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# Structures and Conductivities of the Synthetic Metal Salts of Ethylenedithiotetrathiafulvalene (EDTTTF) and Ethylenedithiodiselenadithiafulvalene (EDTDSDTF): 211-$(EDTTTF)_2IBr_2$, 211-$(EDTDSDTF)_2IBr_2$ and 212-$(EDTTTF)_2AuBr_2$

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**Abstract.** (I): Bis[2-(2-dithiolylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromoiodate(1−), $2C_8H_6S_6^{1/2+}.IBr_2^-$, $M_r = 875\cdot7$, triclinic, $P\bar{1}$, $a = 6\cdot242$ (1), $b = 8\cdot353$ (1), $c = 13\cdot443$ (2) Å, $\alpha = 91\cdot27$ (1), $\beta = 94\cdot48$ (1), $\gamma = 110\cdot06$ (1)°, $V = 655\cdot6$ (2) Å$^3$, $Z = 1$, $D_m = 2\cdot21$, $D_x = 2\cdot217$ g cm$^{-3}$, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71069$ Å, $\mu = 50\cdot84$ cm$^{-1}$, $F(000) = 423$, $T = 296$ (2) K. (II): Bis[2-(2-diselenolylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromoiodate(1−), $2C_8H_6S_4Se_2^{1/2+}.IBr_2^-$, $M_r = 1063\cdot3$, triclinic, $P\bar{1}$, $a = 6\cdot298$ (1), $b = 8\cdot384$ (2), $c = 13\cdot528$ (3) Å, $\alpha = 91\cdot46$ (2), $\beta = 94\cdot48$ (2), $\gamma = 109\cdot60$ (1)°, $V = 669\cdot9$ (3) Å$^3$, $Z = 1$, $D_m = 2\cdot58$, $D_x = 2\cdot635$ g cm$^{-3}$, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71069$ Å, $\mu = 100\cdot68$ cm$^{-1}$, $F(000) = 495$, $T = 296$ (2) K. (III): Bis[2-(2-dithiolylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromoaurate(1−), $2C_8H_6S^{1/2+}.AuBr_2^-$, $M_r = 945\cdot8$, monoclinic, $C2/m$, $a = 7\cdot209$ (2), $b = 29\cdot023$ (8), $c = 6\cdot655$ (1) Å, $\beta = 111\cdot62$ (2)°, $V = 1294\cdot4$ (5) Å$^3$, $Z = 2$, $D_m = 2\cdot44$, $D_x = 2\cdot426$ g cm$^{-3}$, Mo $K\bar{\alpha}$, $\lambda = 0\cdot71069$ Å, $\mu = 95\cdot92$ cm$^{-1}$, $F(000) = 898$, $T = 296$ (2) K. Final $R$ values are 0·0231 (I), 0·053 (II), 0·0262 (III) for 2080, 1837 and 947 observed [$F_o \geq K\sigma(F_o)$, $K = 4\cdot0$ for (I) and (II), $K = 6\cdot0$ for (III)] reflections, respectively. (I) and (II) are isostructural. They retain the metallic state down to 2 K and they are potential superconductors. (III) undergoes a metal-to-semiconductor transition at 125 K under ambient pressure and this is lowered to 25 K under 0·38 GPa pressure.

**Introduction.** Continuing our search for unsymmetrical organic molecules which yield superconducting charge-transfer salts we have synthesized MDTTTF, EDTTTF and EDTDSDTF [for structural formulas corresponding to these and any following abbreviations refer to Hountas, Terzis, Papavassiliou, Hilti & Pfeiffer (1990)], and reported on the structures and conductivities of the salts of MDTTTF and EDTTTF with $I_3^-$ (Hountas *et al.*, 1990). These salts had 1:1 composition and therefore they were poor candidates for affording the superconducting state. It was possible to overcome this limitation by changing the anion from $I_3^-$ to $IBr_2^-$ or $AuBr_2^-$, and salts with the promising 2:1 composition, 211-$(EDTTTF)_2IBr_2$ (I), 211-$(EDTDSDTF)_2IBr_2$ (II) and 212-$(EDTTTF)_2AuBr_2$ (III), were synthesized. [The modifier *MSL*- in front of the compound names is a notation suggested by Williams *et al.* (1987) to convey critical structural features of the donor network.] In this report we present the structures and the conductivity of these salts.

