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Synthesis and characterization of $K_3Cu_{11}Te_{16}$ from supercritical ethylenediamine

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Reaction of copper with potassium polytelluride, K_2Te_5, in supercritical ethylenediamine (305 °C, 2370 psi) led to a new compound with building blocks formed from Cu_8Te_{12} pentagonal dodecahedral cages made with Cu_2Te_3 pentagons; the dodecahedrons are connected by copper atoms and tritelluride fragments to generate tunnels filled with potassium.

Supercritical fluids have been used successfully to synthesize novel compounds at relatively low temperature. We have been exploring the preparation of a number of ternary alkali metal transition metal sulfides[1] and selenides[2,3] by using supercritical amines as the reaction media. To further study the chemistry of transition metal chalcogenides in supercritical amines, we have begun to explore the chemistry of metal tellurides. Synthesis of ternary tellurides has accelerated lately, but there are still only a limited number of ternary alkali metal copper tellurides known, KCuTe,[4] NaCuTe,[5] KCu_3Te_2,[6] $NaCu_3Te_2$,[7] $K_2Cu_5Te_5$,[8] and $K_4Cu_8Te_{11}$[9,10] all of which have been prepared *via* melt reactions. In this paper we report the synthesis and structural characterization of the new compound, $K_3Cu_{11}Te_{16}$.

The new compound, $K_3Cu_{11}Te_{16}$, was prepared from the reaction of Cu powder, K_2Te_5 and Te powder in supercritical ethylenediamine (en).[11] The compound is extremely air and thermally sensitive. This sensitivity inhibits much physical characterization.

The structure of $K_3Cu_{11}Te_{16}$ was studied by single crystal X-ray diffraction.[12] The building block of the structure is a $Cu_8(Te_2)_6$ pentagonal dodecahedral cage shown in Fig. 1. The pentagonal dodecahedron is made of planar Cu_2Te_3 pentagons [average deviation from planarity 0.04(1) Å] each containing a ditelluride edge. The pentagons are connected through the ditelluride with copper to form dodecahedrons. Each adjacent dodecahedral cage shares ditellurides to form columns parallel to the *c* axis. In addition to ditellurides, the structure has tritellurides as bridging groups between the dodecahedral cages along the *a* axis. The central atom of the tritelluride chain also coordinates to a bridging tetrahedral Cu atom which links the dodecahedra together. These tetrahedral copper atoms connect the cages along the *b* axis thereby generating tunnels that are filled with K^+ cations. The average distance across the tunnel is around 6.5 Å. The unit cell view of $K_3Cu_{11}Te_{16}$ is shown in Fig. 2. There are four unique copper atoms tetrahedrally coordinated by tellurium atoms. Bond distances between Cu(3) and Te_2^{2-} ligand and Cu(2) and Te_3^{2-} ligand range from 2.601(2) to 2.670(2) Å and 2.585(2) to 2.738(2) Å, respectively. Both Cu(3) and Cu(2) are part of the dodecahedron and they reside on general positions as do Te(2) and Te(4). Cu(1) is located on an mm2 site between two cages and connects clusters along the *b* axis. Cu(1) has two bonds to tritellurides at 2.634(2) Å and two bonds to ditellurides with an average bond distance of 2.693(4) Å. Cu(4) is also located between two cages and connects them together along the *a* axis. Cu(4) has two bonds to tritellurides and two bonds to ditellurides with bond distances of 2.597(1) and 2.587(1) Å, respectively. Cu(4) and Te(6) reside on 2-fold sites. The average Te–Te distances of the ditellurides in the cluster are 2.80(3) Å, while in the tritelluride they are 2.817(1) Å. There are two unique K^+ cations in the title structure. K(1) is located on an mm2 site in the center of the dodecahedral cage and has twelve interactions with the Te atoms of the dodecahedron. K(1)–Te distances range from 3.647(1) to 3.951(1) Å. K(2) resides in the tunnel and has eight interactions with Te atoms. The average K(2)–Te distance is 3.75(3) Å.

