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Permeable Layers with Large Windows in $[(CH_3CH_2CH_2)_2NH_2]_5In_5Sb_6S_{19}\cdot1.45\ H_2O$: High Ion-Exchange Capacity, Size Discrimination, and Selectivity for Cs Ions

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Zeolitic materials are open-framework silicates and aluminophosphates with enormous structural diversity[1] and applications in catalysis,[2] molecular recognition,[3] separations,[4] and ion exchange.[5] Growing focus, however, is being placed on open-framework compounds with heavier elements that present a different chemical reactivity (e.g., sulfidic vs oxidic). These compounds could combine conventional zeolite functionality with optical and electronic properties or enable processes not possible with zeolites.[6−8] In the chalcogenide family, substantial work has been reported on the construction of group 13 and/or group 14-based systems such as indium sulfides/selenides[6−10] and metal thio-/selenostannates.[6−10] Most of these compounds are constructed with building units involving only tetrahedrally coordinated metal atoms (e.g., GeS_4, InS_4). Heavier aluminophosphate analogs would involve group 13, group 15, and chalcogen elements. Given the different electronegativity and redox properties among group 15 elements, formal open-framework analogs to the aluminophosphates are not expected. Furthermore, because the M−S−M angles are generally smaller than corresponding oxide angles, it leads to different structural varieties.

Here, we describe $[(CH_3CH_2CH_2)_2NH_2]_5In_5Sb_6S_{19}\cdot1.45\ H_2O$ (**1**), which is composed of anionic layers with large windows that allow its organic cations (dipropylammonium, $DPAH^+$) to be rapidly exchanged with other ions. We report that (**1**) has an exceptional Cs^+-exchange specificity and is able to discriminate this ion against all other alkali metal cations, i.e., Li^+, Na^+, K^+, and Rb^+. Divalent cations such as Ca^{2+}, Sr^{2+}, and Ba^{2+}, can also be ion-exchanged into the lattice of **1**. To the best of our knowledge, this is the first example of a chalcogenide exhibiting strong preference for Cs^+ ions. This property is relevant to the field of remediation of radioactive Cs^+ and Sr^{2+} from nuclear waste solutions[11] and points to open-framework chalcogenides as potential alternative materials for remediation.

Compound **1** forms by the reaction of In_2S_3, Sb_2S_3, and S with dipropylamine under hydrothermal conditions.[12] Large platelike pale yellow crystals formed after 5 days, mainly as polysynthetic twins.[13] The compound adopts the space group *P*2/*c* and features extended inorganic layers of $[In_5Sb_6S_{19}]^{5-}$ that are parallel to the *ac*-plane, Figure 1a. The layers are separated by disordered water molecules and two crystallographically unique $DPAH^+$ cations (N1 and N3). The interlayer distance is ~9.5 Å. The closest N···S distances, indicated with dash lines in Figure 1a, are N3−S2 at 3.2768(6) Å, N2−S8 at 3.2970(6) Å, and N1−S4 at 3.3409(6) Å, implying hydrogen bonding between the NH_2 group of the $DPAH^+$ cation and the sulfur atoms of the inorganic framework.

One of the most interesting features of **1** is that the $[In_5Sb_6S_{19}]^{5-}$ slabs are perforated with large elliptical holes or windows. The windows are defined by a 12-membered ring (12 MR, actually a 24-membered ring but we use the terminology used for zeolite rings) within the $[In_5Sb_6S_{19}]^{5-}$

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(12) Synthesis of (**1**): An amount of 0.0408 g (0.125 mmol) of In_2S_3, 0.051 g (0.15 mmol) of Sb_2S_3, and 0.016 g (0.5 mmol) of S were combined and loaded in a 3/8 inch Pyrex tube along with 0.30 mL of 1:1 dipropylamine:water in air. The tube was then evacuated to $<3 \times 10^{-3}$ Torr and flame-sealed. The tube was kept in an oven at ~160 °C for 5 days. The products were isolated in air by filtration and washed with deionized water, ethanol, and ether. The product consists of pale yellow platelike crystals along with some recrystallized Sb_2S_3 (20%). Yield was ~60%. The crystals appear to be stable in air for months. Energy-dispersive spectroscopy (EDS) results: $In_{4.98}Sb_6S_{18.96}$. C, H, N analysis (%): 14.74, 3.48, 2.87 (calcd: 14.70, 3.38, 2.86).

