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Communication

$K_{10}M_4Sn_4S_{17}$ (M = Mn, Fe, Co, Zn): Soluble Quaternary Sulfides with the Discrete $[M_4Sn_4S_{17}]^{10-}$ Supertetrahedral Clusters

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Four cubic compounds are reported that contain the supertetrahedral cluster $[M_4Sn_4S_{17}]^{10-}$ where M = Mn, Fe, Co, Zn. The cluster features a central quadruply bridging sulfide ion (μ_4-S) that holds together four divalent M atoms in a tetrahedral arrangement. This core is capped with four tridentate $[SnS_4]^{4-}$ fragments to complete the structure.

In recent years the discovery of novel inorganic frameworks based on several so-called supertetrahedral chalcogenido clusters, such as $[Ge_4S_{10}]^{4-}$,[1] $[In_{10}S_{20}]^{10-}$,[2] $[In_{33}S_{56}]^{13-}$,[3] and $[Cd_4In_{16}S_{35}]^{14-}$,[4] has finally opened the way to accessing nonoxidic microporous materials with zeolite-like properties.[5-9] These adamantane clusters have been enumerated as members of a homologous series. Their structures represent excised fragments from the diamond or zinc blende lattice,[2,8] and with the exception of $[Ge_4S_{10}]^{4-}$ none has been reported as a discrete molecule. Presumably, these species form in situ under hydrothermal conditions and then get incorporated into the extended inorganic frameworks.

The availability of chalcogenido clusters that can be put into solution could permit more rational synthetic approaches for a wide variety of microporous and mesostructured solids. For example, the adamantane clusters $[Ge_4S_{10}]^{4-}$ and $[Sn_4Se_{10}]^{4-}$ are excellent precursors for a new family of surfactant-templated mesostructured chalcogenide materials containing various linkage metal ions (Pt^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Ga^{3+}, In^{3+}, Sb^{3+}, Sn^{4+}).[10-14] The clusters exist in the soluble compounds $K_4Ge_4Q_{10}$ and $K_4Sn_4Q_{10}$.

Using the polychalcogenide flux technique we have demonstrated the stabilization of a variety of solid-state compounds with extended structures based on discrete chalco-anions such as $[SnS_4]^{4-}$.[15] This synthesis technique, however, is also capable of synthesizing soluble, molecular compounds under appropriate conditions, although this aspect of it has been little investigated. Here we report K_2S_x flux synthesis of $K_{10}Zn_4Sn_4S_{17}$ and $K_{10}Mn_4Sn_4S_{17}$ which contain the supertetrahedral mixed-metal cluster $[M_4Sn_4S_{17}]^{10-}$ (M = Mn, Zn). Interestingly, the Fe and Co analogues could not be prepared in a K_2S_x flux, but the appeal of the $[M_4Sn_4S_{17}]^{10-}$ structural motif prompted us to seek different routes to prepare analogues with these magnetic metals. Thus herein we describe the family $K_{10}Mn_4Sn_4S_{17}$, $K_{10}Fe_4Sn_4S_{17}$, $K_{10}Co_4Sn_4S_{17}$, and $K_{10}Zn_4Sn_4S_{17}$ possessing the discrete supertetrahedral $[M_4Sn_4S_{17}]^{10-}$ cluster. Structurally, this cluster is not a member of the above-mentioned adamantoid homologous series and does not represent an excised fragment from the diamond or zinc blende lattice.

$K_{10}Zn_4Sn_4S_{17}$ and $K_{10}Mn_4Sn_4S_{17}$ form by reaction of Zn (or Mn) and Sn with K_2S_x flux in the 1:1:3:12 ≡ Sn:Zn:K_2S:S (1:1:4:12 ≡ Sn:Mn:K_2S:S) ratio at 500 °C (650 °C) for 2.5 days (4 days). After the reaction mixture was cooled at 5 °C/h and the K_2S_x flux was dissolved with methanol, yellow-red (red) octahedral or cubic crystals were obtained in 90% (and 40%) yield.[16,17] The corresponding polysulfide flux reaction with Fe and Co does not yield the expected analogues and results only in $KFeS_2$ and CoS_2 and several K/Sn/S phases. Instead these compounds require a direct

