

A discrete cubane-like [Cu₇Te] cluster: synthesis and structural characterization of (NBu₄)₄Cu₇As₃Te₁₃

Chwanchin Wang and Robert C. Haushalter*†

NEC Research Institute, 4 Independence Way, Princeton, NJ 08540, USA

The structure of the [Cu₇As₃Te₁₃]⁴⁻ anion contains a discrete cubane-like [Cu₇Te] cluster which is surrounded exclusively by three [As(Te₂)Te₂]³⁻ ligands and resembles the close packing of the Cu metal along the [111] direction.

Recently, much attention has been focused on the soluble binary chalcogenides and polychalcogenides which exhibit a great deal of structural diversity due mainly to the variety of catenation and bonding modes of the chalcogen atoms.¹⁻⁵ In contrast to the large number of binary chalcogenides, comparatively few ternary chalcogenides were reported. Investigation of the ternary M-As-E (M = transition metals and main-group elements; E = S, Se) systems by using the solventothermal technique has produced several compounds.^{6,7} There is a common feature in these structures, that is, a varied degree of condensation of the basic structural units, [AsE₃]³⁻ (E = S and Se) through the chalcogen atoms acting as ligands toward both transition metals and main-group elements. The [AsS₃]³⁻ ligand coordinated to transition-metal compounds was also reported.⁸ While research has been concentrated on the sulfide and selenide systems, only one telluride compound, (NEt₄)₄-Cu₄SbTe₁₂,⁹ containing a [Sb(Te₂)₂Te]³⁻ structural unit was reported. To further the investigation of the telluride systems, we have examined the Cu-As-Te system using the extractive method and report the first telluride containing a [As(Te₂)Te₂]³⁻ ligand which is exclusively used as a tridentate ligand to the Cu atoms.

One gram of an alloy with a nominal composition of K₂CuAsTe₄, prepared from the fusion of K₂Te, KAs, Cu, and Te in stoichiometric proportions, was extracted by dissolving in 10 ml of ethylenediamine that had been freshly distilled from a red K₄Sn₉ solution. The brown extract was filtered and layered with an equal volume of a saturated solution of tetrabutylammonium bromide in ethylenediamine. After one week, (NBu₄)₄Cu₇As₃Te₁₃ was isolated in ca. 12% yield (based on Cu) as small, black elongated hexagonal-like crystals. The composition of the alloy does not seem to be crucial, as the extraction of a more Cu-rich alloy of the composition K₂Cu₃AsTe₄ also yielded the title compound.

The structure† of (NBu₄)₄Cu₇As₃Te₁₃ consists an unprecedented, discrete cubane-like [Cu₇Te] cluster which is exclusively coordinated by three [As(Te₂)Te₂]³⁻ ligands as shown in Fig. 1, **1a**. The As atom in the [As(Te₂)Te₂]³⁻ ligand is bound to a Te₂²⁻ and two Te²⁻ ligands in a trigonal-pyramidal fashion. This ligand is observed in the title compound for the first time but is structurally quite similar to (NBu₄)₃SbTe₄.¹⁰ The As-Te bond distances range from 2.561 to 2.639 Å, comparable to those of [K(2,2,2-crypt)]₂As₂Te₆¹¹ and (NEt₄)₂As₂Te₅.¹² The Te-Te bond distances ranging from 2.720 to 2.735 Å are close to those of (NBu₄)₃SbTe₄¹⁰ and CsAs₂Te₆,¹³ in good agreement with the Te-Te covalent bond distance, 2.74 Å.¹⁴ The three terminal Te atoms from each [As(Te₂)Te₂]³⁻ ligand are bound to a rhombus-like Cu₄ unit with each Te atom coordinated to two Cu atoms having Cu-Te distances in the range 2.523–2.728 Å. The structure of the [Cu₇As₃Te₁₃]⁴⁻ anion is constructed in such fashion that shows a pseudo-threefold axis running through Cu(1) and Te(13)

atoms [Fig. 1, **1b**]. The most striking feature of the anion is that the inner core, which is surrounded by the three [As(Te₂)Te₂]³⁻ ligands, is a cubane-like [Cu₇Te] cluster [Fig. 1, **1c**]. In the [Cu₇Te] cluster, there are two coordination environments of Cu atoms: Cu(1) bound to four Te atoms has a distorted tetrahedral geometry, while the rest of the Cu atoms, each bound to three Te atoms, have a nearly trigonal-planar geometry. It is somewhat surprising that, based on the charge balance, all Cu atoms bear a 1+ charge. Both tetrahedral and trigonal-planar coordination environments of Cu^I ions have been previously reported.^{4,9} The average Cu-Te distance [2.72(3) Å] of the CuTe₄ tetrahedron is

