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Unique Pore Selectivity for Cs^+ and Exceptionally High NH_4^+ Exchange Capacity of the Chalcogenide Material $K_6Sn[Zn_4Sn_4S_{17}]$

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Abstract: Highly selective ion-exchange properties and -exchange capacities of the open framework chalcogenide material $K_6Sn[Zn_4Sn_4S_{17}]$ (**1**) with Cs^+ and NH_4^+ are reported. Because the structure of this framework is known in great detail, these studies are a rare example where structure/property relationships can be directly drawn. **1** possesses three types of micropore cavities. The largest pore of **1** presents an exact fit for Cs^+ and exhibits high selectivity for this ion, as demonstrated by competitive ion-exchange experiments. The next largest pore has a greater capacity (up to four cations) and is well suited for NH_4^+ ions. This leads to a high ammonium-exchange capacity for **1** of 3.06 mequiv/gr, which is close to the NH_4^+-exchange capacities of natural zeolites. The single-crystal structures of ammonium-exchanged products at various stages reveal an unusual mechanism for the exchange process of **1** which involves diffusion of ammonium cations from the large cavity to the small ones of the framework. Thermal analysis of one of these ammonium-exchanged products, in combination with mass spectroscopy, showed the decomposition of NH_4^+ cations to NH_3 and H_2S with the parallel transformation of the exchanged product to a mixture of crystalline phases. Since $K_6Sn[Zn_4Sn_4S_{17}]$ can be grown in suitably large crystals (much larger than most zeolites), it defines an excellent model system in which ion-exchange processes and products can be characterized and studied in detail in various reaction stages.

Introduction

Open framework compounds are of broad scientific interest because of their high impact in catalysis, separations, ion exchange, and green chemistry.[1] Aluminosilicate zeolites are representative examples of such materials that have been studied extensively during the past decades. The huge diversity in structure and pore size of zeolites is not yet reflected in chalcogenide compounds.[1,2] Because of the wider chemical and bonding flexibility, however, the chalcogenides can be more diverse in composition and structure than the zeolites. Indeed, research on chalcogenides in the past decade resulted in isolation of several remarkable open framework compounds with unique structural types.[3−6] Chalcogenides with anionic open frameworks and loosely bound extra framework cations could thus constitute a new class of inorganic ion exchangers with unique exchange properties arising not only from their diversity in pore and channel size but also from the specific affinity of the non-oxidic framework for certain cationic species. In addition, crystalline open framework chalcogenides can offer themselves as suitable models for understanding the mechanism of various ion-exchange processes on the basis of their structure, which is accurately determined (in most cases) by single-crystal X-ray crystallography. Consequently, their ion-exchange properties can

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be better understood and optimized on the basis of the knowledge of the details of the ion-exchange process.

Reports concerning the ion-exchange properties of open framework chalcogenides remain a few.[3f,7] We recently described the open framework sulfide $K_6Sn[Zn_4Sn_4S_{17}]$ (**1**).[7a] **1** consists of penta-supertetrahedral clusters $[Zn_4Sn_4S_{17}]^{10-}$ linked via tetrahedrally coordinated Sn atoms, thus creating a three-dimensional framework, Figure 1a,b. The structure of **1** contains a relatively large cavity (denoted as **K3**, because it is occupied by the K3 atom) with a diameter of ~4.1 Å[8a,b] which communicates through narrow passages (~1−1.5 Å)[8c] with the smaller cavities (denoted as **K1** and **K2**) having a diameter of 2.8−3.2 Å. The structure of **1** is an excellent case of a crystalline open framework material because it possesses three different sized cavities, more than any other open framework material, and each cavity with its own chemical reactivity. The distribution of the six K^+ ions in the three types of cavities can be described as $[K]^{K1}[K]_4^{K2}[K]^{K3}\{Sn[Zn_4Sn_4S_{17}]\}$. In this formalism the K1 cavity contains one K^+ ion, the **K2** cavity contains four K^+ ions and the **K3** cavity contains one K^+ ion. In the structure of $K_5CsSn[Zn_4Sn_4S_{17}]$ (**2a**), prepared with flux synthesis, the Cs atom is located only in the **K3** cavity of the structure (i.e., $[K]^{K1}[K]_4^{K2}[Cs]\{Sn[Zn_4Sn_4S_{17}]\}$) and is not positionally disordered, (Figure 1c) in contrast with the K3 atoms in the structure of **1**. This suggested to us that the Cs^+ ion is likely an exact fit for this cavity, and thus, **1** is possibly highly selective for it. This would be of interest for applications such as the removal and storage of ^{137}Cs from nuclear waste solutions.[9] To check our hypothesis, we decided to perform Cs^+ ion-exchange experiments as well as competitive experiments with the simultaneous presence of other monovalent cations. In addition, we performed comparative studies for the NH_4^+ ion-exchange capacity of **1**. Our motivation to perform ammonium-exchange experiments of **1** was the expectation of strong electrostatic and hydrogen-bonding framework interactions with this ion, coupled with the possible environmental applications of such processes, e.g. the removal of NH_4^+ from the wastewater.[10,11]

Herein we describe a remarkable Cs^+ selectivity of **1** originating from the particular size and shape of its cavities. The selectivity for Cs^+ persists even in the presence of large excess of Li, Na^+, K^+, Rb^+, and it is associated with the **K3** cavity. We also show that **1** exhibits an exceptional ion-exchange capacity for NH_4^+ (in the absence of Cs^+). This high capacity is associated with the activity of the **K2** cavity which accommodates up to four NH_4^+ ions. Through isolation and characterization of different intermediate ammonium-exchanged products, an unusual NH_4^+-exchange mechanism was revealed. The affinity of the framework of **1** for NH_4^+ was found to be higher than that for any other monovalent cation. The ammonium-exchange capacity of **1** is well comparable with that of natural zeolites,[10] extensively used for environmental applications.[11a]

