Ethylenedithio(ethylenedioxo)diselenadithiafulvalene (TOST) and Ethylenediseleno(ethylenedioxo)tetrathiafulvalene (SO): New Unsymmetrical π-Donors containing Three Elements in Group 16 (O, S, and Se)

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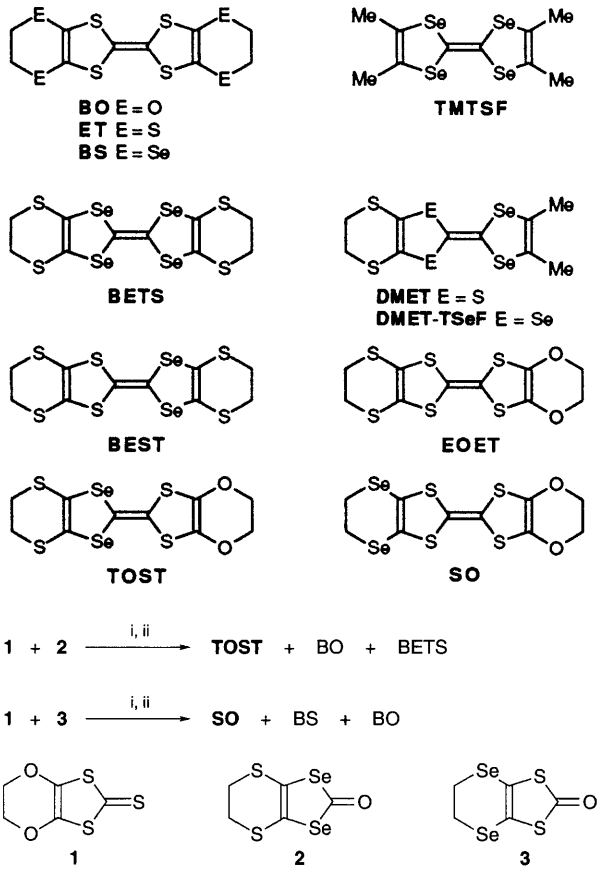
The synthesis and characterization of new unsymmetrical bis(ethylenedithio)tetrathiafulvalene (ET) analogues ethylenedithio(ethylenedioxo)diselenadithiafulvalene (TOST) and ethylenediseleno(ethylenedioxo)tetrathiafulvalene (SO) that contain three elements in group 16 (O, S and Se) and their cation radical salts are reported.

Among a large number of tetrathiafulvalene (TTF) derivatives, bis(ethylenedithio)tetrathiafulvalene (ET) has been the most important modification of the TTF skeleton, and has supplied the largest number of superconducting cation radical salts.[1,2] Furthermore, analogues of the ET molecule, *i.e.* bis(ethylenedithio)tetraselenafulvalene (BETS)[3] and bis(ethylenedioxo)-tetrathiafulvalene (BO),[4] has also given superconducting cation radical salts. In addition to these symmetrical donors, there exist some unsymmetrical combinations of the known superconducting molecular frameworks that can provide superconducting cation radical salts. For example, dimethyl(ethylenedithio)diselenadithiafulvalene (DMET)[5] is based on the ET and tetramethyltetraselenafulvalene (TMTSF) frameworks and dimethyl(ethylenedithio)tetraselenafulvalene (DMET-TSeF)[6] is based on the BETS and TMTSF frameworks. All these considerations induced us to examine the new unsymmetrical ET analogues, ethylenedithio(ethylenedioxo)diselenadithiafulvalene (TOST) and ethylenediseleno(ethylenedioxo)-tetrathiafulvalene (SO). These are based on BETS and BO, or on bis(ethylenediseleno)tetrathiafulvalene (BS)[7] and BO, respectively. Each of them contains three elements from group 16 (O, S and Se), and is expected to have a large polarity, compared with the known unsymmetrical ET analogues, ethylenedioxy(ethylenedithio)tetrathiafulvalene (EOET)[8] and bis(ethylenedithio)diselenadithiafulvalene (BEST).[9] This large polarity would effectively remove some difficulties, *e.g.* difficult separation and purification in the synthesis or disorder in the crystals. We now report their synthesis, characterization,



