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Preparation, structures and physical properties of selenium analogues of DTEDT as promising donors for organic metals

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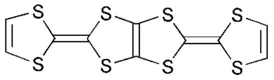
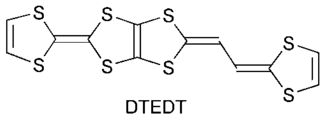
Three selenium analogues of DTEDT [2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene] have been synthesized. They showed four pairs of single-electron redox waves. The E_1 values are a little higher by 0.02–0.05 V than that of DTEDT. On the other hand, the E_2-E_1 values are almost equal to that of DTEDT. Their TCNQ complex and cation radical salts show fairly high electrical conductivities and several salts exhibit metallic conductivities. In particular the ReO_4^- and $Au(CN)_2^-$ salts of DTEDS and the SbF_6^-, TaF_6^- and I_3^- salts of DSEDS exhibited stable metallic behaviour down to 1.5–4.2 K. An X-ray crystal structure analysis of the metallic salt $(DSEDS)_3TaF_6$ reveals that this salt has a two-dimensional β-type packing motif of the donor molecules similar to the superconducting $(DTEDT)_3Au(CN)_2$. The calculated Fermi surface of $(DSEDS)_3TaF_6$ is a two-dimensional closed ellipsoid.

Introduction

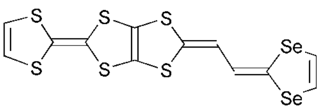
In the course of the development of new donor components for organic conductors, the enhancement of dimensionality of intermolecular interactions has been recognized as an important guideline for realizing stable metallic behaviour down to low temperatures since the discoveries of several two-dimensional stable metals among bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts.[1] A bis-fused TTF, 2,5-bis(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentalene (TTP), in which two TTFs are directly fused with each other, is a promising π-electron framework due to the so-called "ladder-like array" of sulfur atoms similar to BEDT-TTF. We have synthesized a large number of TTP derivatives to date,[2] and found that many of them have produced cation-radical salts metallic down to liquid helium temperature.[2,3] On the other hand, a vinylogue of TTP, 2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DTEDT)[4] has been revealed to be of much interest during the investigation of TTP analogues,[5] because DTEDT has yielded many metallic cation-radical salts stable down to liquid helium temperature and $(DTEDT)_3Au(CN)_2$ is an ambient pressure superconductor below 4 K.[4] Therefore, chemical modification of the DTEDT molecule is a subject of the utmost importance. We have reported the synthesis and properties of DTEDT derivatives with various substituents.[6] On the other hand, the introduction of heavier chalcogen atoms such as selenium to the DTEDT framework is also an attractive modification because of the strengthened transverse chalcogen–chalcogen interaction due to the larger electron clouds of the selenium atoms and the resultant stabilization of the metallic state at low temperature.[7] Such a strong stabilization has been observed in the salts of bis(ethylenedithio)tetraselenafulvalene (BETS),[8] which has yielded many stable metals and a series of organic superconductors λ-$(BETS)_2Fe_xGa_{1-x}Cl_yBr_{4-y}$.[9] Considering the history of the development of new organic donors so far, there are much fewer syntheses of unsymmetrical donors containing 1,3-diselenole rings than of the corresponding 1,3-dithiole donors, because the synthesis of such selenium analogues is usually very difficult. Therefore, systematic study of the selenium analogues is considered to be very useful for the future development of new donors. In this paper, we describe the synthesis and electrochemical properties of three selenium analogues of DTEDT, namely, 2-(1,3-dithiol-2-ylidene)-5-[2-(1,3-diselenol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DTEDS, **1a**) 2-(1,3-diselenol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DSEDT, **2a**) and 2-(1,3-diselenol-2-ylidene)-5-[2-(1,3-diselenol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (DSEDS, **3a**), in which two or four sulfur atoms of the terminal 1,3-



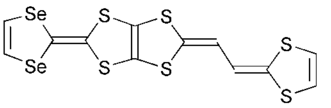
TTP



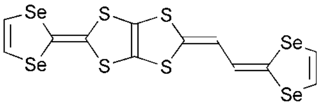
DTEDT



DTEDS(**1a**)



DSEDT(**2a**)



DSEDS(**3a**)

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dithiole rings are exchanged by selenium atoms. Furthermore, conducting properties of their CT complexes and cation radical salts and especially the crystal and band structures of the salt $(DSEDS)_3TaF_6$ are also presented.[10]

Experimental

General

THF was freshly distilled under argon over sodium and benzophenone prior to use. Trimethyl phosphite was distilled under argon by fractional distillation. Melting points were determined with a Yanaco MP-J3 micro melting point apparatus and are not corrected. Microanalyses were performed at the Microanalysis Center, Kyoto University. NMR spectra were recorded on a JEOL FT-NMR Model JNM-EX270 (270 MHz for ^{1}H) spectrometer, and chemical shift values are given in parts per million (ppm) relative to internal tetramethylsilane. Mass spectra were obtained with a Shimadzu Model QP-1000EX spectrometer and IR spectra with BIO-RAD FTS-30 FTIR and Perkin-Elmer 1600 FTIR spectrometers.

