

Synthesis and structure of $\text{KIn}(\text{en})_2\text{SnTe}_4 \cdot 1.5\text{en}$ containing a mixed-metal one-dimensional chain

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The linkage of a coordination compound, $\text{cis-}[\text{In}(\text{en})_2\text{Te}_2]$, and a Zintl anion, $[\text{SnTe}_4]$, into a one-dimensional chain by sharing Te atoms is observed for the first time in the title compound.

Two decades ago, attempts to synthesize the low-dimensional transition-metal chalcogenide complexes that incorporated $[\text{ME}_4]^{n-}$ (M = transition or post-transition metal; E = S, Se) ligands and ethylenediamine (en) were conducted mainly to study the varied degree of the coordinating ability of the ligands and how these ligands affected the overall structure.^{1,2} Based on these studies, it was proposed that these chalcogenide complexes might have low-dimensional structures. Recently, several ternary transition and post-transition metal sulfides and selenides, using, for example, $[\text{As}_x\text{E}_y]^{n-}$ (E = S, Se) as ligands in the construction of low-dimensional structures, were successfully synthesized, by using solvothermal synthesis, and structurally characterized.^{3–5} The non-traditional solvothermal technique has been shown to be an efficient synthetic

technique to obtain new materials with unusual structures which are not accessible by using more common synthetic methods. While the research has been mostly concentrated on the ternary sulfides and selenides, the ternary telluride systems are relatively unexplored. In the telluride system, an early study showed that the one-dimensional chain structures can also be built up by the incorporation of the $[\text{ATe}_4]^{4-}$ (A = Ge, Sn) building blocks in $\text{K}_2\text{HgSnTe}_4$, $(\text{NEt}_4)_2\text{HgSnTe}_4$ and $(\text{PPh}_4)\text{In-GeTe}_4$.⁶ The structures of these ternary tellurides are substitutional variants of the one-dimensional chain compound NaInTe_2 .⁷ During our investigation of the ternary In–Sn–Te system using solvothermal synthesis in ethylenediamine, we have discovered a new compound, $\text{KIn}(\text{en})_2\text{SnTe}_4 \cdot 1.5\text{en}$, which also uses $[\text{SnTe}_4]^{4-}$ as a building block to construct a new one-dimensional chain structure.

The telluride $\text{KIn}(\text{en})_2\text{SnTe}_4 \cdot 1.5\text{en}$ was synthesized by mixing 0.3 g of K_2Te , SnTe , In_2Te_3 and Te in a mole ratio of 1 : 2 : 0.5 : 1.5 with 1 ml of ethylenediamine in an evacuated Pyrex tube (*ca.* 10 ml). The reaction tubes were heated to

