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A Novel Ternary Zintl Anion: Synthesis and Structural Characterization of the $[Cu_4SbTe_{12}]^{3-}$ Anion

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The chemistry of soluble chalcogenide and polychalcogenide complexes has become an increasingly active area of research during the last decade. This is primarily due to the large number of different structural types accessible, which is accentuated by the varying degrees of catenation and bonding modes of the polychalcogenides[1-3] as well as their ability to provide precursors for both the room temperature preparation of novel thin films[4-6] and conducting solids.[7,8] In contrast to the very large number of polysulfide- and polyselenide-based materials, the chemistry of the polytellurides has not been as extensively developed. While most of these polychalcogenide compounds were prepared by more familiar solution-phase syntheses[1] or crystallization from polychalcogenide fluxes,[2] we have focused on the preparation of heteropolyatomic tellurium anions utilizing the methods originally employed by Zintl[9] to generate, but not necessarily to isolate, these materials. One method is the cathodic dissolution of alloy electrodes to produce such tellurides as $Au_3Te_4^{3-}$,[10] $Sb_9Te_6^{4-}$,[11] $Sb_4Te_4^{4-}$,[11] and $GaTe_2(en)_2^{1-}$ [12] as well as other indium, arsenic, and tin tellurides.[13] The other main route to these polyanions, the solvent extraction of intermetallic alloys composed primarily of alkali, main group, and posttransition metals, has produced a variety of telluride clusters such as $Au_2Te_4^{2-}$,[14] $Au_4Te_4^{4-}$,[15] $KAu_9Te_7^{4-}$,[15] $Hg_4Te_{12}^{4-}$,[16] $Hg_2Te_5^{2-}$,[16] $As_{10}Te_3^{2-}$,[17] and others like As_{22}^{4-} [18] and $SnAs_{14}^{4-}$.[18] Extension of this extractive method to quaternary intermetallic materials containing alkali, transition and two main-group metals has led to the isolation and structural characterization of the novel ternary polytelluride $(Et_4N)_3Cu_4SbTe_{12}$ (**1**). Whereas isolated ternary, mixed calcogenide, polysulfide, and polyselenide anionic clusters are known, for example $MoOS_8^{2-}$,[19] $Mo_2O_2S_7^{2-}$,[19] and $W_3OSe_8^{2-}$,[19] to the best of our knowledge, compound **1** represents the first example of a discrete ternary polytelluride anion.

Telluride **1** was synthesized by extracting 0.200 g of an alloy of nominal composition of $KCuSbTe_3$,[20] prepared from the fusion of K_2Te, Cu, Sb_2Te_3, and Te powders in the appropriate molar ratios in quartz tubes under N_2, with 10 mL of ethylenediamine (en) that had been previously dried by distillation from a red solution of K_4Sn_9. The brown extract was filtered and layered with a solution of 0.100 g of Et_4NBr in 10 mL of en which, after 4 days, gave a 13% yield (based on Cu) of **1** as small, dark red crystals insoluble in most common organic solvents. A quantitative analysis of a large number of these crystals in an electron microscope by energy dispersive X-ray analysis gave an average composition of $Cu_4Sb_{0.8}Te_{12.4}$. The composition of the alloy seems to be crucial for the formation of the title compound, as the extraction of the alloy of the composition $K_3Cu_4SbTe_{12}$ (elemental composition as found in the ternary anion) does not yield the aforementioned complex.