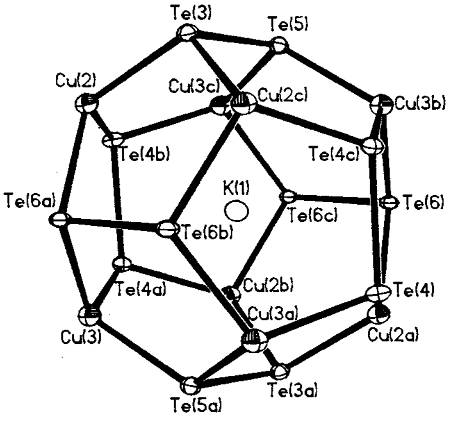

Fig. 1 Structure of KCu_8Te_{12} dodecahedral cage. Selected distances (Å): Te(3)–Te(5) 2.801(2), Te(3)–Cu(2) 2.589(2), Te(3)–Cu(2c) 2.589(2), Te(4)–Te(4c) 2.773(2); Te(4)–Cu(2a) 2.602(2), Te(4)–Cu(3a) 2.601(2), Te(5)–Cu(3b) 2.612(2), Te(5)–Cu(3c) 2.612(2), Te(6)–Te(6c) 2.834(2), Te(6)–Cu(3a) 2.670(2), Te(6)–Cu(3b) 2.670(2). Average angles within the cage: Te–Cu–Te 109(3) and Te–Te–Cu 108(4)°.

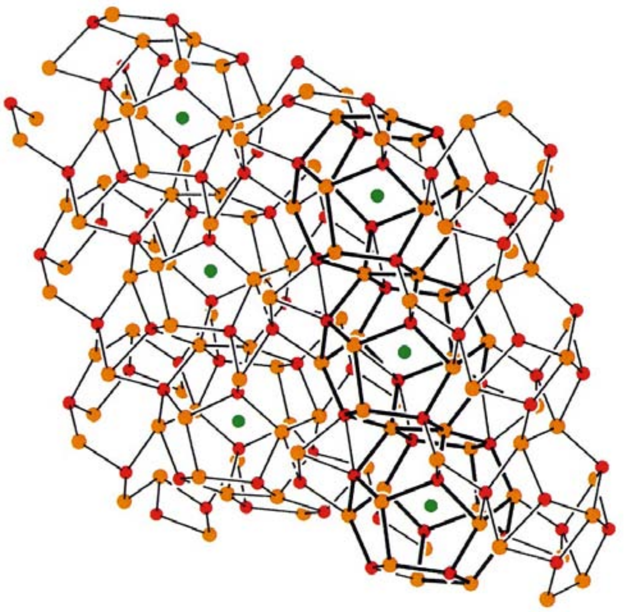

Fig. 2 Packing diagram of $K_3Cu_{11}Te_{16}$. Cu atoms are shown as red spheres, tellurium atoms as orange spheres, and potassium atoms as green spheres.

The formula of $K_3Cu_{11}Te_{16}$ can be written more informatively as $K_3Cu_{11}[(Te_2)_5(Te_3)_2]$. If the formal charges of the ditelluride and tritelluride units are considered to be −2, and that of Cu as +1, the compound is electron precise, and should be a semiconductor. We were not able to do conductivity measurements due to the air-sensitivity of the compound, but the black shiny appearance of the crystals suggests that it is a narrow band gap semiconductor. The copper is presumably oxidized to Cu(I) *via* the oxidative cleavage of the polytelluride chain.

$$2Cu + Te_5^{2-} \longrightarrow 2Cu^+ + Te_2^{2-} + Te_3^{2-}$$

The title compound, $K_3Cu_{11}Te_{16}$, is somewhat similar to $K_4Cu_8Te_{11}$ as synthesized from molten polytelluride flux.[9] Both compounds have the same Cu_8Te_{12} building block. The primary differences between the two are that $K_4Cu_8Te_{11}$ has large tunnels filled with six cations, and has only ditellurides in the structure. In the title compound the dodecahedra are only fused to each other through a shared Te_2^{2-} in the z direction, creating a chain. Along the y direction these chains are linked *via* shared tetrahedral copper atoms while in the x direction another tetrahedral copper atom and a Te_3^{2-} form the bridging units. In contrast, the dodecahedra in $K_4Cu_8Te_{11}$ are more densely packed. Not only are there fused chains similar to $K_3Cu_{11}Te_{16}$, but two such chains are also fused through another shared Te_2^{2-} creating a column. This column connects to four other symmetry related columns through adjacent Cu–Te interactions and another Te_2^{2-}. This anionic arrangement creates large columnar channels that are filled with the counter cation potassium. We have never observed formation of the previously reported flux synthesized $K_4Cu_8Te_{11}$ phase in numerous reactions in supercritical amines.

