New Stable Metallic Salt Based on a Donor Molecule Containing *peri*-Ditellurium Bridges, TMTTeN(SCN)$_{0.88}$

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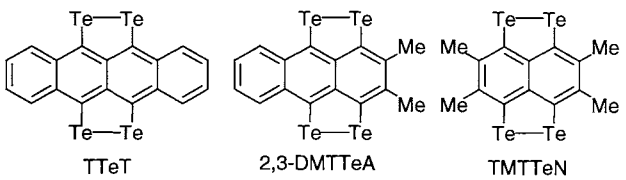
(Received May 18, 1999; CL-990401)

A new stable organic metal, TMTTeN(SCN)$_{0.88}$, where TMTTeN is 2,3,6,7-tetramethylnaphtho[1,8-*cd*:4,5-*c'd'*]bis[1,2]ditellurole, was obtained. The donors are stacked to form columns and three-dimensional network is developed through Te···Te contacts. The salt is highly conductive and keeps metallic behavior down to 4.2 K. Furthermore the salt exhibits Pauli paramagnetic behavior down to 2 K. The extended Hückel tight-binding band calculation was examined.

It is quite well established that the introduction of heavy atoms into the component molecules of synthetic metal, particularly donor molecules, increases the intermolecular interactions in the solid state and leads to larger conduction bandwidths.[1] Among structural modifications of donor molecule in the search for superior electron donors forming organic conductor, tellurium-containing donors have drawn much attention, because the introduced tellurium atoms are expected to produce a novel metallic system in which wide bandwidth and high dimensionality may be realized due to the large electron cloud of tellurium atoms. Furthermore conducting salts based on tellurium-containing donors are interesting from the viewpoints of the crystal structure because the formation of tellurium network seems to be dominant in the construction of the crystal structure.[2,3] In recent years, we have focused on the polyacene donor molecules containing *peri*-ditellurium bridges, for example, TTeT (tetratellurotetracene),[4,5] 2,3-DMTTeA (3,4-dimethylanthra[1,9-*cd*:4,10-*c'd'*]bis[1,2]ditellurole)[2,6] and TMTTeN (2,3,6,7-tetramethylnaphtho[1,8-*cd*: 4,5-*c'd'*]bis[1,2]ditellurole),[3,7] which might be one of the most convincing candidates to provide unique organic metals because the atomic character of tellurium atoms might be reflected more directly than the case of the donors with TTeF (tetratellurafulvalene) framework. Recently we have discovered the TMTTeN salts with $Ag(CN)_2^-$ and $Au(CN)_2^-$ anions showing metallic behavior down to 50 K.[3] They have tetragonal



structures similar to the highly conducting salts composed of donor molecules with TTT (tetrathiotetracene)-like skeletons.[8] The quasi three-dimensional Fermi surfaces of these salts seem to be originated from the tetragonal symmetries of the crystals. In this context, it is very important to obtain new metallic cation radical salt of TMTTeN with different type of crystal structure. In this article, we report the structure and electrical and magnetic properties of a new stable metallic salt, TMTTeN(SCN)$_{0.88}$.

A new cation radical salt of TMTTeN was prepared by electrochemical oxidation in 10% EtOH/1,1,2-TCE (trichloroethane) containing mixed anion salts, tetrabutylammonium salts of SCN^- and ClO_4^- anions, at 40 °C. A constant current of 0.1-0.2 μA was applied for about 2 weeks. Several regular prismatic black single crystals grew on the anode.

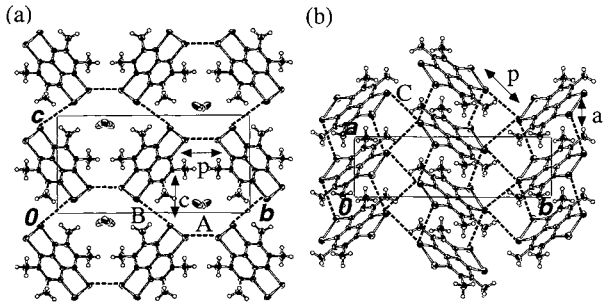


Figure 1. Crystal structure of TMTTeN(SCN)$_{0.88}$ in the (a) *bc*-plane and (b) *ab*-plane. The anion molecules are omitted for clarity in Figure 1(b). Intermolecular Te···Te contacts: A = 4.048(1), B = 4.123(1) and C = 3.788(2) Å. Overlap integrals: a = 82.8, c = -24.4 and p = -7.2x10^{-3}.