The single crystal diffraction data[21] revealed that **1** contains the unprecedented and complicated ternary polytelluride cluster $[Cu_4SbTe_{12}]^{3-}$ (Figure 1) and tetraethylammonium cations. The cluster can be qualitatively described as a tetrahedral array of four Cu^+ coordinated to $SbTe_5^{3-}$ and Te_7^{4-} ligands. The central $[Cu_4Te_6]$ core can be envisioned as a tetrahedron of Cu^+, each edge of which is bridged by a Te atom. This results in the Cu_4 tetrahedron circumscribed by a Te_6 octahedron. The trigonally planar coordinated coppers lie in four of the eight faces of the Te_6 octahedron, giving the $[Cu_4Te_6]$ core approximate $\bar{4}3m$ point symmetry. The trigonal-planar coordination of the Cu results in a unit that differs from the more usual adamantane-like M_4X_6 cages by a tetragonal compression along the four three-fold axes of $\bar{4}3m$ symmetry to yield the trigonal-planar coordination about the metal. The Cu_4 tetrahedron has Cu–Cu distances in the range of 2.740(6)–2.784(6) Å, which is close to the sum of the van der Waals radii of Cu atoms (2.8 Å)[22] and comparable to

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(20) The intermetallic alloy of the nominal composition of $KCuSbTe_3$ is actually a mixture of several known phases and at least one unidentified phase. The known phases were identified by their powder X-ray diffraction patterns, and the amounts were qualitatively estimated from the intensity of their X-ray diffraction peaks. Present were K_2Te_3 (20%), Sb (10%), Te (5%), and Sb_2Te_3 (15%). The remaining 50% of the product, which contains all of the copper, had a powder pattern tentatively indexed to an orthorhombic cell with parameters $a = 22.885(6)$, $b = 11.266(2)$, and $c = 4.528(1)$ Å and $V = 1167$ Å^3. The alloy $KCuSbTe_3$ can also be prepared by the reaction of 0.500 g of K_2Te, 0.309 g of Cu, 0.592 g of Sb, and 1.550 g of Te at 650 °C in a sealed evacuated quartz ampule for 12 h.

(21) Crystal data for $(Et_4N)_3[Cu_4SbTe_{12}]$ (**1**): $C_{24}H_{60}N_3Cu_4SbTe_{12}$; orthorhombic; space group *Pbca* (No. 61); $a = 23.042(4)$ Å; $b = 32.209(6)$ Å; $c = 14.000(4)$ Å; $V = 10\,389(3)$ Å^3; $Z = 8$, $d_{calcd} = 2.938$ g cm^{-3}; μ(Mo Kα) = 87.5 cm^{-1}; $\lambda = 0.7107$ Å; crystal dimensions $0.10 \times 0.10 \times 0.20$ mm^3, $R = 0.050$, $R_w = 0.052$. The date were collected on a Rigaku AFC7R four circle diffractometer at 22 °C equipped with a RU300 18KW rotating anode, in the range of $5° < 2\theta < 45°$ using a ω-scan technique at a scan rate of 45 deg/minute. A total of 7470 reflections were measured, of which 2547 reflections with $I \geq 3\sigma(I)$ were considered as observed. An empirical absorption correction using the program DIFABS was applied. The structure was solved by direct methods (SAPI 91) and refined using the *teXsan* crystallographic software package of Molecular Structure Corporation. There are three crystallographically independent tetraethylammonium cations, one of which exhibits a disorder, with the inner carbon atoms of all the ethyl groups distributed over two different sites of half occupancy. There is no disorder in the terminal carbons or the nitrogen atom of the Et_4N^+ cation.

