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Novel Stable Metallic Salts Based on a Donor Molecule Containing *peri*-Ditellurium Bridges, TMTTeN

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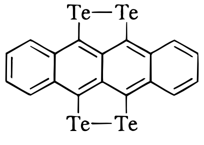
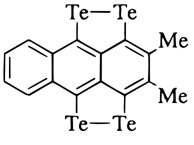
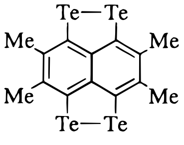
Recent development of organic conductors has been based mostly on the design of two-dimensional (2D) electron states by the introduction of sulfur or selenium atoms to π-electron systems.[1] On the other hand, systems based on tellurium-containing donor molecules have not received much attention because of their low solubility in organic solvents and difficulty of synthesis.[2] Several conducting complexes with tellurium-containing donors have been reported, for example, the cation radical salts of hexamethylenetetratellurafulvalene (HMTTeF)[3] and the tetratellurafulvalene (TTeF) complex.[4] In particular, a polyacene donor molecule containing *peri*-ditellurium bridges would be one of the most promising candidates to give stable organic metals because some tetraselenotetracene (TSeT) complexes with semimetallic ground states were reported two decades ago.[5] However, few cation radical salts and charge transfer complexes of tetratellurotetracene (TTeT) have been reported owing to its extremely poor solubility.[6,7] On the other hand, 3,4-dimethylanthra[1,9-*cd*:4,10-*c′d′*]bis[1,2]ditellurole (2,3-DMTTeA)[8] has supplied a cation radical salt with bromide anion showing high conductivity, but this salt is a semiconductor due to the disorder of the orientation of the anthracene moiety and bromide anion. To overcome the orientational disorder of polyacene donor molecules, we focused on the symmetrical polyacene donor molecule 2,3,6,7-tetramethylnaphtho[1,8-*cd*:4,5-*c′d′*]bis[1,2]ditellurole (TMTTeN), whose solubility to organic solvents is comparatively high due to the four methyl groups. TMTTeN was first synthesized by Otsubo et al.;[9] however, its conducting salts have not been reported so far. We report here the crystal structures, electric and magnetic properties, and three-dimensional (3D) Fermi surfaces of the tight-binding band of stable metallic salts.



TTeT



2,3-DMTTeA



TMTTeN

The radical cation salts of TMTTeN with $Ag(CN)_2^-$ and $Au(CN)_2^-$ were prepared by electrochemical oxidation in 10% EtOH/1,1,2-trichloroethane (TCE) containing tetra-*n*-butylammonium salts of anions at 40 °C.

X-ray crystallographic analyses were performed on a neutral TMTTeN molecule recrystallized from carbon disulfide and also on its $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts.[10−12] Unlike the 2,3-DMTTeA system, TMTTeN has no orientational disorder due to the symmetrical structure of TMTTeN.[10] The structure of the $Ag(CN)_2^-$ salt is shown in Figure 1. The donor molecules are stacked with short interplanar distances of 3.41 Å to form columns along the *c*-axis (Figure 1b). The $Ag(CN)_2^-$ anions are located in the channels formed by the surrounding TMTTeN molecules along which the 4_2 axes exist. These channels are isolated from each other, and the positions of the anions are heavily disordered along the *c*-axis. The population refinement of the Ag atom gave a 2:1 stoichiometry of the complex. There are many intermolecular Te···Te contacts less than the sum of the van der Waals radii (4.1 Å) and a three-dimensional network through tellurium

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(10) X-ray crystallography of $(TMTTeN)(CS_2)$: black rodlike crystal, 0.80 × 0.10 × 0.10 mm, $C_{15}H_{12}Te_4S_2$, triclinic, $P\bar{1}$, $a = 10.812(5)$ Å, $b = 14.588(6)$ Å, $c = 6.295(3)$ Å, $\alpha = 100.49(4)°$, $\beta = 106.75(4)°$, $\gamma = 89.90(4)°$, $V = 933.5(7)$ Å^3, $Z = 2$; Rigaku AFC-5R diffractometer, 296 K, $\omega-2\theta$ mode up to $2\theta = 60°$ ($h + 15$, $k \pm 20$, $l \pm 8$), graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The final R (R_w) was 0.034 (0.033) for 3883 reflections ($I > 3.00\sigma(I)$) of 5445 independent collected reflections. The details of the crystal structure will be reported in the near future.