**Experimental.** All three salts have a great tendency to form twins. In the case of (III), the two individua of the twin are of equal size in most of the crystals and give a pseudo-orthorhombic cell. Once this had been recognized (from the existence of nonsensical systematic absences) the following procedure was used to obtain a 'single' crystal. We started with a very large crystal mounted along the *a* axis. If the oscillation photograph indicated the existence of mirror symmetry, the crystal was cut and the new pieces mounted again along *a*. If the mirror symmetry disappeared the 1*kl* level was recorded in order to estimate the intensity ratio of the two individua from the non-overlapping reflections. We continued to cut

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the crystals until this intensity ratio was better than 9:1. A similar procedure of cutting the crystals in different directions until the intensity ratio improved to better than 9:1 (I) and 8:2 (II) was followed for (I) and (II). We could not improve the ratio further in (II) because we did not have very large crystals to begin with.

Compounds (I) to (III) were prepared by electrocrystallization (Hountas *et al.*, 1990). Crystals used for data collection were 0·05 $\times$ 0·30 $\times$ 0·31 mm (I), 0·02 $\times$ 0·29 $\times$ 0·44 mm (II) and 0·03 $\times$ 0·25 $\times$ 0·45 mm (III). $D_m$ by flotation in $CHCl_3/C_2H_2Br_4$. Intensity data collected on a Syntex $P2_1$ computer-controlled diffractometer with Mo $K\bar{\alpha}$ Nb-filtered radiation. Cell parameters from 15 intermediate $2\theta$ reflections. $\theta$–$2\theta$ scan, $2\theta \leq 50·0°$, scan speed variable 2–20° $min^{-1}$, scan range 1·6° ($2\theta$) plus $\alpha_1 - \alpha_2$ divergence, background counting 0·5 of scan time. Data collected/unique reflections/$R_{int}$ 2990/2328/0·007 (I), 2544/2336/0·016 (II) and 1277/1178/0·010 (III). Range of $hkl$ $0 \rightarrow 7$, $-15 \rightarrow 15$, $-9 \rightarrow 9$ (I), $-6 \rightarrow 7$, $0 \rightarrow 9$, $-16 \rightarrow 16$ (II), $0 \rightarrow 8$, $-34 \rightarrow 0$, $-7 \rightarrow 7$ (III). Three reflections monitored periodically showed < 3·0% intensity fluctuations and no crystal decay. Lp and analytical absorption correction applied [$T_{min}/T_{max}$ 0·26/0·77 (I), 0·14/0·92 (II), 0·13/0·72 (III)] with *SHELX*76 (Sheldrick, 1976). The structures of (I) and (III) were solved by the Patterson method. The final parameters of (I) were used as the starting model for (II). H-atom positions for (I) and (III) were located from a difference Fourier map and refined isotropically; those for (II) were calculated at 1·08 Å and only the temperature factor was refined. Full-matrix refinement based on $F$ with *SHELX*76 minimizing $\sum w\Delta^2$; unit weights gave a satisfactory analysis of variance. An attempt was made to refine (III) and its enantiomorph in space groups $C2$ and $Cm$. While somewhat lower $R$ values were obtained [$R/wR$ = 0·0233/0·0238 ($C2$) and 0·0236/0·0248 ($Cm$) for observed data] bond distances were unsatisfactory, equivalent bonds were far from being equal and the standard deviations were three to five times larger. Refinement proceeded in $C2/m$. Number of parameters refined 166 (I), 145 (II), 87 (III). $wR$ = 0·0252 (I), 0·0579 (II), 0·0266 (III), for observed data. $R/wR$ = 0·0275/0·0306 (I), 0·0727/0·0844 (II), 0·0390/0·0585 (III) for all data. In the last cycles of refinement for (II), certain lines of reflections ($\bar{1}2l$, $13l$, $\bar{3}1l$, $21l$, $50l$, $05l$, $00l$) were given zero weight because it was known from Weissenberg photographs that they were coincident for the two individua of the twin. This left a total of 1837 observed reflections. $\Delta\rho_{max}/\Delta\rho_{min}$ = 0·80/−0·41 (I), 1·01/−1·21 (II), 0·67/−0·79 (III) e Å$^{-3}$. All 'large' peaks in the final difference map were around I and Au atoms. $|\Delta/\sigma|_{max}$ = 0·071 (I), 0·006 (II), 0·091 (III). $S$ = 0·84 (I), 2·25 (II), 2·07 (III). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters of the non-H atoms are given in Table 1,* bond lengths and angles in Table 2. The atom-labeling scheme is shown in Fig 1.

