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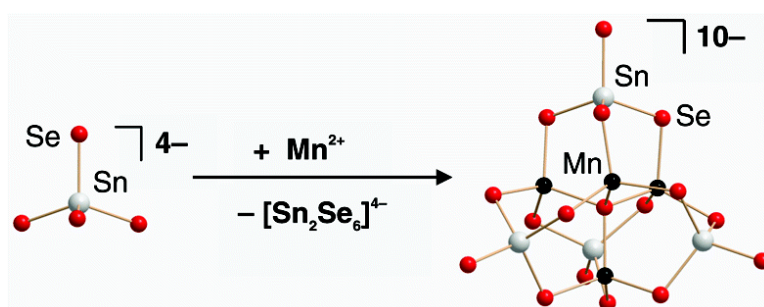
Reactivity of Chalcogenostannate Compounds: Syntheses, Crystal Structures, and Electronic Properties of Novel Compounds Containing Discrete Ternary Anions [M(□-Se)(SnSe)] (M = Zn, Mn)

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Reactivity of Chalcogenostannate Compounds: Syntheses, Crystal Structures, and Electronic Properties of Novel Compounds Containing Discrete Ternary Anions [$M^{II}_4(\mu_4$-Se)(SnSe$_4)_4$]$^{10-}$ (M^{II} = Zn, Mn)

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The synthesis of compounds that contain ternary substructures M/E′/E (M = transition metal, E′ = group 14 or 15 element, E = S, Se, Te) is a field of still increasing research activity.[1−3] In addition to a range of coordination compounds, from [PPh$_4$]$_4$[E′$_2$(ME$_4$)$_4$] (E′ = Sn, M = W, E = S,[4] or E′ = Sn, Pb; M = W, Mo; E = Se[5]) to organometallic species such as [(CO)$_6$Fe$_2$(Sb$_2$S$_6$)][SbS$_6$]$_2$·2SO$_2$[6] or [(PhSnS$_3$)$_2$(CuPPhMe$_2$)$_6$],[7] several ternary or quaternary phases also attracted attention owing to novel structural, optoelectronic or magnetic properties;[8−12] examples are [Co(en)$_3$][CoSb$_4$S$_8$],[8] Rb$_3$[AgGe$_4$Se$_{10}$]·2H$_2$O[9] or [NMe$_4$]$_2$[MnGe$_4$Se$_{10}$].[10] Some of these solids exhibit open framework structures of M/E′/E polymers, others might be viewed as substituted group 14 chalcogenides. The combination of E′/E and M/E units affects optoelectronic features, resulting in, for instance, narrow band gaps and intense photoluminescence. Moreover, linkage of paramagnetic and diamagnetic metal atoms via chalcogenide ligands can produce unusual magnetic behavior, as observed in K$_2$[MnSnS$_4$].[11] Recently, a number of mesoporous solids with M/E′/E substructures were reported that have been generated by surfactant-templated syntheses.[13−15] These reactions were the first successfully to use chalcogenotetrelate salts A$_4$[E′E$_4$],[13] A$_4$[E′$_2$E$_6$],[14] or A$_4$[E′$_4$E$_{10}$][15] (A = Na, K; E′ = Ge, Sn; E = S, Se) as synthons.

In the course of studying the reactivity of chalcogenostannate anions,[16−18] we recently isolated a novel type of quaternary A/M/E′/E compound, [K$_{22}$(H$_2$O)$_7$(MeOH)$_{18}$][SnSe$_4$]$_3$[Co$_4$(μ_4-Se)(SnSe$_4$)$_4$] (**1**).[19] **1** contains the first known discrete ternary M/E′/E anion (E′ = tetrel) besides those of the "pioneer" compounds.[4,5] However, further experiments to explore the electronic or magnetic properties of **1** for comparison with the related polymers were yet not possible, due to very low yields and immediate decomposition of the black crystals upon redissolution. Variation of reactants and reaction conditions has now enabled the isolation of novel compounds in higher yields that contain Mn^{II} or Zn^{II} as transition metal centers and crystallize without additional [SnSe$_4$]$^{4-}$ anions: [K$_{10}$(H$_2$O)$_{16}$(MeOH)$_{0.5}$][M$_4$(μ_4-Se)(SnSe$_4$)$_4$] (M = Zn, **2**; Mn, **3**; Scheme 1).
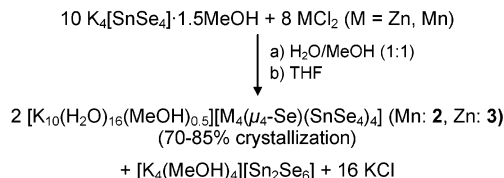
In the formation of the ternary units, [SnSe$_4$]$^{4-}$ anions of the reactant act both as tridentate ligands and as Se^{2-} donors, the latter leading to the generation of [SnSe$_3$]$_2^{4-}$ = [Sn$_2$Se$_6$]$^{4-}$ as coproduct.

