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The selenium analogue of DOET and its conducting salts

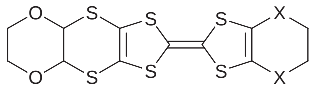
Hiroyuki Nishikawa,*[a]† Hanako Ishikawa,[a] Tatsuo Sato,[a] Takeshi Kodama,[a] Isao Ikemoto,[a] Koichi Kikuchi,*[a] Satoru Tanaka,[b] Hiroyuki Anzai[b] and Jun-ichi Yamada*[b]‡

[a]Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
[b]Department of Material Science, Faculty of Science, Himeji Institute of Technology, 1475-2 Kanaji, Kamigori-cho, Ako-gun, Hyogo 678-1297, Japan

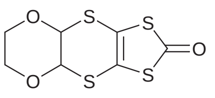
Synthesis and electrochemical properties of the title donor (DOES), electrical conductivities of its radical-cation salts, and crystal structure of $(DOES)_2(AuI_2)_{0.75}$ are described.

We have already disclosed the crystal structure of the metallic $(DOET)_2BF_4$ [DOET = (1,4-dioxanediyl-2,3-dithio)ethylenedithiotetrathiafulvalene] salt.[1] Despite the fact that the 1,4-dioxane ring of DOET is condensed by *cis* fusion,[2] the DOET molecules in this salt form the so-called β-type packing arrangement, and the band structure calculation of this salt reveals nearly two-dimensional character. One interesting modification of the DOET molecule, for inducing appreciable change in the crystal structure, might be to replace the outer sulfur atoms with selenium atoms. In this communication, we report the synthesis and electrochemical properties of the selenium analogue of DOET, *viz.* DOES [(1,4-dioxane-2,3-diyldithio)ethylenediselenotetrathiafulvalene], and the conducting behaviour of its radical-cation salts. Furthermore, the crystal structure of a metallic $(DOES)_2(AuI_2)_{0.75}$ salt is described.

Synthesis of DOES§ was carried out by cross-coupling between ketone **1**[3] and 2 equiv. of thione **2**¶ in the presence of $(MeO)_3P$ in benzene under reflux for 1 h (27% yield).



DOET; X = S
DOES; X = Se



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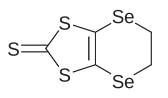

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The electrochemical properties of DOES were investigated by cyclic voltammetry in benzonitrile (0.1 M $Bu^n{}_4NClO_4$, Pt electrode, room temp., scan rate 50 mV s^{-1}). DOES showed two pairs of reversible redox waves, and its E_1 and E_2 values (+0.54, +0.84 V *vs.* SCE) are slightly lower than those of DOET ($E_1 = +0.58$ V, $E_2 = +0.88$ V).

Table 1 Conducting behaviour of the DOES salts

anion	solvent	D:A[a]	σ_{rt}/S cm^{-1} [b]
AsF_6^-	PhCl	5:2	5.1 ($Ea = 52$ meV)
PF_6^-	PhCl	2:1	0.62 ($Ea = 74$ meV)
ClO_4^-	PhCl	2:1	2.3 ($Ea = 3.7$ meV)
BF_4^-	PhCl	3:2	5.0 ($Ea = 34$ meV)
I_3^-	PhCl	2:1	60 ($T_{M-I}{}^d = 250$ K)
AuI_2^-	PhCl	2:0.75[c]	1.4 ($T_{M-I}{}^d = 55$ K)

[a]Determined by elemental analysis. [b]Room temperature conductivity measured by a four-probe technique on a single crystal. [c]Determined by the X-ray analysis. [d]Temperature of a metal-to-insulator transition.

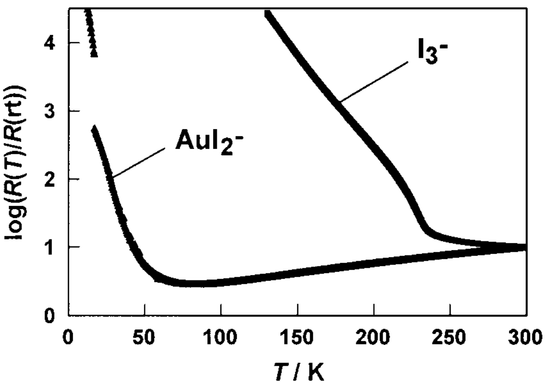

Fig. 1 Temperature dependence of the resistivity of the AuI_2 and I_3 salts of DOES