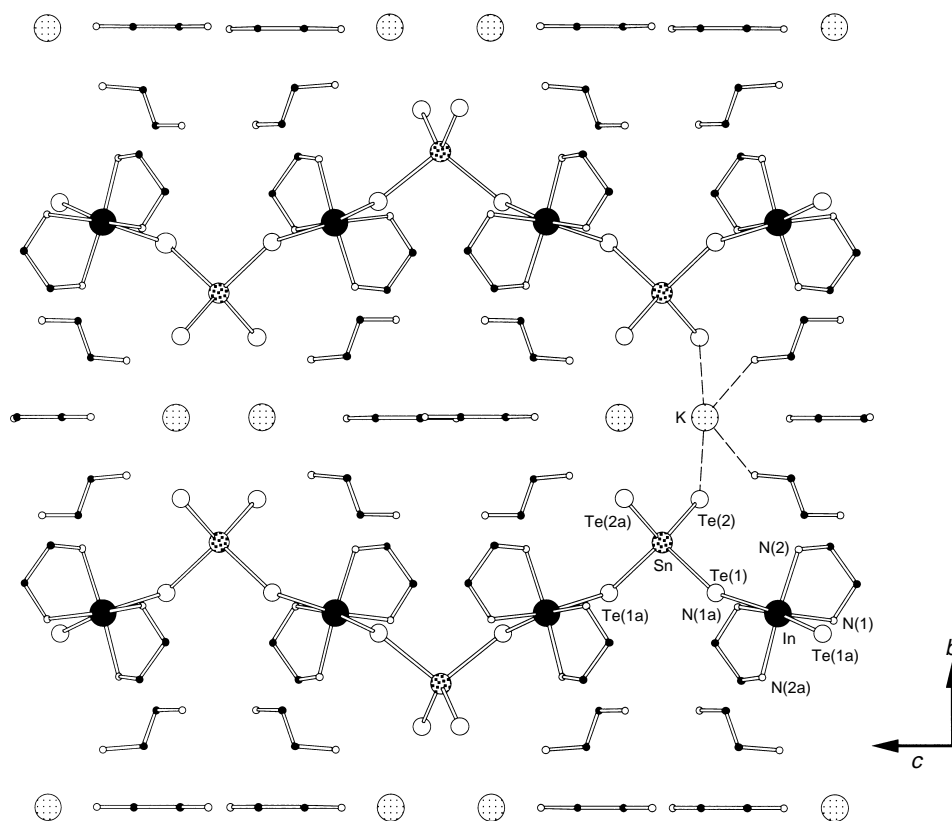


Fig. 1 One-dimensional chain structure of the $[\text{In}(\text{en})_2\text{SnTe}_4]^{1-}$ anion approximately projected onto the bc plane. The anionic chain consists of a corner-sharing of alternating $\text{cis-}[\text{In}(\text{en})_2\text{Te}_2]$ octahedra and $[\text{SnTe}_4]$ tetrahedra. The close contacts between the K and both Te and N atoms are shown as dashed lines. Some selected bond distances (Å) and angles ($^\circ$): Sn–Te(1)/Te(1a), 2.766(2), Sn–Te(2)/Te(2a), 2.691(2), In–Te(1)/Te(1a), 2.827(2), In–N(1)/N(1a), 2.35(1), In–N(2)/N(2a), 2.28(2), Te(1)–Sn–Te(1a), 104.89(9), Te(1)–Sn–Te(2), 110.64(5), Te(1)–Sn–Te(2a), 107.60(5), Te(2)–Sn–Te(2a), 115.0(1), Sn–Te(1)–In, 109.07(5), Te(1)–In–Te(1a), 85.32(7), Te(1)–In–N(1a), 94.2(4), Te(1)–In–N(1), 171.3(4), N(1)–In–N(1a), 87.6(7), N(1)–In–N(2), 75.5(5), N(1)–In–N(2a), 86.2(5), N(2)–In–N(2a), 154.6(8).

150 °C for 12 h and maintained at 150 °C for 3 days followed by cooling to room temp. at a rate of 10 °C h⁻¹. Dark red, cube-like crystals of KIn(en)₂SnTe₄·1.5en were isolated and separated from by-products in ca. 60% yield. Energy dispersive X-ray analysis on selected crystals gave an approximate ratio of 1 : 1 : 1 : 4.3 for K, In, Sn and Te atoms. KIn(en)₂SnTe₄·1.5en can also be successfully synthesized by using the extraction method on an alloy with an exact composition of KInSnTe₄, prepared from the fusion of KIn, Sn and Te in stoichiometric proportions. One gram of the alloy was extracted by dissolving it in 10 ml of ethylenediamine. After three weeks, KIn(en)₂SnTe₄·1.5en was obtained in the container which contained the KInSnTe₄ sludge, and the product of the red-brown extract turned out to be only KInTe₂·2en.⁸ These results also demonstrate one of the advantages of solventothermal synthesis in that it can accelerate the reaction toward the product formation.

