Inorg. Chem. **2004**, *43*, 4106–4108

Inorganic Chemistry
Communication

$[C_6H_5NH(CH_3)_2]_2Te_2I_{10}$: Secondary I···I Bonds Build up a 3D Network

Jacqueline M. Ryan and Zhengtao Xu*

*Department of Chemistry, The George Washington University, 725 21st Street, NW,
Washington, D.C. 20052*

Received April 29, 2004

The crystal structure of $[C_6H_5NH(CH_3)_2]_2Te_2I_{10}$ consists of the *N*,*N*-dimethylanilinium cation and a hitherto unreported tellurium iodide anion $Te_2I_{10}{}^{2-}$ [crystal data: $C_8H_{12}NTeI_5$, monoclinic, $P2_1/c$, $a = 9.4787(2)$ Å, $b = 14.2874(3)$ Å, $c = 13.6869(3)$ Å, $\beta = 95.1918(8)°$, $V = 1845.96(7)$ Å^3, $Z = 4$]. The $Te_2I_{10}{}^{2-}$ dianion is based on two edge-sharing $TeI_6{}^{2-}$ octahedra, and interestingly, it builds up a three-dimensional Te(IV)–I open framework through extensive interconnecting I···I contacts. These I···I contacts (3.66–3.80 Å) are significantly shorter than the corresponding sum of van der Waals radii (4.0 Å) and may potentially promote charge carrier migration throughout the Te–I network. This material can also be drop-cast into thin films from a heated DMF solution.

Organic-templated metal halide frameworks[1,2] have been widely studied for their potentially important properties such as semiconductivity,[1,3−7] porosity,[8−10] and luminescence.[11−13] In particular, the relatively weak metal−halogen bonding (compared with metal−chalcogen bonds, for example) generally improves solution or melt processability for potential applications in thin film devices. Studies in this direction are well illustrated by the hybrid systems based on organic ammonium cations and tin(II) iodide layers.[14−16]

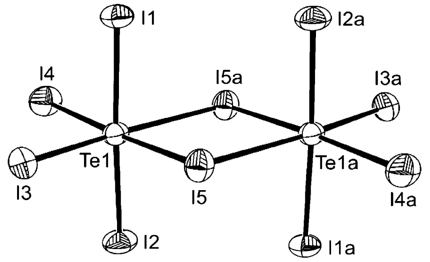


Figure 1. $Te_2I_{10}{}^{2-}$ anion in the crystal structure of **1**, with atom labeling and thermal ellipsoids (50% probability) for the Te and I atoms. Bond lengths: Te1−I1, 2.961(2) Å; Te1−I2, 2.909(2) Å; Te1−I3, 2.779(2) Å; Te1−I4, 2.906(2) Å; Te1−I5, 2.988(2) Å; Te1−I5a, 3.273(2) Å.

One issue in the above tin(II) iodide system is the air-sensitivity of the tin(II) centers, which will likely limit potential practical applications. Our lab is currently studying hybrid Te(IV) iodide systems, in hope of uncovering crystalline compounds with improved air-stability and tunability as potential semiconductors. Besides being generally more stable to air than the Sn(II) systems, Te(IV)−I compounds tend to display significant I···I secondary interactions in the solid state.[17−23] The strength of these secondary bonds lies between those of the typical covalent bonds and van der Waals interaction. As a result, they may, on one hand, serve to integrate the molecular species into extended networks and, on the other, render substantial solubility of the solid product in common solvents.

This paper reports the hybrid tellurium iodide bis(*N*,*N*-dimethylanilinium) ditellurium decaiodide {$[C_6H_5NH(CH_3)_2]_2$-Te_2I_{10}, **1**} as an initial result in efforts along this direction. The crystal structure of **1** consists of the *N*,*N*-dimethylanilinium cation and the distinct dinuclear anion of $Te_2I_{10}{}^{2-}$, which is formed through edge sharing of two $TeI_6{}^{2-}$ octahedral units (Figure 1). To our best knowledge, the $Te_2I_{10}{}^{2-}$ anion represents the first polynuclear tellurium iodide

---

* To whom correspondence should be addressed. E-mail: zxu@gwu.edu.

