

Heterobimetallic Chalcogenidometallate Strands: Synthesis, Structure, Magnetism, and Conductivity

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Supporting Information

ABSTRACT: Two salts with one-dimensional, Si₂-type telluridostannate chain anions {[MSnTe₄]²⁻]_n, Rb₂[HgSnTe₄] (2) and (NMe₄)₂[MnSnTe₄] (3), were prepared by the reactions of [SnTe₄]⁴⁻ anions with Hg²⁺ or Mn²⁺ ions in solution. We present the crystal structures of 2 and 3, as well as the magnetic properties of the previously reported Cs⁺ analogue Cs₂[MnSnTe₄] (1).

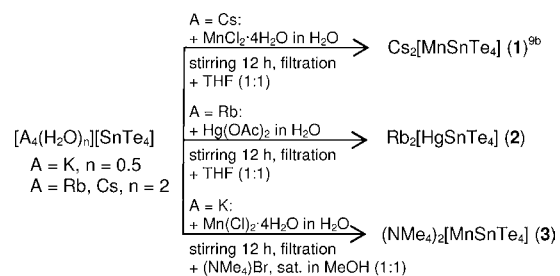
The search for metal chalcogenide based phases with certain structures still represents a great challenge for inorganic and material chemists.¹ One approach is the formation of transition-metal complexes of chalcogenido metallate anions, which show a large variety of structural arrangements depending on the elemental combination and synthesis method. Solid-state syntheses, such as high-temperature synthesis, polychalcogenide flux techniques, or solvothermal methods, tend to result in extended structures of the ternary anions in the quaternary phases. These materials display one-dimensional (1D) arrays as in K₂[Ag₂SnTe₄],^{2a} [Mn(en)₃][CdSnTe₄],^{2b} K₂[HgSnTe₄],^{2c} K₂[Ag₂Sn₂Se₆],^{2d} or K₂[MnSn₂Se₆],^{2e} two-dimensional (2D) layered structures as in K₂[MnSnSe₄]^{3a} or Cs₂[Hg₃Sn₂S₈],^{3b} or three-dimensional (3D) open frameworks as in [Zn₄Sn₃Se₁₃]⁶⁻,^{4a} or Rb₃(AlSe₂)₃(GeSe₂)₇.^{4b} Molecular clusters, like [M₄T₄S₁₇]¹⁰⁻ (M = Mn, Fe, Co, Zn; T = Ge, Sn), are still relatively rare.^{5a,b}

The situation is inverse when using the mild coordinating chemical approach:^{5c} reactions of [T_xE_y]^{q-} anions with transition-metal ions in protic solution at ambient conditions produce molecular anions in most cases. It was possible to isolate a large variety of compounds with ligand-free, ternary anions [M₄Sn₄E₁₇]¹⁰⁻ (M = Mn, Co, Zn, Cd, Hg; E = S, Se, Te), [M₅Sn₅E₁₇]¹⁰⁻ (M = Co, Zn; E = S, Se), or [Mn₆Ge₄Se₁₇]¹⁰⁻.⁶ So far with this approach, only a few compounds with extended ternary anions have been isolated. These are salts of the 3D anionic frameworks {[M₄Sn₃E₁₃]⁶⁻]_n (M = Zn, Cd, Hg; E = Se, Te)^{4a,6a,d,7} or {[MT₄Se₁₀]²⁻]_n (M = Mn, Fe; T = Ge, Sn),⁸ the 2D layered anion {[Mn₆(H₂O)₃Ge₄Se₁₇]⁶⁻]_n^{9a} or 1D strands {[MSnE₄]²⁻]_n (M = Mn, Hg; E = Se, Te).^{2c,7,9b} The latter are unique in terms of

the absence of crystal solvent in the respective salts A₂[MSnE₄] in spite of synthesis in solution.

Here, we report further investigations on this exceptional type of compound regarding the higher-yield synthesis of Cs₂[MnSnTe₄] (1)^{9b} by use of a different reactant, [Cs₄(H₂O)₂][SnTe₄] (see the Supporting Information), the generation of new salts, Rb₂[HgSnTe₄] (2) and (NMe₄)₂[MnSnTe₄] (3), as well as investigations of the magnetic and conductivity properties of the open-shell compound 1. Scheme 1 depicts the syntheses of 1–3, and Figure 1 shows photographs of the manganese compounds 1 and 3.

