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$K_6Cd_4Sn_3Se_{13}$: A polar open-framework compound based on the partially destroyed supertetrahedral $[Cd_4Sn_4Se_{17}]^{10-}$ cluster

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Received (in West Lafayette, IN) 20th February 2004, Accepted 22nd March 2004
First published as an Advance Article on the web 23rd April 2004

$K_6Cd_4Sn_3Se_{13}$ forms in superheated water and has a polar open-framework structure that is based on an octahedral topological motif. It forms from the polymerization of a single $[Cd_4Sn_3Se_{13}]^{6-}$ cluster which formally derives from a $[Cd_4Sn_4Se_{17}]^{10-}$ *via* elimination of one $[SnSe_4]^{4-}$ anion. $K_6Cd_4Sn_3Se_{13}$ exhibits facile ion-exchange properties with suitably sized cations.

Recently, we described the new group of the compounds, $K_{10}M_4Sn_4S_{17}$, (A = alkali metal, M = Zn, Cd, Mn, Fe, Co) all possessing the discrete $[M_4Sn_4S_{17}]^{10-}$ supertetrahedral cluster.[1] Several selenium analogs prepared in solution and crystallized with organic counterions were also described.[2] Unlike other supertetrahedral clusters,[3,4] the motif of $[M_4Sn_4Q_{17}]^{10-}$ (Q = S, Se) does not represent excised fragments from the adamantine zinc-blende lattice. The clusters feature a central quadruply bridging chalcogen ion (μ_4-Q^{2-}) that links to four divalent M atoms in a tetrahedral arrangement to define a $[M_4Q]^{6+}$ core, which is then capped with four tridentate tetrahedral $[SnQ_4]^{4-}$ fragments to complete the structure, Fig. 1A(i). Such clusters are expected to act as precursors for non-oxidic microporous[3,4,5] and mesostructured solids.[6,7] Because of the apparent good stability of the $[M_4Sn_4Q_{17}]^{10-}$ clusters we attempted to prepare extended three-dimensional framework phases that contained it as a building block. Namely we reasoned that the cluster may form spontaneously under hydrothermal reaction conditions if given the appropriate elements. Interestingly, we obtained $K_6Cd_4Sn_3Se_{13}$ a compound whose framework structure is indeed open and three-dimensional (3D)†. To our surprise a fragment reminiscent of the cluster exists as a recognizable unit but it represents a partially destroyed or truncated $[Cd_4Sn_4Se_{17}]^{10-}$ cluster. Here we describe the structure and properties of $K_6Cd_4Sn_3Se_{13}$ and discuss its relationship with that of the respective molecular cluster.‡

$K_6Cd_4Sn_3Se_{13}$ has a contiguous anionic covalent framework of distinctly open character. It forms from a single cluster unit *via* polymerization at six linking sites. This cluster is $[Cd_4Sn_3Se_{13}]^{6-}$ and derives from $[Cd_4Sn_4Se_{17}]^{10-}$ *via* elimination of a single $[SnSe_4]^{4-}$ tetrahedron, see Fig. 1A. This generates three-coordinate Cd atoms and leads to the $[Cd_4Sn_3Se_{13}]^{6-}$ cluster. This species is strongly polar with a three-fold axis of symmetry and belongs to the C_{3v} point group. The extended 3D framework then forms when the three terminal Se atoms act as ligands to Cd atoms in adjacent clusters, Fig. 1B. The coordination geometry of all metal atoms as well as the μ_4-Se(1) atoms is distorted tetrahedral. The cross-linking Se atoms are μ_2-type formig Cd–Se–Sn bridges.

The cluster polymerization results in a simple octahedral geometry around each $[Cd_4Sn_3Se_{13}]^{6-}$ which resembles topologically the Po-structure. This means that each cluster resides in an octahedral cage of six other clusters. This arrangement is clearly seen when each cluster is represented as ball and inter-cluster contacts as sticks, see Fig. 2. Because the polymerization pattern depicted in Fig. 1B demands that the alignment and orientation of the polar clusters is identical, the resulting framework is also polar and adopts rhombohedral *R*3*m* symmetry. As a subgroup of cubic symmetry, the *R*3*m* structure has tunnel voids in this structure running in all three directions. Two of the tunnels are identical and larger (Fig. 1B) than the third. The van der Waals diameter is ~5 Å.

