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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)

By A. Hountas and A. Terzis

Institute of Materials Science, NRC 'Demokritos', Aghia Paraskevi Attikis, 153 10 *Athens, Greece*

G. C. Papavassiliou

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
48 *Vassileos Constantinou Ave.,* 116 35 *Athens, Greece*

and B. Hilti, M. Burkle, C. W. Meyer and J. Zambounis

*Central Research Laboratories, Ciba-Geigy AG, CH-*4002 *Basel, Switzerland*

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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 $K\overline{\alpha}$, λ = 0·71069 Å, μ = 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 $K\overline{\alpha}$, 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 [$I \geq 3·0\sigma(I)$] and 0·0539 (II) for 1692 observed reflections [$I \geq 2·0\sigma(I)$]. (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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MSL- in front of the compound name is a notation suggested by Williams *et al.* (1987) to convey critical structural features of the donor network] does not afford the superconducting state.

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 c^* alternating with Bragg lines. For space-group assignment and data collection these streaks were ignored. D_m measured by flotation. Crystal dimensions 0·05 × 0·30 × 0·36 mm (I) and 0·01 × 0·15 × 0·18 mm (II). Nicolet $P2_1$ diffractometer, θ–2θ scan, $2\theta \leq 50°$, scan speed variable between 1 and 20° min^{-1}, scan range 1·7° (2θ) plus $\alpha_1 - \alpha_2$ separation, background counting 0·5 of scan time. Cell parameters from 15 intermediate 2θ reflections. Data collected/unique reflections/$R_{\rm int}$ 4767/2161/0·017 (I) and 730/696/0·003 (II). Range of hkl $-12 \rightarrow 0$, $0 \rightarrow 9$, $-34 \rightarrow 34$ (I), $0 \rightarrow 14$, $0 \rightarrow 8$, $0 \rightarrow 35$ (II). Three reflections monitored periodically showed < 3% intensity fluctuation and no crystal decay. Lp and analytical absorption corrections applied [$T_{\rm min}/T_{\rm max}$ 0·14/0·65 (I), 0·32/0·90 (II)] with *SHELX76* (Sheldrick, 1976). The structure of (I) was solved by the Patterson method. $\rm AuI_2^-$ is on the mirror plane. The contents of the unit cell of (II) indicated that Au should occupy a special position of multiplicity 4. It was placed at (0,0,0). The rest of the structure was phased after two structure-factor and Fourier-map calculations. The long axis of the donor is a crystallographic twofold axis. The $\rm AuI_2^-$ is disordered and Fig. 1 shows the average structure. During the refinement Au was given a site occupancy of 0·25 and I of 0·5. H atoms were located from a difference map and refined for (I), and placed at calculated positions riding on C atoms at 1·08 Å for (II). Non-H atoms anisotropic, H atoms isotropic. Refinement, based on F, by full-matrix least squares minimizing $\sum w\Delta^2$ with *SHELX76*. Weighting scheme for the last cycles of refinement, $1/w = \sigma^2(F_o) + 0{\cdot}0005|F_o|^2$ for (I), unit weights for (II). Number of refined parameters is 152 (I) and 82 (II). Structures refined to $wR = 0{\cdot}0459$ (I) and 0·0570 (II), $S = 2{\cdot}31$

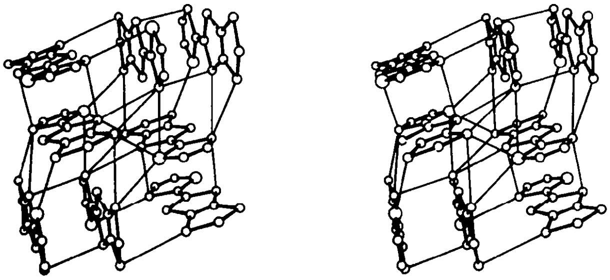


Fig. 1. Stereoview of the dimeric structure in (I). S···S contacts (< 3·6 Å) are indicated by thin lines.