Scheme 1. Syntheses of Compounds 1–3 by the Reaction of Chalcogenidostannates [A₄(H₂O)_n][SnTe₄] with M²⁺



The three compounds crystallize in different space groups: orthorhombic (*Fddd*, 1), tetragonal (*I4̄*, 2), or monoclinic (*C2/c*, 3). All structures have been determined based on single-crystal structure analyses. Figure 2 shows fragments of the crystal structures of novel phases 2 and 3, Figure 3 depicts a part of one ternary anionic strand. As in 1, the 1D anions are arranged as parallel chains that follow the crystallographic *c* (2) or *b* (3) axis, respectively. They are separated and stabilized by the counterions Rb⁺ in 2 and (NMe₄)⁺ in 3. Each Rb⁺ ion is coordinated by eight telluride ligands of the anions in a distorted square-antiprismatic manner (Figure S1 in the Supporting Information), as was already observed in the structure of the K₂[HgSnTe₄]^{6a} homologue (space group

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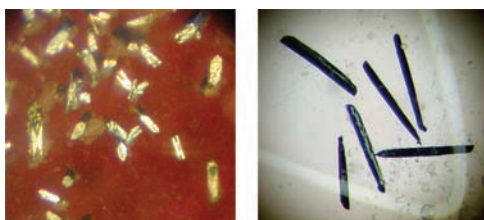


Figure 1. Photographs of crystals of the manganese compounds **1** (left) and **3** (right).

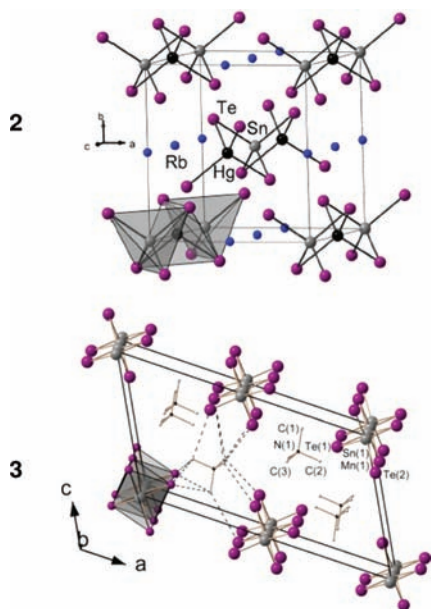


Figure 2. Fragments of the crystal structures of **2** and **3**.



Figure 3. Representation of part of one ternary anionic strand $[\text{MSnTe}_4]^{2-}$, shown for $[\text{HgSnTe}_4]^{2-}$ as an example.

$\bar{1}42m$). In **3**, a better refinement of the single-crystal structure analyses is obtained by distributing the Mn and Sn atoms statistically along the chain, as for some of the reported analogues like $\text{K}_2[\text{HgSnTe}_4]$ (space group $I4/mcm$) or $(\text{NEt}_4)_2[\text{HgSnTe}_4]$ (space group $P4_2/mnm$).^{2c}

In **3**, the $(\text{NMe}_4)^+$ counterions interact via hydrogen bridges with tellurium ligands of the anions. This compound is the second one containing ammonium ions for stabilization of 1D ternary anions besides $(\text{NEt}_4)_2[\text{HgSnTe}_4]$ prepared by the treatment and ion exchange of $\text{K}_2[\text{HgSnTe}_4]$ with $\text{NEt}_4\text{I/en}$.^{2c} As in these phases, the ammonium salt **3** underwent a symmetry reduction with comparison to the related alkali-metal salts $\text{K}_2[\text{HgSnSe}_4]$,⁷ $\text{K}_2[\text{HgSnTe}_4]$,^{2c} **1**,^{9b} and **2**.

The magnetism of compounds with 1D coordination polymers of a heterobimetallic SiS_2 structure type, is unknown yet. By the synthesis of **1** in suitable yields, it was possible to investigate the magnetic behavior of the $\dots\text{Mn}^{\text{II}}[(\mu\text{-Te})_2\text{Sn}(\mu\text{-Te})_2]\text{Mn}^{\text{II}}\dots$ chain via direct-current (dc) susceptibility measurement using a SQUID magnetometer. Figure 4 gives the temperature dependence of the magnetic susceptibility (χ defined as M/H per mole of the Mn site) and the χT product for **1** at 1000 Oe.

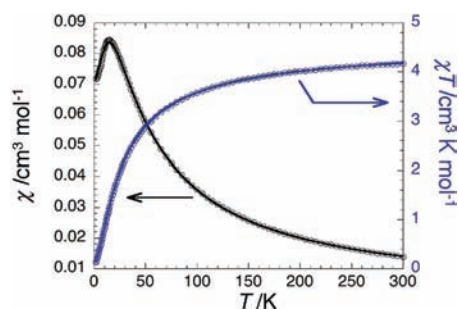


Figure 4. Temperature dependence of the magnetic susceptibility, χ , of **1** at 1000 Oe. The plots show the experimental data of χ versus T and χT versus T (open circles) and the best fits described in the text (lines).