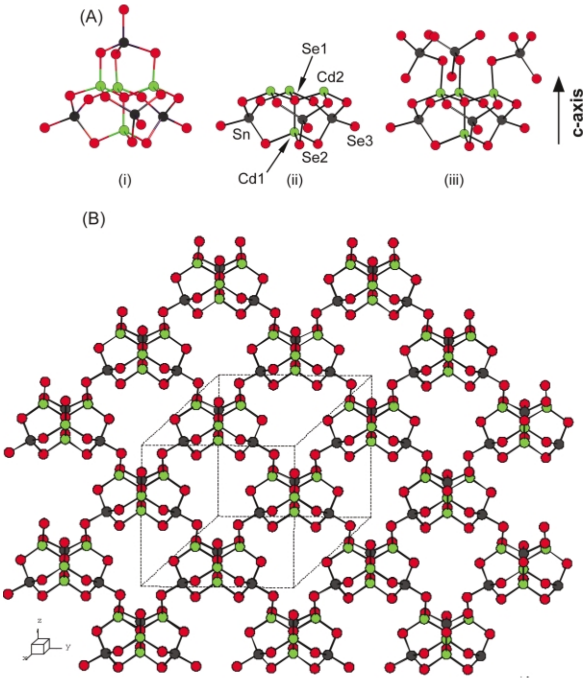

Fig. 1 (A) The structural relationship of (i) $[Cd_4Sn_4Se_{17}]^{10-}$ and (ii) $[Cd_4Sn_3Se_{13}]^{6-}$ clusters. Removal of the $[SnSe_4]^{4-}$ unit reduces the ideal molecular symmetry from T_d to C_{3v}. The resulting truncated cluster has three terminal Se atoms and three coordinatively unsaturated trigonal pyramidal Cd atoms. In (iii) the Cd atoms of the C_{3v} cluster bind to terminal Se atoms of adjacent clusters. These linking sites define the mode of polymerization. (B) The polymerized framework of $^{3}_{\infty}[Cd_4Sn_3Se_{13}]^{6-}$ viewed down one of the tunnels. The K ions are removed for clarity. All clusters are aligned along the *c*-axis. Selected distances (Å): Cd1–Se1 2.574(4), Cd1–Se2 2.656(2), Cd2–Se4 2.619(2), Cd2–Se1 2.6305(17), Cd2–Se3 2.631(2), Sn1–Se4 2.511(2) Sn1–Se2 2.514(2), Sn1–Se3 2.515(2), K1–Se4 3.727(13), K2–Se4 3.89(2), K1–Se3 3.412(8) K1–Se4 3.727(13), K1–Se4 3.727(13), K2–Se2 3.482(11). Red circles are Se, black are Sn and green are Cd atoms.

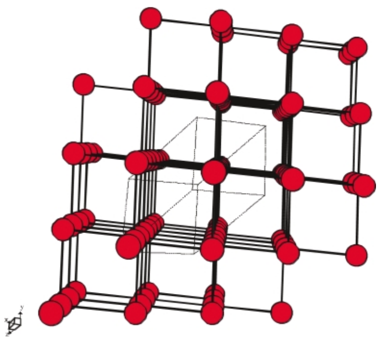

Fig. 2 Skeletal representation of the structure of $^{3}_{\infty}[Cd_4Sn_3Se_{13}]^{6-}$ with emphasis on topology. The red balls represent a single cluster and the overall idealized architecture is that of distorted Po-structure (*i.e* six-coordinate environment).

DOI: 10.1039/b402686a

The structural motif represented by $K_6Cd_4Sn_3Se_{13}$ is unique among open framework chalcogenides several of which include $(Me_4N)_2M(Sn_4Se_{10})$[8] (M = Zn, Cd, Mn, Fe, Co), $[In_{10}Se_{18}]^{6-}$,[5c] and $[Cd_4In_{16}S_{35}]^{14-}$.[5b] In these, the overall topology is close to that of diamond.

Potassium cations occupy the void spaces in the framework but their volume does not fill the available space. This results in a loose packing density and disorder of the K^+ ions as evidenced by split sites and high thermal displacement parameters of K(1) and K(2).[9] This is not unusual in open structures of this type and implies considerable cation mobility in the tunnels.

The open framework structure of the material is in fact accessible to cationic guest species. The mobility of K^+ ions in the new material and the accessibility of the microporous space were probed with ion-exchange reactions. Facile and extensive topotactic ion-exchange was achieved in a single step under mild conditions with LiI, NaI and RbI in water and also by a solid state reaction described earlier.[10] Ion-exchange was confirmed with X-ray diffraction and elemental analysis (EDS: Rb:K ratio 9.7:1) which indicated up to 97% exchange of K ions in the structure. The powder X-ray diffraction patterns of pristine and $Rb_{6-x}K_xCd_4Sn_3Se_{13}$ ($x \sim 0.03$) are nearly identical, Fig. 3.