(1) Papavassiliou, G. C. *Prog. Solid State Chem.* **1997**, *25*, 125.
(2) Mitzi, D. B. *Prog. Inorg. Chem.* **1999**, *48*, 1.
(3) Mitzi, D. B.; Feild, C. A.; Harrison, W. T. A.; Guloy, A. M. *Nature* **1994**, *369*, 467.
(4) Mitzi, D. B.; Wang, S.; Feild, C. A.; Chess, C. A.; Guloy, A. M. *Science* **1995**, *267*, 1473.
(5) Castro-Castro, L. M.; Guloy, A. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2771.
(6) Papavassiliou, G. C.; Koutselas, I. B.; Terzis, A.; Whangbo, M.-H. *Solid State Commun.* **1994**, *91*, 695.
(7) Papavassiliou, G. C.; Koutselas, I. B. *Synth. Met.* **1995**, *71*, 1713.
(8) Martin, J. D.; Greenwood, K. B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2072.
(9) Martin, J. D.; Leafblad, B. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3318.
(10) Sullivan, R. M.; Liu, H.; Smith, D. S.; Hanson, J. C.; Osterhout, D.; Ciraolo, M.; Grey, C. P.; Martin, J. D. *J. Am. Chem. Soc.* **2003**, *125*, 11065.
(11) Mitzi, D. B.; Liang, K. *Chem. Mater.* **1997**, *9*, 2990.
(12) Guloy, A. M.; Tang, Z.; Miranda, P. B.; Srdanov, V. I. *Adv. Mater.* **2001**, *13*, 833.
(13) Sullivan, R. M.; Martin, J. D. *J. Am. Chem. Soc.* **1999**, *121*, 10092.
(14) Chondroudis, K.; Mitzi, D. B. *Chem. Mater.* **1999**, *11*, 3028.
(15) Kagan, C. R.; Mitzi, D. B.; Dimitrakopoulos, C. D. *Science* **1999**, *286*, 945.
(16) Mitzi, D. B.; Dimitrakopoulos, C. D.; Rosner, J.; Medeiros, D. R.; Xu, Z.; Noyan, C. *Adv. Mater.* **2002**, *14*, 1772.
(17) Einstein, F. W. B.; Trotter, J.; Williston, C. S. *J. Chem. Soc.* **1967**, 2018.
(18) Lang, E. S.; Manzoni de Oliveira, G.; Silveira, E. T.; Burrow, R. A.; Vázquez-López, E. M. *J. Organomet. Chem.* **2002**, *664*, 306.
(19) McCullough, J. D.; Knobler, C. *Inorg. Chem.* **1976**, *15*, 2728.
(20) McCullough, J. D. *Inorg. Chem.* **1977**, *16*, 2318.
(21) Kumar, R. K.; Aravamudan, G.; Udupa, M. R.; Seshasayee, M.; Hamor, T. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *C49*, 1328.

10.1021/ic049443k CCC: $27.50

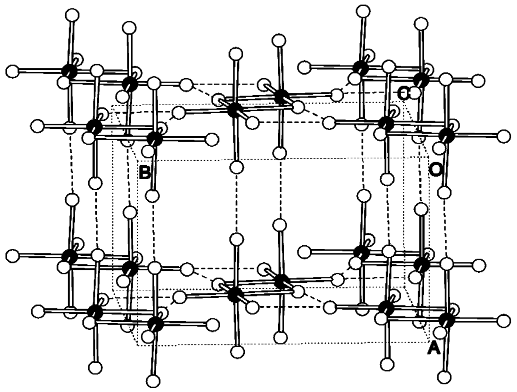
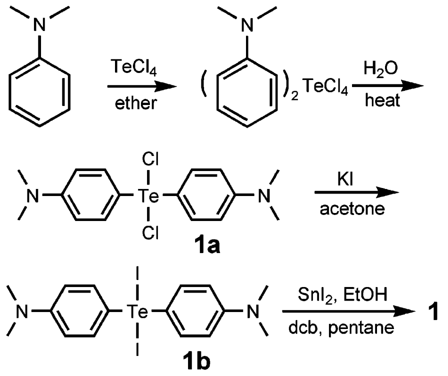