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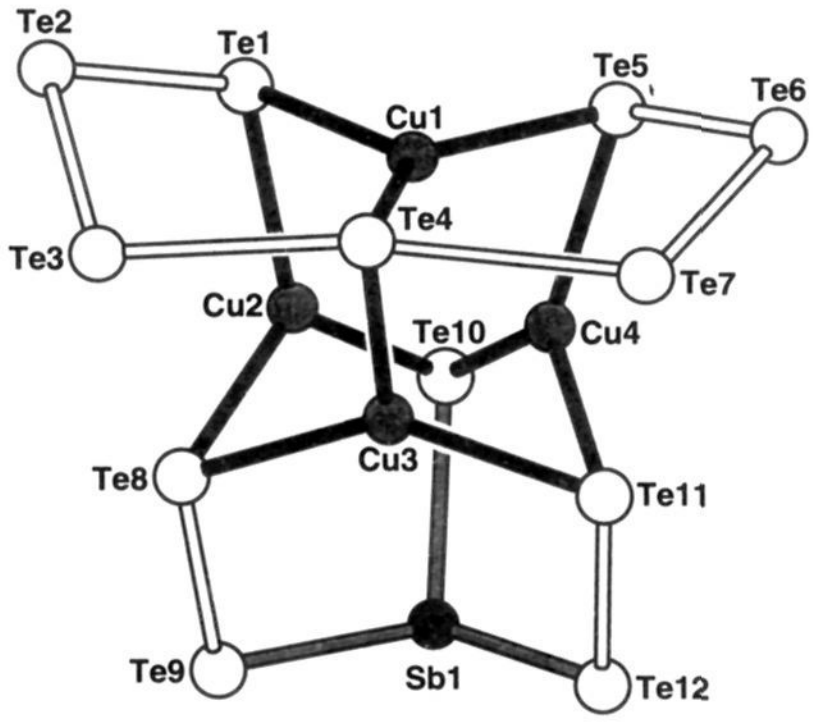

Figure 1. Structure of the $[\mathrm{Cu_4SbTe_{12}}]^{3-}$ anion. Some selected bond distances (Å) and angles (deg): Cu(1)–Te(1), 2.530(5); Cu(1)–Te(4), 2.510(4); Cu(1)–Te(5), 2.532(5); Cu(2)–Te(1), 2.549(5); Cu(2)–Te(8), 2.551(5); Cu(2)–Te(10), 2.546(5); Cu(3)–Te(4), 2.612(5); Cu(3)–Te(8), 2.538(5); Cu(3)–Te(11), 2.522(5); Cu(4)–Te(5), 2.544(5); Cu(4)–Te(10), 2.557(5); Cu(4)–Te(11), 2.552(5); Sb(1)–Te(9), 2.764(4); Sb(1)–Te(10), 2.766(4); Sb(1)–Te(12), 2.759(4); Te(1)–Te(2); 2.774(4); Te(2)–Te(3), 2.709(4); Te(3)–Te(4), 2.961(4); Te(5)–Te(6), 2.778(4); Te(6)–Te(7), 2.701(4); Te(4)–Te(7), 3.166(4); Te(8)–Te(9), 2.786(4); Te(11)–Te(12), 2.819(4); Te(1)–Cu(1)–Te(4), 121.9(2); Te(1)–Cu(1)–Te(5), 110.3(2); Te(4)–Cu(1)–Te(5), 127.6(2); Te(1)–Cu(2)–Te(8), 123.6(2); Te(1)–Cu(2)–Te(10), 117.3(2); Te(8)–Cu(2)–Te(10), 118.9(2); Te(4)–Cu(3)–Te(8), 111.0(2); Te(4)–Cu(3)–Te(11), 112.5(2); Te(8)–Cu(3)–Te(11), 136.5(2); Te(5)–Cu(4)–Te(10), 116.5(2); Te(5)–Cu(4)–Te(11), 122.2(2); Te(10)–Cu(4)–Te(11), 120.9(2); Te(9)–Sb(1)–Te(10), 101.8(1); Te(9)–Sb(1)–Te(12), 101.3(1); Te(10)–Sb(1)–Te(12), 101.5(1); Te(3)–Te(4)–Cu(1), 95.3(1); Te(3)–Te(4)–Cu(3), 87.9(1); Te(7)–Te(4)–Cu(1), 90.3(1); Te(7)–Te(4)–Cu(3), 86.2(1); Te(3)–Te(4)–Te(7), 170.0(1); Cu(1)–Te(4)–Cu(3), 70.3(1).