The yellow $K_6Cd_4Sn_3Se_{13}$ shows an optical energy gap of 2.33 eV, indicating it is a wide gap semiconductor, inset of Fig. 3A. Its optical transparency below 2.33 eV and strongly polar crystal lattice could give rise to interesting non-linear optical properties. The compound decomposes at 280 °C to $K_2CdSnSe_4$ and CdSe and it seems to be accessible only through hydrothermal synthesis. Several attempts to prepare it with a solid state direct combination reaction of K_2Se/Cd/Sn/Se yielded mixtures of $K_2CdSnSe_4$ and CdSe. Interestingly, however, when a mixture of $K_2CdSnSe_4$ and CdSe, having the proper nominal composition, was treated under hydrothermal conditions at 115 °C for 96 h $K_6Cd_4Sn_3Se_{13}$ formed in excellent yield.

In addition to its fascinating structural and reactivity attributes, the framework in $K_6Cd_4Sn_3Se_{13}$ may well serve as a starting model for understanding the structures of mesostructured materials $CPyMSnSe_4$.[6c] The mesostructured systems have periodically arranged nano-sized pores but lack crystalline periodicity in the inorganic framework. As a result their precise crystal structure is not known and this impedes a better understanding of their properties. These solids have covalent frameworks and are templated in solution from long chain surfactants and M^{2+}/$[SnSe_4]^{4-}$ as the inorganic constituents. These are the same structural elements present in $K_6Cd_4Sn_3Se_{13}$. Therefore, compounds such as $K_6Cd_4Sn_3Se_{13}$ with their precisely defined structures could be valuable as model systems, and fragments of their framework may be considered in building mesoporous model structures for simulation studies.

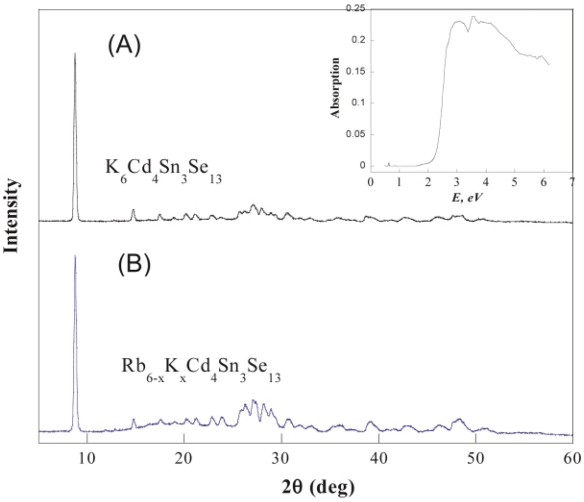

Fig. 3 X-ray diffraction patterns of (A) $K_6Cd_4Sn_3Se_{13}$, (B) ion-exchanged $K_xRb_{6-x}Cd_4Sn_3Se_{13}$ ($x \sim 0.03$); lattice constants: a = 15.174(10), c = 16.613(8) Å. Inset: electronic spectrum of $K_6Cd_4Sn_3Se_{13}$.

Financial support from the National Science Foundation CHE-0211029, (Chemistry Research Group) and DMR-0127644, is gratefully acknowledged.

Notes and references

† The synthesis of $K_6Cd_4Sn_3Se_{13}$ is achieved in two steps: (1) An amount of 0.188 g (1.2 mmol) of K_2Se, 0.176 g (1.6 mmol) Cd, 0.140 g (1.2 mmol) Sn and 0.316 g (4 mmol) Se were combined and melted at ~900 °C. The product was loaded in a 13 mm Pyrex tube along with 0.3 mL of deionized water which was then evacuated to $< 3 \times 10^{-3}$ and flame-sealed. The tube was kept at ~115 °C for 3.5 d. The products were filtered off and washed with water, ethanol and ether. The products were in the form of yellow/orange powder and square-shaped orange crystals. Yield was ~ 72%. The phase is insoluble in water, ethanol, DMF and ethylenediamine. The crystals appear stable in air for days.

‡ Details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany crysdata@fiz-karlsruhe.de) on quoting CSD number 413739. Single crystal X-ray diffraction intensity data were collected on a Bruker SMART platform CCD diffractometer from a crystal of $0.084 \times 0.094 \times 0.101$ mm³ dimensions and Mo-Kα (λ = 0.71073 Å) radiation. An empirical absorption correction was applied to the data using SADABS. The structure was solved with direct methods using SHELX-97. Crystals of $K_6Cd_4Sn_3Se_{13}$ belong to the space group $R3m$ (No. 160) with a = 15.0338(11), b = 15.0338(11), c = 16.512(2) Å, V = 3231.9(6) Å³. Other crystal data: $Z = 3$, $D_c = 3.186$ mg·m^{-3}, $\mu = 15.203$ mm^{-1}; index range $-20 \le h \le 19$, $-19 \le k \le 19$, $-21 \le l \le 21$; total reflections 11764, independent reflections 1849, parameters 53, (R_{int} = 5.93); $R1$ = 4.53%, $wR2$ = 13.44%, GOF = 1.044. CCDC 232407. See http://www.rsc.org/suppdata/cc/b4/b402686a/ for crystallographic data in .cif or other electronic format.

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