$(Me_4N)[M(Te_4)]$ (M = Cu, Ag): The First Layered Metal Polytellurides

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The presence of long Q_x^{2-} (Q = S, Se, Te; $x > 3$) chains as building blocks or linking units for metal atoms in extended frameworks is only a recent phenomenon. Compounds with these characteristics are more likely to have low-dimensional or open structures.[1] Despite the abundance of molecular metal polychalcogenide complexes, analogs with extended solid-state structures are still rare, with a few notable examples. These include the alkali metal salts of α- and β-$KCuQ_4$ (Q = S, Se),[2] K_2PdSe_{10},[3] $KAuQ_5$ (Q = S, Se),[4] K_3AuSe_{13},[4] and $K_2Sn_2S_8$.[5] Polymeric structures with organic counterions are even fewer: $(Ph_4P)AgSe_4$,[6] $(Me_4N)AgQ_5$ (Q = S,[7] Se[8]), $(H_3NCH_2CH_2NH_3)Cu_2S_{10}$,[9] and $(Ph_4P)MSe_{12}$ (M = Ga, In, and Tl).[10] To date, no polymeric metal tetratelluride compound is known. Thus far the longest Te_x^{2-} ligand is the Te_3^{2-} stabilized in $K_4M_3Te_{17}$[11] (M = Zr, Hf) and the binary compound $CrTe_3$.[12] Here we report the synthesis, structural characterization, and semiconducting properties of $(Me_4N)[M(Te_4)]$ (M = Cu (**I**), Ag (**II**)), the first polymeric metal/Te_x^{2-} compounds with a layered structure.

$(Me_4N)[Cu(Te_4)]$ was prepared by the reaction of $(Ph_3P)_3CuCl$, K_2Te_4, and Me_4NCl in a 1:1:1 molar ratio for 30 min in DMF. The black cube-shaped crystals (50% yield) grew upon careful addition of ether to the reaction solution in test tubes. The structure of this material was established with single-crystal X-ray diffraction techniques.[13] The isostructural silver analog was prepared similarly using $AgBF_4$.

$(Me_4N)[M(Te_4)]$ (M = Cu, Ag) contain anionic $[M(Te_4)]^-$ (**I**) layers and noninteracting Me_4N^+ cations situated between the layers, see Figures 1A and 1B. The layers form by interconnection of five-membered MTe_4 rings via a new bridging mode for a Te_4^{2-} ligand which holds three Cu atoms together. Chart I shows the four different bridging modes of a Q_4^{2-} ligand known to result in polymeric $[M(Q_4)]^-$ structures which include α- and β-$[Cu(Q_4)]^-$ (Q = S, Se) and $[Ag(Se_4)]^-$.[6] Variations in connectivity of Q_4^{2-} and M^+ atoms determine the dimensionality of the structures.

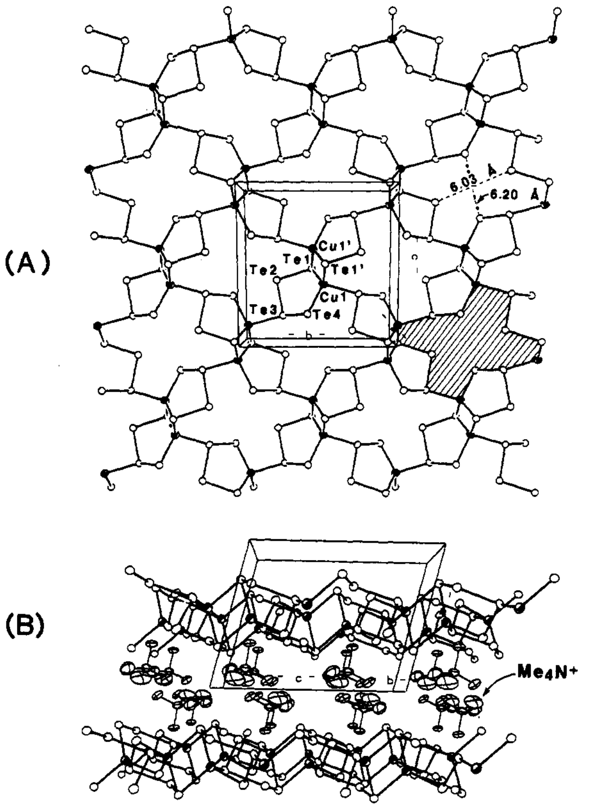

Figure 1. (A) ORTEP representation and labeling scheme of $[Cu(Te_4)]^-$ layer viewed along the *a* axis. The 14-membered ring holes in the layers are shaded for clarity. Selected bond distances (Å) and angles (deg): Cu1–Te1, 2.655(3); Cu1–Te1′, 2.578(3); Cu1–Te3, 2.725(3); Cu1–Te4, 2.578(2); Te1–Te2, 2.762(2); Te2–Te3, 2.791(2); Te3–Te4, 2.759(2); Te1–Cu1–Te1′, 116.99(8); Te1–Cu1–Te3, 92.44(7); Te1–Cu1–Te4, 111.75(9); Te3–Cu1–Te4, 100.38(7); Cu1–Te1–Te2, 97.73(6); Cu1′–Te1–Te2, 96.10(6); Te1–Te2–Te3, 98.55(4); Cu1–Te3–Te2, 96.27(5); Cu1–Te3–Te4, 126.70(7); Te2–Te3–Te4, 96.53(5); Cu1–Te4–Te3, 103.94(7). (B) Structure of $(Me_4N)[Cu(Te_4)]$ viewed along the *b* axis. Shaded ellipsoids represent Cu atoms, and open ellipsoids represent Te atoms. The structure of the $[Ag(Te_4)]^-$ layers is identical. Ellipsoids are drawn at the 50% probability level.