Table 1. *Positional and equivalent isotropic thermal parameters* [$\times 10^4$ (I) *and* (III), $\times 10^3$ (II)] *of the non*-H *atoms with e.s.d.'s in parentheses*

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| (I) | | | | |
| I | 0 | 0 | 0 | 356 |
| Br | −1822·1 (9) | 2506·9 (6) | 44·7 (4) | 542 |
| S(1) | 2257 (2) | 7953 (1) | 6403·7 (8) | 408 |
| S(2) | 7248 (2) | 9612 (1) | 6616·0 (8) | 387 |
| S(3) | 2556 (2) | 6133 (1) | 4298·3 (7) | 341 |
| S(4) | 7538 (2) | 7800 (1) | 4506·2 (7) | 363 |
| S(5) | 2275 (2) | 4621 (1) | 2271·9 (8) | 380 |
| S(6) | 8269 (2) | 6662 (2) | 2524·0 (8) | 438 |
| C(1) | 3475 (7) | 9306 (5) | 7443 (3) | 463 |
| C(2) | 5727 (7) | 10069 (5) | 7534 (3) | 437 |
| C(3) | 4842 (6) | 8244 (5) | 5904 (3) | 320 |
| C(4) | 4962 (6) | 7479 (5) | 5013 (3) | 310 |
| C(5) | 4021 (6) | 5855 (5) | 3287 (3) | 308 |
| C(6) | 6314 (6) | 6643 (5) | 3382 (3) | 331 |
| C(7) | 4392 (7) | 4250 (5) | 1554 (3) | 432 |
| C(8) | 6386 (7) | 5833 (6) | 1409 (3) | 428 |
| (II) | | | | |
| I | 0 | 0 | 0 | 34 |
| Br | −172·7 (3) | 253·4 (2) | 5·0 (1) | 54 |
| Se(1) | 212·5 (2) | 789·5 (2) | 641·1 (1) | 50 |
| Se(2) | 740·8 (2) | 964·3 (2) | 663·3 (1) | 43 |
| S(3) | 257·7 (4) | 612·7 (4) | 427·0 (2) | 31 |
| S(4) | 749·5 (4) | 773·8 (4) | 447·9 (2) | 33 |
| S(5) | 229·8 (5) | 466·9 (4) | 223·5 (2) | 34 |
| S(6) | 821·1 (5) | 664·8 (4) | 249·6 (2) | 40 |
| C(1) | 346 (2) | 930 (2) | 750·2 (9) | 44 |
| C(2) | 573 (2) | 1009 (2) | 760·0 (9) | 44 |
| C(3) | 486 (2) | 819 (1) | 587·1 (8) | 26 |
| C(4) | 496 (2) | 746 (1) | 498·7 (8) | 30 |
| C(5) | 402 (2) | 585 (1) | 325·2 (7) | 30 |
| C(6) | 627 (2) | 663 (1) | 335·0 (8) | 32 |
| C(7) | 437 (2) | 427 (2) | 153 (1) | 44 |
| C(8) | 634 (2) | 583 (2) | 138·2 (8) | 35 |
| (III) | | | | |
| Au | 0 | 0 | 10000 | 487 |
| Br | 2185 (2) | 0 | 8085 (2) | 859 |
| S(1) | 850 (2) | 1753·0 (4) | 7370 (2) | 372 |
| S(3) | −856 (2) | 2865·5 (4) | 2632 (2) | 362 |
| S(5) | −1030 (2) | 3871·4 (5) | 2151 (2) | 451 |
| C(1) | 400 (8) | 1230 (2) | 6079 (9) | 442 |
| C(3) | 0 | 2078 (2) | 5000 | 290 |
| C(4) | 0 | 2542 (2) | 5000 | 299 |
| C(5) | −410 (8) | 3402 (2) | 3914 (7) | 351 |
| C(7) | −900 (10) | 4335 (2) | 3990 (10) | 513 |