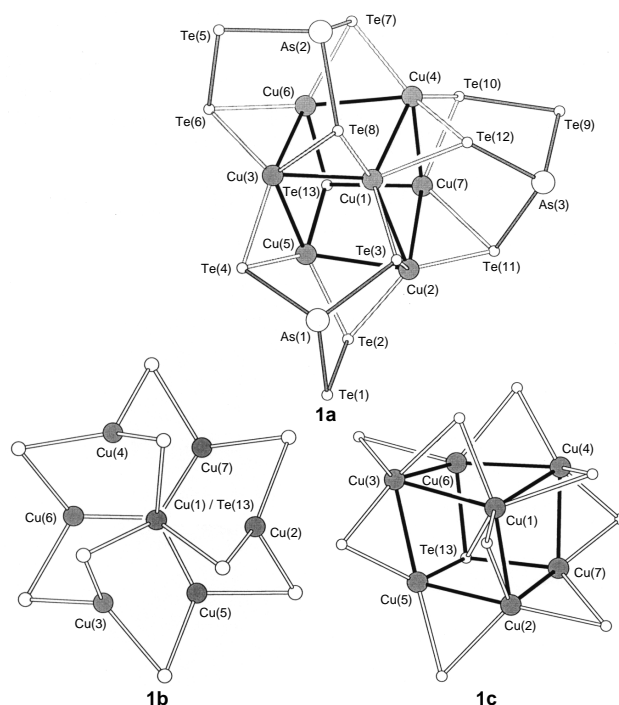


Fig. 1 Structure of the [Cu₇As₃Te₁₃]⁴⁻ anion **1a** which shows a pseudo-threefold axis running through Cu(1) and Te(13) atoms **1b**. Some selected bond distances (Å): Te(1)–Te(2) 2.735(3), Te(1)–As(1) 2.632(4), Te(2)–Cu(2) 2.552(4), Te(2)–Cu(5) 2.599(4), Te(3)–As(1) 2.615(4), Te(3)–Cu(2) 2.549(4), Te(3)–Cu(1) 2.685(4), Te(4)–As(1) 2.603(4), Te(4)–Cu(5) 2.534(4), Te(4)–Cu(3) 2.523(4), Te(5)–Te(6) 2.738(3), Te(5)–As(2) 2.608(4), Te(6)–Cu(3) 2.543(4), Te(6)–Cu(6) 2.614(4), Te(7)–As(2) 2.625(4), Te(7)–Cu(6) 2.542(4), Te(7)–Cu(4) 2.542(4), Te(8)–As(2) 2.602(4), Te(8)–Cu(3) 2.544(4), Te(8)–Cu(1) 2.728(5), Te(9)–Te(10) 2.720(4), Te(9)–As(3) 2.639(4), Te(10)–Cu(4) 2.560(4), Te(10)–Cu(7) 2.623(4), Te(11)–As(3) 2.619(4), Te(11)–Cu(2) 2.544(4), Te(11)–Cu(7) 2.546(4), Te(12)–As(3) 2.561(4), Te(12)–Cu(4) 2.553(4), Te(12)–Cu(1) 2.702(4), Te(13)–Cu(5) 2.501(4), Te(13)–Cu(6) 2.491(4), Te(13)–Cu(7) 2.500(4), Te(13)–Cu(1) 2.764(4), Cu(1)–Cu(2) 2.698(5), Cu(1)–Cu(3) 2.660(5), Cu(1)–Cu(4) 2.667(5), Cu(1)–Cu(5) 2.764(5), Cu(1)–Cu(6) 2.770(5), Cu(1)–Cu(7) 2.814(7), Cu(2)–Cu(5) 2.691(5), Cu(2)–Cu(7) 2.764(5), Cu(3)–Cu(5) 2.785(6), Cu(3)–Cu(6) 2.659(5), Cu(4)–Cu(6) 2.760(5), Cu(4)–Cu(7) 2.683(5). The inner core of the anion shows a cubane-like [Cu₇Te] cluster in which both the Cu–Cu contacts and the Cu–Te bonds are highlighted with bold lines **1c**. Some of the atoms are omitted for clarity.

slightly longer than that [2.55(4) Å] of the trigonal planar CuTe₃. Another interesting feature is that the Cu₇ unit resembles close packing of the Cu metal along the [111] direction. The average Cu–Cu distance is 2.73(5) which is about 0.17 Å longer than that in Cu metal. The Cu₇ unit is then capped with a Te(13) atom at the bottom corner to complete a cube. The Te(13) atom within the cube has an umbrella-shaped coordination to a Cu₄ unit which shows one long [2.764(4) Å] and three short (2.491–2.501 Å) Te–Cu distances. This results in a compression of a regular cube along the body diagonal containing Cu(1) and Te(13) and, concomitantly, in the formation of two different coordination environments of Cu atoms. The cube is compressed to the extent that a bonding interaction of 2.764(4) Å develops between Cu(1) and Te(13). It is also notable that the Te atoms in the structure exhibit two [Te(1), Te(5), Te(11)], three {all the terminal Te atoms in [As(Te₂)Te₂]³⁻ ligand} and four [Te(13)] coordination environments.

To our knowledge, the 23-atom anionic cluster of the title compound represents the largest ternary telluride Zintl anion that has been synthesized to-date. We and others⁹ have demonstrated that both [As(Te₂)Te₂]³⁻ and [Sb(Te₂)₂Te]³⁻ ligands can be used as building blocks in the construction of larger Zintl anions. Our results further suggest the possibility of obtaining much larger clusters or extended structures by the use of ligands with formulae [M(Te₂)_{3-x}Te_x]³⁻ (M = As, Sb; x = 0–3).

Footnotes

* E-mail: bobh@symyx.com

† Present address: Symyx Technologies, 420 Oakmead Parkway, Sunnyvale CA 94086, USA.

‡ *Crystal data* for C₆₄H₁₄₄As₅Cu₇N₄Te₁₃: space group *Pna*2₁ (no. 33), *a* = 18.473(3), *b* = 22.809(6), *c* = 24.443(6) Å, *U* = 10299(3) Å³, *Z* = 4, *D_c* = 2.096 g cm⁻³, μ(Mo-Kα) = 60.16 cm⁻¹. 9916 unique reflections were collected of which 3964 had *I* ≥ 3σ(*I*). An empirical absorption correction was applied. The structure was solved by direct method and refined by full-matrix least-squares to a final *R* = 0.039 (*R_w* = 0.038) with anisotropic thermal parameters for As, Cu, and Te atoms and isotropic thermal parameters for non-hydrogen atoms. CCDC 182/495.

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