Crystal structures and electrical conductivities of cation-radical salts of a tellurium-containing donor: 3,4-dimethylanthra [1,9-*cd* : 4,10-*c*′*d*′]bis[1,2]-ditellurole

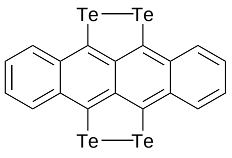
Masahiro Nakata,[a] Akiko Kobayashi,*[a] Taro Saito,[a] Hayao Kobayashi,[b] Kazuo Takimiya,[c] Tetsuo Otsubo[c] and Fumio Ogura[d]

[a] *Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*
[b] *Institute for Molecular Science, Myodaiji, Okazaki 444, Japan*
[c] *Department of Applied Chemistry, Faculty of Engineering, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan*
[d] *Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Umenobe-1, Takaya, Higashi-Hiroshima 739-21, Japan*

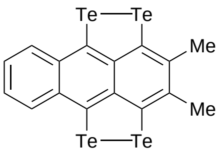
The crystal structures and conducting properties of various cation-radical salts of a tellurium-containing polyacene donor molecule, 3,4-dimethylanthra[1,9-*cd* : 4,10-*c*′*d*′]bis-[1,2]ditellurole, are described; the Br^- salt shows a relatively high conductivity at room temperature.

In the field of molecular conductors, systems based on tellurium-containing donor molecules have not received as much attention as systems based on sulfur- or selenium-containing donors.[1] Only a few conducting complexes with tellurium-containing donors have been reported, including the cation-radical salts of hexamethylenetetratellurafulvalene (HMTTeF)[2] and the tetratellurafulvalene (TTeF)–TCNQ complex.[3] By incorporating heavy chalcogen atoms such as tellurium into donor molecules, a new metallic system with a wider bandwidth and a higher dimensionality is expected to appear.[1] In particular, a polyacene donor molecule containing *peri*-ditellurium bridges might reflect the atomic character of tellurium more directly than a donor with a tetratellurafulvalene framework, and is expected to show novel physical properties. Tetratellurotetracene (TTeT) is well known as a donor molecular containing *peri*-ditellurium bridges,[4] but few cation-radical salts or charge transfer complexes of TTeT have been reported because of its extremely poor solubility.[5] We report here the first examples of cation radical salts of a polyacene donor with *peri*-ditellurium bridges, 3,4-dimethylanthra-[1,9-*cd* : 4,10-*c*′*d*′]bis[1,2]ditellurole (2,3-dimethyltetratelluroanthracene: 2,3-DMTTeA), the synthesis of which was first reported by Takimiya and co-workers.[6] 2,3-DMTTeA is an unsymmetrical polyacene molecule with an anthracene framework, two Te–Te bridges and two methyl groups. The solubility of 2,3-DMTTeA in organic solvents is high due to the two methyl groups. Therefore, we can examine the complexes of this donor with the usual chemical or electrochemical methods using organic solvents.

Single crystals of the cation-radical salts were obtained by electrochemical oxidation of 2,3-DMTTeA in a THF solution of Bu_4N (Table 1). A standard H-shaped cell and platinum electrodes were used and a constant current (0.1–1.0 μA) was applied for 7–15 days. Needle- or plate-shaped black crystals grew on the anode.



TTeT



2,3-DMTTeA

The electrical resistivities of the salts were measured by a four-probe method along the donor-stacking axes of the single crystals. The resistivities of all the salts showed semiconducting temperature dependence. However, the Br^- salt has quite a high room temperature conductivity (1.3×10^3 S cm^{-1}) and a very low activation energy (0.010 eV) (Fig. 1). Room temperature conductivities, activation energies and stoichiometries of the salts are listed in Table 1.

X-ray structure analyses were performed on neutral 2,3-DMTTeA and its cation-radical salts with ClO_4^-, BF_4^-, ReO_4^-, PF_6^-, AsF_6^- and Br^- counter anions.†,‡ The BF_4^- and ReO_4^- salts are isomorphous with the ClO_4^- salt, and the PF_6^- salt is isomorphous with the AsF_6^- salt. The common feature to all the structures is the disorder of the donor molecules caused by their unsymmetrical shape, which makes the 2,3-DMTTeA molecules appear as if they have a tetracene framework instead of their actual anthracene framework. One possible reason why the donor molecules have this orientational disorder is that the formation of the Te···Te network is dominant in the construction

Table 1 Composition and electrical conductivities of 2,3-DMTTeA salts

Anion	Donor : anion ratio	Form	σ_{293}/S cm^{-1}	E_a/eV
ClO_4^-	3 : 2[a]	plate	7.1×10^{-3}	0.16
BF_4^-	3 : 2[a]	plate	9.7×10^{-3}	0.17
ReO_4^-	3 : 2[a]	plate	5.5×10^{-3}	0.16
PF_6^-	5 : 1[b]	plate	5.6×10^{-2}	0.077
AsF_6^-	5 : 1[b]	plate	1.2×10^{-1}	0.068
Br^-	2 : 1[b]	needle	1.3×10^{3}	0.010

[a] Determined from the X-ray crystal structure analysis. [b] Determined by elemental analysis.