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(1) Yaghi, O. M.; Sun, Z.; Richardson, D. A.; Groy, T. L. *J. Am. Chem. Soc.* **1994**, *116*, 807.
(2) Li, H. L.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *Science* **1999**, *283*, 1145.
(3) Wang, C.; Bu, X. H.; Zheng, N. F.; Feng, P. Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 1959.
(4) Li, H. L.; Kim, J.; Groy, T. L.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2001**, *123*, 4867.
(5) Li, H. L.; Eddaoudi, M.; Laine, A.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **1999**, *121*, 6096.
(6) Wang, C.; Bu, X. H.; Zheng, N. F.; Feng, P. Y. *J. Am. Chem. Soc.* **2002**, *124*, 10268.
(7) Wang, C.; Bu, X. H.; Zheng, N. F.; Feng, P. Y. *Chem. Commun.* **2002**, 1344.
(8) Wang, C.; Li, Y. Q.; Bu, X. H.; Zheng, N. F.; Zivkovic, O.; Yang, C. S.; Feng, P. Y. *J. Am. Chem. Soc.* **2001**, *123*, 11506.
(9) Bu, X. H.; Zheng, N. F.; Li, Y. Q.; Feng, P. Y. *J. Am. Chem. Soc.* **2002**, *124*, 12646.

(10) Trikalitis, P. N.; Rangan, K. K.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **2002**, *124*, 2604.
(11) Wachhold, M.; Kanatzidis, M. G. *Chem. Mater.* **2000**, *12*, 2914.
(12) Wachhold, M.; Rangan, K. K.; Lei, M.; Thorpe, M. F.; Billinge, S. J. L.; Petkov, V.; Heising, J.; Kanatzidis, M. G. *J. Solid State Chem.* **2000**, *152*, 21.
(13) Wachhold, M.; Rangan, K. K.; Billinge, S. J. L.; Petkov, V.; Heising, J.; Kanatzidis, M. G. *Adv. Mater.* **2000**, *12*, 85.
(14) Trikalitis, P. N.; Rangan, K. K.; Bakas, T.; Kanatzidis, M. G. *Nature* **2001**, *410*, 671.
(15) Kanatzidis, M. G.; Liao, J. H.; Marking, G. A. U.S. Patent 5 531 936, 1996. Liao, J. H. Ph.D. Dissertation, Michigan State University, 1993.
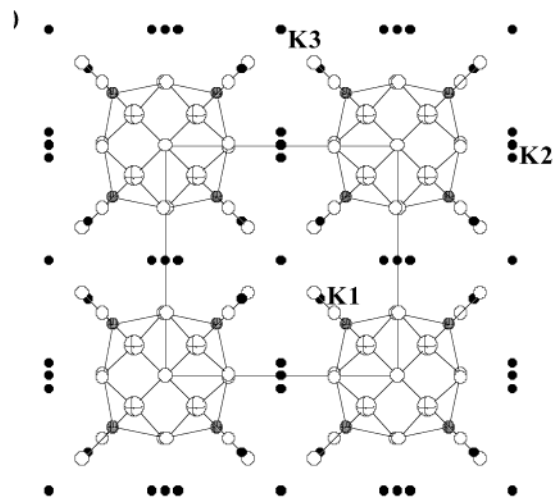
Figure 1. A [100] view of the cubic unit cell of $K_{10}M_4Sn_4S_{17}$ (M = Co). The M, Sn, S and K atoms are indicated as large crossed, small gray, small open, and small black circles, respectively.

combination of K_2S, Fe (or Co), Sn, and S at 650 °C in the exact stoichiometric ratio of 5:4:4:12.[18]

The crystal structure of $K_{10}M_4Sn_4S_{17}$ (M = Zn, Mn, Fe, Co) is cubic and features discrete molecular clusters shown in Figure 1.[19] The structure of the $[M_4Sn_4S_{17}]^{10-}$ cluster is highly symmetrical with a T_d point group symmetry, see Figure 2. We have also isolated the cadmium analogue $[Cd_4Sn_4S_{17}]^{10-}$ as its Cs^+ salt, but this and other systems will be reported later.

