$; $[K_{36}Cl(H_2O)_{11}(CH_3OH)_{32}]$; $[K_6(H_2O)_3]$; M^{II} = Co, Zn, Mn, Cd, Hg)[5,6b] was shown to have discrete supertetrahedral clusters that belong to the penta-supertetrahedral series P*n*.[1a,2a,2b] This cluster type is an assembly of four $\{MQ_4\}$ (T1) and one $\{QM_4\}$ (anti-T1) structural units, in which M is the metal ion and Q is the chalcogen atom (see Figure 1a). The $[M_4M'_4S_{17}]^{10-}$ clusters have four terminal S atoms, which are potential binding sites to other clusters or metal centers, and can thus serve as building blocks for framework materials. However, to date no pertinent reports regarding such systems have appeared even though frameworks consisting of the partially destroyed P1 selenido clusters $[Cd_4Sn_3Se_{13}]^{6-}$ and $[Hg_4Sn_3Se_{13}]^{6-}$ were recently reported.[6]

Herein we describe $A_{5-x}K_{1+x}Sn[Zn_4Sn_4S_{17}]$($A = K^+$, Rb^+, Cs^+; $x = 0,4,5$), the first examples of compounds consisting of intact $[Zn_4Sn_4S_{17}]^{10-}$ clusters linked with Sn^{4+} centers. They feature a new type of open framework and have excellent chemical stability. Furthermore, we report the surprising finding that one-fifth of the K^+ ions play an important templating role in stabilizing the framework. The A^+ ions fill relatively large voids and exhibit remarkably facile ion-exchange properties similar to those of small-pore zeolites.

The synthesis of $K_6Sn[Zn_4Sn_4S_{17}]$[7] (**1**) was carried out by using the alkali polychalcogenide flux method,[8] with a K_2S/S ratio of 1:8–1:10 (that is, in a flux of relatively low basicity). For reasons that will become apparent below, we also succeeded in isolating the isostructural $CsK_5Sn[Zn_4Sn_4S_{17}]$ (**2**) and $RbK_5Sn[Zn_4Sn_4S_{17}]$ (**3**).[9]

Compound **1** crystallizes in the tetragonal acentric $I\bar{4}m2$ space group.[10] The noncentrosymmetric character of **1** is apparent when one looks at the (010) projection of the unit cell (Figure 1b). The critical building unit of **1** is the $[Zn_4Sn_4S_{17}]^{10-}$ cluster, which features a central tetrahedral $\{Zn_4S\}^{6+}$ core capped with four tridentate $\{SnS_4\}^{4-}$ fragments (see Figure 1a). To form the 3D framework, the cluster uses all four terminal S atoms to coordinate to four linking Sn atoms (Sn1), which in turn bind to four clusters (Figure 1c). This creates a full diamondlike framework with a zinc-blende (ZnS) topology (Figure 1d). Fourfold inversion rotation axes (−4) pass through the Sn1 atoms and the intracluster S1 atoms of the structure (Figure 1c).

The connection of tetrahedral chalcogenide clusters with metal linkers is a rational way to build open-framework compounds, yet it is still a relatively uncommon structural feature among the known crystalline examples. Generally in the latter compounds, the clusters tend to link by sharing terminal chalcogen atoms (μ_2-S or μ_2-Se). An exception to this is the $(Me_4N)_2[MGe_4Q_{10}]$ (M = Mn, Fe, Co, Zn, Cd) and

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[**] Financial support from the National Science Foundation (DMR-0443785 and CHE-0211029 Chemistry Research Group) is gratefully acknowledged.