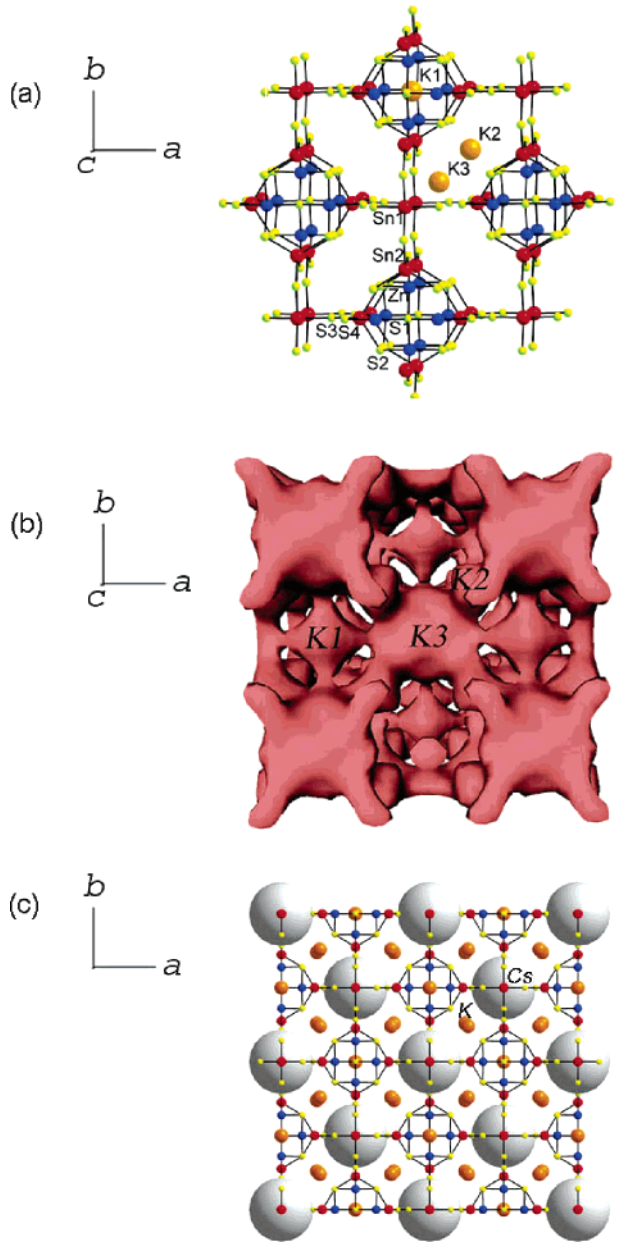

Figure 1. (a) The $\{Sn[Zn_4Sn_4S_{17}]^{6-}\}$ framework of **1** viewed down the *c*-axis. For clarity, **K2** and **K3** are shown in only one of the sub-sites. (b) Plot of the void space of **1** with labeling of the three types of cavities according to the potassium atoms located on each cavity. The diameter of the channel connecting the **K1** and **K3** cavities is ~1.00 Å and that connecting the **K2** and **K3** cavities is ~1.5 Å. (c) The structure of **2a** with the Cs atoms represented by oversized spheres to show the available space around them. The exchange product **2b** has an almost identical framework with that of **2a**, but the Cs cavity of **2b** is slightly larger than that of **2a**, which causes a positional disorder of Cs atoms in **2b**.

Experimental Section

Materials. Sn was purchased from CERAC Inc., 325 mesh, 99.8%. Zn was purchased from Johnson Matthey/AESAR, −325 mesh,

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>99.5%. Sublimed sulfur was purchased from J. T. Baker Chemical Co., >99.5%. Potassium metal, NH_4I, CsCl, and RbI were purchased from Aldrich Chemical Co. The preparation of K_2S is described in ref 12. The synthesis of **1** was accomplished with a polysulfide flux reaction.[7a]

Cs^+ Ion-Exchange Experiment with Polycrystalline Powder. In a suspension of **1** (0.012 mmol, 20 mg) in water (10 mL), excess of CsCl (0.36 mmol, 61 mg) was added as a solid. The mixture was kept under magnetic stirring at room temperature for ~12 h. Then, the yellowish-white crystalline material was isolated by filtration, washed several times with water, acetone, and ether. Energy dispersive spectroscopy (EDS) analysis on the exchanged material **3** gave an average formula "$Cs_{1.2}K_{4.4}Zn_{4.8}Sn_5S_{17}$".

Cs^+ Ion-Exchange Experiment with Single Crystals of 1 at 70 °C. Single crystals of **1** were placed in a water solution of CsCl (0.39 mmol, 65 mg). Then, the mixture was heated at 70 °C and kept undisturbed at this temperature for 2 weeks. The crystals were then isolated by filtration, washed several times with water, acetone, and ether. EDS analysis on several of them revealed the average formula "$K_{4.5}Cs_{1.3}Zn_{4.5}Sn_{5.2}S_{17}$". Single-crystal analysis showed that the exchanged crystals were $K_5CsZn_4Sn_5S_{17}$ (**2b**).

Cs^+ Ion-Exchange Experiment in the Presence of Large Excess of RbI. In a suspension of compound **1** (0.047 mmol, 77 mg) in water (20 mL), CsCl (0.047 mmol, 7.8 mg), and RbI (0.47 mmol, 100 mg) were added as solids. The mixture was kept under magnetic stirring for ~12 h. Then, the yellowish-white crystalline material was isolated by filtration and washed several times with water, acetone, and ether. EDS analyses on the exchanged solid **4** gave the average formula "$K_{1.8}Rb_{3.1}Cs_{0.5}Zn_{4.0}Sn_{4.8}S_{17}$".

NH_4^+ ion-Exchange Experiment with Polycrystalline Powder or Single Crystals of 1 at Room Temperature. The NH_4^+ ion-exchange experimental routes are identical to the Cs^+ ones described above, except that NH_4I was used instead of CsCl. A 12 h reaction of NH_4I with polycrystalline powder of **1** yielded an exchanged product with the formula $K_2(NH_4)_4Zn_4Sn_5S_{17}\cdot 3H_2O$ (**5**) based on N, H (Calculated: H, 1.38%; N, 3.49%. Found: H, 1.33%; N, 3.57%) and TGA analyses (see below). EDS analysis on the exchanged solid gave the formula "$K_{1.4}Zn_{4.8}Sn_{5.1}S_{17}$". The same reaction with single crystals of **1** gave an exchanged product with the formula $K_5(NH_4)Zn_4Sn_5S_{17}$ (**6**), as determined by single-crystal X-ray analysis. EDS analysis on several crystals of the exchanged material gave the formula "$K_{4.5}Zn_{4.5}Sn_{5.2}S_{16.8}$". The same reaction of NH_4I with single crystals of **1** allowed to run for 48 h gave $K_{4.6}(NH_4)_{1.4}Zn_4Sn_5S_{17}$ (**7**), according to single-crystal X-ray analysis. EDS analysis on several crystals of the exchanged material gave the formula "$K_{4.7}$ $Zn_{4.5}Sn_{5.2}S_{16.9}$".

NH_4^+ Ion-Exchange with Single Crystals of 1 at 70 °C. Single crystals of **1** were placed in a water solution (10 mL) of NH_4I (0.24 mmol, 35 mg). The mixture was then heated at 70 °C and left undisturbed at this temperature for 1 week. The crystals were then isolated by filtration, washed several times with water, acetone, and ether. EDS on several of them revealed the average formula "$K_{0.6}Zn_{4.5}Sn_{5.2}S_{17}$". Single-crystal X-ray refinement indicated the exchanged crystals correspond to $K(NH_4)_5Zn_4Sn_5S_{17}$ (**8**) (see below).