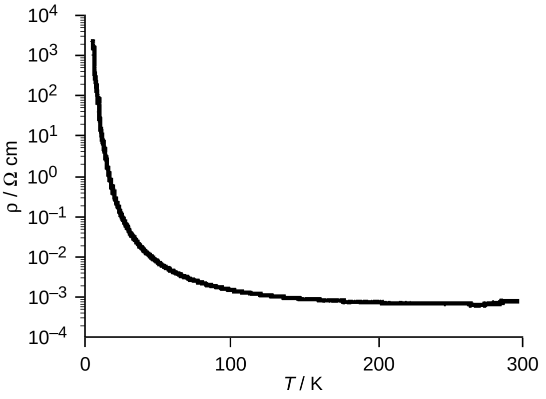


Fig. 1 Electrical resistivity of $(2,3\text{-DMTTeA})_2Br$

of the crystal structures. This disorder, which is absent from the sulfur or selenium isologue of 2,3-DMTTeA,[6b] is considered to reflect the character of tellurium atoms. In addition, the anions are also disordered in the AsF_6^- and Br^- salts. In spite of their disordered structures, however, all were refined with R factors of 3–9%, because the donor molecules contain heavy tellurium atoms.

The structure of $(2,3\text{-DMTTeA})_3(ClO_4)_2$ is shown in Fig. 2. There are donor stacks along the c axis, and in each stack, two crystallographically independent donor molecules, A and B in Fig. 2, overlap with their long axis 90° rotated. This rotated overlapping arrangement causes the very small value of the calculated intermolecular overlap integral§ between A and B ($< 1 \times 10^{-3}$). On the other hand, B and B′, which are crystallographically equivalent, are almost eclipsed and the overlap integral between them is 10×10^{-3}, so they may be regarded as forming a dimer. The weak interaction between A and B causes the dimer to be isolated, which causes the poor conductivity of this salt.

The AsF_6^- salt has donor stacks along the a axis. There is a short interstack Te···Te contact (3.83 Å) which is shorter than the intermolecular Te···Te distance within the stack (4.16 Å). Therefore, two-dimensional character is expected in its conducting properties.

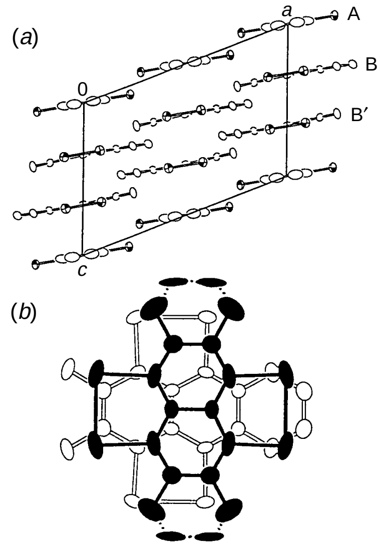


Fig. 2 (*a*) Crystal structure of $(2,3\text{-DMTTeA})_3(ClO_4)_2$ projected onto the *ac* plane. ClO_4^- anions are omitted for clarity. (*b*) Overlapping mode of the donor molecules of $(2,3\text{-DMTTeA})_3(ClO_4)_2$ projected onto the molecular plane. While molecule A (coloured black) has a disordered tetracene structure, molecule B (coloured white), is not disordered.

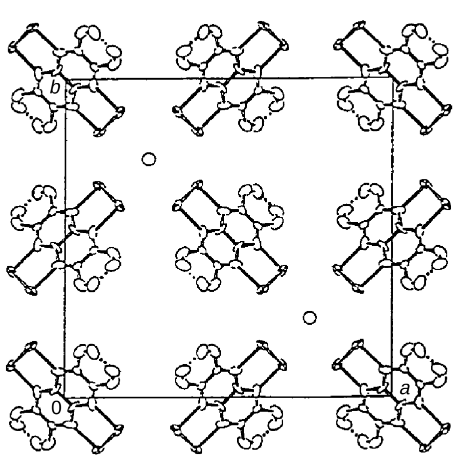


Fig. 3 Crystal structure of $(2,3\text{-DMTTeA})_2Br$ projected onto the *ab* plane

In the Br^- salt (Fig. 3), the donor stacking structure is isomorphous with the tetragonal structure of $(TSeT)_2Cl$, reported by Shibaeva and Kaminskii in 1978 (TSeT = tetraselenotetracene).[7] There exist donor stacks along the c axis, and in each stack there are very close Te···Te intermolecular contact (3.70 Å). Between neighbouring stacks, however, no short contacts are found. Therefore, this structure may be called quasi-one-dimensional. In addition, the Br^- anions are disordered along the c axis, which is responsible for the semiconducting property of this salt.