1-[4,5-Bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]-2-(4,5-carbonyldithio-1,3-dithiol-2-ylidene)ethane (6)

To a solution of 4,5-(diethoxyphosphorylmethylene)dithio-1,3-dithiol-2-one (**4**) (1.00 g, 3.03 mmol) and 2-formylmethylidene-4,5-bis(methoxycarbonyl)-1,3-diselenole (**5**) (1.07 g, 3.03 mmol) in 95 ml of dry THF was added dropwise 0.5 M LDA (6.70 ml, 3.35 mmol) for 15 min at −78 °C under argon. After additional stirring for 15 min at −78 °C, 100 ml of propan-2-ol was added and the precipitate was filtered and washed with propan-2-ol and *n*-hexane and dried *in vacuo*. The resultant solid was dissolved in dichloromethane and column chromatographed on silica gel with dichloromethane as the eluent and evaporated *in vacuo*. Obtained as brown microcrystals (768 mg, 1.45 mmol) in 48% yield; mp 194–195 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 3006, 2954, 1723, 1706, 1664, 1618, 1574, 1430, 1271, 1243, 1009, 788; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.09 (d, J = 11 Hz, 1H), 5.64 (d, J = 11 Hz, 1H), 3.55 (s, 6H); MS *m*/*z* (relative intensity) 526 (12), 527 (8), 528 (50), 529 (45), 530 (M$^+$, 90), 531 (42), 532 (100), 533 (18), 534 (40); Anal. Calcd. for $C_{13}H_8O_5S_4Se_2$: C, 29.44; H, 1.52. Found: C, 29.30; H, 1.69%.

2-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-5-{2-[4,5-bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]ethylidene}-1,3,4,6-tetrathiapentalene (1b)

The ketone **6** (189 mg, 0.357 mmol) and 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**7**) (200 mg, 0.800 mmol) were stirred in a solution of trimethyl phosphite (6 ml) and toluene (6 ml) at 110 °C under argon for 2 h. The reaction mixture was cooled to room temperature and *n*-hexane (30 ml) was added, the resultant precipitate was filtered, washed with *n*-hexane, and then dried *in vacuo*. The precipitate was column chromatographed on silica gel with dichloromethane as the eluent and evaporated. Obtained as greenish dark brown microcrystals (142 mg, 0.193 mmol) in 52% yield; mp 198–199 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 3002, 2949, 1742, 1708, 1693, 1573, 1558, 1429, 1282, 1236, 1023, 668; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.14 (d, J = 11 Hz, 1H), 5.62 (d, J = 11 Hz, 1H), 3.85 (s, 6H), 3.81 (s, 6H); Anal. Calcd. for $C_{20}H_{14}O_8S_6Se_2$: C, 32.79; H, 1.93. Found: C, 32.72; H, 2.04%.

2-(1,3-Dithiol-2-ylidene)-5-[2-(1,3-diselenol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (1a)

A mixture of **1b** (141 mg, 0.192 mmol) and LiBr·H_2O (404 mg, 3.85 mmol) in HMPA (15 ml) was held under vacuum for 1 h to eliminate traces of amines in the solvent. The mixture was stirred at 90 °C for 1 h and then at 130 °C for 1 h under bubbling argon gas. The reaction mixture was cooled to room temperature, and methanol (50 ml) was added. The resultant precipitate was filtered and washed with methanol and *n*-hexane, and dried *in vacuo*. The precipitate was silica gel column chromatographed with CS_2 as the eluent. Obtained as orange microcrystals (60 mg, 0.12 mmol) in 62% yield; mp 197 °C (decomp.) (recrystallized from chlorobenzene); IR (KBr) ν (cm^{-1}) 3051, 1537, 1506, 1273, 967, 811, 798, 722, 643, 617; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.83 (q, J = 6.5 Hz, 2H), 6.16 (d, J = 11 Hz, 1H), 6.02 (s, 2H), 5.62 (d, J = 11 Hz, 1H); MS *m*/*z* (relative intensity) 494 (4), 495 (10), 496 (20), 497 (29), 498 (50), 499 (62), 500 (M$^+$, 90), 501 (64), 502 (100), 503 (27), 504 (50), 505 (11), 506 (12); Anal. Calcd. for $C_{12}H_6S_6Se_2$: C, 28.80; H, 1.21. Found: C, 29.00; H, 1.37%.

1-[4,5-Bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]-2-(4,5-thiocarbonyldithio-1,3-dithiol-2-ylidene)ethane (13)

To a solution of 4,5-(diethoxyphosphorylmethylene)dithio-1,3-dithiole-2-thione (**11**) (1.00 g, 2.89 mmol) and 2-formylmethylidene-4,5-bis(methoxycarbonyl)-1,3-dithiole (**12**) (751 mg, 2.89 mmol) in 100 ml of dry THF was added dropwise 0.5 M LDA (6.4 ml, 3.2 mmol) for 10 min at −78 °C under argon. After additional stirring for 20 min at −78 °C, 90 ml of propan-2-ol was added and the precipitate was filtered and washed with propan-2-ol and *n*-hexane and dried *in vacuo*. Obtained as reddish brown microcrystals (1.15 g, 2.53 mmol) in 88% yield; mp 226–227 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 3005, 2945, 1730, 1706, 1578, 1519, 1430, 1284, 1252, 1062, 1030, 792; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 5.78 (d, J = 11 Hz, 1H), 5.63 (d, J = 11 Hz, 1H), 3.58 (s, 6H); MS *m*/*z* (relative intensity) 452 (M$^+$, 100), 453 (20), 454 (32), 455 (6), 456 (5); Anal. Calcd. for $C_{13}H_8O_4S_7$: C, 34.50; H, 1.78. Found: C, 34.36; H, 1.70%.

The analogue **14** was obtained by a similar procedure to that mentioned above.

1-[4,5-Bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]-2-(4,5-thiocarbonyldithio-1,3-dithiol-2-ylidene)ethane (14)

Obtained in 74% (1.16 g, 2.13 mmol) from **11** (1.00 g, 2.89 mmol) and **5** (1.02 g, 2.89 mmol) in 100 ml of dry THF after washing with propan-2-ol and *n*-hexane; mp 247 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 2987, 2945, 1730, 1698, 1560, 1522, 1431, 1277, 1227, 1071, 1006, 965, 802; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.05 (d, J = 11 Hz, 1H), 5.59 (d, J = 11 Hz, 1H), 3.54 (s, 6H); MS *m*/*z* (relative intensity) 540 (4), 541 (7), 542 (17), 543 (15), 544 (46), 545 (34), 546 (M$^+$, 84), 547 (38), 548 (100), 549 (22), 550 (43), 551 (8), 552 (10); Anal. Calcd. for $C_{13}H_8O_4S_5Se_2$: C, 28.57; H, 1.47. Found: C, 28.45; H, 1.72%.