Competitive Ion-Exchange Experiment of 1 with Equimolar Quantities of CsCl, RbI, and NH_4I. Single crystals of **1** were placed in 15 mL of water, and then, 0.24 mmol each of CsCl, RbI, and NH_4I were added to the suspension of **1**. The mixture was heated at 70 °C for a week without stirring. EDS analysis on several crystals of the final product was consistent with a formula of "$K_{0.4}Rb_2CsZn_4Sn_5S_{17}$". Single-crystal X-ray diffraction analysis revealed the formula $KCsRb_{1.29}(NH_4)_{2.71}Zn_4Sn_5S_{17}$ (**9**) for the exchanged product (see below).

Powder X-ray Diffraction (PXRD). The samples were examined by X-ray powder diffraction for identification and to assess phase purity. Powder patterns were obtained using a CPS 120 INEL X-ray powder diffractometer with Ni-filtered Cu Kα radiation operating at 40 kV and 20 mA and equipped with a position-sensitive detector. Samples were ground and spread on a glass slide. The purity of phases was confirmed by comparison of the X-ray powder diffraction patterns to ones calculated from single-crystal data using the NIST Visualize 1.0.1.2 software.

EDS Analyses. The analyses were performed using a JEOL JSM-6400V scanning electron microscope (SEM) equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. Data acquisition was performed with an accelerating voltage of 25 kV and 40 s accumulation time.

IR Spectroscopy. Infrared spectra (IR) in the mid-IR region [4000−600 cm^{-1}, diffuse reflectance infrared Fourier transform (DRIFT) method] were recorded with a computer-controlled Nicolet 750 Magna-IR series II spectrometer equipped with a TGS/PE detector and silicon beam splitter in 2-cm^{-1} resolution.

H, N Analyses and Mass Spectroscopy. Elemental H, N analyses were obtained on a Perkin-Elmer Series II CHNS/O analyzer 2400. Pyrolysis mass spectra were obtained with a TRIO-1 mass spectrometer. Samples were heated at 20 °C/min, and the volatile products were ionized by electron ionization.

Thermal Analysis. A Shimatzu DSC 50, differential scanning calorimeter (DSC), calibrated with indium, tin, and zinc standards, was used. Samples of about 10 mg were used for each test, placed in an aluminum crucible, and were heated from ambient temperature to 500 °C in a 20 mL/min flow of N_2.

Thermogravimetric analysis (TGA) was carried out with a Shimatzu TGA 50. Samples (10 ± 0.5 mg) were placed in quartz crucible. Samples were heated from ambient temperature to 500 °C in a 20 mL/min flow of N_2. Heating rate of 10 °C/min was used, and continuous records of sample temperature, sample weight, and its first derivative (DTG) were taken.

Single-Crystal X-ray Crystallography. A Siemens SMART Platform CCD diffractometer, operating at room temperature and using graphite-monochromatized Mo Kα radiation, was used for data collection. Cell refinement and data reduction were carried out with the program SAINT.[13] An empirical absorption correction was performed on the data using SADABS.[14] The structures were solved with direct methods using SHELXS, and least-squares refinement was done against F^2 using routines from the SHELXTL software.[15] The protons of the NH_4^+ ion could not be located in the structures of the exchanged materials, with the exception of the structure of **4**, for which the hydrogen atoms were located in a difference Fourier map and refined isotropically. Selected crystal data for the structures of **2b**, **4**−**7** are given in Table 1. Further details of the crystal structure investigations may be obtained by the crystallographic information files (CIF) of **2b**, **4**−**7** (see Supporting Information).

Results and Discussion

The goals of this study were to understand the ion-exchange properties of $K_6Sn[Zn_4Sn_4S_{17}]$ which presents a stable open framework motif similar to those of small pore zeolites, and to explore those chemo- and cavity-specific responses to a variety of mono-valent ions that distinguish this material from the zeolites. This section first presents ion-exchange synthetic routes to the variously exchanged materials (i.e. Cs^+, Rb^+, NH_4^+, etc.) and a variety of competitive experiments. The occupation of the various cavities in the framework is discussed on the basis

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(13) Siemens Analytical X-ray Instruments Inc., 1995.

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(15) The Cs^+ ion of the ion-exchange product **2b** is disordered in the cavity. Interestingly, when $K_5CsSn[Zn_4Sn_4S_{17}]$ is prepared by direct solid-state synthesis, the Cs^+ ion is found ordered in the structure. This may be explained by taking into account the slightly larger size of the cavity hosting the Cs^+ ion in **2b** [9.690(3) × 6.046(1) $Å^2$] compared to the corresponding [9.563(1) × 5.975(6) $Å^2$] cavity in **2a**.

Table 1. Selected Data for the Ion-Exchanged Compounds Reported in This Work

cmpd	cell parameters[a] and *R* values	type of synthesis (reaction temperature)	chemicals used for ion-exchange/ reaction time
$K_6Sn[Zn_4Sn_4S_{17}]$[b] (**1**)	a = 13.7425(7) Å, c = 9.7272(5) Å, V = 1837.04(16), R1(F) = 0.0452, wR2(F^2) = 0.0878	solid-state reaction (400 °C)	–
$K_5CsSn[Zn_4Sn_4S_{17}]$[b] (**2a**)	a = 13.7684(11) Å, c = 9.5630(9) Å, V = 1812.8(5), R1(F) = 0.0669, wR2(F^2) = 0.1277	solid-state reaction (400 °C)	–
$K_5CsSn[Zn_4Sn_4S_{17}]$ (**2b**)	a = 13.843(2) Å, c = 9.690(3) Å, V = 1856.8(7), R1(F) = 0.0682, wR2(F^2) = 0.1795	ion-exchange reaction of single crystals of **1** (70 °C)	CsCl/ 10 d
$K_{4.36}Cs_{1.2}Zn_{4.8}Sn_5S_{17}$ (**3**)	–	ion-exchange reaction of polycrystalline **1** (25 °C)	CsCl/ 12 h
$K_{1.8}Rb_{3.1}Cs_{0.5}Zn_{4.0}Sn_{4.8}S_{17}$ (**4**)	–	ion-exchange reaction of polycrystalline **1** (25 °C)	CsCl, RbI/ 12 h
$K_2(NH_4)_4Zn_4Sn_5S_{17}\cdot 3H_2O$ (**5**)	–	ion-exchange reaction of polycrystalline **1** (25 °C)	NH_4I/ 12 h
$K_5(NH_4)Zn_4Sn_5S_{17}$ (**6**)	a = 13.8142(9) Å, c = 9.6824(12) Å, V = 1847.7(3), Z = 2, R1(F) = 0.0554, wR2(F^2) = 0.1239	ion-exchange reaction of single crystals of **1** (25 °C)	NH_4I/ 12 h
$K_{4.59}(NH_4)_{1.41}Zn_4Sn_5S_{17}$ (**7**)	a = 13.829(5) Å, c = 9.810(7) Å, V = 1876.0(15), Z = 2, R1(F) = 0.0685, wR2(F^2) = 0.1326	ion-exchange reaction of single crystals of **1** (25 °C)	NH_4I/ 48 h
$K(NH_4)_5Zn_4Sn_5S_{17}$ (**8**)	a = 13.8455(6) Å, c = 10.0731(9) Å, V = 1931.0(2), Z = 2, R1(F) = 0.0243, wR2(F^2) = 0.0786	ion-exchange reaction of single crystals of **1** (70 °C)	NH_4I/ 7 d
$KCsRb_{1.29}(NH_4)_{2.71}Zn_4Sn_5S_{17}$ (**9**)	a = 13.8184(4) Å, c = 10.0456(7) Å, V = 1918.19(16), Z = 2, R1(F) = 0.0468, wR2(F^2) = 0.0825	ion-exchange reaction of single crystals of **1** (70 °C)	NH_4I, CsCl, RbI/ 7 d

[a] All compounds crystallize in the tetragonal space group $\bar{I}4m2$ (no. 119). [b] From ref 7a.