(13) Compound (**1**) crystal data: The single-crystal X-ray diffraction data was collected with a STOE IPDS diffractometer at 100 K. A platelike crystal with dimensions $0.178 \times 0.245 \times 0.042$ mm^3 was chosen for data collection. An analytical absorption correction based on face-indexing was applied. The structure was solved with direct methods using SHELX-97. The PLATON SQUEEZE program was applied to obtain better refinement for the highly disordered organic cations and water molecule. Space group: *P*2/*c* with $a = 17.638(4)$ Å, $b = 9.4889(19)$ Å, $c = 26.369(5)$ Å, $b = 115.47(3)°$, $V = 3984.2(14)$ Å^3. Other crystal data: $Z = 2$, $D_{calcd} = 2.041$ g cm^{-3}, $m = 3.942$ mm^{-1}; index range $-22 \leq h \leq 20$, $-12 \leq k \leq 12$, $-32 \leq l \leq 31$; total reflections 29779, independent reflections 8185, parameters 228, R1 = 5.84 %, wR2 = 15.47 %, GOF = 1.096.

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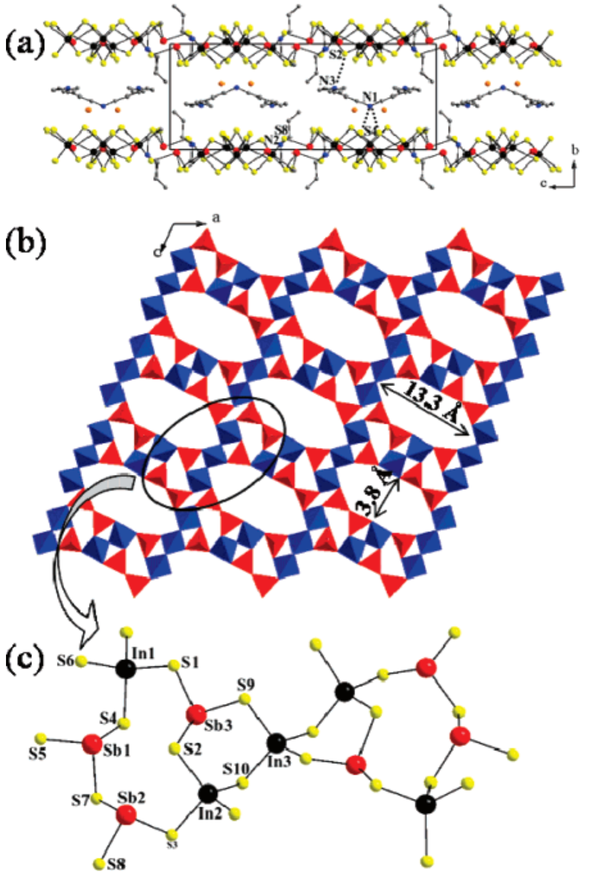

Figure 1. (a) Structure of (**1**) viewed down the *a*-axis. The closest N···S distances are illustrated with dash lines. All hydrogen atoms in the cation were removed for clarity. (b) Polyhedral view of a $[In_5Sb_6S_{19}]^{5-}$ layer, blue tetrahedra are InS_4 units, and red trigonal pyramids are SbS_3 fragments. (c) Secondary building-unit in $[In_5Sb_6S_{19}]^{5-}$. Black atoms are In, red atoms are Sb, yellow atoms are S. Orange atoms are O selected bond distances (Å): In1−S1 2.451(2), In1−S4 2.476(2), In1−S5 2.442(2), In1−S6 2.419(2), In2−S2 2.469(2), In2−S3 2.461(3), In2−S8 2.464(3), In2−S10 2.403(3), In3−S9 2.462(3), In3−S10 2.425(3), Sb1−S4 2.426(2), Sb1−S5 2.423(2), Sb1−S7 2.442(2), Sb2−S3 2.413(3), Sb2−S7 2.460(2), Sb2−S8 2.416(3), Sb3−S1 2.424(2), Sb3−S2 2.441(3), Sb3−S9 2.420(3).