Scheme 1 *Reagents and conditions*: i, $P(OEt)_3$, benzene, reflux; ii, SiO_2, CS_2–CH_2Cl_2

Table 1 Cyclic voltammetric data[a]

Donor	$E_1^{1/2}$/V	$E_2^{1/2}$/V	ΔE/V
ET	0.13	0.45	0.32
BO	0.02	0.34	0.32
BS	0.09	0.43	0.34
BETS	0.30	0.55	0.25
TOST	0.13	0.44	0.31
SO	0.04	0.38	0.34

[a] *vs.* 0.01 mol dm^{-3} $Ag/AgNO_3$ in PhCN with 0.1 mol dm^{-3} Bu_4NBF_4, glassy carbon working electrode, scan speed 100 mV s^{-1}, room temperature.

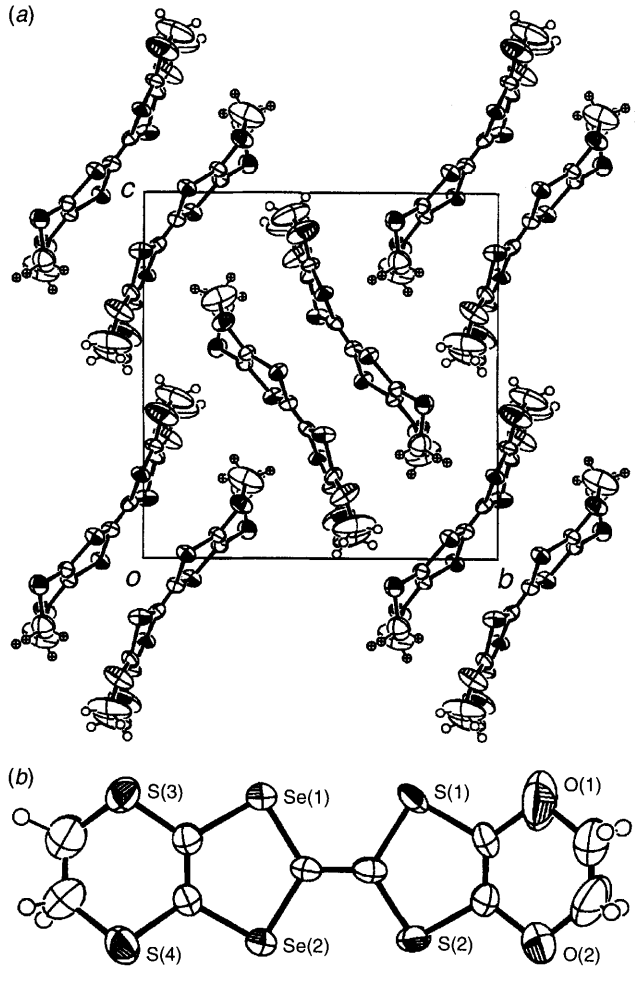


Fig. 1 Crystal structure of TOST (only the major orientation is shown for clarity); (*a*) packing diagram, (*b*) top view of the molecule

Table 2 Cation radical salts of TOST and SO

Donor	Anion	Donor–anion ratio	Shape[c]	ρ_{rt}/Ω cm	Temperature dependence[d]
TOST	$AuCl_2$	2:1[a]	N	0.03	T_{MI} = 194 K
	$AuBr_2$	2:1[a]	N	0.12	T_{MI} = 242 K
	AuI_2	2:1[a]	N	0.11	E_a[e] = 6 meV
	$Au(CN)_2$	2:1[a]	N	0.19	E_a[e] = 41 meV
	I_3	—	N	—	Insulator
	PF_6	—	P	0.19	E_a[e] = 18 meV
	AsF_6	2:1[a]	P	0.39	E_a[e] = 13 meV
	TaF_6	2:1[a]	P	0.38	E_a[e] = 8 meV
	$GaCl_4$	2:1[b]	P	1.9	Metallic down to 4.2
	$FeCl_4$	2:1[b]	P	0.31	Metallic down to 4.2
SO	$AuBr_2$	2:1[b]	R	0.05	Metallic down to 4.2
	I_3	1:1[b]	P	—	Insulator

