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Bis(ethylenedioxy)diselenadithiafulvalene (BEDO-STF)

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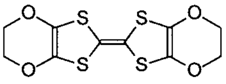
As a new promising π-donor for organic metals and superconductors, the title compound has been synthesized without the use of highly toxic CSe_2 or H_2Se gas; the preparation of stable organic metals including a new κ-type salt is also mentioned.

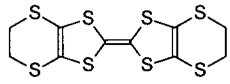
Bis(ethylenedioxy)tetrathiafulvalene (BO)[1] is one of the most successful π-donors derived from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET), the flagship molecule of the organic π-donors.[2] BO has supplied a large number of metallic cation radical salts with various inorganic or organic counter anions[3] and two superconducting salts are also known.[4,5] The most distinguished feature of the BO molecule compared with other TTF derivatives is the existence of the ethylenedioxy group, and the effect of the oxygen substitution on the electronic state and crystal structure has been of interest. However, X-ray structure analysis of the BO salt is usually difficult due to the low quality and small size of the single crystals obtained, and further research on the physical properties has been prevented.

From the viewpoint of the improvement of the crystal quality and fine tuning of the electronic state of the cation radical salts, we have tried to introduce selenium atoms into the inner frame of the parent BO molecule. Several modifications of the BO skeleton have been reported by our group and others;[6,7] however, all these donors contain only two oxygen atoms on the skeleton. The origin of the characteristic features of the BO molecule, *e.g.* CH···O type hydrogen bonding and high solubility, must be due to the existence of *two* ethylenedioxy groups on the edges of the skeleton, and we have decided therefore to fix the outer part of the BO framework and modify the inner TTF moiety. The selenium substitution method is well-known as the one of the most effective methods of stabilizing metallic and/or superconducting states at low temperature, and the disadvantage of the selenium substitution, lowering of the solubility, should be reduced in the present case by the two ethylenedioxy groups. Our goal is the synthesis of the all selenium-substituted π-donor bis(ethylenedioxy)tetraselenafulvalene (BEDO-TSeF); however, it is usually difficult to synthesize TSeF analogues without using the highly toxic and foul-smelling reagents, CSe_2 or H_2Se gas. As the first step of the project, we planned to substitute half of the TTF sulfur atoms of BO with selenium atoms without using the above troublesome reagents. Here we report the synthesis and properties of a novel BO analogue, bis(ethylenedioxy)diselenadithiafulvalene **1** (BEDO-STF). The preparation, conductivity and crystal structures of metallic cation radical salts are also mentioned.

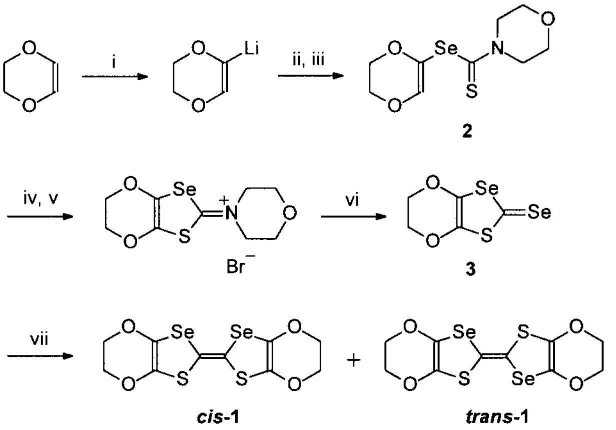
The synthesis of **1** is outlined in Scheme 1. The starting material is commercially available 2,3-dihydro-1,4-dioxine and the key intermediate of the present route is thiocarbonyl selenoester **2**. Highly viscous 5-lithio-2,3-dihydro-1,4-dioxine was obtained by treatment of neat 2,3-dihydro-1,4-dioxine with 1 equiv. of BuLi at 0 °C.[8] To a THF solution of 5-lithio-2,3-dihydro-1,4-dioxine was added powdered selenium at −35 °C to give an orange solution of 2,3-dihydro-1,4-dioxine-5-selenolate. After cooling to −78 °C, morpholine-4-thiocarbonyl chloride was added in one portion and the key intermediate **2** was obtained in 68% isolated yield as a cream–white powder. Synthesis of selone **3** from **2** was achieved *via* the same procedure as for the synthesis of 4,5-ethylenedioxy-1,3-dithiole-2-seleone,[1] except for the selenocarbonyl synthesis, in which we used the NaSeH–AcOH method[9] to avoid the use of H_2Se gas. Treatment of the selone **3** with triethyl phosphite in refluxing benzene gave the title compound **1** as deep-red microcrystals‡ which had good solubility towards the usual organic solvents.