DOI: 10.1002/ange.200500214

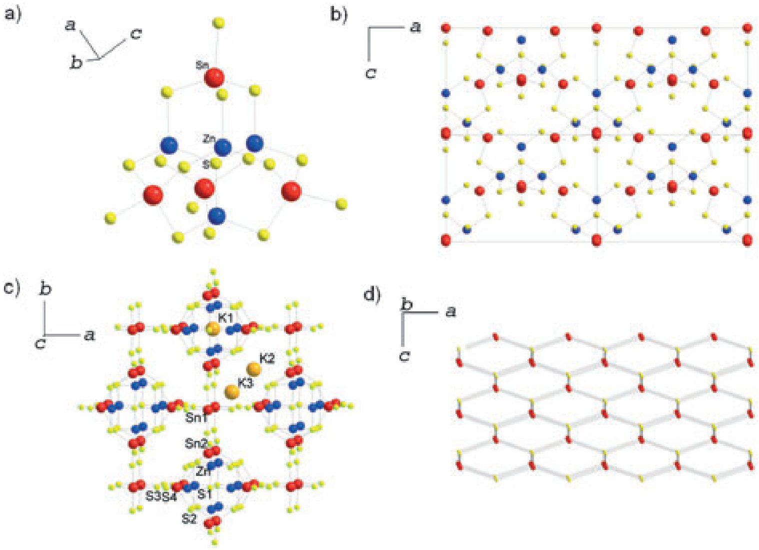

Figure 1. a) The $[Zn_4Sn_4S_{17}]^{10-}$ P1 cluster. b) A [010] projection showing the absence of a center of symmetry in the structure of compound **1**. Yellow, red, and blue balls represent S, Sn, and Zn atoms, respectively. K ions were removed for clarity. c) The $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ framework viewed down the *c* axis. For clarity, K3 is shown in only one of the several subsites that are partially occupied by this ion. Selected distances [Å] and angles [°]: Sn1-S3 2.397(2), Sn2-S4 2.342, Sn-S2 2.3497(16), Sn2-S3 2.428(2), Zn-S1 2.3287(9), Zn-S2 2.3369(15), Zn-S4 2.353(2), K1-S2 3.4460(16), K2-S4 3.3637(15), K2-S2 3.145(2), K3-S3 3.791(3), K3-S4 3.253(5), Sn(1)-S(2)-Sn(2) 104.42(9). d) Skeletal version of the structure of $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ depicting the topological relationship to diamond. The yellow balls are $[Zn_4Sn_4S_{17}]^{10-}$ clusters, and red balls are linking Sn atoms (Sn1).

$A_n[MGe_4Se_{10}]\cdot m\,H_2O$ ($A = Rb$, Cs; $M = Ag$: $n = 3$, $m = 2$; $M = Mn$: $n = 2$, $m = 3$) families, which feature adamantane clusters linked by tetrahedral M^{2+} centers.[11,12]

The most prominent aspect of the framework we describe here is the nature of the open space available in it. There are two types of large cavities: one that accommodates the K2 atoms and one that accommodates the K3 atoms. The K3 cavity is larger and both are indicated in Figure 2a, b. Out of the six K atoms in the formula, one atom is accommodated in site K1, one atom is in site K3, and four atoms are in site K2. K1 is in a tight eight-coordinate square-prismatic environment of S atoms. The K1–S2 bond length is 3.446(2) Å. Atoms K1, K2, and K3 occupy different environments in the tunnel network. K3 is in the largest cavity with a diameter of ≈9.7 Å and K2 is in the next largest cavity with a diameter of ≈6 Å. The atoms in the K3 site were modeled with several split subsites over the cavity.[14]

We can obtain a better understanding of the empty space in the $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ framework if we plot the isosurface[13] that lies between the framework atoms and the voids (see Figure 2c, d). From this perspective, the relative size, shape, and interconnection of the cavities are revealed. It is apparent from these plots that the tunnel network in the structure is three-dimensional with a diamondlike topology similar to the topology of the filled space. Each cavity is not spherical but square and "pancake" in shape with the short dimension being parallel to the tetragonal *c* axis, Figure 2c, d. The two types of cavities (K2 and K3) communicate through narrow passages that are only ≈2 Å wide. This feature accounts for the observed selectivity in the ion-exchange properties observed for this framework (see below).

The K1 site seems to be an exact fit for this framework (see Figure 2c), and the role of this atom seems pivotal to the stability of the structure. This aspect was suggested by the results of experiments aimed at preparing analogues with larger alkali atoms such as $Rb_6Sn[Zn_4Sn_4S_{17}]$ and $Cs_6Sn[Zn_4Sn_4S_{17}]$; the experiments did not succeed. This lack of success implied that a K atom might be needed to occupy a K1 site to stabilize the framework. Conversely, the large cavities of K2 and K3 suggested that the K^+ ions are potentially very mobile and that it might be possible to replace them with larger Rb^+ or Cs^+ ions. Indeed compounds **2**, **3**, $Rb_5KSn[Zn_4Sn_4S_{17}]$ (**4**), and $(A_{5-x}K_x)KSn[Zn_4Sn_4S_{17}]$ ($A = Rb$, Cs) are all possible and can be prepared by high-temperature solid-state synthesis as well as topotactic ion-exchange reactions at room temperature.