As the $CuTe_4$ rings in **I** come together to form layers, they form planar $[Cu_2Te_2]$ rhombic units located at the center of symmetry. The Cu–Cu distance in the $[Cu_2Te_2]$ unit is 2.735(4) Å, which is close to the sum of van der Waals radii of Cu atoms, 2.80 Å, and a little longer than those found in β-$[Cu(S_4)]^-$ (2.607(1) and 2.661(1) Å).[14] The five-membered ring of $CuTe_4$ adopts an envelope conformation as the Cu(1), Te(1), Te(2), and Te(3) atoms lie in an almost perfect plane (0.01 Å of mean deviation), with the Te(4) atom lying 2.17 Å above it. The Cu–

[†] A. P. Sloan Foundation Fellow, 1991–1993. Camille and Henry Dreyfus Teacher-Scholar, 1993–1995.

(1) (a) Haradem, P. S.; Cronin, J. L.; Krause, R. L.; Katz, L. *Inorg. Chem. Acta* **1977**, *25*, 173–179. (b) Kanatzidis, M. G. *Chem. Mater.* **1990**, *2*, 353–363. (c) Park, Y.; Liao, J.-H.; Kim, K.-W.; Kanatzidis, M. G. In *Inorganic and Organometallic Polymers and Oligomers*; Harrod, J. F., Laine, R. M., Eds.; Kluwer Academic Publishers: Netherlands, 1991; pp 263–276.

(2) Kanatzidis, M. G.; Park, Y. *J. Am. Chem. Soc.* **1989,** *111*, 3767–3769.

(3) Kim, K.-W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1992,** *114*, 4878–4883.

(4) Park, Y.; Kanatzidis, M. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 914–915.

(5) Liao, J.-H.; Kanatzidis, M. G. *Inorg. Chem.* **1993**, in press.

(6) Kanatzidis, M. G.; Huang, S.-P. *J. Am. Chem. Soc.* **1989**, *111*, 760–761.

(7) Banda, R. M. H.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *Polyhedron* **1989**, *8*, 2379–2383.

(8) Huang, S.-P.; Kanatzidis, M. G. *Inorg. Chem.* **1991**, *30*, 1455–1466.

(9) Kiel, G.; Gattow, G.; Dingeldein, T. *Z. Anorg. Allg. Chem.* **1991**, *596*, 111–119.

(10) Dhingra, S.; Kanatzidis, M. G. *Science* **1992**, *258*, 1769–1772.

(11) Keane, P. M.; Ibers, J. A. *Inorg. Chem.* **1991**, *30*, 1327–1329.

(12) Klepp, K. O.; Ipser, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 911.

(13) (a) Single-crystal X-ray data were collected on a Rigaku AFC6S diffractometer using Mo radiation. Crystal data for $(Me_4N)[Cu(Te_4)]$: monoclinic $P2_1/c$ (No. 14), $Z = 4$, $a = 9.519(7)$ Å, $b = 11.240(6)$ Å, $c = 12.007(5)$ Å, $\beta = 103.73(4)°$, and $V = 1248(1)$ Å^3 at 23 °C, $2\theta_{max} = 50.0°$, $\mu = 109.04$ cm^{-1}, $d_{calc} = 3.45$ g/cm^3; number of data collected, 2472; number of unique data having $F_o^2 > 3\sigma(F_o^2)$, 1292; final $R = 0.033$ and $R_w = 0.036$. A crystal with dimensions of 0.06 × 0.06 × 0.08 mm was mounted on a glass fiber with epoxy. The data were collected using a $\omega/2\theta$ scan with 4 deg/min scan speed. Data for $(Me_4N)[Ag(Te_4)]$: $P2_1/c$ (No. 14), $Z = 4$, $a = 9.357(2)$ Å, $b = 11.494(3)$ Å, $c = 12.163(2)$ Å, $\beta = 102.06(2)°$, and $V = 1279(1)$ Å^3 at 23 °C, $2\theta_{max} = 50.0°$, $\mu = 104.9$ cm^{-1}, $d_{calc} = 3.59$ g/cm^3; number of data collected, 3297. number of unique data having $F_o^2 > 3\sigma(F_o^2)$, 1868; final $R = 0.025$ and $R_w = 0.033$. All equivalent reflections were averaged. An empirical absorption correction (based on ψ scans) was applied to the data, followed by a DIFABS[13b] correction to the isotropically refined structures. The structures were solved with SHELXS-86 and refined with the TEXSAN package[13c] of crystallographic programs. The homogeneity of the products was confirmed by comparison of the observed X-ray powder diffraction pattern to the one calculated from the single-crystal data. (b) Walker, N.; Stuart, D. DIFABS: An Empirical Method for Correcting Diffractometer Data for Absorption Effects *Acta Crystallogr.* **1983**, *A39*, 158–166. (c) *TEXSAN*: *Single Crystal Structure Analysis Software, Version 5.0*; Molecular Structure Corporation: The Woodlands, Texas,