layer. The size of this window is ~13.3 × 3.8 Å^2 (excluding the van der Waals radii of S atoms), enough for large molecules or ions to pass through it. These windows are pseudo-hexagonally arranged to give a chicken-wire mesh appearance to the layers. This leads to ~40% of the layer area to be holes and causes 60% of the total volume of a unit cell to be accessible space (calculated by PLATON,[14] excluding the cations and water molecules). A polyhedral view is shown in Figure 1b. One crystallographically unique DPAH$^+$ (N2) is sandwiched between two windows, supporting the structure. The windows of a slab are aligned with those of adjacent slabs, forming straight pseudo-channels perpendicular to the layers. This imparts a 3D character to the compound and makes it reminiscent of some zeolitic structures with such large aperture, e.g., aluminophosphates VPI-5.[15] A closer example is a dipropylamine-templated indium sulfide $[(C_3H_7)NH_2]_3H{-}In_6S_{11}$[16] which is also a layered compound (though not isostructural) composed of 12 MRs by corner-/edge-sharing InS_4 tetrahedra.

The secondary building unit (SBU) of each $[In_5Sb_6S_{19}]^{5-}$ slab may be defined as the fragment with the same formula as the compound, see Figure 1c. The $[In_5Sb_6S_{19}]^{5-}$ SBU consists of two identical bicyclic subfragments, which are composed of fused 5 and 3 MRs of corner-sharing InS_4 tetrhedra and SbS_3 trigonal pyramids, respectively, sharing the In3 atom.

Because of the large windows in **1**, the organic cations are readily exchangeable with other cationic species such as Rb$^+$, Cs$^+$, and the alkaline earth cations Ca^{2+}, Sr^{2+}, and Ba^{2+}. Interestingly, the specific window size in the $[In_5Sb_6S_{19}]^{5-}$ layers causes a strong preference for Cs$^+$ ions, more than any other alkali metal cation. Within a single ion-exchange step, Cs$^+$ could replace up to 85% of the organic species according to elemental analysis. Taking the molecular weight into account, the exchange capacity of (**1**) for Cs$^+$ (4.25 mequiv/mmol or 1.72 mequiv/g) is surprisingly high,[17] compared to $K_6Zn_5Sn_4S_{17}$[18] and microporous titanosilicates (e.g., 2.25 mequiv/mmol or 4.19 mequiv/g), the latter is one of the best Cs$^+$ exchangers.[19] In fact, complete replacement of DPAH$^+$ by Cs$^+$ ions can be achieved with two successive reactions, generating $Cs_5In_5Sb_6S_{19}$. Correspondingly, the PXRD pattern of $Cs_5In_5Sb_6S_{19}$ showed a clear shift from 9.81[20] to 7.72 Å in the *d*-spacing of the basal (010) reflection, consistent with the smaller size of Cs$^+$ ion. Under scanning electronic microscope (SEM) examination, striated surfaces can be seen in crystals of the pristine compound **1**. After exchange with Cs$^+$, these features were less-discernible but the crystals retained their original shape, Figure 2a. The color of $Cs_5In_5Sb_6S_{19}$ is golden yellow (instead of the pale yellow pristine compound) and the optical energy gap decreased from 2.62 to 2.38 eV, see Figure 2b.

Interestingly, however, only 37% of the cations can be exchanged by Rb$^+$, 12% by Li$^+$, and only trace amount of Na$^+$ and K$^+$.[21] These partially exchanged products, e.g., $(DPAH)_{5-x}Rb_xIn_5Sb_6S_{19}$ ($x \approx 1.8$) showed only a slight shift of the interlayer distance, from 9.81 to 9.11 Å. The elemental analysis results and exchange yields of the ion-exchanged products are given in the Supporting Information.