A refinement of the crystal structures of **2** and **3** showed unequivocally that the K1 and K2 sites are occupied exclusively by K atoms. The largest site of K3 is occupied exclusively by Rb^+ and Cs^+ cations. However, refinement of the structure of the ion-exchanged material **4** showed that only K1

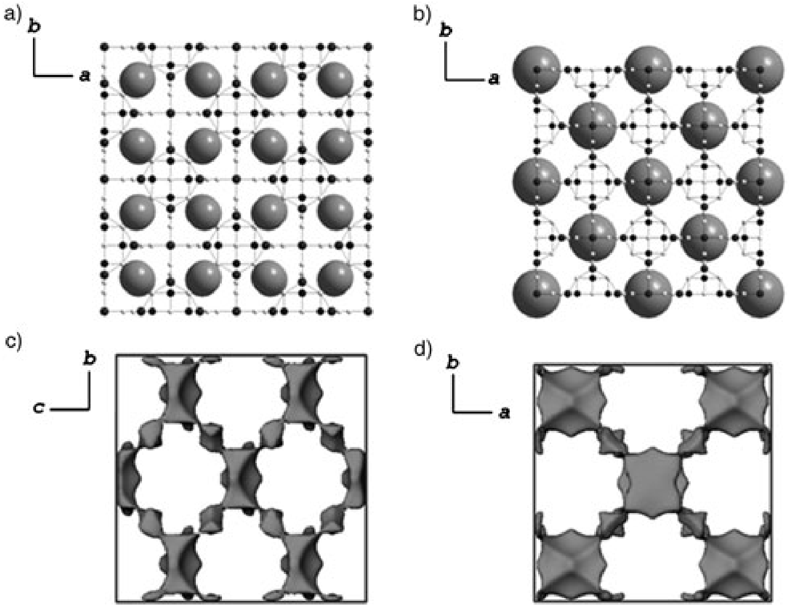

Figure 2. a) A [010] projection of the structure of **1** with the K2 sites represented by oversized spheres to show the available space around them. The diameter of the cavity hosting K2 is ≈6.0 Å. b) The same projection with the K3 sites now shown as oversized spheres. The diameter of the cavity hosting the K3 atoms is ≈9 Å. c) Depiction of the void space in $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ viewed down the [100] direction of the isosurface representing the atom-free space in $\{KSn[Zn_4Sn_4S_{17}]\}^{5-}$ (2 Å from the van der Waals radius). d) The isosurface viewed down the [001] direction. The cavities containing the K3 atoms are square shaped "pancakes", whereas the cavities hosting the K2 atoms serve as connecting channels between the pancake-shaped cavities.

remains intact after ion-exchange (see below). Furthermore, analogues of **1** with larger metal ions, such as Hg^{2+} and Cd^{2+}, or with selenium analogues could not be isolated, possibly because they create larger K1 cavities thereby destabilizing the structure.[15] Because of these results, we are tempted to view the K1 site as a major reason for the stability of this structure type and likely to play the role of template. In this context and because it does not seem to be exchangeable, K1 must be considered as part of the framework whereas K2 and K3 are extraframework ions.

Since the extraframework K^+ ions are loosely bound, they are readily exchanged for other types of ions in solution. Complete ion exchange was achieved in a single-step reaction by stirring compound **1** in water for a few hours at room temperature with excess RbI and CsI.[16] The powder X-ray diffraction (XRD) patterns of compound **1** and those of the ion-exchanged material **4** are almost identical with the exception of a small shift of the diffraction peaks to lower 2θ angles (as expected) in the pattern of compound **4** (see Figure 3 a, b). Energy-dispersive spectroscopy (EDS) analysis of the exchanged material was consistent with the formula of $Rb_5KSn_5Zn_4S_{17}$.