DOES formed a 1:1 charge-transfer complex with TCNQ (tetracyanoquinodimethane), the room temperature conductivity of which was rather low ($\sigma_{rt} < 10^{-6}$ S cm^{-1}). Thus, we examined the preparation of the radical-cation salts by controlled-current electrochemical oxidation[4] in chlorobenzene containing the corresponding tetrabutylammonium salt. As summarized in Table 1, the salts with octahedral and tetrahedral anions (AsF_6^-, PF_6^-, ClO_4^-, and BF_4^-) exhibited semiconducting behaviour with activation energies ranging from 3.7 meV to 74 meV. On the other hand, the salts with linear anions (I_3^- and AuI_2^-) displayed metallic behaviour. The temperature dependence of their resistivities is shown in Fig. 1. The resistivity of the AuI_2 salt shows metallic temperature dependence to 83 K, and gradually increases until 55 K where a metal-to-insulator transition occurs.|| While the resistivity of the I_3 salt increases slightly with decreasing temperature around room temperature, its temperature dependence is very small and a clear transition to insulator takes place at 250 K.||

The X-ray crystal analysis of the AuI_2^- salt of DOES** revealed that this salt has a β-type crystal structure, like $(DOET)_2BF_4$ (Fig. 2). The anion AuI_2^- is aligned almost

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†E-mail: hiron@comp.metro-u.ac.jp.

‡E-mail: yamada@sci.himeji-tech.ac.jp.

§Physical and spectroscopic data for DOES: orange cryst.; mp 168–171 °C (decomp.); MS (*m*/*z*) 538 ($M^+ + 2$), 536 (M^+); ^1H NMR ($CDCl_3$) δ 3.25 (s, 2 H), 3.40 (m, 2 H), 3.63 (m, 2 H), 3.99 (m, 2 H), 5.31 (s, 2 H). The preliminary X-ray study of DOES confirmed that the dioxane ring was condensed by *cis* fusion like that of the DOET molecule.

¶Thione **2** was prepared by reaction of $(Bu_4N)_2[Zn(dsit)_2]$ (dsit = 4,5-diselenolato-1,3-dithiole-2-thione) with 1,2-dibromoethane in THF under reflux in 97% yield.[5]

||The transition temperature of this salt was estimated by the derivative of the Arrhenius plot of its resistivity.

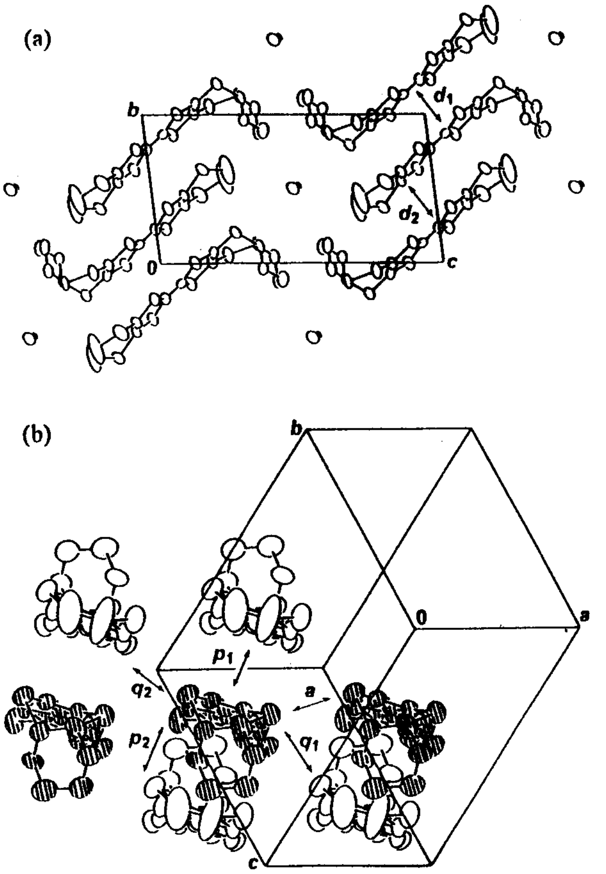

Fig. 2 Crystal structure showing: (a) intermolecular face-to-face distances: $d_1 = 3.47$ Å, $d_2 = 3.78$ Å; (b) intermolecular overlap integrals ($\times 10^{-3}$) p_1, p_2, q_1, q_2 and a are 21.31, 22.72, 7.51, 8.51 and −3.15, respectively