(11) X-ray crystallography of the $Ag(CN)_2^-$ salt: black needlelike crystal, 0.40 × 0.03 × 0.03 mm, $TeAg_{0.12}C_{3.75}N_{0.25}H_3$, $M = 192.7$, tetragonal, $P4_2/ncm$, $a = 18.2911(9)$ Å, $c = 5.352(1)$ Å, $V = 1790.5(4)$ Å^3, $Z = 16$; Rigaku AFC-7R diffractometer, 296 K, $\omega-2\theta$ mode up to $2\theta = 60°$ ($h + 25$, $k + 18$, $l - 7$), graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The final R (R_w) was 0.035 (0.034) for 927 reflections ($I > 3.00\sigma(I)$) of 1582 independent collected reflections.

(12) X-ray crystallography of the $Au(CN)_2^-$ salt: black needlelike crystal, 0.30 × 0.07 × 0.07 mm, $TeAu_{0.12}C_{3.75}N_{0.25}H_3$, $M = 203.8$, tetragonal, $P4_2/ncm$, $a = 18.322(1)$ Å, $c = 5.350(3)$ Å, $V = 1795.9(9)$ Å^3, $Z = 16$; Rigaku AFC-7R diffractometer, 296 K, $\omega-2\theta$ mode up to $2\theta = 60°$ ($h + 25$, $k + 18$, $l - 7$), graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The final R (R_w) was 0.042 (0.044) for 947 reflections ($I > 3.00\sigma(I)$) of 1586 independent collected reflections.

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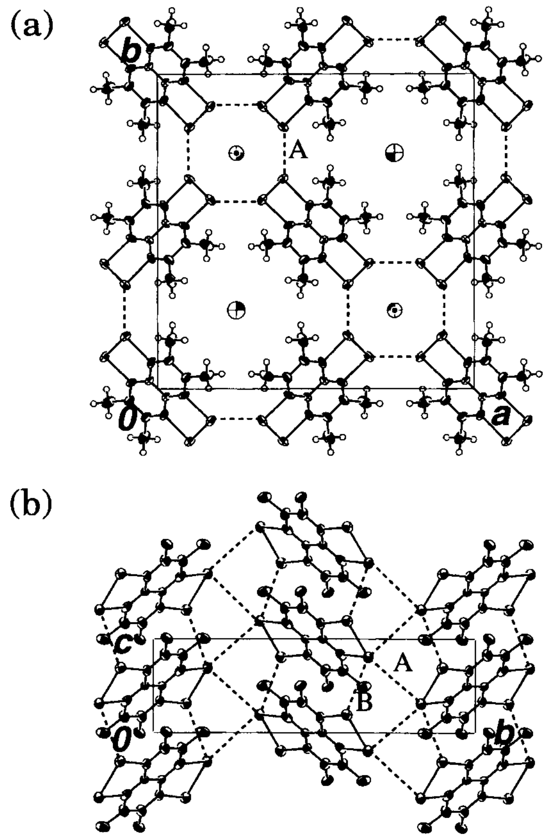

Figure 1. (a) Crystal structure of $(TMTTeN)_2Ag(CN)_2$ projected onto the *ab* plane. (b) Donor arrangement of $(TMTTeN)_2Ag(CN)_2$. Intermolecular Te···Te contacts: $A = 4.0199(8)$, $B = 3.709(1)$ Å. These figures are shown by an ORTEP 50% probability plot.

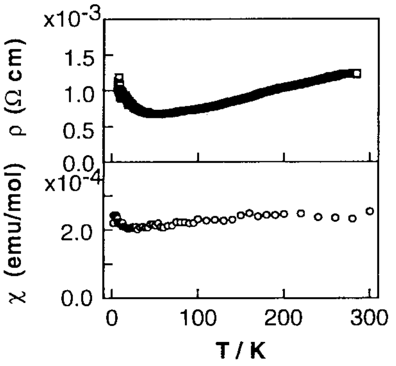

Figure 2. Electrical resistivity and paramagnetic susceptibility of $(TMTTeN)_2Ag(CN)_2$.

atoms is developed. The structure of $TMTTeN_2Au(CN)_2$ is almost the same as that of the $Ag(CN)_2$ salt.