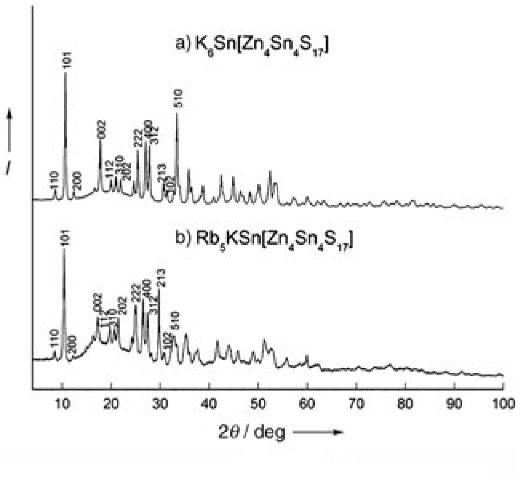

Figure 3. XRD ($Cu_{K\alpha}$ radiation) diagrams (with indexing of selected reflections) of: a) pristine $K_6Sn[Zn_4Sn_4S_{17}]$ and b) ion-exchanged $Rb_5KSn[Zn_4Sn_4S_{17}]$. c) SEM images of a single crystal of pristine $K_6Sn[Zn_4Sn_4S_{17}]$. d) A single crystal of ion-exchanged $Rb_5KSn[Zn_4Sn_4S_{17}]$.

Even whole single crystals of compound **1** can be ion-exchanged to give compound **4**,[17] which could be characterized by single-crystal X-ray diffraction. Figure 3 c,d depicts typical well-formed crystals of pristine and ion-exchanged material. Crystallographic analysis on such a single crystal confirmed the replacement of only five of the K atoms (K2 and K3 from the large cavities),[18] whereas the K1 site remained totally unaffected. Again this result is consistent with the view that K1 may be necessary to form the $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ framework.

The pale-yellow compound **1** and the analogues **2** and **3** show an optical energy gap of ≈ 2.87 eV, which indicates that they are semiconductors with wide band gaps. They also have high optical transparency to electromagnetic radiation, which begins from 2.87 eV and extends down to 0.30 eV as determined from combined IR–near-IR–UV/Vis spectroscopy. The high transparency and the noncentrosymmetric lattice of **1** prompted us to check for possible nonlinear optical (NLO) behavior. We note that the crystal structures of compounds **1**–**4** have the same topology and belong to the same point group $-42m$ as that of $AgGaS_2$. The latter has attained special interest for middle- and deep-IR applications due to its large NLO coefficients and high transmission in the IR region.[19] By using a pulsed Nd-YAG laser on polycrystalline samples of **1**, we observed the presence of a second harmonic generation (SHG) signal. More quantitative experiments are needed, however, to fully assess the NLO behavior of **1**–**4** materials.

In conclusion, $\{Sn[Zn_4Sn_4S_{17}]\}^{6-}$ is the first extended framework based on supertetrahedral $[M_4M'_4S_{17}]^{10-}$ clusters (P1) linked through metal ions. The compound is an ion-exchange material with properties reminiscent of those of small-pore zeolites. We are currently investigating the ion-exchange properties in more detail and the possibility of synthesizing mesostructured open frameworks by using discrete soluble P1 chalcogenide clusters and various metal linkers.[20]

Received: January 19, 2005
Published online: May 11, 2005

Keywords: cluster compounds · ion exchange · nonlinear optics · semiconductors · zeolites

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[7] $K_6Sn[Zn_4Sn_4S_{17}]$ (**1**): A mixture of Sn (0.5 mmol), Zn (0.4 mmol), K_2S (1 mmol), and S (8 mmol) was sealed under vacuum ($\approx 10^{-4}$ torr) in a 9-mm silica tube, heated ($\approx 40\,°C\,h^{-1}$) to 400 °C for 96 h, and then cooled to 25 °C at a rate of $6\,°C\,h^{-1}$. The excess flux was removed with *N*,*N*-dimethylformamide (DMF) to reveal a mixture of pale yellow polyhedral crystals of **1** and orange crystals of $K_2Sn_2S_5$. In some preparations, the product contained a small quantity of S_8, which could be removed by washing with CS_2. Treating the mixture of **1** and $K_2Sn_2S_5$ with aqueous K_2CO_3 (pH 9–10) completely dissolved the ternary phase, and pure compound **1** was obtained (yield ≈30–60%). EDS analysis on several crystals of **1** gave an average composition of $K_{5.6}Sn_{5.2}Zn_4S_{17.2}$.