BO



ET



Scheme 1 *Reagents and conditions*: i, BuLi (1 equiv.), 0 °C; ii, Se, THF, −35 °C; iii, morpholine-4-thiocarbonyl chloride, −78 °C (68%); iv, Br_2, CH_2Cl_2; v, 110 °C; vi, Se, $NaBH_4$, AcOH–EtOH (11%); vii, $P(OEt)_3$, benzene, reflux (12%)

The doubling of the all ^{13}C NMR signals of **1** demonstrates the existence of *cis-* and *trans*-isomers. It was impossible to separate these isomers by the usual chromatography methods; however, isolation of the neutral isomer is not always necessary for the preparation of conducting salts, as has been shown for other mixed chalcogenofulvalenes.[10]

Cyclic voltammetry measurements were taken at room

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‡New compounds were characterized by elemental and/or spectral analyses. *Selected data* for **1**: deep-red microcrystals; ^1H NMR ($CDCl_3$, 500 MHz): δ 4.267 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ (minor isomer) 66.15, 66.54, 102.06, 121.62, 126.57; δ (major isomer) 66.18, 66.48, 101.34, 122.19, 125.74; MS (EI, 70 eV): 416 (100%, M^+ for $C_{10}H_8O_4S_2{}^{80}Se_2$), 388 ($M^+ - C_2H_4$, 27%), 300 ($M^+ - C_4H_4O_2S$, 38%), 252 ($M^+ - C_4H_4O_2Se$, 69%); Calc. for $C_{10}H_8O_4S_2Se_2$: C, 29.00; H, 1.95. Found: C, 28.94; H, 2.03%.

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Table 1 Cyclic voltammetric data for **1** and related π-donors. Values are given in V *vs.* the ferrocene/ferrocenium couple

donor	$E_{1/2}{}^1$/V	$E_{1/2}{}^2$/V	ΔE/V
ET	0.06	0.38	0.32
BO	−0.05	0.27	0.32
BEDO-STF **1**	0.01	0.30	0.29

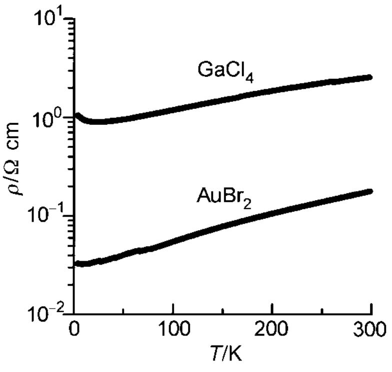

Fig. 1 Temperature dependence of the resistivity for the $AuBr_2$ and $GaCl_4$ salts of **1**

temperature using a glassy-carbon working electrode in benzonitrile at 100 mV s^{-1} with 0.1 M Bu_4NBF_4 and measured *vs.* a 0.01 M $Ag/AgNO_3$ reference. Table 1 summarizes the half-wave potentials of **1** and related π-donors *vs.* the potential of the ferrocene/ferrocenium couple. The donor **1** showed two reversible redox waves. As expected from the selenium substitution of the TTF skeleton, the first redox potential ($E_{1/2}{}^1$) is at a slightly higher voltage than that of the parent BO; however, the difference between the first and second redox potentials ($\Delta E = E_{1/2}{}^2 - E_{1/2}{}^1$), which reflects the on-site coulombic repulsion, is 0.03 V smaller than those of BO and ET. The decrease in ΔE must be due to the larger size of the 4p atomic orbital on the inner selenium atoms and is promising for the preparation of stable metallic salts.