While (PPh₄)InGeTe₄⁶ adopts a one-dimensional chain structure which is composed of alternating [InTe₄] and [GeTe₄] tetrahedra, the structure[‡] of KIn(en)₂SnTe₄·1.5en, which is not isostructural with (PPh₄)InGeTe₄, is also built up from a one-dimensional chain with alternating [In(en)₂Te₂] octahedra and [SnTe₄] tetrahedra instead (Fig. 1). In the structure of KIn(en)₂SnTe₄·1.5en, the In atom lies a twofold axis and is coordinated by two ethylenediamine and two Te atoms forming a distorted *cis*-[In(en)₂Te₂] octahedron. The In-Te distances [2.827(2) Å] are comparable to those of the one-dimensional chain compound, Na₅In₂Te₆, (2.706–2.853 Å),⁹ and are significantly longer than those in (PPh₄)InGeTe₄ [2.686(2) Å].⁶ In the *cis*-[In(en)₂Te₂] octahedron, the *trans* In-N(2) distances are slightly shorter than the *cis* In-N(1) distances, but neither is very different from those observed in the nitrogen-ligated complexes.¹⁰ The Sn atom lies on a twofold axis and is bound to four Te atoms, forming a slightly distorted [SnTe₄] tetrahedron which shares two Te atoms with the neighboring *cis*-[In(en)₂Te₂] octahedra. The terminal Sn-Te bond distances [2.691(2) Å] are slightly shorter than those of the shared ones [2.766(2) Å] and are close to those observed in dimeric species, (NMe₄)₄Sn₂Te₆¹¹ and Cs₄Sn₂Te₇.¹² The *cis*-[In(en)₂Te₂] octahedra and [SnTe₄] tetrahedra then share two Te corners in the construction of the unusual one-dimensional [In(en)₂SnTe₄]-chain propagating along the *c* axis. There is only one crystallographically unique K⁺ ion, located near the Te(2) atoms, that has close contact with four terminal Te(2) atoms (3.90–4.00 Å) and two N atoms [2.70(3) Å] from the ethylenediamine. A similar strong interaction between the K and the N atoms has been observed in (PPh₄)₂[K₂Au₄Te₄(en)₄]¹³ and K₆In₂Te₆·4en.¹⁴ In Fig. 1, the unbound ethylenediamines are located in a large cavity (ca. 12 Å diameter across the K⁺ ions), created by the surrounding K⁺ ions, *cis*-[In(en)₂Te₂] octahedra and [SnTe₄] tetrahedra. Although the X-ray crystallography can not discern the difference between In and Sn atoms, the assignment of each atom in a specific position can be empirically confirmed by the use of bond valence sum calculations.¹⁵ The bond valence sum calculation for In³⁺ and Sn⁴⁺ ions in KIn(en)₂SnTe₄·1.5en, based on the structure mentioned above, results in the respective sums of 3.16 and 4.09.¹⁶ When the In and Sn atoms are exchanged, the results are 3.62 and 3.53 for In³⁺ and Sn⁴⁺ ions, respectively. Thus, the results obtained from the bond valence

sum calculation favor the assignment of the *cis*-[In³⁺(en)₂Te₂] octahedron and the [Sn⁴⁺Te₄] tetrahedron.

KIn(en)₂SnTe₄·1.5en represents the first example using both a Zintl anion, [SnTe₄], and a coordination compound, *cis*-[In(en)₂Te₂], in the construction of a one-dimensional chain compound. Recently, a similar strategy using the *cis*-octahedral units, incorporated with either tetrahedral or octahedral units, in the formation of the heteroatomic one-dimensional chain structures was reported in transition-metal hydroxo-complexes.¹⁷ The investigation on the post-transition metal systems, based on this strategy, may lead to the discovery of new materials with unusual structures and properties.

Footnotes and References

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‡ Crystal data for KIn(en)₂SnTe₄·1.5en: orthorhombic, space group *Cmca* (no. 64), *a* = 26.069(8), *b* = 15.278(4), *c* = 14.972(4) Å, *U* = 5962(2) Å³, *Z* = 8, *D_c* = 2.432 g cm⁻³, *μ*(Mo-Kα) = 56.04 cm⁻¹. 2922 unique reflections were collected at 273 K of which 1601 had *I* ≥ 3σ(*I*). An empirical absorption correction was applied. The structure was solved by direct methods and refined by the teXsan crystallographic software package of Molecular Structure Corporation to a final *R* = 0.044 (*R_w* = 0.060). All K, In, Sn and Te atoms were refined anisotropically. The carbon and nitrogen atoms of two ethylenediamines were refined isotropically while those of the third ethylenediamine, located on special positions, were fixed. The hydrogen atoms were calculated but not refined. Although the isotropic thermal parameter of K⁺ ion is about four times larger than those of Te atoms, the refinement of a disordered model for splitting the K⁺ ion was unsuccessful. However, the occupancy factor of the K⁺ ion was refined and is close to unity. CCDC 182/540.

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