2-[4,5-Bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]-5-{2-[4,5-bis(methoxycarbonyl)-1,3-dithiol-2-ylidene]ethylidene}-1,3,4,6-tetrathiapentalene (2b)

Trimethyl phosphite (20 ml) was added to a refluxing toluene solution (60 ml) of the thione **13** (400 mg, 1.22 mmol) and 4,5-bis(methoxycarbonyl)-1,3-diselenol-2-one (**9**) (828 mg, 1.83 mmol) under argon and the mixture was stirred for 2 h under reflux. The reaction mixture was cooled to room temperature and added *n*-hexane (100 ml), the resultant precipitate was filtered, washed with *n*-hexane, and then dried *in vacuo*. The precipitate was column chromatographed on silica gel with dichloromethane as the eluent. Obtained as greenish dark brown microcrystals (460 mg, 0.628 mmol) in 52% yield; mp 195–196 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 3000, 2950, 1736, 1723, 1707, 1566, 1519, 1431, 1274, 1224, 1090, 1007, 708; ^{1}H-NMR (CS_2–$CDCl_3$, 270 MHz) δ 6.07 (d, $J = 11$ Hz, 1H), 5.96 (d, $J = 11$ Hz, 1H), 4.088 (s, 6H), 4.084 (s, 6H); Anal. Calcd. for $C_{20}H_{14}O_8S_6Se_2$: C, 32.79; H, 1.93. Found: C, 32.91; H, 2.05%.

The analogue **3b** was obtained by a similar procedure to that mentioned above.

2-[4,5-Bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]-5-{2-[4,5-bis(methoxycarbonyl)-1,3-diselenol-2-ylidene]ethylidene}-1,3,4,6-tetrathiapentalene (3b)

Obtained in 33% yield (249 mg, 0.301 mmol) from **14** (300 mg, 0.915 mmol) and **9** (750 mg, 1.37 mmol) after column chromatography on silica gel with dichloromethane as the eluent; mp 193 °C (decomp.) (recrystallized from 1,2-dichloroethane); IR (KBr) ν (cm^{-1}) 2998, 2948, 1727, 1700, 1560, 1521, 1430, 1242, 1067, 1009, 735; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.1–6.0 (m, 1H), 5.6–5.4 (m. 1H), 3.602 (s, 3H), 3.597 (s, 3H), 3.588 (s, 3H), 3.578 (s, 3H); Anal. Calcd. for $C_{20}H_{14}O_8S_4Se_4$: C, 29.07; H, 1.71. Found: C, 29.14; H, 1.89%.

2-(1,3-Diselenol-2-ylidene)-5-[2-(1,3-dithiol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (2a)

A mixture of **2b** (466 mg, 0.636 mmol) and $LiBr \cdot H_2O$ (2.00 g, 19.1 mmol) in HMPA (100 ml) was held under vacuum for 1 h to eliminate traces of amines in the solvent. The mixture was stirred at 90 °C for 1 h and then at 130 °C for 1 h under bubbling argon gas. The reaction mixture was cooled to room temperature, and extracted three times with benzene. The organic layers were washed three times with distilled water and dried over Na_2SO_4, and the solvent was evaporated *in vacuo*. The residue was column chromatographed on silica gel with CS_2 as the eluent. Obtained as orange microcrystals (132 mg, 0.264 mmol) in 41% yield; mp 211 °C (decomp.) (recrystallized from chlorobenzene); IR (KBr) ν (cm^{-1}) 3036, 2986, 1528, 1516, 1502, 1282, 1251, 968, 814, 803, 720, 635, 609, 581; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.96 (s, 2H), 6.02–5.94 (m, 2H), 5.81 (d, $J = 11$ Hz, 1H), 5.69 (d, $J = 11$ Hz, 1H); MS *m/z* (relative intensity) 494 (4), 495 (12), 496 (18), 497 (30), 498 (50), 499 (59), 500 (M^+, 89), 501 (67), 502 (100), 503 (30), 504 (49), 505 (10), 506 (12); Anal. Calcd. for $C_{12}H_6S_6Se_2$: C, 28.80; H, 1.21. Found: C, 28.88; H, 1.34%.

The analogue **3a** was obtained by a similar procedure to that mentioned above.

2-(1,3-Diselenol-2-ylidene)-5-[2-(1,3-diselenol-2-ylidene)ethylidene]-1,3,4,6-tetrathiapentalene (3a)

Obtained in 47% yield (72 mg, 0.12 mmol) from **3b** (210 mg, 0.254 mmol) and $LiBr \cdot H_2O$ (799 mg, 7.62 mmol) in HMPA (50 ml) after column chromatography on silica gel with CS_2 as the eluent; mp 210–211 °C (decomp.) (recrystallized from chlorobenzene); IR (KBr) ν (cm^{-1}) 3028, 1538, 1530, 1516, 1505, 1273, 1235, 966, 818, 800, 724, 620, 525; ^{1}H-NMR (CS_2–C_6D_6, 270 MHz) δ 6.92 (s, 2H), 6.83 (q, $J = 6.5$ Hz, 2H), 6.15 (d, $J = 11$ Hz, 1H), 5.63 (d, $J = 11$ Hz, 1H); MS *m/z* (relative intensity) 585 (3), 586 (6), 587 (12), 588 (17), 589 (26), 590 (37), 591 (43), 592 (67), 593 (61), 594 (M^+, 94), 595 (70), 596 (100), 597 (48), 598 (85), 599 (32), 600 (42), 601 (9), 602 (14); Anal. Calcd. for $C_{12}H_6S_4Se_4$: C, 24.25; H, 1.02. Found: C, 24.55; H, 1.23%.