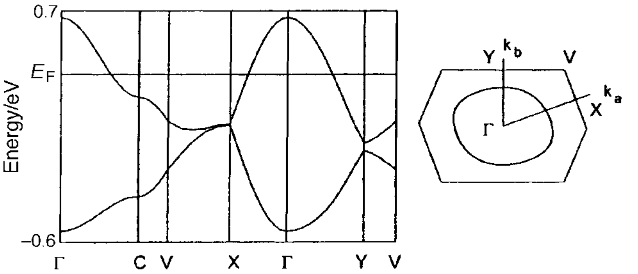

Fig. 3 Energy band structure and Fermi surface of $(DOES)_2(AuI_2)_{0.75}$

parallel to the *a* axis and the length of the anion (4.492 Å) is nearly 2/3*a*. In the oscillation photographs the diffuse lines were also observed at 3/4, 3/2, 9/4 and 3*a**. These facts indicate the 4/3*a* periodicity of the anion without the three-dimensional order. Namely, three sites for the anion are occupied by Au and I atoms with 3/4 occupancy to make the array such as ····I-Au-I-V-I-Au-I-V···· (V = vacancy) along the *a* axis and there is no correlation between these arrays. Fig. 2(b) shows the donor arrangement of $(DOES)_2(AuI_2)_{0.75}$. The DOES molecules are stacked along the [110] direction with some dimerization, so as to avoid the steric hindrance of the bulky dioxane rings. Although the intradimer and interdimer face-to-face distances (intradimer: 3.47 Å; interdimer: 3.78 Å) are larger than those in $(DOET)_2BF_4$ (intradimer: 3.50 Å; interdimer: 3.77 Å), the donor stack in $(DOES)_2(AuI_2)_{0.75}$ is much more uniform because the ratio of overlap integral p_1/p_2 is close to 1.0 compared with the value of $(DOET)_2BF_4$ [0.94 for $(DOES)_2(AuI_2)_{0.75}$, 1.6 for $(DOET)_2BF_4$]. The pattern of chalcogen contacts of $(DOES)_2(AuI_2)_{0.75}$ is similar to that of $(DOET)_2BF_4$, hence $(DOES)_2(AuI_2)_{0.75}$ has the 2D energy dispersion relation and closed Fermi surface shown in Fig. 3. Because the band filling of this salt increased by 8.3% compared with that of $(DOET)_2BF_4$, the area of the Fermi surface is smaller than in the case of $(DOET)_2BF_4$.

In conclusion, when comparing the crystal structure of $(DOES)_2(AuI_2)_{0.75}$ with that of $(DOET)_2BF_4$, the substitution of sulfur atoms of DOET with selenium atoms has a minor influence on the donor arrangement. However, this modification yields a metallic salt of different stoichiometry, which can realize a different band filling. The next aim of our ongoing investigation is further development of the metallic DOET and DOES salts and clarification of their crystal structures.

References

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**Crystal data for $(DOES)_2(AuI_2)_{0.75}$: $(C_{24}H_{20}O_4S_{12}Se_4(AuI_2)_{0.75}$, $M = 1411.06$, triclinic, space group $P\bar{1}$, $a = 6.814(3)$, $b = 9.197(5)$, $c = 16.491(8)$ Å, $\alpha = 94.49(4)$, $\beta = 96.45(4)$, $\gamma = 109.71(5)°$, $V = 959.3(9)$ Å^3, $Z = 1$, $D_c = 2.442$ g cm^{-3}, $\mu = 98.395$ cm^{-1}, $F(000) = 662.75$. The data were collected on a Mac Science MXC18 diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–2θ scan technique to a maximum 2θ of 60°. The structure was solved by direct methods using CRYSTAN (MacScience, Japan), and refined by full-matrix least-squares analysis (anisotropic for S and Se atoms) to $R = 0.082$ and $R_w = 0.093$ for 2501 independent reflections $[I \geqslant 2\sigma(I)]$. The refinement was carried out by assuming that the specific position (0, 0.5, 0.5) and the general ones for the anion are occupied by Au and I atoms, respectively. The occupancies for these sites were fixed to 0.586 (weight is 0.293) and 0.873, considering that every site is occupied by both Au (1/4 occupancy) and I (1/2 occupancy) atoms. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/95.