The electrical resistivities of the salts were measured by the four-probe method along the *c*-axes of the crystals. The $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts show high room temperature conductivities (500−1000 S cm^{-1}). Both salts exhibited similar temperature dependencies of the resistivities. Figure 2 shows the resistivity behavior of $TMTTeN_2Ag(CN)_2$. The resistivity decreased down to 50 K and then increased very slowly down to 4 K, where the resistivity was less than 10^{-3} Ω cm. The low-temperature behavior was somewhat sample-dependent, which will be related to the anion disorder. This behavior indicates that $TMTTeN_2Ag(CN)_2$ is essentially metallic down to low temperature. The magnetic susceptibility of $TMTTeN_2Ag(CN)_2$ was measured with a SQUID magnetometer down to 2 K. The paramagnetic susceptibility of $TMTTeN_2Ag(CN)_2$ corrected by subtracting the diamagnetic contribution and that of the small low-temperature Curie term due to the paramagnetic impurities and/or lattice defects was almost constant throughout the temperature range, indicating the paramagnetism of the metal electrons ($2.5-2.0 \times 10^{-4}$ emu/mol ($TMTTeN_2Ag(CN)_2$)) (Figure 2). No anomaly corresponding to the gradual resistivity increase around 50 K was observed. Therefore the complex is the first system based on *peri*-ditellurium-bridged donors having a metallic ground state. The magnitude of paramagnetic susceptibility is about half that of a well-known κ-type ET superconductor (ET = bis(ethylenedithio)tetrathiafulvalene) (5×10^{-4} emu/mol),[13] suggesting the large bandwidth of $TMTTeN_2Ag(CN)_2$.

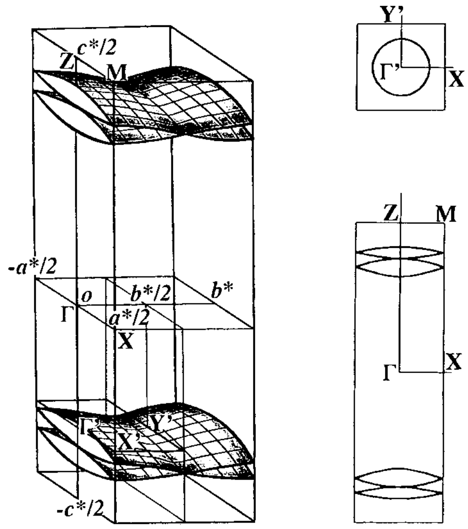

Figure 3. Three-dimensional Fermi surfaces of $(TMTTeN)_2Ag(CN)_2$ obtained by the extended Hückel tight-binding band calculation and their cross sections by the plane through ΓXZ and Γ′X′Y′, where $\Gamma = (0, 0, 0)$, $X = (a^*/2, 0, 0)$, $Z = (0, 0, c^*/2)$, $\Gamma' = (0, 0, -0.34c^*)$, $X' = (a^*/2, 0, -0.34c^*)$, and $Y' = (0, b^*/2, -0.34c^*)$.

The extended Hückel tight-binding band was calculated.[14] Despite the stacking structure of TMTTeN molecules, the one-dimensionality of the intermolecular interaction is rather weak: $t_\parallel/t_\perp \approx 7$, where $t_\parallel$ (≈0.6 eV) and $t_\perp$ are the intermolecular interactions parallel and perpendicular to the *c*-axis (molecular stacking axis), respectively. This is due to the 3D network between the protruding Te atoms. Owing to the tetragonal lattice symmetry, the band energies are doubly degenerated on the XM line (see Figure 3), which renders the Fermi surfaces composed of two corrugated one-dimensional Fermi surfaces quasi-3D. The Fermi surfaces are closed in the a^*c^* and b^*c^* planes and also in the plane perpendicular to c^* (an example of the cross section of the Fermi surface by the plane (Γ′X′Y′) perpendicular to the c^*-axis is presented) (Figure 3). As mentioned before, the analogous Se-donor system $TSeT_2Cl$ shows a metal−semimetal transition around 20 K, where the susceptibility drop indicating the reduction of the Fermi surfaces has been observed.[5] The stability of the metallic state of $TMTTeN_2Ag(CN)_2$ is attributable to the stronger three-dimensionality of the band structure.

Supporting Information Available: Three X-ray crystallographic files, in CIF format, are available. Access information is given on any current masthead page.

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(14) Slater type atomic orbitals were used for the calculation of molecular orbitals. The exponent ζ and the ionization potential (eV) are as follows: Te 5s, 2.112, −20.00; Te 5p, 1.827, −11.00; Te 5d, 1.500, −6.80; C 2s, 1.625, −21.4; C 2p, 1.625, −11.4; H 1s, 1.0, −13.6.