Figure 2. Packing of the $Te_2I_{10}^{2-}$ anions in the crystal structure of **1**: black spheres, Te; white spheres, I; dashed lines, I···I contacts.

Scheme 1



anion reported so far (although tellurium bromide and chloride anions with similar structures have previously been uncovered).[24−26] Interestingly, the crystal structure of **1** reveals that the $Te_2I_{10}^{2-}$ dianions interact with one another through extensive I···I contacts, integrating the inorganic anions into a three-dimensional open network (Figure 2). These I···I distances (ranging from 3.66 to 3.80 Å) are significantly shorter than the corresponding sum of van der Waals radii (4.0 Å),[27] and figure rather prominently in comparison with the smaller TeI_6^{2-} systems, where I···I interactions across the TeI_6^{2-} ions are much weaker (e.g., >4.0 Å).[28−30]

The making of crystalline samples of **1** takes several steps from *N*,*N*-dimethylaniline and $TeCl_4$ (Scheme 1). Reaction of *N*,*N*-dimethylaniline and $TeCl_4$ in ether forms the adduct bis(dimethylaniline) tellurium tetrachloride, which was subsequently converted into bis(4-dimethylaminophenyl) telluridichloride (**1a**) in boiling water. Compound **1a** was then subjected to a halogen exchange reaction with potassium iodide to produce bis(dimethylaminophenyl) telluridiiodide (**1b**). These reactions have already been reported,[31] and further details are given as Supporting Information. The title compound (**1**) was obtained as a crystalline solid from diffusing pentane vapor into a mixture of compound **1b** and tin(II) iodide dissolved in ethanol and 1,2-dichlorobenzene (dcb).[32] Both the single crystals and powder samples of **1** are black and air-stable. The samples are also soluble in polar solvents such as ethanol and *N*,*N*-dimethylformamide (DMF), and thin films can be deposited from a heated DMF solution (Figure S4 in Supporting Information).

Compound **1** crystallized in the space group $P2_1/c$, and the unit cell contains one tellurium, five iodine atoms, and one *N*,*N*-dimethylanilinium cation in the asymmetric unit.[33] The two edge-sharing TeI_6^{2-} fragments of the $Te_2I_{10}^{2-}$ anion are related by a center of symmetry (Figure 1), and the octahedral bonding geometry around the Te(IV) center is distorted. The strongest distortion occurs along the I3−Te1−I5a direction (bond lengths: I3−Te1, 2.78 Å; Te1−I5a, 3.27 Å), while the distances of the other four Te−I bonds are all within 2.90−3.00 Å (Figure 1). Overall, the condensed $Te_2I_{10}^{2-}$ anion contains six iodine atoms on the equatorial plane and four iodine atoms at the apical positions of the individual octahedron units.

The $Te_2I_{10}^{2-}$ anions form I···I contacts with one another, building up a three-dimensional framework that consists of distinct layers parallel to the crystallographic [100] plane (Figure 2). Within the layer, the equatorial iodine atoms (i.e., I3, I4, I5) from the constituent $Te_2I_{10}^{2-}$ anions are aligned to be on the same plane. The pattern of I···I contacts within the layer can be better seen in Figure 3a. The pattern is simple: only one type of linkage is formed between neighboring $Te_2I_{10}^{2-}$ anions, and it is based upon one I3 atom simultaneously touching upon one I4 atom and one I5 atom (distances: I3−I4′, 3.80 Å; I3−I5′, 3.76 Å, Figure 3a). Such I···I linkages thus connect each $Te_2I_{10}^{2-}$ anion to four

---

(22) Rao, G. V. N. A.; Seshasayee, M.; Aravamudan, G.; Radha, K. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1018.