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(20) (a) Single-crystal diffraction data was collected at 100 K, and powder XRD was obtained at room temperature; therefore, there is a slight shift to lower 2θ (~ .32 Å in *d*-spacing fo the (010) reflection) in the experimental PXRD pattern compared to the calculated one. (b) Single-crystal diffraction of $(DPAH)_{5-x}Cs_xIn_5Sb_6S_{19}$ from the ion-exchange experiment was performed at 100 K. Space group: $C2/m$ with $a = 25.874(4)$ Å, $b = 14.927(2)$ Å, $c = 17.663(2)$ Å, $\beta = 115.42(1)°$, $V = 6161(2)$ Å^3. However, because of the deteriorated quality of the ion-exchanged single crystal, the refinement of the structure is not satisfactory. Nevertheless, the framework connectivity could be confirmed to be the same as the pristine material.

(21) A typical ion-exchange experiment was performed as follows: A specific amount of AI (A = Li, Rb, Cs), ACl (A = Na, K), or $AECl_2$ (AE = Ca, Ba) was dissolved in ~5 mL of deionized water at 75 °C in a glovebox. An amount of ~15 mg of $(DPAH)_5In_5Sb_6S_{19}$ was then added in the salt solutions. The mixture was kept at 75 °C without stirring for ~24 h. The products were isolated in air by filtration and washed with water, ethanol, and ether. The crystallinity of the sample was confirmed by X-ray diffraction before and after ion-exchange.

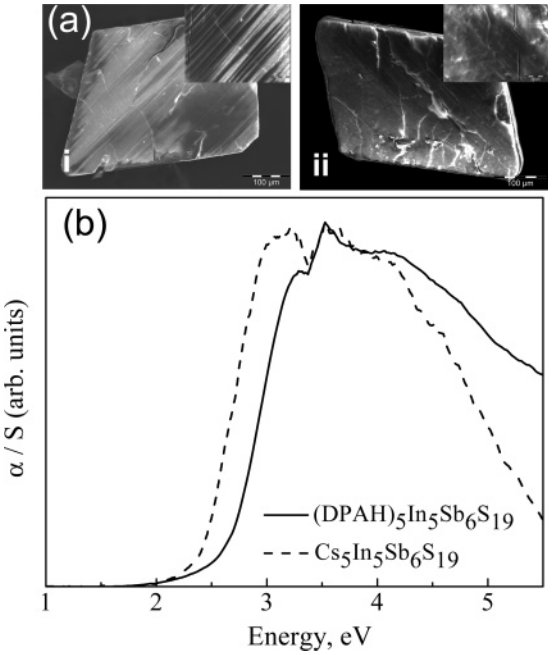

Figure 2. (a) SEM images of (i) the pristine compound (**1**) and (ii) the Cs^+-exchanged product. Insets are a magnified image of the surface of each crystal. (b) Optical absorption spectra of $(DPAH)_5In_5Sb_6S_{19}$ (solid) and $Cs_5In_5Sb_6S_{19}$ (dash).

Compound **1** is stable in the pH range of 4.3−10.0 (HCl and NaOH were used to adjust the pH values) at room temperature. Cs^+ exchange was successful in this range with vigorous shaking for ∼24 h. After two successive steps at pH 4.3, $Cs_5In_5Sb_6S_{19}$ as the major phase with its (010) reflection at *d*-spacing 7.72 Å. We also observe the partially exchanged $(DPAH)_{5-x}Cs_xIn_5Sb_6S_{19}$ as a minor phase with d_{010} at 9.06 Å.

In competitive experiments at neutral pH, using equimolar amounts of alkali metal cations Na^+, K^+, Rb^+, and Cs^+, the uptake of Cs^+ by **1** was 10 times greater than that of Rb^+ and orders of magnitude higher than those of Na^+ or K^+, as they were not observed to enter the structure. Using a molar 10:10:10:1 ratio of Na^+, K^+, Rb^+, and Cs^+ in an ion-exchange reaction, we observed the following respective distribution of in the exchanged product 1:1.5:6:4. Despite the initial 10-fold excess of Rb^+ over Cs^+, the ratio of Rb^+:Cs^+ was less than 1.5 in the final product. A ratio of Na^+:Cs^+ = 20:1 in a competitive exchange experiment gave a 2:2.3 ratio of Na^+ to Cs^+ in the product (i.e., $(DPAH)_{0.7}Na_2Cs_{2.3}In_5Sb_6S_{19}$).