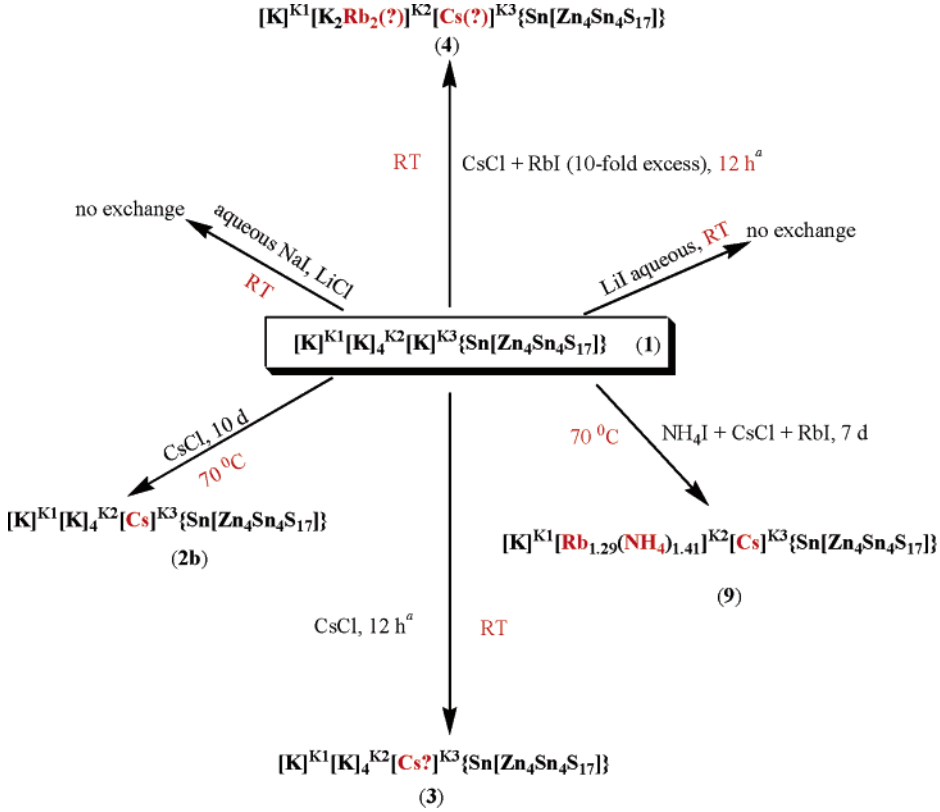
of the X-ray crystal structure of a series of exchanged materials including intermediates. A systematic organization of the ion-exchange chemistry with regard to cage specificity and affinity is then presented. Finally, results of ammonium-exchange chemistry are discussed and compared with previous results using conventional ion-exchange materials, followed by a discussion of plausible ion motional pathways through a flexible chalcogenide framework to explain the unusual experimental observations.

Affinity for Cs^+. The ion-exchange experiments of **1** with Cs^+ in aqueous solution showed that only a single Cs atom per formula unit can be inserted into the framework, specifically in the **K3** cavity (Scheme 1). Unambiguous confirmation for this was obtained from the X-ray analysis of single crystals of $K_5CsZn_4Sn_5S_{17}$ **2b**, which were isolated by a long (10−14 d) ion-exchange reaction of single crystals of **1** with aqueous CsCl solution at 70 °C. Ion-exchange reactions with the use of ground polycrystalline powder of **1** instead of its single crystals resulted in exchanged product with nearly the same composition as **2b**. However, due to the higher external surface area, the reactions with powder samples can be completed much faster (less than 24 h) than those with single crystals. **2b** is isostructural to **1,** proving that the exchange process is topotactic.[15]

The **K3** cavity in the framework is suitably sized for Cs^+ ions, which explains its selectivity for this ion. To demonstrate this assessment we ran further experiments using equimolar mixtures of CsCl/RbI/NH_4I and obtained $KCsRb_{1.29}(NH_4)_{2.71}Zn_4Sn_5S_{17}$ (**9**) (Scheme 1). The refinement of the X-ray structure of **9** showed the exclusive presence of Cs^+ in the largest, **K3** cavity, Figure 2d.[16] The Rb^+ and NH_4^+ ions were placed in the

(16) The Cs atom in **9** is also positionally disordered inside the cavity. As in the case of the structure of **2b**, the fact that the Cs cavity of **9** is larger (10.046 by 6.029 Å^2) than of **2a** (9.563 by 5.975 Å^2) leads to a higher mobility for Cs^+ in **9**, presumably allowing the positional disorder in the cavity.

Scheme 1. Representation of the Alkali (Li, Na, Rb, Cs)-Exchange Reactions of **1** and the Competitive (Cs, Rb, NH_4) Exchange Experiments



[a] Reaction with polycrystalline powder of **1**. All other reactions were with single crystals of **1**. Bracket superscripts **K1**, **K2**, **K3** denote the type of cavity the ion occupies. The question marks refer to the positions of exchange cations that have been assigned tentatively because of lack of structural data. All reactions were in aqueous solution.