(23) Bird, P. H.; Kumar, V.; Pant, B. C. *Inorg. Chem.* **1980**, *19*, 2487.

(24) Kozawa, K.; Uchida, T. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *C49*, 267.

(25) Hauge, S.; Janickis, V.; Maroy, K. *Acta Chem. Scand.* **1999**, *53*, 992.

(26) Hauge, S.; Maroy, K. *Acta Chem. Scand.* **1996**, *50*, 1095.

(27) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(28) Kiriyama, H.; Mizuhashi, Y.; Ootani, J. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 581.

(29) Abriel, W.; Du Bois, A. *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*, 1187.

(30) Srivastava, P. C.; Schmidt, H. G.; Roesky, H. W. *Z. Naturforsch., B: Chem. Sci.* **1995**, *50*, 695.

(31) Morgan, G. T.; Burgess, H. *J. Chem. Soc.* **1929**, 1103.

(32) Inside an argon-filled glovebox, **1b** (30.5 mg, 0.049 mmol) and SnI_2 (36.6 mg, 0.098 mmol) were dissolved in 1,2-dichlorobenzene (dcb, anhydrous, 3.0 mL) and ethanol (anhydrous, 2.0 mL). The solution was filtered and the filtrate collected in a small vial. The vial was then placed in a jar that had previously been charged with a mixture of dcb (anhydrous, 8.0 mL) and pentane (anhydrous, 8.0 mL). Slow vapor exchange between the reaction mixture (in the vial) and the reservoir (in the jar) over two weeks yielded black, blocklike crystals suitable for X-ray dataset collection (yield: 18.4 mg, 43% based on **1b**). X-ray powder diffraction studies indicated a single phase consistent with the single crystal structure. EDX (using a Shimadzu energy dispersive fluorescence X-ray spectrometer, Rayny series, EDX-700/800) spectrometry of the product indicated the Te/I ratio to be 1.0/5.2. The EDX measurement also indicated a small amount of Sn-containing impurities (amorphous) in the product (Sn/Te ratio about 1/10). Experiments for better product purity and for characterizing the other products are ongoing (also see Supporting Information for a proposed equation of the overall reaction, Figure S5).

(33) The X-ray dataset of **1** was collected from a black, blocklike crystal (0.15 × 0.10 × 0.10 mm^3) on a Nonius kappaCCD system using Mo Kα ($\lambda = 0.71073$ Å) radiation. The absorption effects were minimized by scaling and averaging of redundant measurements. The structure was solved and refined by full-matrix least-squares on F_o^2 using SHELXL 97. Crystal data: $C_8H_{12}NTeI_5$, monoclinic, $P2_1/c$, $a = 9.4787(2)$ Å, $b = 14.2874(3)$ Å, $c = 13.6869(3)$ Å, $\beta = 95.1918(8)°$, $V = 1845.96(7)$ Å^3, $Z = 4$, $T = 293$ K, $\mu = 9.952$ mm^{-1}, $R_{\mathrm{int}} = 2.6\%$, R1/wR2 = 6.54/18.48% for 4210 unique observed reflections [$I > 2\sigma(I)$] and 136 variables (R1/wR2 = 7.91/19.06% for all data).