X-Ray structure analysis was performed.[9] The composition of the obtained salt was determined to be TMTTeN(SCN)$_{0.88}$ by the population refinement and no ClO_4^- anion was discovered, which is consistent with the result of EPMA (electron probe microanalyses) measurement showing no trace of chlorine atom. The SCN^- salt was also prepared from the solution without the ClO_4^- anions. But the obtained crystals were very small in spite of the similar shape of the crystal. The projections of the crystal structure of the SCN^- salt in the *bc*- and *ab*-planes are shown in Figure 1. The donor molecules are stacked to form columns along the *a*-axis with an intermolecular interplane distance of 3.62 Å. The anions are located in the channels surrounded by the TMTTeN molecules. The donor molecules are inclined with a dihedral angle of 72.2° between adjacent two donor columns. The crystal structure is not isostructural to the earlier reported structures of the $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts with tetragonal lattices.[3] That is, penetration of the SCN^- anion into the

TMTTeN lattice leads to a modification of the packing of the TMTTeN molecules along the *c*-axis of the crystals, but the arrangements of TMTTeN molecules are almost the same as those of the $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts along the other two axes. On the other hand, there are some positional disorder of the SCN^- anions along the *a*-axis (the donor stacking axis), which result in ellipsoids of anisotropic temperature factors elongated along the *a*-axis. As shown in Figure 1, there are many intermolecular Te···Te contacts less than the sum of the van der Waals radii (4.2 Å) and three-dimensional network through the tellurium atoms is developed.

The electrical resistivities were measured by the four-probe method along the *a*-axis (the donor stacking axis) of the crystals. The salt shows very high room-temperature conductivities (400-600 S cm^{-1}) similar to those of the $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts (500-1000 S cm^{-1}).[3] Figure 2 shows that the temperature dependence of electrical resistivity is metallic down to low temperature (4.2 K). Especially, this SCN^- salt has no slight increase of resistivity, which was observed below 50 K in the case of the $Ag(CN)_2^-$ and $Au(CN)_2^-$ salts.[3] That is, the SCN-salt is a genuine stable metal down to low temperature. The magnetic susceptibility of the salt was measured by SQUID magnetometer at 3 Tesla down to 2 K. The susceptibility of neutral TMTTeN crystals was also measured in order to estimate the diamagnetic contribution of TMTTeN. The paramagnetic susceptibility of $TMTTeN(SCN)_{0.88}$ is almost constant throughout the temperature range, indicating Pauli paramagnetism of the system [1.6-1.9 x 10^{-4} emu mol^{-1}], where corrections of the diamagnetic contribution and the small low-temperature Curie term due to the paramagnetic impurities and/or lattice defects were made. (Figure 2) The small paramagnetic susceptibility suggests the large bandwidth of $TMTTeN(SCN)_{0.88}$ similar to that of the $Ag(CN)_2^-$ salt (2.0-2.5 x 10^{-4} emu mol^{-1}).[3] Thus, as indicated by the low-temperature resistivity behavior, the salt is considered to keep stable metallic nature down to liquid helium temperature.

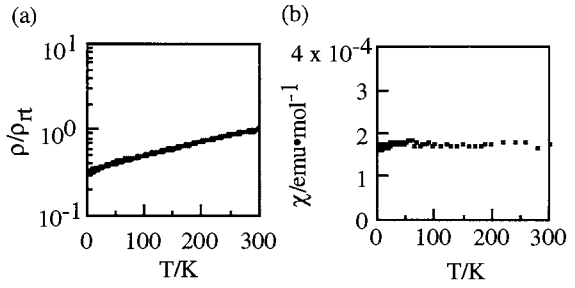


Figure 2. Temperature dependencies of (a) electrical resistivity and (b) paramagnetic susceptibility of $TMTTeN(SCN)_{0.88}$.