**Discussion.** (I) and (II) are isostructural. In all three of these structures the donors display the ($\alpha$,$L$) interstack–intrastack packing mode (Williams *et al.*, 1987) with ($a$) the 'corrugated sheet' network of short interstack S···S, S···Se and Se···Se interactions (Fig. 2), and ($b$) the anions occupying positions between these 'sheets' (Fig. 3). Both of these features

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52261 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *of the cations with e.s.d.'s in parentheses*

For (II) substitute Se(1) and Se(2) for S(1) and S(2), respectively, and for (III) substitute Au for I.

| | (I) | (II) | (III) |
|---|---|---|---|
| I—Br | 2·706 (1) | 2·693 (1) | 2·363 (1) |
| C(1)—C(2) | 1·324 (6) | 1·35 (2) | 1·34 (1) |
| C(1)—S(1) | 1·727 (4) | 1·83 (1) | 1·716 (5) |
| C(2)—C(2) | 1·727 (4) | 1·85 (1) | |
| S(1)—C(3) | 1·738 (2) | 1·87 (1) | 1·744 (4) |
| S(2)—C(3) | 1·740 (4) | 1·87 (1) | |
| C(3)—C(4) | 1·365 (5) | 1·34 (1) | 1·346 (9) |
| C(4)—S(3) | 1·735 (3) | 1·74 (1) | 1·740 (4) |
| C(4)—S(4) | 1·733 (4) | 1·74 (1) | |
| S(3)—C(5) | 1·750 (4) | 1·76 (1) | 1·749 (5) |
| S(4)—C(6) | 1·746 (4) | 1·75 (1) | |
| C(5)—C(6) | 1·349 (5) | 1·34 (1) | 1·345 (9) |
| C(5)—S(5) | 1·746 (4) | 1·74 (1) | 1·744 (5) |
| C(6)—S(6) | 1·740 (4) | 1·74 (1) | |
| S(5)—C(7) | 1·800 (4) | 1·79 (1) | 1·797 (6) |
| S(6)—C(8) | 1·797 (4) | 1·80 (1) | |
| C(7)—C(8) | 1·502 (5) | 1·50 (2) | 1·48 (1) |
| C(2)—C(1)—S(1) | 117·8 (3) | 119·7 (9) | 117·7 (4) |
| C(1)—C(2)—S(2) | 117·7 (3) | 118·5 (9) | |
| C(1)—S(1)—C(3) | 94·8 (2) | 93·8 (5) | 95·0 (3) |
| C(2)—S(2)—C(3) | 94·8 (2) | 93·5 (5) | |
| S(1)—C(3)—S(2) | 114·9 (2) | 114·4 (5) | 114·5 (4) |
| S(1)—C(3)—C(4) | 122·3 (3) | 122·2 (7) | 122·8 (2) |
| S(2)—C(3)—C(4) | 122·8 (3) | 123·3 (7) | |
| C(3)—C(4)—S(3) | 122·7 (3) | 123·2 (8) | 122·6 (2) |
| C(3)—C(4)—S(4) | 122·2 (3) | 122·4 (8) | |
| S(3)—C(4)—S(4) | 115·1 (2) | 114·4 (6) | 114·7 (2) |
| C(4)—S(3)—C(5) | 95·6 (2) | 96·1 (5) | 95·7 (2) |
| C(4)—S(4)—C(6) | 95·4 (2) | 95·6 (5) | |
| S(3)—C(5)—C(6) | 116·5 (3) | 115·9 (8) | 117·0 (2) |
| S(4)—C(6)—C(5) | 117·1 (3) | 117·6 (8) | |
| S(3)—C(5)—S(5) | 114·7 (2) | 115·2 (6) | 114·3 (3) |
| S(4)—C(6)—S(6) | 114·4 (2) | 113·9 (6) | |
| C(6)—C(5)—S(5) | 128·7 (3) | 128·9 (8) | 128·7 (2) |
| C(5)—C(6)—S(6) | 128·5 (3) | 128·4 (8) | |
| C(5)—S(5)—C(7) | 100·6 (2) | 100·4 (5) | 100·9 (3) |
| C(6)—S(6)—C(8) | 101·1 (2) | 100·9 (5) | |
| S(5)—C(7)—C(8) | 113·9 (3) | 113·8 (8) | 115·3 (2) |
| S(6)—C(8)—C(7) | 113·8 (3) | 113·3 (8) | |