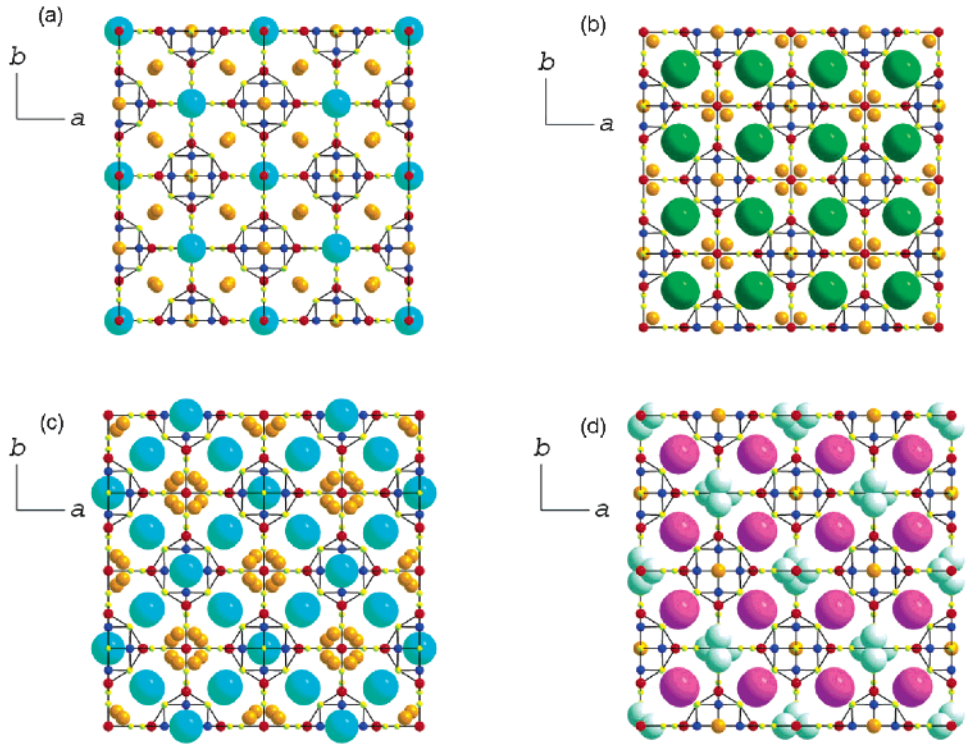


Figure 2. The structures of the exchanged products: (a) $K_5(NH_4)Zn_4Sn_5S_{17}$ (**6**); (b) $K_{4.59}(NH_4)_{1.41}Zn_4Sn_5S_{17}$ (**7**); (c) $K(NH_4)_5Zn_4Sn_5S_{17}$ (**8**); (d) $KCsRb_{1.29}(NH_4)_{2.71}Sn_5Zn_4S_{17}$ (**9**). The incoming cations in each case are depicted as large balls (N, cyan; mixed K/N, green; Cs, gray; mixed Rb/N, purple).

K2 cavity, whereas the **K1** cavity did not exchange its cation. This result indicates that five of the six K^+ ions of **1** (K2 and K3, Figure 1b) exhibit high framework mobility and can be exchanged with Cs^+, Rb^+, and NH_4^+ while simultaneously

sorting the cations according to size, Figure 2d. Only the K1 atom of **1**, which is tightly bound in a square prismatic site, remained in the exchanged material **9**, Figure 2d. The significance of this K atom for the stabilization of the framework has been discussed.[7a]

Additional exchange experiments were performed using equimolar amounts of **1** and CsCl while adding a 10-fold excess of RbI. The exchanged material **4** contained 0.5−1 Cs^+, 3−3.5 Rb^+, and ∼2 K^+ per formula unit, based on EDS analysis. Large excess of Li^+ and Na^+ ions cannot displace Cs^+ as the framework exhibits no preference for these ions at all (see below).[7a] The results show the strong preference of (**1**) to adsorb Cs^+ ions even when is in relatively low concentration in the initial solution and with the simultaneous presence of large excess of other competing cations (Rb^+) which can easily exchange K^+ ions of **1**.[7a] The selectivity of **1** for Cs^+ is therefore remarkable, and this compound could be promising for further environmentally related investigations involving Cs^+ separations. The cavity-dependent ion-exchange behavior and reactivity patterns of **1** based on the $[K]^{K1}[K]_4^{K2}[K]^{K3}\{Sn[Zn_4Sn_4S_{17}]\}$ formalism are summarized in Scheme 1.

Selectivity and Affinity of the $\{Sn(Zn_4Sn_4S_{17}]\}^{6-}$ Framework for Li, Na, K, Cs^+, Rb^+, NH_4^+. Interestingly, the framework exhibits absolutely no selectivity for Li^+ and Na^+ ions because of the large hydration sphere of these ions that prevents them from entering the framework.[7a] The affinity of the framework of **1** for NH_4^+ seems to be higher than that for any other monovalent cation studied here. The competitive ion-exchange experiments with the simultaneous presence of NH_4I, RbI, and CsCl showed that the framework can exchange the 54.2% of its exchangeable K^+ by NH_4^+, while 25.8 and 20% of the exchangeable K^+ are replaced by Rb^+ and Cs^+ respectively. This gave rise to $KCsRb_{1.29}(NH_4)_{2.71}Sn_5Zn_4S_{17}$ (**9**), in which the various cations are selectively distributed in the three cavities according to their size. However, the pore selectivity of the framework revealed by the structure of **9** [Figure 2d**)**] is as follows: **K3** cavity, Cs = 100%; **K2** cavity, Rb = 32.25%, NH_4^+ = 67.75%; **K1** cavity, K = 100%.

NH_4^+ Ion-Exchange Capacity. A series of NH_4^+-exchanged products have been isolated (see Table 1 and Scheme 2). FT-IR spectroscopy in the mid-infrared region showed the presence of characteristic NH_4^+ absorptions at 3136 and 1400 cm^{-1}.[17] However, NH_4^+-exchange reactions with single crystals of **1** stopped at various intermediate stages gave us the opportunity to completely characterize the exchanged materials with X-ray crystallography and obtain key insights into the ion-exchange process.

Specifically, reacting single crystals of **1** with excess of NH_4I for 12 h yielded the exchanged product $K_5(NH_4)Zn_4Sn_5S_{17}$ (**6**) (Figure 2a**)**, with one NH_4^+ replacing the disordered K3 of **1**. A longer reaction (48 h) of single crystals of **1** with excess of NH_4I gave $K_{4.59}(NH_4)_{1.41}Zn_4Sn_5S_{17}$ (**7**) (Figure 2b**)** with 1.4 NH_4^+ ions replacing equivalent amount of K^+ ions of (**1**). Surprisingly, only K atoms from the **K2** cavity of the framework (which is one of the small cavities of the framework) were replaced by NH_4^+, while the largest cavity of the structure (**K3** one) was still occupied only by the highly disordered K3 atom (Figure 2b).

(17) Nakamoto, K. *Infrared and Raman spectra of inorganic and coordination compounds*, 3rd ed.; John Wiley & Sons: New York, 1977; pp 132−146.