To confirm the potential ability of the π-donor **1**, cation radical salts were prepared *via* galvanostatic oxidation. Two conducting salts ($AuBr_2$ and $GaCl_4$ salts) were obtained and both salts are fundamentally metallic down to 4.2 K (Fig. 1). Large thick plate crystals of the $GaCl_4$ salt were harvested and X-ray structure analysis was performed on a single crystal.§ The donor–anion ratio is 2:1 and disorder of the selenium and sulfur atoms has been observed in all four positions. It is known that the parent BO molecule tends to construct similar types of donor arrangements in most cases,[3] however the present $GaCl_4$ salt forms a so-called κ-type arrangement, which is well-known as the most promising for construction of a two-dimensional electronic state (Fig. 2). The calculated Fermi surface is a closed two-dimensional one and is also in accordance with the stable metallic feature.

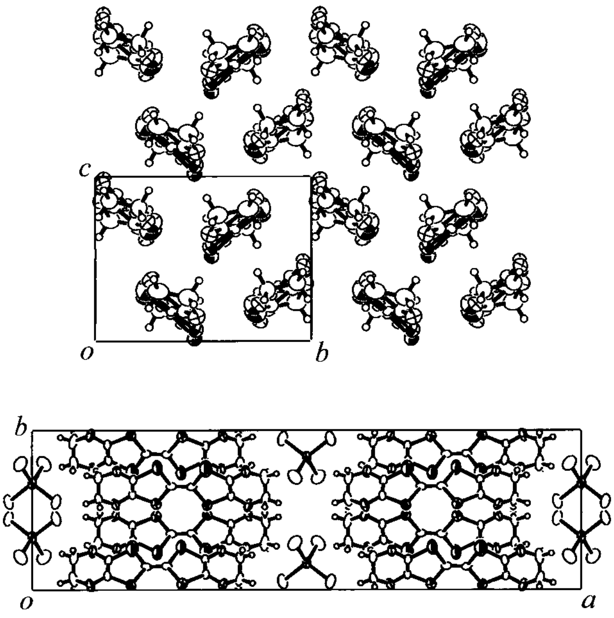

Fig. 2 Crystal structures of κ-($\mathbf{1}$)$_2$GaCl$_4$: top, donor layer arrangement viewed along the *a* axis and bottom, crystal packing viewed along the *c* axis

In conclusion, we have synthesized the first selenium-substituted BO analogue using a newly developed CSe_2- and H_2Se-free synthetic method and obtained a large single crystal of a new κ-type salt suitable for X-ray structure analysis. Examination of the other metallic and superconducting salts is in progress.

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§X-Ray diffraction data were collected on a Rigaku AFC6S automatic four-circle diffractometer with monochromated Mo-Kα ($\lambda = 0.71069$ Å) radiation up to $2\theta = 60.2°$. The structure was solved by direct methods and refined with full-matrix least-squares methods using reflections with $I \geqslant 3\sigma(I)$. The data were corrected for Lorentz and polarization effects. Anisotropic thermal parameters were used for non-hydrogen atoms except for disordered sulfur atoms. All calculations were performed using the teXsan program package of MSC. *Crystal data* for $(\mathbf{1})_2GaCl_4$: $(C_{10}H_8O_4S_2Se_2)_2(GaCl_4)$, $M = 1039.95$, *monoclinic*, space group $C2/c$ (#15), $a = 36.14(1)$, $b = 10.532(5)$, $c = 8.073(3)$ Å, $\beta = 94.46(3)°$, $V = 3063(1)$ Å^3, $Z = 4$, $\mu = 63.18$ cm^{-1}, $D_c = 2.255$ g cm^{-3}, $F(000) = 1996.0$, $R = 0.074$, $Rw = 0.046$, GOF = 3.00 for 2420 observed reflections out of 4735 unique reflections.

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 1145/107.

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