General procedure for preparation of TCNQ complexes and I_3^- salts (except for the I_3^- salt of 1a)

Hot solutions of donor molecule and TCNQ or tetra-*n*-butylammonium triiodide in chlorobenzene were mixed, and the resultant precipitate was collected by filtration. The TCNQ complexes were washed with CS_2 and CH_3CN, and dried *in vacuo*. I_3^- salts were washed with CS_2 and MeOH, and dried *in vacuo*. The ratio of donor and TCNQ or I_3^- was determined by elemental analysis or energy dispersion spectroscopy (EDS).

General procedure for preparation of cation radical salts

Cation radical salts of **1a** and **3a** were prepared by electrochemical oxidation in chlorobenzene containing *ca.* 5% absolute ethanol at a constant current of 0.2–0.3 μA in the presence of the corresponding tetra-*n*-butylammonium salts at 20 °C, except for the I_3^- salt of **1a** which was obtained by a diffusion technique (also containing 10% absolute ethanol). The crystals obtained were washed with EtOH and were air-dried at room temperature. The ratio of donor and anion was determined by energy dispersion spectroscopy (EDS) and X-ray crystallographic analysis.

Electrochemical measurement

The cyclic voltammetry system used in this experiment was composed of a Yanaco polarographic analyzer Model P-1100, a Graphtec *x*–*y* recorder Model WX-1200. The measurement was performed in benzonitrile containing a donor molecule (0.2 mM) and tetra-*n*-butylammonium perchlorate (0.1 M) as a supporting electrolyte by use of platinum working and counter electrodes, and a Yanaco saturated calomel electrode (SCE) Model MR-P2A as reference electrode (scan rate: 50 mV s^{-1}).

Electrical conductivity measurement

Electrical conductivity was measured using the four-probe method on a Huso Electro Chemical System HECS 994 Multi-channel 4-terminal conductometer. Electrical contacts were achieved with gold paste.

X-Ray crystal structure analysis of (DSEDS)$_3$TaF$_6$‡

Crystal data: $C_{12}F_2H_6S_4Se_4Ta_{0.33}$, $M = 691.97$, triclinic, space group $P1$, $a = 6.438(1)$, $b = 19.151(2)$, $c = 3.930(1)$ Å, $\alpha = 92.69(2)$, $\beta = 95.76(2)$, $\gamma = 93.70(1)°$, $U = 480.4(2)$ Å^3, $Z = 1$, $D_c = 2.39$ g cm^{-3}, μ(Mo-Kα) $= 9.947$ mm^{-1}, $F(000) = 320.09$. A black plate crystal of dimensions $0.48 \times 0.15 \times 0.03$ mm^3 was used for X-ray measurement at 293 K on a Rigaku AFC7R diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. 3035 reflections measured and 2803 unique ($R_{int} = 0.032$). The structure was solved by a direct method (SHELXS86).[11] The anion molecule is disordered and the site occupancy of the anion molecule was refined to 0.33 by a population refinement on fixing the thermal parameters. The non-hydrogen atoms were refined anisotropically except for the fluorine atoms in the anion which were refined isotropically. Hydrogen atoms were included but not refined. The structure was refined by full-matrix least squares to $R = 0.043$, $Rw = 0.047$, GOF $= 2.37$ (1825 reflections $[I > 3.0\sigma(I)]$).

Band structure calculations

The transfer integrals, band structure and Fermi surface were calculated by a tight-binding method based on the extended Hückel approximation.[12] Slater type atomic orbitals were used

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‡CCDC reference number 1145/222. See http://www.rsc.org/suppdata/jm/b0/b002790l/ for crystallographic files in .cif format.

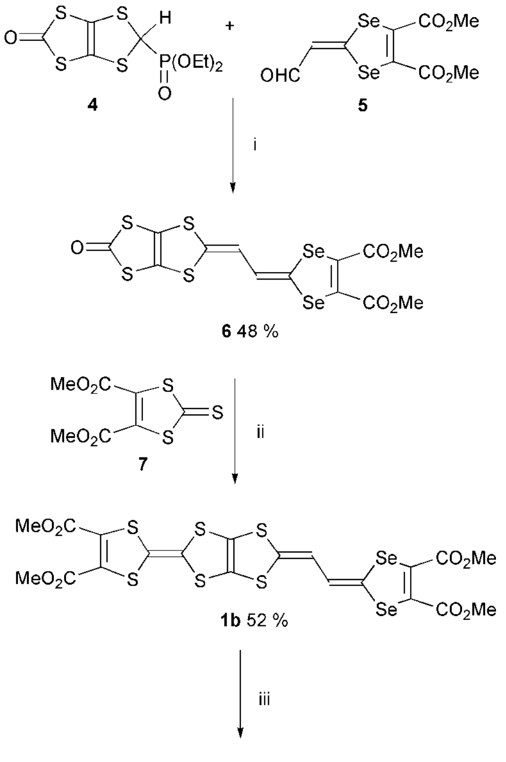
for the calculation of molecular orbitals. The exponent ζ and the ionization potential (eV) are: Se 4s, 2.112, −20.0; Se 4p, 1.827, −11.0; Se 4d, 1.500, −6.8; S 3s, 2.122, −20.0; S 3p, 1.827, −11.0; S 3d, 1.500, −5.4; N 2s, 1.950, −26.0; N 2p, 1.950, −13.4; C 2s, 1.625, −21.4; 2p, 1.625, −11.4; H 1s, 1.0 −13.6.