The divalent Ca^{2+}, Sr^{2+}, and Ba^{2+} seem to be more preferred by **1** over Li^+, Na^+, K^+, and possibly even Rb^+ ions. In a single-step reaction, the $(DPAH)_{5-2x}M_xIn_5Sb_6S_{19}$ were obtained with $x \approx 1.4$ for M = Ca; $x \approx 2.0$ for Sr; and $x \approx 1.1$ for Ba. Although Sr^{2+} ions gave the highest exchange yield, in a competitive experiment with all three divalent ions present in equimolar concentration, Ba^{2+} replaced the most organic species (52%), followed by Sr^{2+} (24%) and Ca^{2+} (12%) ions. Given that Cs^+ and Ba^{2+} have similar size, the selectivity of **1** seems to be a function of size-match between the cations and the aperture of the inorganic $[In_5Sb_6S_{19}]^{5-}$ framework. Therefore, the facile ion-exchange properties of **1** appear to be linked to its perforated layers. This notion is also supported by the lack of any ion-exchange properties of a similarly lamellar compound $[(CH_3)_2NH_2]_2In_2Sb_2S_7$[22] whose layers lack the large windows of **1**.

Thermogravimetric analysis (TGA) of the products before and after the ion-exchange was performed to probe thermal stability and confirm the loss of the organic cations. The weight loss for $(DPAH)_5In_5Sb_6S_{19}$ started at ∼64 °C, possibly because of water in the structure (calcd, 1.1%; found in TGA, 1.3%). From 110 to 247 °C, a weight loss of ∼22.5% was observed, which was higher than what would be expected from the removal of only the organic species. This indicates the simultaneous removal of sulfur probably as H_2S. The powder XRD pattern of the residue obtained from the TGA indicated $InSbS_3$[23] and a small amount of Sb_2S_3. In contrast, the TGA curve of the Cs^+-exchanged compound only showed an ∼4% weight loss that began at room temperature and ended at ∼98 °C, mostly because of the absorbed solvent molecules. This result confirmed that almost all organic cations were replaced by Cs^+, forming $Cs_5In_5Sb_6S_{19}$.

$(DPAH)_5In_5Sb_6S_{19}$ is a rare example of a layered architecture with large enough apertures to enable guest cations to diffuse in and out of the material through the layers. In this regard, it acts and behaves like a three-dimensional framework. The selectivity for alkali/alkaline earth metal cations is as follows

$$Cs^+ > Ba^{2+} > Sr^{2+} > Ca^{2+} > Rb^+ \gg K^+, Na^+, Li^+$$

This order of selectivity, however, also shows that the softer Lewis acidic cations are preferred over harder ones. The trend suggests that the chalcogenide nature of the compound with its soft basic framework has a significant influence. The lower selectivity for the smaller alkali metal ions is believed to be due to their large hydrated spheres.

To conclude, $(DPAH)_5In_5Sb_6S_{19}$ appears to be an excellent ion-exchanger with particular specificity for Cs^+ ions and to a lesser degree for divalent Sr^{2+} and Ba^{2+} ions. The exchange capacity for Cs^+ is comparable to some of the best known microporous oxides and chalcogenides. This exceptional behavior described here is attributed to the holes in the layers of the material as well as the affinity of the sulfide framework for the softer, unhydrated Cs^+ ion. Thus, $(DPAH)_5In_5Sb_6S_{19}$ is a bona fide example of how structure affects function and as such it contributes to our understanding of structure/property relationships.

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Supporting Information Available: Crystallographic data for compound (**1**) (CIF file) and additional information about the ion-exchange reactions and products (elemental analyses, X-ray powder diffraction patterns, etc) (PDF). This material is available free of charge via http://pubs.acs.org.

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