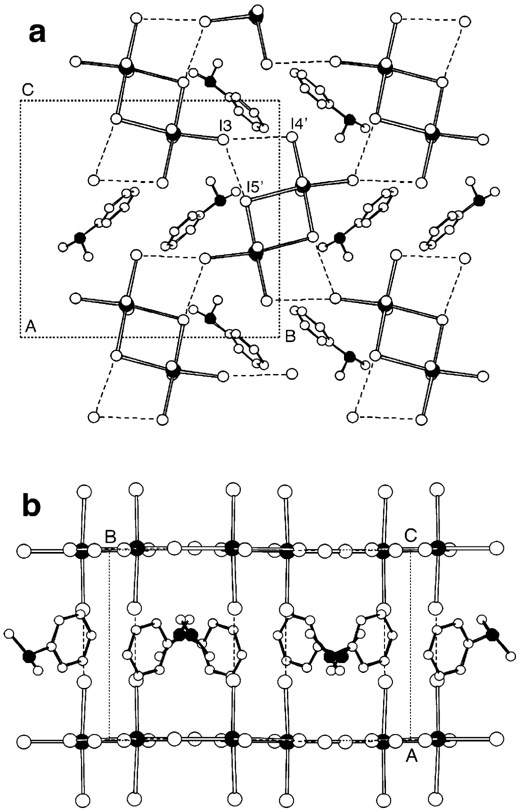


Figure 3. Overall crystal structures of **1**: (a) along the *a*-axis and (b) along the *c*-axis. Large empty spheres, I; large black spheres (partially eclipsed by the I atoms in a), Te; small white, C; small black, N.

neighboring anions, establishing a 2D network parallel to the [100] plane.

The layers are aligned eclipsing one another along the *a*-axis, with the apical iodine atoms forming I···I contacts that complete the 3D network (Figures 2 and 3b). Compared with the I···I contacts (distances: 3.80 and 3.76 Å) within the individual layers, the ones across the layers (distance: 3.66 Å) are markedly shorter, approaching the short intermolecular I···I contact of 3.50 Å in the crystal structure of diiodine.[34]

The organic cations in the crystal structure of **1** are organized into pairs (Figure 3a). Each pair consists of two centrosymmetrically related *N*,*N*-dimethylanilinium cations, interacting through the face-to-face stacking of the aromatic rings (shortest C···C contact: 3.55 Å). The *N*,*N*-dimethylanilinium cation pairs take up the interstices within the inorganic framework (Figure 3) and can be considered as being confined between the neighboring layers of $Te_2I_{10}^{2-}$ anions (Figure 3b). The relative orientation of the organic cation pairs between the inorganic layers can be seen in Figure 3a; namely, they are related by the 2_1 axis in the *b* direction. Finally, a short contact of 3.59 Å is observed between the nitrogen atom from the organic cation and one apical iodine atom (I1) from the inorganic framework, suggesting the existence of an N−H···I ionic hydrogen bond (sum of van der Waals radii of N and I: 3.70 Å[27]).

In summary, compound **1** represents a solution-processable organic−inorganic tellurium halide composite featuring extensive I···I contacts among the constituent $Te_2I_{10}^{2-}$ anions. Such intermolecular I···I contacts link the individual $Te_2I_{10}^{2-}$ anions into a three-dimensional network and may potentially promote charge carrier migration across the $Te_2I_{10}^{2-}$ anions. We are studying the electronic properties of **1** for potential use in semiconductive devices. Studies are also ongoing to exchange the *N*,*N*-dimethylanilinium cation in compound **1** with elongated organic cations so as to improve the self-assembly properties and solution processability.

Acknowledgment. J.M.R. is a GWU Undergraduate Gamow Fellow. We thank the X-ray Structural Characterization Laboratory at the Chemistry Department supported by University of Massachusetts and National Science Foundation (Grant CHE-9974648), and Dr. A. Chandrasekaran for data collection and structure solution and refinement for compounds **1** and **1a**. We also thank Mr. Kunhao Li, Ms. Kristin K. Scanlon, and Mr. Mark J. Wagner for help with characterizing compounds **1** and **1a**.

Supporting Information Available: Synthesis and crystallization of **1**, **1a**, and **1b**. Full crystallographic data in CIF format for **1** and **1a**. Figures (S1 and S2) of the crystal structure of **1a**. X-ray powder diffraction patterns for bulk samples and thin films of **1**, Figures S3 and S4. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049443K

---

[34] Van Bolhuis, F.; Koster, P. B.; Migchelsen, T. Ac*ta Crystallogr.* **1967**, *23*, 90.