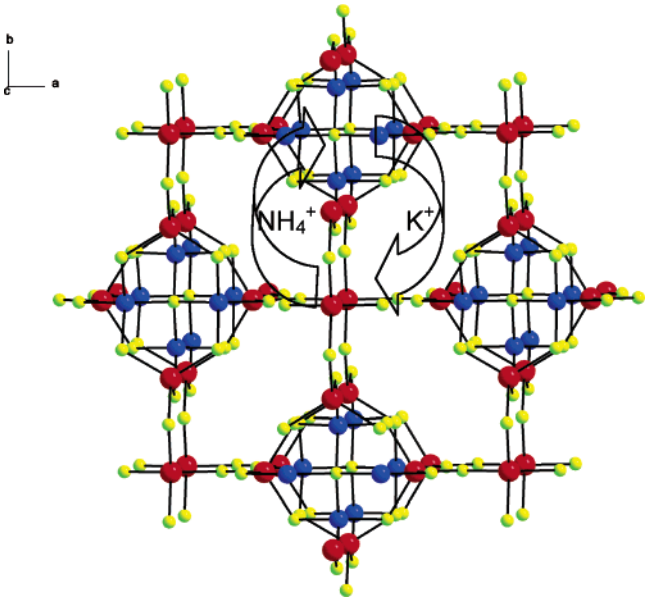


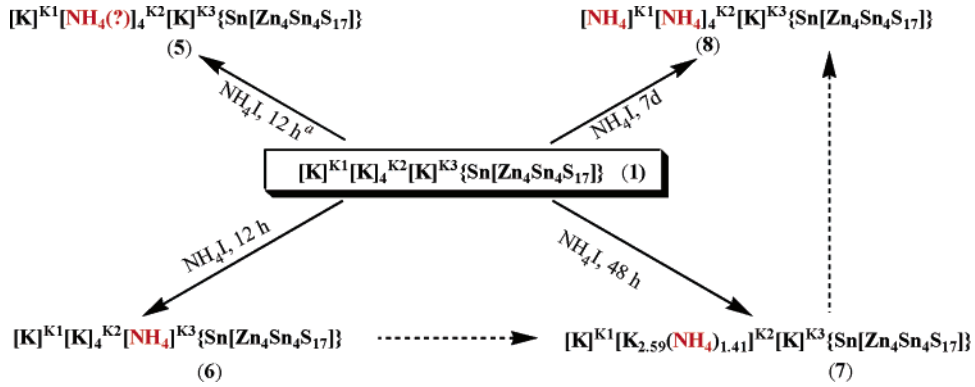
Figure 3. Schematic representation of the possible mechanism of the ammonium-exchange of **1**, employing a diffusion of NH_4^+ from the largest to the small cavities of the framework with the parallel movement of K^+ ions in the opposite direction.

An even more interesting result was obtained by treating single crystals of (**1**) with excess of NH_4I at 70 °C for 1 week. The exchanged material $K(NH_4)_5Zn_4Sn_5S_{17}$ (**8**) (Figure 2c**)** contained five NH_4^+ ions and only one K^+ ion. The refinement of the structure of **8** showed that four NH_4^+ ions were located in the **K2** cavity of the framework. Much to our surprise, the fifth ammonium ion replaced the K1 ion, which as mentioned above is believed to be tightly bound to the framework and tends not to be exchangeable. As in the case of **7**, the **K3** cavity of **8** is occupied by a highly disordered K^+ ion, which is the only one that was not replaced by NH_4^+.

To replace the last K^+ ion of **8** by NH_4^+ occupying the **K3** cavity, crystals of **8** were treated (for 1 week at 70 °C) with excess of NH_4I. X-ray refinement revealed an exchanged product with number and positions of ammonium ions (four NH_4^+ in the **K2** cavity and another one in the **K1** cavity) identical to that of **8**. In another experiment, crystals of **1** were treated with NH_4I for 14 days at 70 °C, to isolate the "$(NH_4)_6Sn[Zn_4Sn_4S_{17}]$" compound containing only NH_4^+ ions. Refinement of crystal structure in this case also showed an exchanged product with number and positions of ammonium ions identical to that of **8**. The inability of the last K^+ ion occupying the **K3** cavity is puzzling, and it may be due to kinetic factors. Alternatively, it is possible that **8** is the thermodynamically stable ammonium-exchanged product (i.e. a $(NH_4)_6Sn[Zn_4Sn_4S_{17}]$ is prone to collapse), while **6** and **7** could be intermediate kinetic phases formed earlier. Scheme 2 summarized the NH_4^+ ion-exchange behavior and reactivity pattern of **1** as a function of experimental conditions.

Another intermediate in the NH_4^+-exchange process is **5** which was isolated from room-temperature ion-exchange reactions using ground polycrystalline powder of **1** with excess of NH_4I for 12 h. **5** has the formula $K_2(NH_4)_4Zn_4Sn_5S_{17}\cdot 3H_2O$, based on % H, % N elemental analysis and thermal analysis measurements (see below). Although there are no single-crystal data for **5** (it was isolated in polycrystalline form), from the above discussion we expect the **K2** cavity of the framework to

Scheme 2. Time-Dependent NH_4^+-Exchange Processes Leading to Compounds **5**−**8**[b]



[a] Reaction with polycrystalline powder of **1**. [b]The cavity site occupation of the NH_4+ ions is indicated in red.

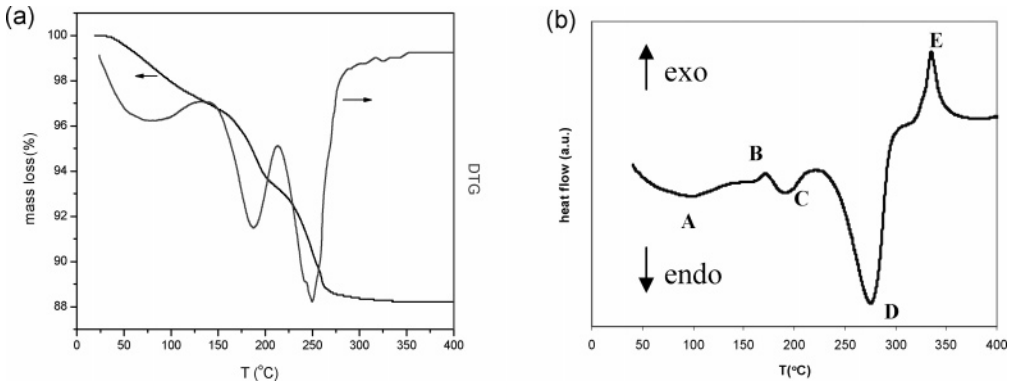


Figure 4. (a) TGA and DTG (first derivative) curves for $K_2(NH_4)_4Zn_4Sn_5S_{17}\cdot 3H_2O$ (**5**). (b) DSC thermogram of the same material. The thermal events are indicated in letters **A**−**E**. The measurements were performed under nitrogen atmosphere and the heating rate used was 10 °C/min.

be the probable location of the 4 NH_4^+ ions in **5**. The high surface area in this case permits the insertion of water into the structure in contrast to the single-crystal studies which did not show the presence of water.