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[9] $K_5CsSn[Zn_4Sn_4S_{17}]$ (**2**) and $K_5RbSn[Zn_4Sn_4S_{17}]$ (**3**): A mixture of Sn (0.5 mmol), Zn (0.4 mmol), K_2S (0.9 mmol), Cs_2S or Rb_2S (0.1 mmol), and S (8 mmol) was sealed under vacuum ($\approx 10^{-4}$ torr) in a 9-mm silica tube, heated ($\approx 40\,°C\,h^{-1}$) to 400 °C for 96 h, and then cooled to room temperature at a rate of $6\,°C\,h^{-1}$. The excess flux was removed with DMF to reveal a mixture of pale yellow polyhedral crystals of **2** or **3** (yield 30–50% based on Sn) and orange crystals of $K_2Sn_2S_5$. The ternary phase was removed by washing with K_2CO_3. EDS analysis on several crystals of **2** and **3** gave compositions of $K_{5.1}CsSn_{5.1}Zn_{4.6}S_{17.6}$ and $K_{4.6}RbSn_5Zn_{4.7}S_{16.8}$, respectively.

[10] Crystal data: $K_6Sn_5Zn_4S_{17}$, space group $I\bar{4}m2$ (No. 119), $a = 13.7425(7)$, $c = 9.7272(5)$ Å, $V = 1837.04(16)$, $Z = 2$, $R1(F) = 0.0452$, $wR2(F^2) = 0.0878$; $K_5CsSn_5Zn_4S_{17}$, space group $I\bar{4}m2$, $a = 13.7684(11)$, $c = 9.5630(9)$ Å, $V = 1812.8(5)$, $Z = 2$, $R1(F) = 0.0669$, $wR2(F^2) = 0.1277$; $K_5RbSn_5Zn_4S_{17}$, space group $I\bar{4}m2$, $a = 13.7687(10)$, $c = 9.7767(6)$ Å, $V = 1853.4(2)$, $Z = 2$, $R1(F) = 0.0553$, $wR2(F^2) = 0.0762$. Further details on the investigation of the crystal structure may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD-415015, CSD-415016, and CSD-415018 (for the compounds $K_6Sn_5Zn_4S_{17}$, $K_5CsSn_5Zn_4S_{17}$, and $K_5RbSn_5Zn_4S_{17}$, respectively).

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[14] The split-occupancy sites and possible rattling of these ions inside the cages explains the much higher thermal-displacement parameters of K3 and K2 relative to that of K1.

[15] Reactions aiming to form $K_6Sn[M_4Sn_4S_{17}]$ analogues ($M = Hg^{2+}$, Cd^{2+}, Co^{2+}, Fe^{2+}) or the Se analogue of **1** led to other quaternary and ternary phases. However, compounds with Sn atoms partially replaced by Ge, or Zn atoms partially replaced by other divalent atoms (such as Hg^{2+} or Cd^{2+}) have been isolated, and these results will be published elsewhere. Efforts to prepare $K_6Ge[Zn_4Ge_4S_{17}]$ resulted instead in $K_{10}Zn_4Ge_4S_{17}$.[4]

[16] Interestingly, the material exhibits selectivity against Li and Na ions. In water these have a strongly held hydration sphere that prevents the large hydrated ions from entering the structure. Preliminary ion-exchange experiments of compound **1** with CsCl at room temperature showed that only one K^+ ion can be exchanged by one Cs^+ ion. Crystallographic analysis of the exchanged material showed that only the K3 ions were exchanged with Cs ions.

[17] A typical ion-exchange experimental route for the preparation of compound **4** is as follows: An excess of solid RbI (0.2 mmol) was added to a suspension of compound **1** (0.01 mmol) in water (20 mL). The mixture was stirred for ≈12 h. Then, the yellowish-white crystalline material was isolated by filtration, washed several times with water, acetone, and ether (in this order), and dried in air.

[18] $Rb_5KSn_5Zn_4S_{17}$ (ion-exchanged), space group $I\bar{4}m2$, $a = 13.8354(10)$, $c = 9.8893(9)$ Å, $V = 1893.0(3)$, $Z = 2$, $R1(F) = 0.0793$, $wR2(F^2) = 0.1519$. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-415017.

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