The isotypic compounds **2** and **3** were unambiguously characterized by single-crystal X-ray diffraction.[20] The highly charged, ternary anions in **2** and **3**, [M$_4$Sn$_4$Se$_{17}$]$^{10-}$ (M = Zn, Mn), are topologically related to that in **1**, and thus to a series of binary [M$_8$E$_{17}$] clusters (M = Cd, Zn; E = S, Se, Te)[21−24] that are, however, always coated by covalently bound ligands. In contrast to **1** and the cited binary clusters, the Zn/Sn/Se or Mn/Sn/Se anions in **2** and **3** show a significant distortion from idealized T_d symmetry that leads to chiral molecules (C_2 site symmetry) and chiral crystals. Depending on the individual crystal selected for the X-ray measurement, space groups are $P4_32_12$ or $P4_12_12$ without significant racemic
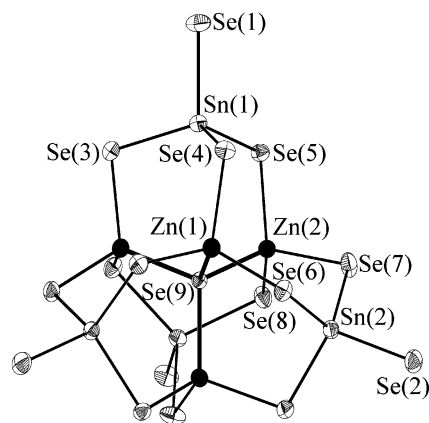
Figure 1. Structure of the ternary anion observed in **2**. Thermal ellipsoids are drawn to 50% probability.

Scheme 1. Synthesis of **2** and **3**

$$10\ K_4[SnSe_4]\cdot 1.5MeOH + 8\ MCl_2\ (M = Zn, Mn)$$

a) H$_2$O/MeOH (1:1)
b) THF

$$2\ [K_{10}(H_2O)_{16}(MeOH)_{0.5}][M_4(\mu_4\text{-Se})(SnSe_4)_4]\ (Mn:\ \textbf{2},\ Zn:\ \textbf{3})$$
(70−85% crystallization)

$$+\ [K_4(MeOH)_4][Sn_2Se_6] + 16\ KCl$$

twinning (Flack parameters are 0.01(3) maximum). The structure of the ternary anion in **2** is shown in Figure 1 as an example.

The anionic substructures of **2** and **3** are based on four barrelane-type cages [M$_3$Se$_4$Sn] (M = Zn, Mn) that are formally condensed by sharing a central [SeM$_4$] unit. Four additional selenide ligands form the corners of a large tetrahedron with Se···Se edges of 10.580(1)−10.712(1) Å in **2** or 10.714(1)−10.863(1) Å in **3**. Chirality of the molecules is induced by formal rotation of the [SnSe$_4$] "caps" of the terminally Se-ligated barrelane cages by about 13−20° around the Sn(1)···Se(9) or Sn(2)···Se(9) axes, each in the same rotational sense within one enantiomer (13.99(3)− 17.35(3)° in **2**, 13.55(2)−19.95(3)° in **3**).

The ternary anions are separated by a complex counterion aggregation of H$_2$O or MeOH coordinated K$^+$ cations that interact with the M/Sn/Se clusters via Se···K contacts.