To obtain further confirmation for the formula of **5** and quantitate the amount of water, we studied its thermal behavior in detail by means of the TGA and DSC techniques. Based on the thermogravimetric curve, Figure 4a, the sample starts to lose mass immediately upon heating. Three stages of mass loss can be recognized until the mass remains stable after 350 °C. The DSC thermogram, Figure 4b, showed five characteristic and well-defined thermal events. The first event (**A**) is a broad endothermic peak between 27 and 160 °C. This corresponds to the first stage of mass loss (3.30%) occurring from 27 to 160 °C (Figure 4a**)** and can be assigned to loss of three water molecules (calculated mass loss = 3.37%). X-ray powder diffraction of the material obtained at this stage showed that it retains its framework structure **(**Figure 5).

The second event (**B**) in the DSC is a very weak and exothermic peak which is almost masked by the third endothermic peak (**C**) at 190 °C. Following this, we also observe endothermic peak (**C**) at 180 °C and endothermic peak (**D**) at 275 °C. The exothermic peak (**B**) is assigned to a partial decomposition of **5**, according to the PXRD results (see below)**-**. The (**C**) and (**D**) peaks correspond to the second and third stages of mass loss in the TGA curve from 160 to 310 °C. The total mass loss in these two stages is ∼8.50% and are consistent with four NH_3 and two H_2S molecules (calculated mass loss = 8.49%). The NH_3 gas is produced from the decomposition of NH_4^+. H_2S is formed by the attack of the H^+ on the sulfide

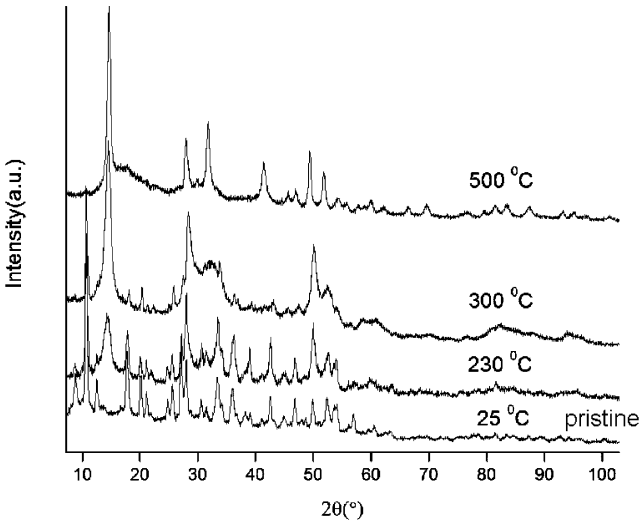


Figure 5. Powder X-ray diffraction patterns of the DSC-derived residues at 230, 300 , and 500 °C as well as of the pristine material **5**. The pattern of the DSC residue at 150 °C (not shown here for clarity) is identical to that of pristine **5**.

atoms of the framework. The simultaneous release of NH_3 and H_2S was also confirmed by pyrolysis mass spectroscopy of **5**. In addition, no H and a negligible amount of N (by C, H, N analysis) were detected for the final residue at 500 °C, and the mid-IR spectrum of this residue indicated absence of NH_4^+ peaks.

The final event on heating is an exothermic peak (**E**) at 330 °C which can be assigned to a crystallization process, as suggested by PXRD studies.

X-ray diffraction analysis of the DSC residue at 230 °C showed the formation of SnS_2 as indicated by the strong peak at $2\theta = 14.4°$, Figure 5. The PXRD pattern of the residue at 300 °C (just before the final exothermic phenomenon), indicates that **5** is still present, but the intensity of the peak from SnS_2 at $2\theta = 14.4°$ has increased, Figure 5. In addition, an amorphous underlying background in the PXRD pattern of the residue at 300 °C is easily observed, Figure 5. The PXRD pattern of the residue at 500 °C corresponds clearly to a mixture of crystalline phases [SnS_2 (main phase), ZnS, and possibly ternary "K Sn S" phases] containing no features of the pristine **5**. Thus, the final exothermic process observed in the DSC plot can be assigned as a crystallization of a glassy phase resulting from the decomposition of **5** after step (**D**) and giving rise to the aforementioned amorphous background in the X-ray diffraction pattern.

Mechanism of the NH_4^+-Exchange Process. The structures of the intermediate NH_4^+-exchange products **6**, **7**, as well as that of the maximally exchanged end product **8**, imply a specific kind of movement or diffusion of NH_4^+ ions during the exchange process from the **K3** cavity [structure of **6**] to the **K2** [structures of **7** and **8**] and even to the **K1** ones [structure of **9**] of the framework (Figure 3 and Scheme 2). This mechanism is quite surprising. The **K1** cavity, although it is similar in size to the **K2**, is less accessible because the passage between the **K1** and **K3** cavities (~1.0 Å) is substantially narrower than that between the **K2** and **K3** cavities (~1.5 Å).[8c] In general, the diameters of these passages in the framework of **1** are significantly smaller than the diameter of a K^+ ion (~3.0 Å for eight-coordinated K^+ ions, such as K1 and 2.8 Å for six-coordinated atoms such as K2).[18] At the narrowest point the passage between the **K1** and **K3** cavities is ~2.3 Å (equal to the S3···S4 distance excluding van der Waals radii), which is less than the diameter of one K^+ ion. In addition, at the narrowest point of the passage the K···S distance of a K^+ ion passing from the **K2** to the **K3** cavity (S3···S3 ≈ 3.9 Å) would be ~1.95 Å, which is much less than the sum of the van der Waals radii of K^+ and S^{2-} (3.2−3.3 Å). Thus, one would expect that **1** should not be able to exchange more than one K^+ ion, i.e., the K3 atom located in the largest cavity of the framework. Furthermore, we would expect that the movement of the K2 and K1 atoms through the tunnel network would be restricted by the small size of the **K1**−**K3** and **K2**−**K3** pore windows. However, **1** not only can exchange five from its six K^+ ions by NH_4^+, but it can also exchange the tightly bound K1 atom located in the less accessible cavity of the framework!

The observed cation-exchange capability of **1** could be due to an expansion/contraction phenomenon during the exchange process in which the absorption of water molecules into the framework may play a role.[19] Such insertion could cause the expansion of the crystal volume of **1** and thus, the expansion of its pores and pore windows facilitating the movement of the K^+ ions through the tunnel network. An indication for the ability of **1** to expand is the significantly larger volume (1931 Å^3) of the ammonium-exchanged product **8** compared to that (1837 Å^3) of **1** itself. The NH_4^+ ion has nearly equal diameter (2.9 Å) to that of K^+ (2.8−3.0 Å), and thus, we would expect that the volume of **8** to be very close to that of **1**. Additional indications concerning the possible swelling of the structure of **1** during the ion-exchange process come from the structures of the exchange products **2b** and **7**. The cavities in **2b** and **7** hosting the Cs atoms are larger than the same Cs-hosting cavity in **2a**, a compound prepared by solid-state reaction. This enlargement of the Cs cavity in **2b** and **7** implies swelling of the framework because of the insertion of water molecules during the ion-exchange process.