The cluster, which finds a selenium analogue reported during the preparation of our manuscript,[20] features a central

(16) Preparation of $K_{10}Zn_4Sn_4S_{17}$: A mixture of Sn (0.5 mmol), Zn (0.5 mmol), K_2S (1.5 mmol), and S (6.0 mmol) was sealed under vacuum ($<10^{-3}$ Torr) in a silica tube and heated (50 °C/h) to 500 °C for 60 h, followed by cooling to room temperature at 5 °C/h. The excess flux was removed with MeOH to reveal brownish-white cubic crystals of $K_{10}Zn_4Sn_4S_{17}$ (~90% yield based on Zn). The crystals are moderately air stable (a few days). Microprobe analysis (EDS) gave an average composition of "$K_{10.2}Zn_4Sn_{4.4}S_{18.2}$". This compound could be also prepared by direct stoichiometric reaction analogously to K_{10}-$Co_4Sn_4S_{17}$ (see footnote 18).
(17) Preparation of $K_{10}Mn_4Sn_4S_{17}$: A mixture of Sn (0.5 mmol), Mn (0.5 mmol), K_2S (2.0 mmol), and S (6.0 mmol) was sealed under vacuum ($<10^{-3}$ Torr) in a silica tube and heated (50 °C/h) to 650 °C. The reaction mixture was kept at this temperature for 96 h, followed by cooling to room temperature at 5 °C/h. The excess flux was removed with MeOH to reveal a mixture of red cubic crystals of $K_{10}Mn_4Sn_4S_{17}$ (40% yield based on Mn) and orange octahedral crystals of K_2MnSnS_4 (~50%). The red crystals are air-stable for approximately 5 h, after which some deterioration could be observed. (Albertelli, G. D.; Cowen, J. A.; Hoff, C. N.; Kaplan, T. A.; Mahanti, S. D.; Liao, J. H.; Kanatzidis, M. G. *Phys. Rev. B* **1997**, *55*, 11056.) The SEM/EDS average composition of the red crystals was "$K_{10.7}Mn_4Sn_{4.6}S_{18.9}$". This compound could not be prepared by direct stoichiometric reaction.
(18) $K_{10}Co_4Sn_4S_{17}$: A mixture of Sn (2.0 mmol), Co (2.0 mmol), K_2S (2.5 mmol), and S (6.0 mmol) was sealed under vacuum ($<10^{-3}$ Torr) in a silica tube and heated (50 °C/h) to 650 °C. The reaction mixture was kept at this temperature for 60 h, followed by cooling to room temperature at 5 °C/h. Deep blue-green crystals were recovered from the ampule (~95% yield based on Co). These crystals are moderately air stable (for a few days). EDS analysis on several crystals gave an average composition of "$K_{11.2}Co_4Sn_{4.2}S_{17.6}$". The iron compound K_{10}-$Fe_4Sn_4S_{17}$ was identified by its X-ray powder diffraction pattern.
(19) Crystal data: $K_{10}Zn_4Sn_4S_{17}$, cubic, space group $F\bar{4}3c$ (No. 219), $a = 19.923(3)$ Å, $T = 273$ K, $V = 7907.7(2)$ Å^3, $Z = 8$, R1$(F) = 0.0474$, wR2$(F^2) = 0.1155$; $K_{10}Co_4Sn_4S_{17}$, cubic, space group $P\bar{4}3m$ (No. 215), $a = 9.9332(13)$ Å, $V = 980.1(2)$ Å^3, $Z = 1$, R1$(F) = 0.0089$, wR2$(F^2) = 0.0213$; $K_{10}Mn_4Sn_4S_{17}$, cubic, space group $P\bar{4}3m$ (No. 215), 10.064(2) Å, 1019.5(4) Å^3, $Z = 1$, R1$(F) = 0.0209$, wR2$(F^2) = 0.0422$.
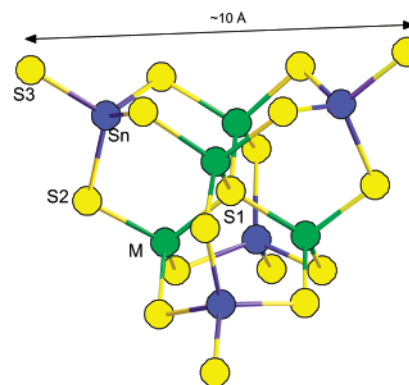
Figure 2. Structure of a single $[M_4Sn_4S_{17}]^{10-}$ cluster with labeling scheme. The two-sided arrow indicates the distance between two terminal sulfide atoms.