2 and **3** belong to the rare examples of polynuclear manganese or zinc complexes that are exclusively bridged by "inorganic" selenide ligands. Most of the Zn/Se or Mn/Se complexes reported until now, including the above mentioned [Zn$_8$(μ_4-Se)(SePh)$_{12}$Cl$_4$]$^{2-}$ cluster,[21] are sterically stabilized by organic groups. The most closely related compounds are still the Mn/E/Se species (CP)$_2$-[MnSnSe$_4$] (CP = cetylpyridinium),[13] [Mn(en)$_3$]$_2$[Mn$_4$(en)$_9$(SbSe$_4$)$_4$]· 2H$_2$O[12] or the Mn/Ge/Se polymer quoted at the outset.[10]
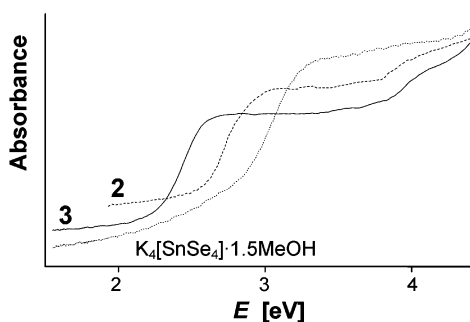
Figure 2. Solid-state UV−vis spectra of **2** (dashed line), **3** (solid line), and the reactant $K_4[SnSe_4] \cdot 1.5MeOH$ (dotted line), recorded as suspensions in Nujol.

To gain insight in the optoelectronic properties of **2** and **3**, we recorded UV−vis spectra of the quaternary compounds **2** or **3**, and of the starting material $K_4[SnSe_4] \cdot 1.5MeOH$ (Figure 2).

An onset of absorption is observed at $E = 2.57$ eV (482 nm, **2**) and $E = 2.27$ eV (546 nm, **3**) which we assign to the energy differences of the lowest electronic excitation within the compounds. Absorption plateaus are reached at 2.90 eV (428 nm, **2**) or 2.56 eV (484 nm, **3**), consistent with the colors of the respective reaction solutions and crystals (**2**: yellow, **3**: orange).

A comparison to the starting material $K_4[SnSe_4] \cdot 1.5MeOH$, $E = 2.77$ eV, illustrates the decrease of the excitation energy upon substitution of $[SeM_4]$ units for solvated K^+ ions and thereby linkage of previously well-separated $[SnSe_4]$ tetrahedra by transition metal centers. The energy values that correspond to the lowest electronic excitations of **2** and **3** are similar to E_g of the topologically related binary phases (ZnSe: 2.7 eV,[25] MnSe: 2.5 eV[26]), although the $[(\mu_4\text{-}Se)M_4(\mu_2\text{-}Se)_{12}]$ cores of **2** (M = Zn) or **3** (M = Mn) represent only small (distorted) fragments of the Wurtzite-type topology of ZnSe or γ-MnSe.

The only known compounds that feature $[SnSe_4]^{4-}$ coordinated Zn or Mn atoms are the mesoporous solids $(CP)_{4-2x}[M_xSnSe_4]$ (CP = cetylpyridinium; M = Zn, Mn; $x = 1.0-1.3$),[13] with optical gaps of 2.5 eV (M = Zn) or 2.0 eV (M = Mn). Clearly, both the incorporation of surfactant micelles in a three-dimensional network and the separation of ternary cluster molecules by solvated K^+ ions have a similar effect on the optical behavior of M/E′/E aggregates.

First ESR experiments of **3** showed distinct paramagnetism, indicating free electrons ($g \approx 2.0$) without spin−orbit coupling at the Mn^{II} centers.[27] This agrees with the d^5 configuration of Mn^{II} ($L = 0$). Hence, coupling and thus quenching of spins via the central Se ligand was not observed, giving rise to a high-spin ground state with an expected total spin of $S = 10$. Quantum chemical investigations of the ternary anions $[M_4Sn_4Se_{17}]^{10-}$ (M = Zn, Mn), employing density functional theory (DFT) methods and provision of mirror charges, confirm this: while the Zn/Sn/Se cluster anion represents a closed-shell situation even by using the unrestricted Kohn−Sham (UKS) modus, 20 unpaired electrons are calculated for the ground state of the Mn/Sn/Se species. A Mullikan population analysis of the spin density reveals five spins per Mn center. The corresponding energy gaps are calculated to 2.46 eV for M = Zn or 1.24 eV for M = Mn (DFT models typically underestimate E_g).

Future investigations will focus on the magnetism of **3**, and on the synthesis of further compounds by the described method.

Supporting Information Available: Crystallographic and refinement details, experimental details, methods of spectroscopy and DFT calculations (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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