Results and discussion

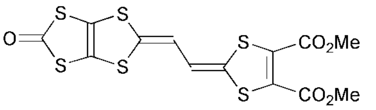
Synthesis

DTEDS (**1a**) was synthesized by a similar method to DTEDT as shown in Scheme 1. Thus, a ketone derivative of the phosphonate reagent for Wittig–Horner reaction (**4**)[6a] was treated with lithium diisopropylamide (LDA) in the presence of 2-formylmethylidene-4,5-bis(methoxycarbonyl)-1,3-diselenole (**5**)[7] to give the corresponding vinylogous diselenadithiafulvalene (DSDTF) **6** in 48% yield. Then the ketone **6** was cross-coupled with 4,5-bis(methoxycarbonyl)-1,3-dithiole-2-thione (**7**) in refluxing trimethyl phosphite and toluene (1 : 1, v/v), and afforded the tetrakis(methoxycarbonyl)-DTEDS **1b** (52% yield). The parent DTEDS was obtained in 62% yield by demethoxycarbonylation of **1b** with an excess of LiBr·H_2O in HMPA at 90–130 °C.

On the other hand, the bis- or tetrakis-methoxycarbonyl-substituted DSEDT and DSEDS derivatives could not be obtained by the cross-coupling reaction of the ketones **6** or **8** with 4,5-bis(methoxycarbonyl)-1,3-diselenol-2-one (**9**) or even with 1,3-diselenole-2-selone (**10**). Therefore the corresponding thione derivatives of vinylogous TTF (**13**) and DSDTF (**14**) were prepared by the Wittig–Horner reaction of the thione derivative of phosphonate **11**[13] and the corresponding 2-formylmethylidene-4,5-bis(methoxycarbonyl)-1,3-dichalcogenole (**12** and **5**) in 88 and 74% yields, respectively (Scheme 2). They were reacted with the 4,5-bis(methoxycarbonyl)-1,3-diselenol-2-one (**9**) to give the tetrakis(methoxycarbonyl) substituted DSEDT (**2b**) and DSEDS (**3b**) in 52 and 33% yields, respectively. After the demethoxycarbonylation by the same procedure as for the case of DTEDS, DSEDT (**2a**) and DSEDS (**3a**) were obtained in yields of 41 and 47%, respectively. These three selenium analogues are stable in air and less soluble in organic solvents than DTEDT.



Scheme 1 *Reagents and conditions*: i, 0.5 M LDA (1 equiv.), THF, −78 °C, 30 min; ii, $P(OMe)_3$ (100 equiv.), toluene, 110 °C, 2 h; iii, LiBr·H_2O (20 equiv.), HMPA, 90 °C, 1 h and 130 °C, 1 h.



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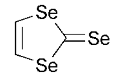

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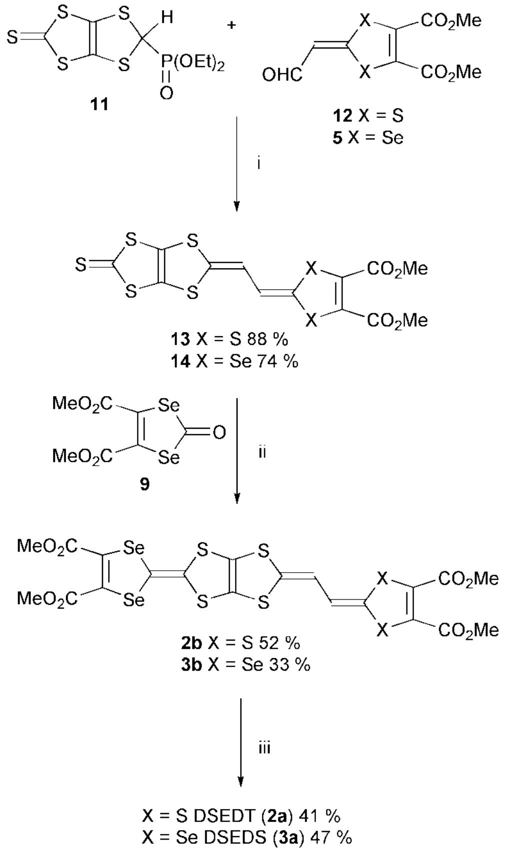
Electrochemical properties

The electrochemical properties of the selenium analogues were investigated by cyclic voltammetry. Fig. 1 shows cyclic voltammograms of **3a** in benzonitrile. All the selenium analogues **1a**–**3a** showed four pairs of single-electron redox waves corresponding to the existence of four redox-active 1,3-dichalcogenole parts. Their redox potentials are summarized in Table 1 together with those of the related compounds. The first oxidation potentials (E_1) of **1a** and **3a** are a little higher by 0.05 and 0.06 V than that of DTEDT under the identical conditions due to the exchange of selenium for sulfur atoms. The E_1 value of DSEDT (**2a**) is comparable to that of DTEDT, suggesting that introduction of selenium atoms in only the TTF moiety of DTEDT has little tendency to raise the E_1 value, in contrast to introduction of selenium in the vinylogous TTF moiety. This is the same situation as the case of the bis(methylthio) substitution on each side of DTEDT.[6a] Furthermore this increase of the E_1 value of **1a** compared to that of **2a** is almost same as that of **15** relative to **16** (0.06 V). These results suggest that the positive charge in the cation radical state tends to lie on the vinylogous tetrachalcogenafulvalene moiety. On the other hand, the E_2-E_1 values of **1a**–**3a** are almost the same as that of DTEDT, indicating that the on-site Coulombic repulsion in



Scheme 2 *Reagents and conditions*: i, 0.5 M LDA (1 equiv.), THF, −78 °C, 30 min; ii, $P(OMe)_3$ (100 equiv.), toluene, 110 °C, 2 h; iii, LiBr·H_2O (20 equiv.), HMPA, 90 °C, 1 h and 130 °C, 1 h.