Swelling phenomena during the ion-exchange processes are well-known for ion-exchange resins[19] but are rare in crystalline frameworks. Inorganic ion-exchangers with three-dimensional structures, such as the zeolites, usually exhibit rigid framework structures that do not favor swelling processes. Thus, ion-exchange properties in these materials are controlled almost exclusively by pore and channel sizes. This could be related to the bond angles around the oxygen vis-à-vis sulfur atoms. In zeolites, the Al−O−Si angles are wide (~160−180°). It is possible that in the sulfide compounds such as $K_6Sn[Zn_4Sn_4S_{17}]$ where the M−S−M′ angles average at ~110° allow for a certain degree of "breathing" action for the framework. This could happen by bending around this angle, thereby cooperating to enable ion diffusion between pores. An example of a chalcogenide exhibiting highly elastic framework was recently described.[20] Although negligible for zeolites and other oxidic inorganic ion exchangers with 3D-frameworks, expansion−contraction phenomena may be important in chalcogenide frameworks and thus could expand the scope of the ion-exchange process in unique ways.

Another explanation for ion diffusion through the structure could involve a cooperative "breathing" action of the framework which allows it to expand and increase the passage windows between cavities concomitantly with ion motion. Such a cooperative process has been invoked to explain ion mobility in amorphous materials and glasses, particularly those that contain mixed alkali ions.[21] Such framework action implies flexibility and low rigidity, and the chalcogenide framework with its small M−S−M′ angles and their ability to vary is likely to possess these attributes.

Comparison of the Cation-Exchange Capacities (CEC) of 1 with Other Crystalline Inorganic Ion Exchangers. Natural and synthetic zeolites have been extensively studied for their ammonium-exchange properties.[10,11] Their ammonium-exchange capacities vary from 1 to 4.18 mequiv/gr (Table 2). **1** has a maximum ammonium-exchange capacity of 3.06 mequiv/gr (theoretical CEC = 3.6 mequiv/gr), which was calculated on the basis of the formula of the exchanged product **8**. The framework density of **1** (2.955 g/cm^3) is much higher than that of zeolites. For example, the density of sodium phillipsite (Na-PHI), exhibiting (to the best of our knowledge) the highest ammonium-exchange capacity among zeolites and other inorganic ion exchangers, is 2.17 g/cm^3. Taking into account the density difference between compound **1** and Na-PHI, the normalized ammonium-exchange capacity of **1** is calculated equal to 4.17 mequiv/gr, which is very close to the NH_4^+-exchange capacity of Na-PHI (4.18 mequiv/gr).

(18) Information about the ionic radii of all elements can be found in http://abulafia.mt.ic.ac.uk/shannon/ptable.php.
(19) Helfferish, F. *Ion Exchange*, Dover Publications: New York, 1995; pp 100−125.
(20) Trikalitis, P. N.; Ding, N.; Malliakas, C.; Billinge, S. J. L.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2004**, *126*, 15326.
(21) Davidson, J. E.; Ingram, M. D.; Bunde, A.; Funke, K. *J. Non-Crystal. Solids* **1996**, *203*, 246.

Table 2. Maximum Ammonium Ion-Exchange Capacities of Various Zeolites and $K_6Sn[Zn_4Sn_4S_{17}]$

ion exchanger	CEC (mequiv/gr)	ref
Na-SOD[a]	0	10a
NaCs-RHO[a]	1.65	10a
Na-LTA[a]	2.56	10a
Na-FAU(X)[a]	3.20	10a
clinoptilolite	1.35	10b
mordenite	1.05	10b
Na-FAU(Y)[a]	3.04	10c
Na-PHI[a]	4.18	10d
$K_6Sn[Zn_4Sn_4S_{17}]$	**3.06** (uncorrected value) **4.17** (normalized for density difference value)	**present work**

[a] Na-SOD: sodium sodalite; NaCs-RHO: zeolite RHO; Na-LTA: sodium-Linde type A; Na-FAU(X):sodium-faujasite (X); Na-FAU(Y): sodium-faujasite (Y); Na-PHI: sodium-phillipsite.

The Cs^+-exchange capacity of **1** is lower (0.6 mequiv/gr) than that of various zeolites and zirconium−titanium silicate materials (1.86−4.19 mequiv/gr).[9] However, the selectivity of **1** for Cs^+ is very high and unique among chalcogenide materials.

Concluding Remarks

Each of the three distinct cavities of the open framework chalcogenide compound $K_6Sn[Zn_4Sn_4S_{17}]$ (**1**) shows facile and specific ion-exchange properties with NH_4^+, Rb^+, and Cs^+ reminiscent those of the natural zeolites. The largest pore in the framework exhibited a unique selectivity and high affinity for Cs^+, which has been demonstrated by competitive exchange experiments using equimolar amounts of Rb^+, Cs^+, and NH_4^+. The selectivity for Cs^+ is high even when it is in relatively low concentration and in the presence of excess of several competitive cations. Thus, $K_6Sn[Zn_4Sn_4S_{17}]$ seems to be a promising material for the ^{137}Cs remediation of nuclear wastes. Ion-exchange experiments of **1** with Cs^+ solutions of various concentrations and analyses of Cs^+ in the solutions after ion exchange will be the subject of future studies.

The NH_4^+-exchange properties of **1** are also significant and they involve a different cavity in the structure. Among monovalent ions, the affinity of **1** for NH_4^+ ions is the highest as proven by competitive ion-exchange experiments. The ammonium-exchange capacity of **1** is well comparable to that of natural and synthetic zeolites, even though the zeolites have much larger pores and pore windows than those of **1**. The mechanism for the ion-exchange seems to be quite unusual, employing a movement of NH_4^+ from the largest cavity to small ones of the framework of **1**. This diffusion mechanism leads to a final product with NH_4^+ ion replacing even the most inaccessible K^+ (**K1** cavity) of the pristine material **1** and exiting completely the largest cavity **K3**. Because the cavities communicate with each other through narrow "necked" regions of ∼2 Å, it is remarkable the ions of NH_4^+, Cs^+ which are larger than the "neck" connecting the cavities can pass through and diffuse throughout. For the first time the elasticity of a chalcogenide framework, that can possibly allow swelling phenomena, may be implicated in the observed ion-exchange properties of **1**. Overall, the results of the ion-exchange experiments of **1** with alkali metals and NH_4^+ revealed the potential of using open framework chalcogenides with loosely bound cations as ion exchangers for specific situations. Although they cannot be expected to replace zeolites in any way, in some cases they can be alternatives to these and other oxidic open framework materials. Finally, because $K_6Sn[Zn_4Sn_4S_{17}]$ and other open framework chalcogenides can generally afford larger crystals than zeolites can, they can serve as model systems for studying mechanisms of various ion-exchange processes as well as guest−host interactions with single-crystal scattering techniques.

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Supporting Information Available: Crystallographic information files (CIF) for compounds **2b** and **6**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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