Table 1. Selected Bond Distances in $[M_4Sn_4S_{17}]^{10-}$ Clusters (M = Zn, Co, Mn)[a]

M	μ_4-S—M	μ_2-S—M	S_t—Sn	μ_2-S—Sn	μ_4-S—S_t
Zn	2.315(1)	2.345(4)	2.329(4)	2.407(3)	6.198(4)
Co	2.2970(10)	2.314(1)	2.329(1)	2.392(1)	6.285(2)
Mn	2.372(1)	2.419(1)	2.334(2)	2.401(1)	6.175(1)

[a] The μ_4-S—S_t distance could be considered as a "cluster radius".

quadruply bridging sulfide ion (μ_4-S) that holds together four divalent M atoms in a tetrahedral arrangement defining a $[M_4S]^{6+}$ core. This tetrahedral core is capped with four tridentate thio-stannate $[SnS_4]^{4-}$ fragments to complete the structure. Alternatively, $[M_4Sn_4S_{17}]^{10-}$ can be regarded as deriving from the fusion of four barrellane-like fragments converging to a single point which is the μ_4-S atom in the center. Three S atoms from the $[SnS_4]^{4-}$ fragments serve to bind the M^{2+} atoms in the core, while the fourth S atom remains terminal. Thus the $[M_4Sn_4S_{17}]^{10-}$ cluster which more descriptively can be expressed as $[(M_4S)(SnS_4)_4]^{10-}$ has four terminal sulfur atoms potentially available for binding to other metals or bridging other clusters. This feature makes it potentially an exciting starting precursor for linkage isomerization chemistry with a variety of metal ions. Selected bond distances for three compounds are given in Table 1. The distances from central sulfur atoms (μ_4-S) to the divalent metal centers (M = Zn, Co, Mn) in $[M_4S]^{6+}$ are the shortest (see Table 1).

The angles around M and Sn atoms are slightly distorted from the ideal tetrahedral bond angle and range from 107.9° to 111.8° and from 108.3° to 110.6°, respectively.

There are three different potassium cations in the structure. The terminal sulfur atoms are coordinated by three K1 atoms forming a pyramid around S_t with bond distances 3.080–3.110 Å. The μ_2-S atoms interact with two K1 ions, one K2 ion, and one K3 ion at distances in the range 3.23–3.65 Å. The K3 atom in $K_{10}Co_4Sn_4S_{17}$ shows a very large thermal parameter after anisotropic refinement and therefore was modeled as a split site with ~50% occupancy.

Despite its T_d point group symmetry and tetrahedral bonding topology, the $[M_4Sn_4S_{17}]^{10-}$ cluster represents a

(20) (a) Zimmermann, C.; Melullis, M.; Dehnen, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 4269. (b) Dehnen, S.; Brandmayer, M. K. *J. Am. Chem. Soc.* **2003**, *125*, 6618–6619.
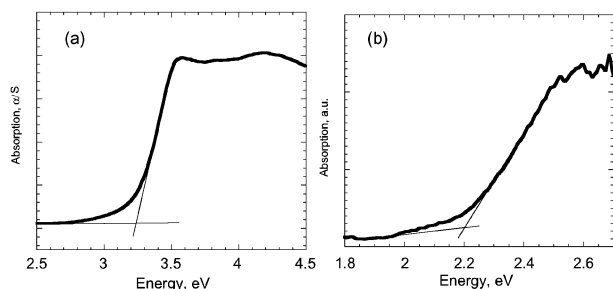
Figure 3. Solid-state optical absorption spectrum of (a) $K_{10}Zn_4Sn_4S_{17}$ (powder sample, diffuse reflectance mode) and (b) $K_{10}Mn_4Sn_4S_{17}$ (single crystal, transmission mode).