The band structure calculation was carried out by the extended Hückel method by using Slater-type atomic orbitals (Figure 3).[10] The overlap integral along the stack is fairly large (a = 82.8x10^{-3}) compared to the others (c = -24.4x10^{-3} and p = -7.2x10^{-3}) due to the stacking structure of TMTTeN molecules. On the other hand, the interstack overlap integral c is about three times larger than p because of the parallel arrangement of two TMTTeN molecules in the interaction c in contrast to the almost orthogonal one of the interaction p. As shown in Figure 3(a), the band dispersions are doubly degenerated on the YM line. The large bandwidth is consistent with the observed small Pauli susceptibility and the expected large intermolecular interactions

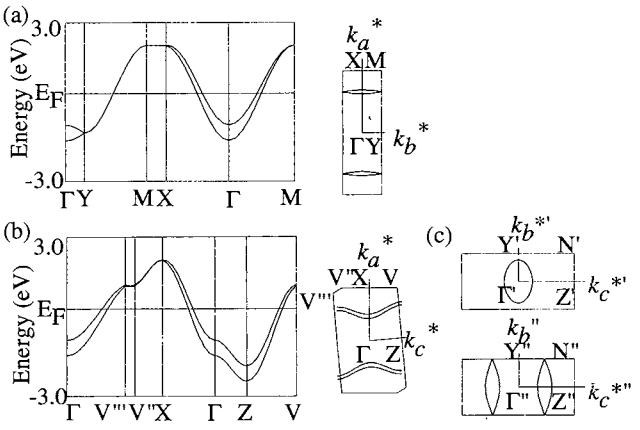


Figure 3. Energy band structures and sections of Fermi surface of $TMTTeN(SCN)_{0.88}$ obtained by the extended Hückel tight-binding band calculation. Γ=(0, 0, 0), X=(*a**/2, 0, 0), Y=(0, *b**/2, 0), Z=(0, 0, *c**/2), Γ'=(0.23*a**, 0, 0), Y'=(0.23*a**, *b**/2, 0), Z'=(0.23*a**, 0, *c**/2), Γ''=(0.28*a**, 0, 0), Y''=(0.28*a**, *b**/2, 0) and Z''=(0.28*a**, 0, *c**/2).

in the organic metals based on the tellurium containing donors. The Fermi surface of the SCN^- salt is open along the *b** and *c** directions, however, the intermolecular interactions between the donor columns are not so weak due to the three-dimensional network mediated by the protruded tellurium atoms. As shown in Figure 3(c), cross-sections of the Fermi surface perpendicular to the *a**-axis indicate two or quasi two-dimensional metallic state. Consequently, the Fermi surfaces are considered to be fairly stable against the nesting of the Fermi surfaces. This may be an origin of the stable metallic state of the SCN^- salt.

In conclusion, we have obtained a new stable metal of TMTTeN complex with the new type of the donor arrangement. The resistivity decreases smoothly down to 4 K. Small Pauli susceptibility is consistent with the calculated large bandwidth.

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9 X-Ray crystallographic data of the SCN^- salt: $Te_2C_7H_6(SCN)_{0.44}$, M = 370.88, monoclinic, space group $P2_1/a$, a = 5.419(3), b = 17.493(2), c = 8.941(2) Å, β = 94.77(3)°, V = 844.7(5) Å^3, Z = 4, D_{calc} = 3.172 g cm^{-3}. 2013 unique reflections and 1223 observed [$I > 3.00\sigma(I)$]. The final R (Rw) and GOF values are 0.035 (0.034) and 1.24, respectively.

10 Slater type atomic orbitals were used for the calculation of molecular orbitals. The exponent ζ and the ionization potential (eV) are: 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.