are characteristics of the $\beta$ form of ET superconductors. A third characteristic of these superconductors is that these 'sheets' are related by translation. This is the case in the present (I) and (II), but in (III) the anions occupy positions on the mirror plane and the 'corrugated sheets' are related by mirror symmetry (Fig. 3). This new feature changes the pattern of H···anion interactions (Fig. 4). In (I) and (II) the H···anion contacts are almost identical to those of the $\beta$ form of ET superconductors. While the characteristic *A*- and *B*-site terminal groups (Whangbo, Williams, Schultz, Emge & Beno, 1987; Terzis, Hountas & Papavassiliou, 1988) are preserved in (III) the number and pattern of H···anion interactions is different (Fig. 4). The H-atom positions used for the calculation of H···anion interactions were calculated at 1·08 Å and $sp^3$ geometry for the ethylene and $sp^2$ geometry for the vinylene C atoms (even though most H-atom positions were located from difference Fourier maps and subsequently refined) so that comparisons with the $\beta$ form of ET salts (Williams *et al.*, 1987; Whangbo *et al.*, 1987) would be more meaningful.

In going from (I) to (II) the anion remains the same and S(1) and S(2) of the donor are substituted by larger Se atoms. This, as it turns out, leaves the hydrogen pocket formed by 12 donor molecules (Fig. 4) essentially unchanged and the H···anion interactions in (I) and (II) are almost identical. On the other hand, the larger Se atoms increase in number and shorten significantly the chalcogen–chalcogen contacts (Fig. 2, Table 3). Three new interstack contacts, Se(1)···Se(2)···, Se(1)···S(3) and Se(1)···S(4), now

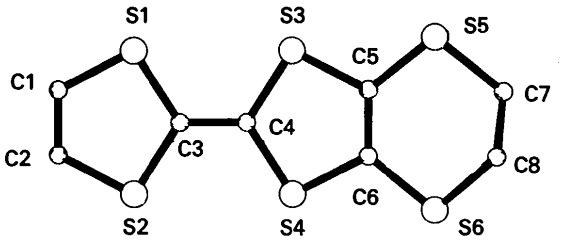
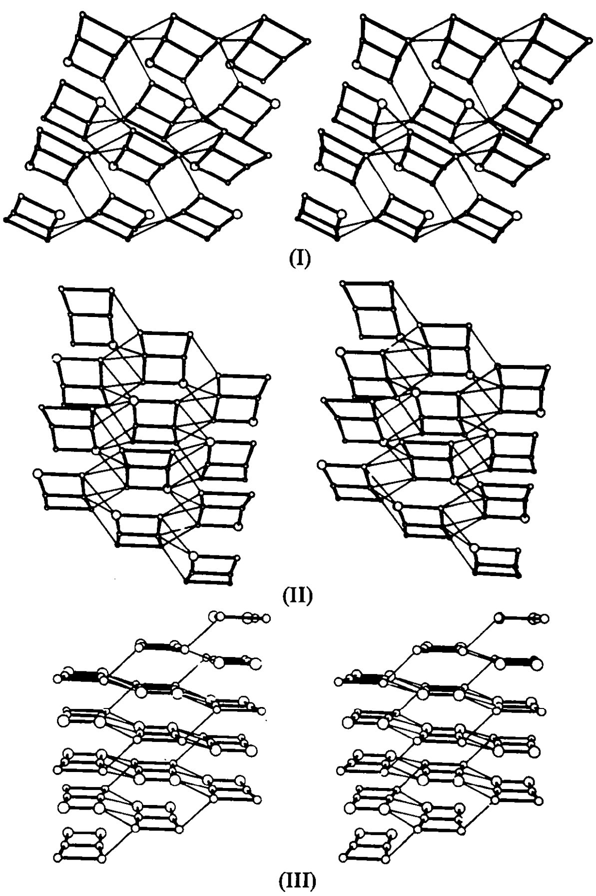