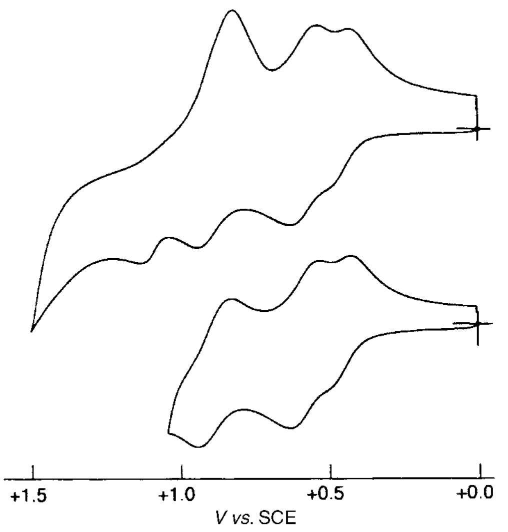
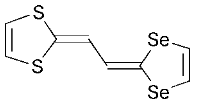


Fig. 1 Cyclic voltammograms of **3a** in benzonitrile.

the dication state is similarly decreased compared to TTF and **16**.



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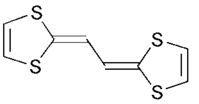

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Conducting properties of CT complexes and cation radical salts

The composition and electrical properties of conducting salts of **1a**–**3a** are summarized in Table 2. The 1 : 1 complex of DTEDS (**1a**) and tetracyano-*p*-quinodimethane (TCNQ) showed high conductivity ($\sigma_{rt} = 20$ S cm^{-1}) and metallic temperature dependence of resistivity around room temperature on a compressed pellet (Fig. 2), while the compressed pellet of DTEDT-TCNQ shows semiconductive temperature dependence. DTEDS has also yielded several high conducting cation-radical salts ($\sigma_{rt} = 10^{-1}$–10^{2} S cm^{-1}) with various anions on single crystals. Among them, the ReO_4^- and $Au(CN)_2^-$ salts showed metallic temperature dependence down to 1.5 K (Fig. 2), although several DTEDS salts displayed semiconducting behaviour dissimilar to the case of DTEDT salts, in which almost all the salts showed metallic conductivity regardless of the shape of the anions.[4] Unfortunately the $Au(CN)_2^-$ salt of DTEDS did not show any superconducting transition down to 1.5 K in contrast to the corresponding superconducting salt of DTEDT. On the other hand, the TCNQ and I_3^- salts of DSEDT **2a** showed semiconducting behaviour on compressed pellets. However their activation energies are very small (0.009–0.006 eV), suggesting their metallic nature on a single crystal measurement. Considering the results that these two donors (DTEDS and DSEDT) afforded unexpectedly many semiconducting salts in comparison to the DETDT salts which are all metallic down to liquid helium temperature, the selenium exchange of only one terminal 1,3-dithiole ring may weaken the intermolecular interaction both in the stacking and transverse directions due to the unsymmetrical shape of donors. DSEDS (**3a**) has also given highly conducting salts ($\sigma_{rt} = 10^{0}$–10^{1} S cm^{-1}) as listed in Table 2. The temperature dependence of DSEDS salts is shown in Fig. 3. The TCNQ complex showed room temperature conductivity of 25 S cm^{-1} and metallic temperature dependence even on a compressed pellet. The metal-to-semiconductor transition temperature of this complex (220 K) is lower than that of the DTEDS-TCNQ complex (260 K). This result suggests that the selenium substitution of both the terminal 1,3-dithiole rings slightly stabilizes the metallic conductivity. The I_3^- salt of DSEDS showed metallic conducting behaviour down to 220 K and little temperature dependence to 4.2 K ($R_{4.2\,K}/R_{rt} \approx 2.5$) on a compressed pellet,

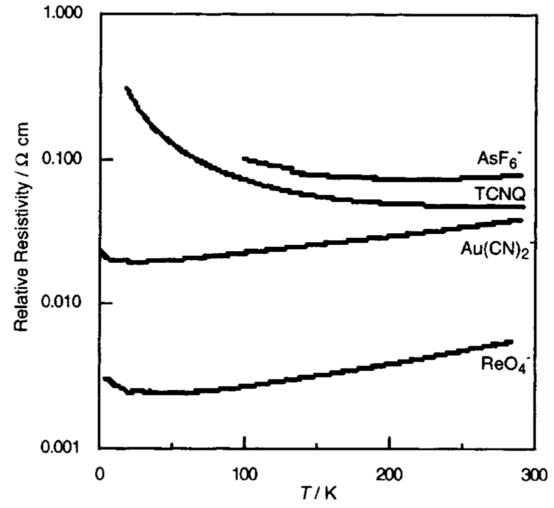

Fig. 2 Temperature dependence of resistivity of cation radical salts of **1a**.

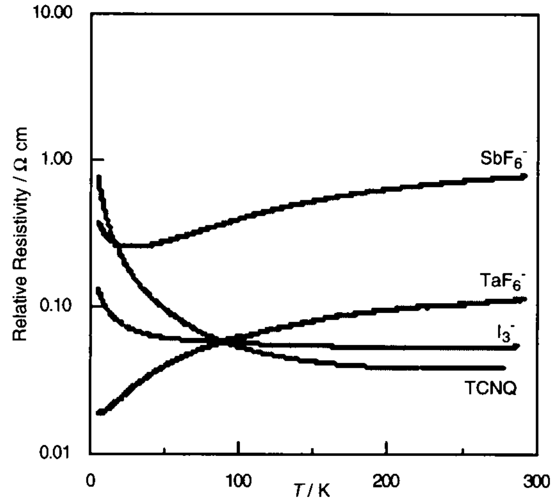

Fig. 3 Temperature dependence of resistivity of cation radical salts of **3a**.