those found in $[\mathrm{Cu(Te_4)}]^{1-}$[22] of 2.735(4) Å and $[\mathrm{Cu_4(S_4)_x(S_5)_{3-x}}]^{2-}$ from 2.675(6) to 2.772(6) Å.[23] A similar $\mathrm{Cu_4L_6}$ core has also been stabilized by the lighter congeners (S and Se) in $[\mathrm{Cu_4(S_4)_x(S_5)_{3-x}}]^{2-}$[23] and $[\mathrm{Cu_4(Se_4)_x(Se_5)_{3-x}}]^{2-}$.[24]

The tellurium ligation of the $\mathrm{Cu_4}$ tetrahedron can be conceptually viewed as arising from $\mathrm{SbTe_5}^{3-}$ and $\mathrm{Te_7}^{4-}$ moieties. The novel $[\mathrm{Sb(Te)(Te_2)_2}]^{3-}$ unit has Sb in a trigonal-pyramidal coordination environment with the Sb bound to a Te^{2-} and two $\mathrm{Te_2}^{2-}$ ligands. The three terminal Te atoms from the $[\mathrm{Sb(Te)(Te_2)_2}]^{3-}$ ligand are bound to a triangular face of the $\mathrm{Cu_4}$ unit comprised of Cu(2), Cu(3) and Cu(4) (Figure 1). While the $\mathrm{SbTe_5}^{3-}$ ligand makes only three Cu–Te contacts, the remaining Te atom contacts to the $\mathrm{Cu_4}$ group are via what is formally a $\mathrm{Te_7}^{4-}$ ligand. The Te atoms Te(1), Te(4), and Te(5) of the $\mathrm{Te_7}^{4-}$ unit each bridge one edge of the Cu tetrahedron, giving a total of six Cu–Te bonds for the $\mathrm{Te_7}$ unit. If the $\mathrm{Te_7}^{4-}$ interaction with only Cu(1) is considered, the geometry of the $\mathrm{MTe_7}$ unit is quite similar to that recently reported for the $\mathrm{HgTe_7}^{2-}$[25,26] and $\mathrm{AgTe_7}^{3-}$[27] anions. In these anions, the central Te atom of the $\mathrm{Te_7}$ chain that is coordinated to the metal had contacts of 2.962(4) and 3.258(8) Å in the $\mathrm{HgTe_7}^{2-}$ and 2.866(2) and 3.230(2) Å in the $\mathrm{AgTe_7}^{3-}$, which are longer than the more usual Te–Te bonds of 2.7–2.8 Å typically observed in many polytellurides that are coordinated to metal centers. In $\mathrm{Cu_4SbTe_{12}}^{3-}$, the expansion of the adjacent Te–Te contacts about the central Te atom of the $\mathrm{Te_7}$ unit are likewise lengthened, as would be expected from the addition of another M–Te interaction to this central Te, to values of 2.961(4) Å for Te(3)–Te(4) and 3.166(4) Å for Te(4)–Te(7). Somewhat similar lengthening of certain internal Te–Te bonds of polytelluride complexes are observed in $\mathrm{AuTe_7}^{3-}$[27] and $\mathrm{Au_2Te_{12}}^{4-}$,[28] resulting in unusual $\mathrm{Te_5}^{4-}$ ligands. The other Te–Te bonds in **1** are in the range of 2.701(4)–2.819(4) Å within the more typical range for polytellurides.

In summary, the synthesis and structural characterization of the first ternary polytelluride cluster, $[\mathrm{Cu_4SbTe_{12}}]^{3-}$, demonstrates that extension of our earlier investigations involving en extraction of quaternary intermetallic phases is a promising pathway to novel cluster materials that compliments the solution-phase and flux growth methodologies. In addition to the $[\mathrm{Cu_4SbTe_{12}}]^{3-}$ cluster reported here, we have successfully synthesized and structurally characterized other ternary and quaternary polyanions containing coinage and main-group metal tellurides.

Supplementary Material Available: Tables of crystal data, data collection, solution and refinement parameters, atomic coordinates, bond lengths and angles, and anisotropic displacement coefficients and torsion angles (32 pages); table of observed and calculated structure factors for **1** (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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