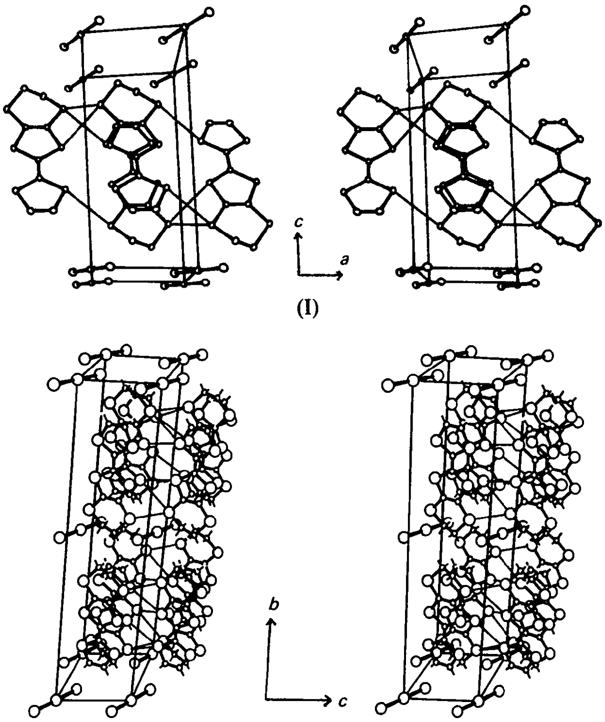
Fig. 1. Atom numbering for (I). For (II) substitute S(1) and S(2) by Se(1) and Se(2). For (III) substitute the ethylene C(7)—C(8) group by a methylene C(7) group.


(I)

(II)

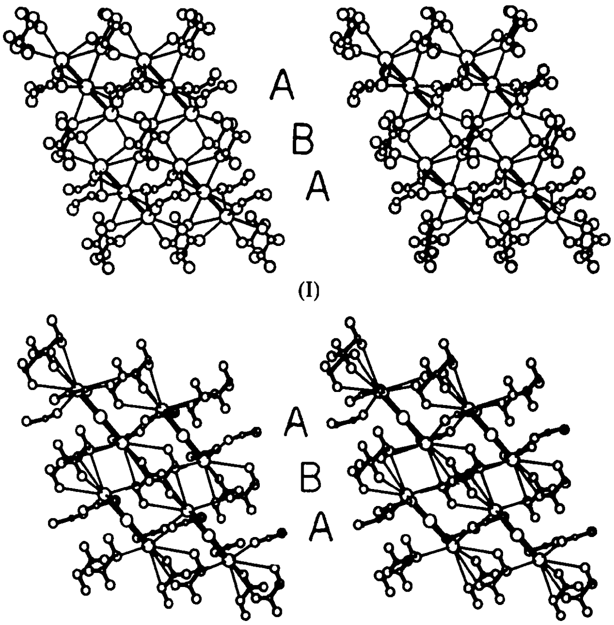
(III)

Fig. 2. Stereoviews of the 'corrugated sheet' of chalcogen–chalcogen contacts. To improve clarity only S and Se atoms are drawn, and S(1) and Se(1) are given a larger radius. 'Contacts' for (III) are between 3·60 and 3·68 Å (see Table 3).