Table 1 Redox potentials of **1a**–**3a** and related compounds^a

	E_1	E_2	E_3	$E_4{}^b$	E_2-E_1
1a	+0.42	+0.54	+0.81	+1.13	0.12
2a	+0.39	+0.52	+0.87	+1.08	0.13
3a	+0.43	+0.55	+0.87	+1.11	0.12
DTEDT	+0.37	+0.50	+0.81	+1.05	0.13
TTF	+0.35	+0.77			0.42
15	+0.35	+0.50			0.15
16	+0.29	+0.49			0.20

^{a}0.1 M Bu_4NClO_4 in PhCN, Pt electrode, 25 °C, *V vs.* SCE, scan rate 50 mVsec^{-1}. ^{b}Irreversible steps. Anodic peak potentials.

Table 2 Composition and electrical properties of donor·(anion)$_x$

Donor	Acceptor	x^a	σ_{rt}/S cm^{-1b}	Conducting behaviour
1a	TCNQ	1.0^c	20^d	$T_{MI} = 260$ K
	BF_4^-	—^{e}	10	$E_a = 0.011$ eV
	ReO_4^-	0.43 (Re)	180	M^f down to 1.5 K
	$GaCl_4^-$	1.3 (Ga)	0.54	$E_a = 0.$ 11 eV
	PF_6^-	0.63 (P)	10	$E_a = 0.010$ eV
	AsF_6^-	0.41 (As)	13	$T_{MI} = 200$ K
	I_3^-	0.56 (I)	0.58	$E_a = 0.023$ eV
	$Au(CN)_2^-$	0.47 (Au)	26	M^f down to 1.5 K
2a	TCNQ	0.80^c	8.7^d	$E_a = 0.009$ eV
	I_3^-	0.41 (I)	9.6^d	$E_a = 0.003$ eV
3a	TCNQ	1.0^c	25^d	$T_{MI} = 220$ K
	SbF_6^-	0.32 (Sb)	1.3	M^f down to 4.2 K
	TaF_6^-	0.33 (X)^g	9.0	M^f down to 4.2 K
	I_3^-	0.41 (I)	18^d	M^f down to 4.2 K

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. [b] Room temperature conductivity measured along the long axis on a single crystal using the four-probe technique. [c] Determined based on elemental analyses. [d] Measured on a compressed pellet. [e] The contents of light elements such as B and F were not reliably determined by the EDS. [f] M designates metallic. [g] Determined based on X-ray crystal structure analysis.

suggesting its stable metallic nature. The SbF_6^- and TaF_6^- salts of **3a** also retained their metallic behaviour down as low as 4.2 K (Fig. 3).

Crystal structure of $(DSEDS)_3TaF_6$

The crystal structure of the TaF_6^- salt of DSEDS (**3a**) which is metallic down to 4.2 K was investigated by X-ray crystal structure analysis. There is only one donor molecule in the unit cell. The anion molecule is disordered and the site occupancy of the anion molecule was refined to 0.33 by a population refinement on fixing the thermal parameters. Thus, the donor-to-anion ratio was determined to be 3 : 1, similar to that of the superconducting $(DTEDT)_3Au(CN)_2$ salt. Fig. 4 shows the structure of the DSEDS molecule in the salt $(DSEDS)_3TaF_6$. The molecular framework is almost flat and has a crooked structure toward the molecular short axis. As shown in Fig. 5, the packing motif of donor layers is the so-called β-type and is very close to that of $(DTEDT)_3Au(CN)_2$. From the *P*1 space group symmetry the donor stack is completely uniform with an intermolecular interplanar distance of 3.58 Å and all the donors point in the same direction. The overlap mode of the face-to-face stack is the so-called ring-over-bond type and the slip distance along the molecular long axis is 1.6 Å as shown in Fig. 6. There are several side-by-side intermolecular Se–Se or Se–S contacts less than the sum of the van der Waals radii between donor molecules (dotted lines in Fig. 5), indicating strong two-dimensional intermolecular interaction.

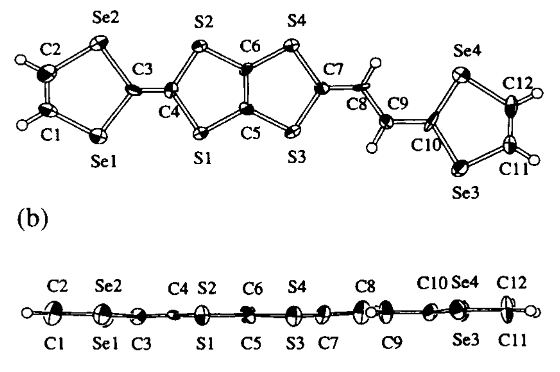

Fig. 4 (a) Donor structure of $(DSEDS)_3TaF_6$ and (b) the side view.