(14) The minimum Ag–Ag distance in the Ag_2Te_2 unit is 2.901(1) Å. Te(4) is lifted 2.30 Å above the Ag(1)Te(1)Te(2)Te(3) plane.

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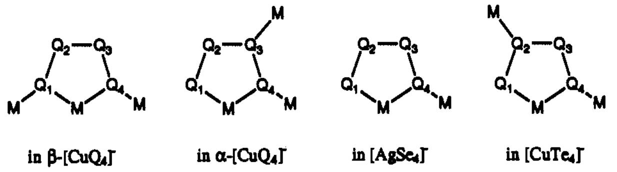
Chart I



in β-$[CuQ_4]^-$ in α-$[CuQ_4]^-$ in $[AgSe_4]^-$ in $[CuTe_4]^-$

Te distances fall into two categories. Shorter distances with an average of 2.60(4) Å involve the terminal Te atoms, and longer ones at 2.725(3) Å are associated with the internal Te atom of the Te_4^{2-} chain. This behavior was also seen in α-$[Cu(Q_4)]^-$ (Q = S, Se). The Te–Te distances in the Te_4^{2-} ligand range from 2.759(2) to 2.791(2) Å, with an average of 2.77(2) Å.

The most interesting feature of the layers are the large holes made of 14-membered rings (see Figure 1A). The dimensions of the rings, defined by the closest oppositely lying Te atoms, are 6.034(2) and 6.195(3) Å, respectively. The conformation of this ring is puckered, with the four Te atoms (two Te(4) and two Te(2)) pointed inwards, defining a square-planar site. The Me_4N^+ cations assemble nicely as a double layer between the $[CuTe_4]^-$ layers, raising the possibility for ion-exchange studies with other cations, see Figure 1B. The layered structural motif is retained even with $EtMe_3N^+$ as the counterion, suggesting the possible existence of a whole family of isostructural lamellar $(RMe_3N)[M(Te_4)]$ materials. $(RMe_3N)[M(Te_4)]$ represents a new addition to the already known broader AMQ_x family (A = Ph_4P, Me_4N, K, Rb, Cs; M = Cu^+, Ag^+, Au^+; Q = S, Se, Te), all of which feature low-dimensional structures.

$(Me_4N)[M(Te_4)]$ are diamagnetic semiconductors (thermally activated conduction) with a room temperature electrical conductivity of ~5×10^{-4} S/cm.[15] These materials start to steeply absorb light in the near-infrared region, as shown in the optical spectrum in Figure 2, suggesting bandgaps (determined from diffuse reflectance measurements) of 0.80 and 0.90 eV for the Cu and Ag analogs, respectively. Thermoelectric power measurements on single crystals indicate p-type semiconductivity (S_{rt} ~ 230 μV/K for both compounds). With the stable layered structure of $(RMe_3N)[M(Te_4)]$ and the recent report of layered $(Ph_4P)[In(Se_6)_2]$, we find further support for the notion that Q_x^{2-} ligands can provide the structural elements for building a variety of open semiconductor frameworks.

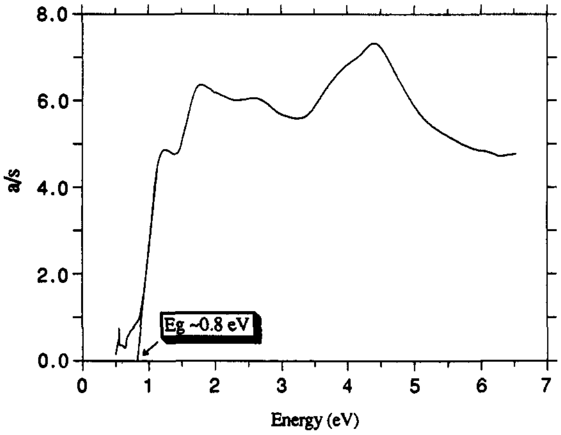


Figure 2. Optical absorption spectrum of $(Me_4N)[Cu(Te_4)]$ derived from diffuse reflectivity measurements.

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Supplementary Material Available: Tables of atomic coordinates and anisotropic thermal parameters of all atoms, bond distances and angles, and calculated and observed powder patterns (6 pages); listing of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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[15] The electrical conductivity measurements were carried out on single crystals using the four-probe method. A SQUID susceptometer was used to measure the magnetic susceptibility.