(III)

Fig. 3. Stereoviews of the molecular packing. (II) is similar to (I).



(I)

(III)

Fig. 4. Stereoviews of H···anion interactions. (II) is similar to (I). Only the terminal ethylene and vinylene groups and the anions are shown. Light lines indicate H···I (< 3·43 Å) and H···Br [< 3·20 Å (I), < 3·30 Å (II)] interactions.

Table 3. S···S (< 3·7 Å), S···Se (< 3·9 Å) *and* Se···Se (< 4·0 Å) *interstack distances*

Those distances marked with an asterisk are considered contacts, taking the van der Waals radii of S and Se to be 1·80 and 1·93 Å, respectively. For (II) substitute Se(1) and Se(2) for S(1) and S(2). See Fig. 2.

| | (I) | (II) | (III) |
|---|---|---|---|
| S(1)···S(2) | > 3·7 | 3·755 (2)* | |
| S(1)···S(3) | > 3·7 | 3·702 (2)* | 3·605 (2) |
| S(1)···S(4) | > 3·7 | 3·726 (3)* | |
| S(1)···S(5) | 3·546 (1)* | 3·566 (2)* | 3·632 (2) |
| S(2)···S(3)† | > 3·7 | 3·778 (3) | |
| S(2)···S(4) | 3·692 (1) | 3·686 (3)* | |
| S(2)···S(6) | 3·496 (1)* | 3·496 (3)* | |
| S(3)···S(4)† | 3·672 (1) | 3·682 (4) | |
| S(3)···S(6) | 3·593 (2)* | 3·652 (4) | |
| S(5)···S(6) | 3·508 (2)* | 3·532 (5)* | |
| S(5)···S(5) | — | — | 3·678 (2) |

† Intrastack distance.

appear and the intrastack distance Se(2)···S(3) of 3·778 (3) Å is not much longer than 3·73 Å, the sum of the van der Waals radii (Table 3). It is seen therefore that the substitution of the two S atom by Se is structurally advantageous, since it greatly improves the chalcogen–chalcogen contacts without affecting adversely the H···anion interactions, and both of these are significant criteria for possible superconductivity (Williams *et al.*, 1987).

In going from (I) to (III) the donor remains the same and the anion, $IBr_2^-$ (which has a length of 9·3 Å as estimated from the sum of the two bond lengths and the van der Waals radii of the terminal atoms), is substituted with the shorter $AuBr_2^-$ (8·6 Å). This changes both the H···anion interactions (Fig. 3) and the pattern of S···S contacts of which there is now not one below 3·6 Å. Furthermore, there is now an energetically unfavorable H···H interaction (Whangbo *et al.*, 1987) [H(7*A*)···H(7*A*)(*x*, 1 − *y*, *z*) = 2·00 (4) Å] while there is no H···H distance less than 2·40 Å in (I) and (II). This is clearly an unfavorable substitution and it is reflected in the conductivity of this salt. While (I) and (II) retain the metallic state down to 2 K and their conductivity behavior makes them candidates for superconductivity (Papavassiliou *et al.*, 1988), since the room-temperature conductivity $\sigma_{RT}$ is $10^3\ \Omega^{-1}\ cm^{-1}$ and the normalized resistance *R*(2 K)/*R*(295 K) is about 0·01, (III) undergoes a metal-to-semiconductor transition at 125 K under ambient pressure and this transition takes place at 25 K under 0·33 GPa pressure (Hilti, Mayer, Pfeiffer, Terzis & Papavassiliou, 1989).