We have obtained the first single crystals of the molecular conductors based on a donor molecule with *peri*-ditellurium bridges. The higher conductivity of the Br^- salt suggests the possibility of molecular metals with novel tellurium-based conduction passways, if the disorder in the crystal structure can be eliminated.

Footnotes

† *Crystal data* for 2,3-DMTTeA: monoclinic, space group $P2_1/c$, $a = 9.976(5)$, $b = 5.137(1)$, $c = 16.186(1)$ Å, $\beta = 104.28(2)°$, $V = 803.8(3)$ Å^3, $Z = 2$, $D_c = 2.944$ g cm^{-3}, $R = 0.057$ for 1200 reflections. For $(2,3\text{-DMTTeA})_3(ClO_4)_2$: monoclinic, space group $C2/m$, $a = 16.538(3)$, $b = 14.681(2)$, $c = 11.612(4)$ Å, $\beta = 111.48(2)°$, $V = 2623(1)$ Å^3, $Z = 2$, $D_c = 2.958$ g cm^{-3}, $R = 0.037$ for 2568 reflections. For $(2,3\text{-DMTTeA})(AsF_6)_{0.2}$: monoclinic, space group $P2_1/a$, $a = 4.155(2)$, $b = 19.898(3)$, $c = 11.572(7)$ Å, $\beta = 94.85(9)°$, $V = 953.3(6)$ Å^3, $Z = 2$, $D_c = 2.614$ g cm^{-3}, $R = 0.066$ for 1400 reflections. For $(2,3\text{-DMTTeA})_2Br$: tetragonal, space group $P4_2/ncm$, $a = 18.655(2)$, $c = 5.438(3)$ Å, $V = 1892(1)$ Å^3, $Z = 2$, $D_c = 2.641$ g cm^{-3}, $R = 0.093$ for 578 reflections.

The data were collected on a Rigaku automated four-circle diffractometer (AFC5R, AFC7R) with graphite monochromated Mo-Kα radiation. The structures were solved by direct methods (SHELX86, SIR92) and refined by full-matrix least-squares methods using reflections with $I \geqslant 3\sigma(I)$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1822/382.

‡ Intramolecular bond lengths of the neutral 2,3-DMTTeA: Te–Te = 2.664(2), C–Te = 2.11(1) Å.

§ Intermolecular overlap integrals were calculated using the HOMO obtained by the extended Hückel MO calculation.

References

1 D. O. Cowan and A. Kini, *The Chemistry of Organic Selenium and Tellurium Compounds*, ed. S. Patai, Wiley, London, 1987, vol. 2, pp. 463–494; D. O. Cowan, R. McCullough, A. Bailey, K. Lerstrup, D. Talham, D. Herr and M. Mays, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1992, **67**, 277.

2 K. Kikuchi, K. Yakushi, H. Kuroda, I. Ikemoto, K. Kobayashi, M. Honda, C. Katayama and J. Tanaka, *Chem. Lett.*, 1985, 419; Z. S. Li, S. Matsuzaki, R. Kato, H. Kobayashi, A. Kobayashi and M. Sano, *Chem. Lett.*, 1986, 1105.

3 D. O. Cowan, M. D. Mays, T. J. Kistenmacher, T. O. Poehler, M. A. Beno, A. M. Kini, J. M. Williams, Y. K. Kwok, K. D. Carlson, L. Xiao, J. J. Novoa and M. H. Whangbo, *Mol. Cryst. Liq. Cryst.*, 1990, **181**, 43.

4 D. J. Sandman, J. C. Stark and B. M. Foxman, *Organometallics*, 1982, **1**, 739.

5 R. Kato, H. Kobayashi and A. Kobayashi, *Physica B + C*, 1986, **143**, 304.

6 (*a*) K. Takimiya, Y. Aso, T. Otsubo and F. Ogura, *Bull Chem. Soc. Jpn.*, 1991, **64**, 2091; (*b*) For the sulfur and the selenium isologues of 2,3-DMTTeA, see K. Takimiya, A. Ohnishi, Y. Aso, T. Otsubo, F. Ogura, K. Kawabata, K. Tanaka and M. Mizutani, *Bull. Chem. Soc. Jpn.*, 1994, **67**, 766.

7 R. P. Shibaeva and V. F. Kaminskii, *Sov. Phys. Crystallogr. Engl. Transl.*, 1978, **23**, 669; I. F. Shchegolev and E. B. Y. Yagubskii, *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, 1982, vol. 2, pp. 385–434.

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