[a] Determined by EPMA measurements. [b] Determined by X-ray analysis. [c] N = needles, P = plates, R = rods. [d] Single crystal, four-probe method; T_{MI} = temperature of the metal–semiconductor transition; E_a = activation energy. [e] Around room temperature.

electrochemical properties and preparation of some metallic cation radical salts.

The unsymmetrical π-donors TOST and SO were synthesized by the cross-coupling reaction of thione **1**[4,8] and ketone **2**[3] or ketone **3**[10] with excess $P(OEt)_3$ in refluxing benzene (Scheme 1).† Both TOST and SO are highly soluble in most organic solvents, due to their large polarity.

The donor abilities of these new π-donors were examined by measuring their redox potentials. Table 1 shows cyclic voltammetric data for the new donors and related donor molecules. All show two reversible redox waves. The $E_1^{1/2}$ value of TOST is the same as that of ET and ΔE ($=E_2^{1/2} - E_1^{1/2}$) value is smaller than that of ET. The $E_1^{1/2}$ value of SO shows a small positive shift from that of BO and the ΔE value is the same as that of BS. These results confirm that TOST and SO have enough donor ability to construct molecular metals.

The crystal structure of the neutral TOST molecule was examined by X-ray diffraction (Fig. 1).‡ The space group is $P2_1/n$ and its crystal structure, based on a pair of TOST molecules, is isomorphrous to that of ET,[11] BS[7] and BETS.[9] Orientational disorder of the TOST molecule was observed, with a small fraction (*ca.* 19%) of the TOST molecules packed with the positions of the BETS fragment ($C_5H_4S_2Se_2$) and BO fragment ($C_5H_4O_2S_2$) exchanged.§

Some cation radical salts were prepared from TOST and SO by the galvanostatic oxidation in chlorobenzene at 20 °C (Table 2). Among them, $(TOST)_2FeCl_4$, $(TOST)_2GaCl_4$ and $(SO)_2AuBr_2$ exhibit metallic resistivity behaviour down to 4.2 K. Preliminary crystal structure analyses showed that $(TOST)_2FeCl_4$ and $(TOST)_2GaCl_4$ form the κ-type molecular packing and $(SO)_2AuBr_2$ is isostructural with β″-$(ET)_2AuBr_2$.[12] Details of the physical properties and crystal structures are under investigation and will be reported soon.

This work was partially supported by a Grant-in-Aid for scientific research on Priority Area 'Novel Electronic States in Molecular Conductors' (Area No. 253/06243105) from the Ministry of Education, Science and Culture of Japan.

Received, 26th July 1995; Com. 5/04950D

Footnotes

† Typical procedure was as follows: To a refluxing benzene solution (20 ml) of a mixture of **1** (242 mg) and **2** (379 mg), or **1** (173 mg) and **3** (241 mg), was added 10 cm^3 of $P(OEt)_3$ and the reaction mixture was then refluxed for 3 h. After the removal of benzene and $P(OEt)_3$ under reduced pressure, separation of crude TOST (or SO) was achieved by silica gel column chromatography (CS_2–CH_2Cl_2 = 5:1). The second wine-red (or red) fraction was collected and recrystallization from dichloromethane–hexane gave TOST (or SO). TOST: deep wine-red crystals (259 mg, 46% based on random coupling); mp 195 °C (decomp.); ^1H NMR ($CDCl_3$) δ 3.30 (4 H s) and 4.25 (4 H s); *m/z* 448 (M^+, 61%), 420 ($M^+ - C_2H_4$, 25), 332(87), 304(38) and 88(100). SO: orange–red crystals (189 mg, 42% based on random coupling); mp 184 °C (dec.); ^1H NMR ($CDCl_3$) δ 3.34 (4 H s) and 4.26 (4 H s); *m/z* 448 [M^+ ($C_{10}H_8O_2S_2{}^{80}Se_2$), 40%], 420 ($M^+ - C_2H_4$, 33), 392 ($M^+ - 2C_2H_4$, 12), 332(22), 304(37) and 88(100).