Kanatzidis *et al.* have synthesized a number of alkali metal copper tellurides by using the flux method.[10] For these reactions, they have observed a general trend that lower temperature and more acidic (longer-chained) Te_x^{2-} ($x = 4, 5$) favor polychalcogenide compounds, while higher temperature and more basic (shorter-chained) Te_x^{2-} ($x = 2, 3$) tend to form monochalcogenides. Based on our reaction conditions of relatively low temperature and long chain polytelluride (305 °C and K_2Te_5), it appears that our compound follows this trend.

Acknowledgements

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Notes and references

1 M. Emirdag, G. L. Schimek and J. W. Kolis, *Acta Crystallogr., Sect. A*, in the press.

2 M. Emirdag, G. L. Schimek and J. W. Kolis, *J. Solid State Chem.*, in the press.

3 M. Emirdag, G. L. Schimek and J. W. Kolis, *J. Chem. Cryst.*, in the press.

4 Y. Park, Ph.D. Dissertation, Michigan State University, 1992.

5 G. Savelsberg and H. Schäfer, *Z. Naturforsch., Teil B*, 1978, **33**, 370.

6 K. O. Klepp, *J. Less-Common Met.*, 1987, **128**, 79.

7 G. Savelsberg and H. Schäfer, *Mater. Res. Bull.*, 1981, **16**, 1291.

8 Y. Park, D. C. Degroot, J. Schindler, C. R. Kannewurf and M. G. Kanatzidis, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1325.

9 Y. Park and M. G. Kanatzidis, *J. Chem. Mater.*, 1991, **3**, 781.

10 X. Zhang, Y. Park, T. Hogan, J. L. Schindler, C. R. Kannewurf, S. Seong, T. Albright and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1995, **117**, 10300.

11 The synthesis of $K_3Cu_{11}Te_{16}$ was achieved by combining 30 mg Cu powder (0.47 mmol), 52 mg K_2Te_5 (0.072 mmol), and 44 mg Te powder (0.34 mmol) in 0.7 ml of ethylenediamine (en) in a $\frac{1}{4}$ inch quartz tube. The tube was sealed under vacuum and placed in a high-pressure autoclave. The autoclave was counter-pressured to 2370 psi, placed in a furnace, and heated at 305 °C for one day. Tubes were opened under argon and washed with ethylenediamine and tetrahydrofuran using standard Schlenk techniques. After the crystals were dried under vacuum, they were placed in mineral oil. Shiny black column crystals were recovered with over 90% yield. They are extremely air sensitive.

12 Crystal data for $K_3Cu_{11}Te_{16}$. The single crystal X-ray diffraction data for the title compound were collected at room temperature on a four circle Rigaku AFC7R diffractometer (Mo-K$\alpha = 0.71073$ Å, graphite monochromator). The unit cell was based on the indexing of 25 reflections with a 2θ range of 36.89–44.32°. Three standard reflections were measured every 100 reflections with decay = −1.6%. $2\theta_{max} = 50°$, $M = 2857.90$, gray column, 0.064 × 0.064 × 0.034 mm. Orthorhombic *Imma*, $Z = 4$, $a = 23.642(3)$, $b = 19.577(2)$, $c = 6.958(2)$ Å, $V = 3220.5(9)$ Å^3, $D_c = 5.89$ g cm^{-3}, μ(Mo-Kα) = 21.701 mm^{-1}. Refinement on F, 1255 observed reflections [$I > 3\sigma(I)$], 80 parameters (all atoms anisotropic), $R = 0.031$, $Rw = 0.037$, $S = 2.59$, maximum and minimum residual electron density: 1.28 and −1.01 e Å^{-3}. The structure was solved with direct methods and refined by full matrix least-square techniques explained as in previous work.[1] CCDC reference number 186/1408.

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