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# Structures of the New Superconductor $(MDTTTF)_2AuI_2$ ($T_c$ = 4·5 K) and the Organic Metal $(EDTTTF)_2AuI_2$ (MDTTTF = Methylenedithiotetrathiafulvalene and EDTTTF = Ethylenedithiotetrathiafulvalene)

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**Abstract.** (I): Bis[2-(2-dithiolylidene)dithiolo[4,5-*d*]dithiol]ium diiodoaurate(1−), $2C_7H_4S_6^{1/2+}.AuI_2^-$, $M_r$ = 1011·76, orthorhombic, *Pbnm*, $a$ = 10·797 (2), $b$ = 7·789 (2), $c$ = 28·991 (7) Å, $V$ = 2438·1 (9) Å$^3$, $Z$ = 4, $D_m$ = 2·69, $D_x$ = 2·775 g cm$^{-3}$, Mo $K\bar{\alpha}$, $\lambda$ = 0·71069 Å, $\mu$ = 94·73 cm$^{-1}$, $F(000)$ = 1876, $T$ = 296 (2) K. (II) Bis[2-(2-dithiolylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium diiodoaurate(1−), $2C_8H_6S_6^{1/2+}.AuI_2^-$, $M_r$ = 1039·89, orthorhombic, *F*222, $a$ = 12·473 (3), $b$ = 7·238 (2), $c$ = 29·650 (6) Å, $V$ = 2676 (1) Å$^3$, $Z$ = 4, $D_m$ = 2·50, $D_x$ = 2·579 g cm$^{-3}$, Mo $K\bar{\alpha}$, $\lambda$ = 0·71069 Å, $\mu$ = 86·30 cm$^{-1}$, $F(000)$ = 1940, $T$ = 296 (2) K. Final $R$ values are 0·0343 (I) for 583 observed reflections [$I \geq 3{\cdot}0\sigma(I)$] and 0·0539 (II) for 1692 observed reflections [$I \geq 2{\cdot}0\sigma(I)$]. (I) becomes superconducting at 4·5 K and (II) is a metal down to 125 K. (I) consists of dimers of donors with strong intradimer and interdimer S···S contacts with an interdimer angle of 79·3 (1)°.

**Introduction.** Continuing our search for superconducting charge-transfer salts we have reported on the structures and conductivities of $(EDTTTDF)I_3$ and $(MDTTTF)I_3$, both semiconductors (Hountas, Terzis, Papavassiliou, Hilti & Pfeiffer, 1990), $(EDTTTF)_2IBr_2$ and $(EDTDSDTF)_2IBr_2$, possible superconductors, and $(EDTTTF)_2AuBr_2$, a metal down to 125 K (Terzis, Hountas, Papavassiliou, Hilti & Pfeiffer, 1990). We have now used the unsymmetrical donors EDTTTF and MDTTTF [for structural formulas for these and other abbreviations, refer to Hountas *et al.* (1990)] and the linear anion $AuI_2^-$ to synthesize the title compounds. Only six years ago, in a review (Lyubovskaya, 1983) of the structural charactictics of organic metals and superconductors, it was accepted that the donors must be symmetrical and they should pack in regular stacks. This was true until recently when the rule for columnar packing was invalidated by the discovery of the superconductors $(BEDTTTF)_2Cu(NCS)_2$ (Urayama *et al.*, 1987) and $K(BEDTTTF)_2I_3$ (Kato *et al* 1987). The requirement for symmetrical donors was given up with the discovery of the superconductors $(DMET)_2X$ [$X$ = $Au(CN)_2^-$, $AuI_2^-$, $AuBr_2^-$, $AuCl_2^-$, $I_3^-$, $IBr_2^-$] (Kikuchi *et al.*, 1987). One of these, $(DMET)_2AuBr_2$, breaks both of the above mentioned rules, *i.e.* DMET is an unsymmetrical donor and there are no stacks in the structure. The present compound $(MDTTTF)_2AuI_2$ (I) also breaks both requirements and its $T_c$ of 4·5 K at ambient pressure is the highest known to date for an unsymmetrical donor, while 222-$(EDTTTF)_2AuI_2$ [the modifier

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