‡ *Crystal data* for TOST: $C_{10}H_8O_2S_4Se_2$, M_W = 446.33, monoclinic, space group $P2_1/n$, a = 6.531(2), b = 14.524(3), c = 15.149(3) Å, β = 92.16(2)°, V = 1435.9(5) $Å^3$, Z = 4, D_c = 2.065 gm^{-3}, $F(000)$ = 864.0, R = 0.056, R_w = 0.062, GOF = 2.69 for 2216 observed reflections out of 4357 unique reflections. X-ray diffraction data were collected on a MAC Science automatic four-circle diffractometer with monochromated Mo-Kα (λ = 0.71069 Å; 50 kV, 300 mA) radiation up to 2θ = 60°. The intensities were corrected for Lorentz and polarization effects. The analytical absorption correction was carried out. The structure was solved by the direct method and refined with full-matrix least-squares method using reflections with [$I \geqslant 4\sigma(I)$]. Anisotropic thermal parameters were used for non-hydrogen atoms. All calculations were performed with use of a TEXSAN program package of MSC. Orientational disorder of the TOST molecule was observed (see text). It was impossible to refine the full parameters for the minor orientation due to the small fraction. Therefore, refinement of the occupancy ratio for the two possible orientations was performed with a part of the atomic parameters for the minor orientation. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The authors thank one of the referees for his helpful and constructive comments, which helped to clarify the existence of the orientational disorder.

References

1 D. Jerome, *Science*, 1991, **252**, 1509.
2 J. M. Williams, A. J. Schultz, U. Geiser, K. D. Carlson, A. M. Kini, H. H. Wang, W. K. Kwok, M-H. Whangbo and J. E. Schirber, *Science*, 1991, **252**, 1501.
3 R. Kato, H. Kobayashi and A. Kobayashi, *Synth. Met.*, 1993, **55–57**, 2780.
4 T. Suzuki, H. Yamochi, G. Srdanov, K. Hinkelmann and F. Wudl, *J. Am. Chem. Soc.*, 1989, **111**, 3108.
5 K. Kikuchi, Y. Honda, Y. Ishikawa, K. Saito, I. Ikemoto, K. Murata, H. Anzai, T. Ishiguro and K. Kobayashi, *Solid State Commun.*, 1988, **66**, 405 and references therein.
6 R. Kato, S. Aonuma, Y. Okano, H. Sawa, M. Tamura, M. Kinoshita, K. Oshima, A. Kobayashi, K. Bun and H. Kobayashi, *Synth. Met.*, 1993, **61**, 199.
7 P. J. Nigrey, B. Morosin and E. Duesler, *Synth. Met.*, 1988, **27**, B481 and references therein.
8 A. M. Kini, T. Mori, U. Geiser, S. M. Budz and J. M. Williams, *J. Chem. Soc., Chem. Commun.*, 1990, 647.
9 A. Kobayashi, R. Kato, T. Naito and H. Kobayashi, *Synth. Met.*, 1993, **55–57**, 2078.
10 J.-M. Fabre, S. Chakroune, A. Javidan and L. Zannik, International Conference on Science and Technology of Synthetic Metals (ICSM '94), Seoul, July, 1994, MON P234.
11 H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito and H. Inokuchi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 301.
12 T. Mori, F. Sakai, G. Saito and H. Inokuchi, *Chem. Lett.*, 1986, 1875.