different structural motif than the adamantane-type supertetrahedral clusters found in many open framework structures. The $[M_4Sn_4S_{17}]^{10-}$ cluster is constructed from six-membered rings having only the boat conformation where the adamantoid homologues contain the chair conformation. The all-boat conformation presents terminal sulfide atoms and ensures that this cluster cannot have higher order homologues like the adamantoid homologues.[1,2] Therefore, this cluster is a "singularity" among supertetrahedral species and represents a highly attractive alternative fundamental building block for the construction of new types of extended and open framework solids. In fact the $[Zn_4Sn_4S_{17}]^{10-}$ cluster was observed earlier in the solid-state compound $K_6Sn[Zn_4Sn_4S_{17}]$ in which a Sn^{4+} center serves to link the clusters to a three-dimensional framework.[15]

The compounds reported here exhibit well-defined electronic absorption spectra in the solid state with sharp optical absorption edges associated with energy gaps of 2.3 eV for $K_{10}Mn_4Sn_4S_{17}$, 2.2 eV for $K_{10}Fe_4Sn_4S_{17}$, 1.8 eV for $K_{10}Co_4Sn_4S_{17}$, and 3.1 eV for $K_{10}Zn_4Sn_4S_{17}$ (Figure 3). Because of the molecules in these compounds, the optical absorptions are due to the local excitations between cluster molecular orbitals rather than across electron bands. They are likely due to charge-transfer transitions from filled, S-based p-orbitals and empty Sn-based or M-based orbitals. In addition absorptions that are attributed to d−d transitions (in the region 0.6−1.0 eV) are observed in the Fe and Co analogues. The presence of this high-symmetry cluster can be readily detected from the characteristic signature-like vibrations in the infrared spectrum.[21]

An important feature to highlight is that all compounds exhibit solubility in water, and even in some organic solvents such as formamide. The degree of solubility decreases as $K_{10}Co_4Sn_4S_{17} > K_{10}Fe_4Sn_4S_{17} > K_{10}Mn_4Sn_4S_{17} > K_{10}Zn_4Sn_4S_{17}$ in water, and $K_{10}Co_4Sn_4S_{17} > K_{10}Mn_4Sn_4S_{17}$ in formamide. The solubility of these molecules makes them attractive precursors for the surfactant-templated synthesis of meso-structured metal sulfides incorporating the $[M_4Sn_4S_{17}]^{10-}$ building block.[22]

Supporting Information Available: Tables of crystallographic details, atomic coordinates, bond length and angles, and anisotropic thermal parameters for all compounds. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

(21) Infrared spectroscopy: All three compounds display relatively similar far-IR spectra, due to the similar crystal structure, but the spectra are complicated by the numerous possible vibrational modes of the polyatomic species. FT-IR spectra were recorded as pressed CsI pellets with a Nicolet 740 FT spectrometer in 4 cm^{-1} resolution. For $K_{10}Zn_4Sn_4S_{17}$, absorption frequencies are 418.1 (s), 392.9 (w, m), 373.3 (s), 351.8 (s), 326.7 (m), 303.4 (s), 279.1 (s), 253.9 (m); for $K_{10}Co_4Sn_4S_{17}$, 418.1 (s), 389.2 (w, m), 367.7 (s), 352.8 (s), 326.9 (s), 301.5 (m), 281 (m, w), 254.8 (m); for $K_{10}Mn_4Sn_4S_{17}$, 419.0 (s), 394.7 (w, m), 369.6 (s, w), 355.4 (s), 326.6 (m), 302.4 (m), 285 (m), 253.7 (m); (s) strong, (m) medium, (w) wide.
(22) Trikalitis, P.; Palchik, O.; Kerr, T.; Kanatzidis, M. G. Manuscript in preparation.