Structures of the New Superconductor (MDTTTF)$_2$AuI$_2$ ($T_c = 4.5$ K) and the Organic Metal (EDTTTF)$_2$AuI$_2$ (MDTTTF = Methyleneedithiotetrahiafulvalene and EDTTTF = Ethylenedithiotetrahiafulvalene)

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(Received 27 February 1989; accepted 19 May 1989)

Abstract. (I): Bis[2-(dithiolyletidene)dithiolo[4,5-d]dithiol]ium diodoaurate(1$^-$), 2C$_7$H$_4$S$_2$Au$_2$.M$_r$, $M_r = 1011.76$, 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 $K_{α}$, $λ = 0.71069$ Å, $μ = 94.73$ cm$^{-1}$, $f(000) = 1876$, $T = 296$ (2) K. (II): Bis[2-(dithiolyletidene)-5,6-dihydro-dithiolo[4,5-b]dithiino]ium diodoaurate(1$^-$), 2C$_7$H$_4$S$_2$Au$_2$.M$_r$, $M_r = 1039.89$, orthorhombic, $F222$, $a = 12.473$ (3), $b = 7.238$ (2), $c = 29.650$ (6) Å, $V = 2676$ (1) Å$^3$, $Z = 4$, $D_m = 2.50$, $D_x = 2.797$ g cm$^{-3}$, Mo $K_{α}$, $λ = 0.71069$ Å, $μ = 86.30$ cm$^{-1}$, $f(000) = 1940$, $T = 296$ (2) K. Final R values are 0.0343 (I) for 583 observed reflections [$I ≥ 3σ(I)$] and 0.0539 (II) for 1692 observed reflections [$I ≥ 2σ(I)$]. (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° (I$^c$).

Introduction. Continuing our search for superconducting charge-transfer salts we have reported on the structures and conductivities of (EDTTTF)$_2$I$_2$ and (MDTTTF)$_2$I$_2$, both semiconductors (Hountas, Terzis, Papavassiliou, Hilti & Pfeiffer, 1990), (EDTTTF)$_2$IBr$_2$ and (EDTTSF)$_2$IBr$_2$, possible superconductors, and (EDTTTF)$_2$AuBr$_2$, 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 characteristics 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)$_2$Cu(NCS)$_2$ (Urayama et al., 1987) and K(BEDTTTF)$_2$I$_3$ (Kato et al., 1987). The requirement for symmetrical donors was given up with the discovery of the superconductors (DMET)$_2$X [X = Au(CN)$_2$-, AuI$_2$-, AuBr$_2$-, AuCl$_2$-, I$_2$-, IBr$_2$-] (Kikuchi et al., 1987). One of these, (DMET)$_2$AuBr$_2$, 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)$_2$AuI$_2$ (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)$_2$AuI$_2$ [the modifier
Experimental. The title compounds were prepared by electrocrystallization (Hountas et al., 1990). All examined crystals of (II) were of poor quality and showed streaks along the alternating with Bragg lines. For space-group assignment and data collection these streaks were ignored. $D_m$ measured by flotation. Crystal dimensions $0.05 \times 0.30 \times 0.36$ mm (I) and $0.01 \times 0.15 \times 0.18$ mm (II). Nicolet P2, diffractometer, $\theta$–$2\theta$ scan, $2\theta \leq 50^\circ$, scan speed variable between 1 and 20$^\circ$ min$^{-1}$, scan range $1^\circ$–$7^\circ$ ($2\theta$) plus $\alpha_1 - \alpha_2$ separation, background counting 0.5 of scan time. Cell parameters from 15 intermediate $2\theta$ reflections. Data collected/unique reflections $R_{int}$

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

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

![Fig. 1. Stereoview of the dimeric structure in (I). S--S contacts ($<3.6$ Å) are indicated by thin lines.](image-url)
(I) and 9·32 (II) for observed data. The opposite enantiomorph for (II) was tested but refined only to \( wR = 0·0615 \) and \( S = 9·61 \). \( R/wR = 0·0519/0·0568 \) (I) and 0·0696/0·0738 (II) for all data. \( \Delta \rho_{\text{max}}/\Delta \rho_{\text{min}} = 1·35/−1·82 \) (I) and 0·98/−1·05 (II) e Å\(^{-3}\). The large peaks in the final difference Fourier map were around the Au and I positions. \( |\Delta \rho|_{\text{max}} = 0·079 \) (I) and 0·017 (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters for the non-H atoms are given in Table 1,* and bond distances and angles in Table 2. The atom-labeling scheme is shown in Fig. 2.

**Discussion.** The packing arrangement of (I) is similar to that of \((\text{DMET})_2\text{AuBr}_3\) (Kikuchi *et al.*, 1987). It consists of trimers of donor molecules with strong intrameric and interdimer S···S contacts, Fig. 1. The intrameric distance is 3·35 Å and the interdimer angle is 79·3°. These S···S contacts generate the ‘sheet network’ of donors and these sheets are separated by the anions, Fig. 3. There are several I···H interactions at distances less than 3·35 Å, the pattern of which is shown in Fig. 4. A very short Au···I contact of 3·703 (1) Å and an Au···Au III···Au angle of 159·6 (1)° generate the anion network also shown in Fig. 4. These crystals become superconducting with a transition temperature, \( T_c \), of 3·5 K under ambient pressure (Papavassiliou *et al.*, 1988). More recent measurements raise the \( T_c \), under ambient pressure, to 4·5 K (Kini *et al.*, 1989; Hilti, Mayer, Pfeiffer, Terzis & Papavassiliou, 1989). This \( T_c \) is the highest known to date for an unsymmetrical donor.

The packing arrangement in (II) is reminiscent of the (TMTSF)_2X salts (Williams & Carneiro, 1986) and the (PEDTTTF)_2X salts (Terzis, Psycharis, Hountas & Papavassiliou, 1988), i.e. the donor stacks pack in-phase (Terzis *et al.*, 1988) with S···S contacts in the plane of the donor, Fig. 1, and not

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* Lists of observed and calculated structure factors, anisotropic thermal parameters of the non-H atoms and atomic and isotropic thermal parameters for the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52263 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fig. 2. Atom numbering for (II). For (I) substitute the ethylene C(7)···C(8) group by a methylene C(7).

Fig. 3. Stereoview of the molecular packing. For (II) S···S contacts (<3·6 Å) are indicated by thin lines and the average structure of the disordered Au\(_3^1\) ion is shown.

Fig. 4. Stereoview of (I) showing the Au···I interactions (3·703 Å) with double lines and the interactions between the terminal methylene and vinylene groups of the donor and the Au\(_3^1\) anions. Thin lines indicate H···I (<3·35 Å) interactions.
1987) as in the (EDTTTF)$_2$X salts and the superconducting (ET)$_2$X salts (Williams et al., 1987). These crystals show metallic behavior down to 125 K at ambient pressure (Terzis et al., 1988) and the metallic behavior is extended down to 30 K at 0.48 GPa pressure (Hilti et al., 1989).

References