Compound **1** is paramagnetic, following roughly a Curie–Weiss law down to 35 K [$C = 4.7(1) \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -32(1) \text{ K}$]. The Curie constant indicates that the $S = 5/2 \text{ Mn}^{\text{II}}$ spin is well present. The Weiss constant reveals the presence of weak antiferromagnetic interactions between the magnetic centers. On the basis of the 1D structure of the ternary coordination polymer, a Heisenberg chain model of classical $S = 5/2$ spins ($H = -2J \sum S_i S_{i+1}$)¹⁰ was used to model the data and to estimate the intrachain magnetic interaction between Mn^{II} spins through a $[\text{SnTe}_4]$ bridge. The least-squares fitting of both χ versus T and χT versus T data led to an excellent agreement with the experiment, with $J_{\text{Mn-Mn}}/k_B = -1.88(1) \text{ K}$ and $g = 1.99(5)$, which is in good agreement with the values usually found for Mn^{II} ions.

Another open question concerns the conductivity properties of these types of compounds. Infinite strands of (semi)metal atoms, on the one hand, and lined cations, on the other hand, would allow for two possible conductivity processes, in principle, electronic conductivity, with all variants, and ionic conductivity. Therefore, impedance spectroscopic measurements on a pellet of single crystals of **1** were performed. From the frequency-dependent complex impedance of sample **1**, $Z(\nu) = Z'(\nu) + iZ''(\nu)$, the real part of the conductivity $\sigma'(\nu)$ was calculated according to eq 1.

$$\sigma'(\nu) = \frac{d}{A} \frac{Z'(\nu)}{[Z'(\nu)]^2 + [Z''(\nu)]^2} \quad (1)$$

Here, d and A denote the thickness and area of the sample, respectively. The $\sigma'(\nu)$ spectra were characterized by low-frequency plateaux. In this plateau regime, the conductivity is identical with the bulk dc conductivity σ_{dc} reflecting long-range charge transport in the sample. In Figure 5, we show an Arrhenius plot of σ_{dc} .

At room temperature, we find $\sigma_{\text{dc}} \approx 3 \times 10^{-5} \text{ S cm}^{-1}$, i.e., relatively fast charge transport. Furthermore, the Arrhenius data are characterized by a relatively strong curvature with an

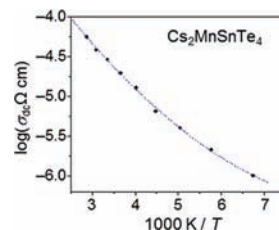


Figure 5. Arrhenius plot of the dc conductivity, σ_{dc} , of **1**.

apparent activation energy decreasing with decreasing temperature to 148 K. This is indicative of charge transport due to polaronic hopping, i.e., hopping of localized electrons, e.g., between transition-metal centers in different valence states,^{11–13} and accords with the relatively small optical absorption energy of 1.51 eV (Figure S2 in the Supporting Information). In contrast, ion hopping in solid materials manifests usually in an Arrhenius-type temperature dependence of the dc conductivity.¹¹ At ambient and subambient temperatures, polaronic transport in solids can often be described by a variable-range hopping approach. In the case of 3D hopping, the conductivity data follow Mott's $T^{-1/4}$ law (eq 2).¹²

$$\sigma_{\text{dc}} = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (2)$$

In Figure 6, $\log \sigma_{\text{dc}}$ is plotted versus $(1/T)^{1/4}$. The data do, indeed, lie on a straight line, showing that Mott's law is valid.

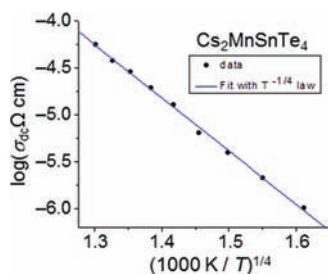


Figure 6. Fit of the dc conductivity of **1** with Mott's $T^{-1/4}$ law.

From the fit, we obtain $T_0 = 2.9 \times 10^7$ K. These results provide a strong indication that the charge transport in $\text{Cs}_2[\text{MnSeTe}_4]$ can be described as 3D polaron hopping. The origin of this conductivity is not clear yet because the valence of the Mn centers seems to be well-defined and localized, as shown by the magnetic properties of **1**. Nevertheless, a small but significant mixed valency on the Mn sites (compensated for by vacancies on the Cs sites) might be relevant for the polaron hopping process, while it might not be detectable by magnetic measurements. Conductivity measurements on single crystals of **3** has not produced reproducible results so far, possibly because of contact problems.

In summary, a hetero(semi)metallic combination of elements, namely, Cs, Mn, Sn, and Te, within a chalcogenidotetrelate phase can produce extended nonionic charge transport. Besides the syntheses of two novel salts with 1D telluridostannate anions $\{[\text{MSnTe}_4]^{2-}\}_n$ ($M = \text{Mn, Hg}$), we have reported the observation of charge transport due to polaron hopping, as well as antiferromagnetic coupling of the transition-metal centers in **1**.

■ ASSOCIATED CONTENT

Supporting Information

Details of experimental techniques and crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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