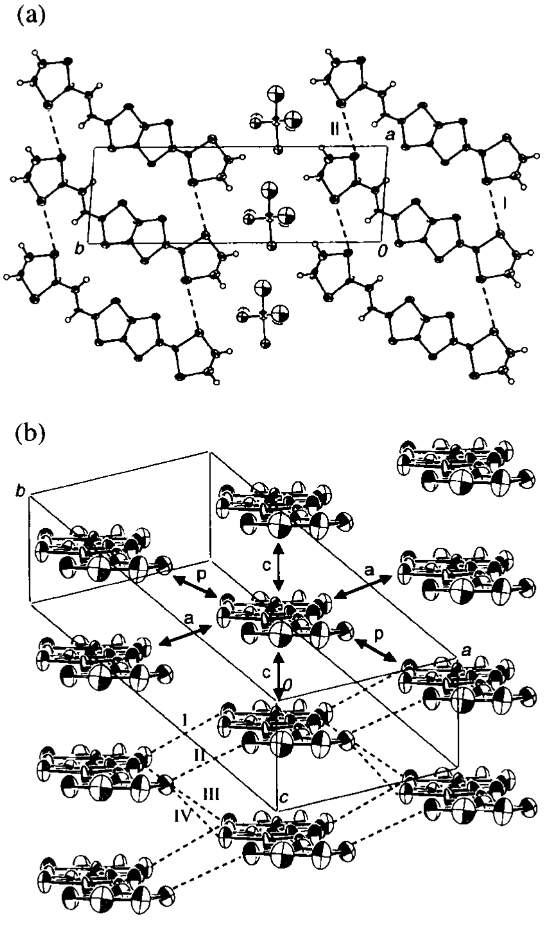

Fig. 5 Crystal structures of $(DSEDS)_3TaF_6$ viewed (a) along the *c*-axis and (b) along the molecular long axis. The intermolecular contacts: I Se(1)–Se(2) 3.633(3) and II Se(3)–Se(4) 3.648(3) Å along the [100] direction; III Se(2)–S(1) 3.638(5) and IV Se(3)–S(4) 3.494(4) Å along the [101] direction.

Band structure of $(DSEDS)_3TaF_6$

A tight-binding band calculation was performed on the basis of the extended Hückel approximation on a donor layer (*ac* plane) of $(DSEDS)_3TaF_6$. The dispersion relation and Fermi surface are shown in Fig. 7. The overlap integral along the donor stacking c (-36.2×10^{-3}) is much larger than that between the stacks p (-6.45×10^{-3}) and a (-1.88×10^{-3}), indicating relatively strong one-dimensional character of this salt. Compared to the $(DTEDT)_3Au(CN)_2$, one-dimensionality of this salt is stronger than that of DTEDT salt due to the larger c/p (5.6) and c/a (19.2) values that of $(DTEDT)_3Au(CN)_2$ [c/p (3.7) and c/a (12.2)]. This situation is probably derived from the

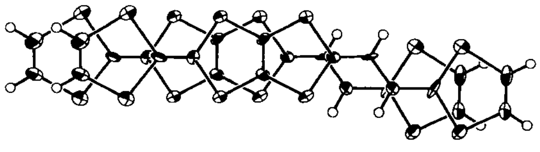

Fig. 6 Overlap mode of the donor molecules in $(DSEDS)_3TaF_6$.

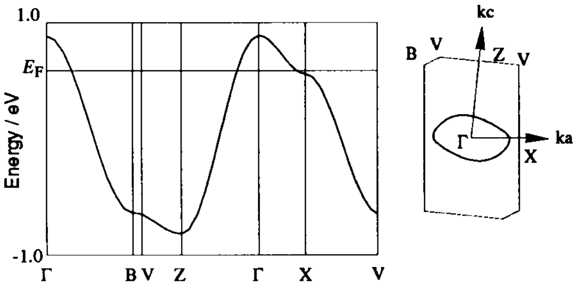

Fig. 7 Band dispersion and Fermi surface of $(DSEDS)_3TaF_6$.

introduction of the large selenium atoms into only the outer 1,3-dithiole ring(s), which might weaken the side-by-side interaction between the central tetrathiapentalene frameworks of the adjacent molecules because the atomic coefficients of the chalcogen atoms of the tetrathiapentalene moiety are larger than those of the outer 1,3-dichalcogenoles in the highest occupied molecular orbital (HOMO).[4,6] The Fermi surface derived from these overlap integrals is a two-dimensional closed ellipsoid, which contributes to the stable metallic behaviour of this salt.

Conclusion

In summary, we have synthesized three selenium analogues of the bis-fused donor DTEDT to investigate the effects of selenium substitution on their physical properties. Studies on the effect of the selenium exchange on the E_1 value suggested that the positive charge in the cation radical state tends to lie on the vinylogous tetrachalcogenafulvalene moiety. The selenium analogues have yielded highly conducting TCNQ complex and cation radical salts (10^{-1}–10^2 S cm^{-1}). The $Au(CN)_2^-$ and ReO_4^- salts of DTEDS and the SbF_6^-, TaF_6^- and I_3^- salts of DSEDS showed stable metallic temperature dependence down to 1.5–4.2 K. Among them, $(DSEDS)_3TaF_6$ salt has a two-dimensional β-type packing motif of the donor molecules almost the same as the superconducting $(DTEDT)_3Au(CN)_2$ salt and a two-dimensional closed elliptical Fermi surface. Generally speaking, it is very difficult to control the crystal structure and donor packing motif of the molecular conductors. In the BEDT-TTF conducting salts, this has yielded many polymorphs, such as over ten kinds of I_3^- salts, even using only one kind of counter anion. Furthermore, exchange of the sulfur atoms with the seleniums has often completely changed the original crystal structure as is observed in the BETS system. On the other hand, the TTP system has a strong tendency to form the same β-type donor packing pattern regardless of the shapes of anion molecules because such a packing pattern is electronically and structurally stable due to a flat molecular structure of the TTP system and is suitable for the realization of stable metallic behaviour. In the present $(DSEDS)_3TaF_6$ salt, the packing motif is almost the same as the superconducting $(DTEDT)_3Au(CN)_2$ in spite of the selenium exchange and incorporation of an anion of a different shape. The realization of the same donor packing as for superconductors is considered to be the shortest way to develop new organic superconductors. We believe that selenium analogues of DTEDT could be promising candidates to afford new superconducting salts, though the present salts unfortunately showed no superconducting transition down to 4 K.

Acknowledgements

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