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

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

	x	y	z	$U_{\rm eq}$(Å^2)
(I)				
Au	4704·8 (5)	4863·4 (6)	2500	456
I(1)	3235·2 (8)	2311 (1)	2500	541
I(2)	6241·0 (8)	7335 (1)	2500	549
S(1)	47 (2)	2161 (2)	820·0 (7)	314
S(2)	2140 (2)	4572 (2)	802·1 (6)	315
S(3)	−52 (2)	2183 (2)	−293·3 (6)	264
S(4)	2065 (2)	4610 (2)	−311·0 (6)	288
S(5)	−11 (2)	1974 (3)	−1347·6 (6)	355
S(6)	2183 (2)	4359 (3)	−1361·5 (6)	402
C(1)	712 (8)	2760 (10)	1339 (3)	414
C(2)	1659 (8)	3810 (10)	1335 (3)	408
C(3)	1070 (6)	3365 (8)	484 (2)	241
C(4)	1035 (6)	3378 (8)	20 (2)	244
C(5)	572 (6)	2711 (8)	−826 (2)	231
C(6)	1539 (6)	3802 (8)	−836 (2)	258
C(7)	982 (8)	3360 (10)	−1689 (3)	432
(II)				
Au	0	0	0	51
I	178·3 (3)	152·2 (5)	−3·4 (3)	81
S(1)	116·6 (4)	4 (3)	177·5 (2)	91
S(3)	116·4 (4)	−7 (4)	286·4 (2)	93
S(5)	141·4 (4)	−2 (3)	385·0 (2)	76
C(1)	53 (2)	−32 (4)	124·9 (6)	42
C(3)	0	0	209·5 (8)	71
C(4)	0	0	255·5 (8)	85
C(5)	53 (1)	−10 (10)	339·2 (6)	64
C(7)	53 (2)	−53 (5)	429·7 (8)	76

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

	(I)	(II)
Au—I(1)	2·484 (4)	2·544 (1)
Au—I(2)		2·541 (1)
C(1)—C(2)	1·41 (4)	1·31 (1)
C(1)—S(1)	1·77 (2)	1·731 (8)
C(2)—S(2)		1·736 (8)
S(1)—C(3)	1·74 (1)	1·746 (7)
S(2)—C(3)		1·752 (6)
C(3)—C(4)	1·37 (3)	1·347 (9)
C(4)—S(3)	1·72 (1)	1·751 (6)
C(4)—S(4)		1·754 (6)
S(3)—C(5)	1·76 (2)	1·733 (7)
S(4)—C(6)		1·743 (7)
C(5)—C(6)	1·34 (4)	1·347 (9)
C(5)—S(5)	1·75 (2)	1·736 (7)
C(6)—S(6)		1·730 (7)
S(5)—C(7)	1·76 (2)	1·814 (8)
S(6)—C(7)		1·786 (9)
C(7)—C(8)	1·55 (2)	
I(1)—Au—I(2)		177·9 (1)
C(2)—C(1)—S(1)	112 (1)	119·1 (6)
C(1)—C(2)—S(2)		117·1 (6)
C(1)—S(1)—C(3)	96 (1)	94·4 (4)
C(2)—S(2)—C(3)		95·0 (4)
S(1)—C(3)—S(2)	114 (1)	114·3 (4)
S(1)—C(3)—C(4)	123·1 (7)	123·0 (5)
S(2)—C(3)—C(4)		122·7 (5)
C(3)—C(4)—S(3)	122·2 (7)	122·2 (5)
C(3)—C(4)—S(4)		122·2 (5)
S(3)—C(4)—S(4)	116 (1)	115·7 (4)
C(4)—S(3)—C(5)	95·5 (9)	94·3 (3)
C(4)—S(4)—C(6)		94·2 (3)
S(3)—C(5)—C(6)	116 (1)	118·1 (5)
S(4)—C(6)—C(5)		117·5 (5)
S(3)—C(5)—S(5)	114 (1)	123·9 (5)
S(4)—C(6)—S(6)		123·2 (5)
C(6)—C(5)—S(5)	128 (1)	118·0 (5)
C(5)—C(6)—S(6)		119·4 (5)
C(5)—S(5)—C(7)	100 (1)	93·7 (4)
C(6)—S(6)—C(7)		93·8 (4)
S(5)—C(7)—C(8)	116 (2)	
S(5)—C(7)—S(6)		113·5 (5)

(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. $\Delta\rho_{max}/\Delta\rho_{min} = 1·35/-1·82$ (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. $|\Delta/\sigma|_{max} = 0·079$ (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 $(DMET)_2AuBr_2$ (Kikuchi *et al.*, 1987). It consists of dimers of donor molecules with strong intradimer and interdimer S···S contacts, Fig. 1. The intradimer 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—I···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 out-of-phase with bifurcated S···S contacts as is the case with the similar salts of $(EDTTTF)_2X$ ($X = IBr_2^-$, $AuBr_2^-$) (Terzis *et al.*, 1990). However, the intrastack packing is of the α mode (Williams *et al.*,

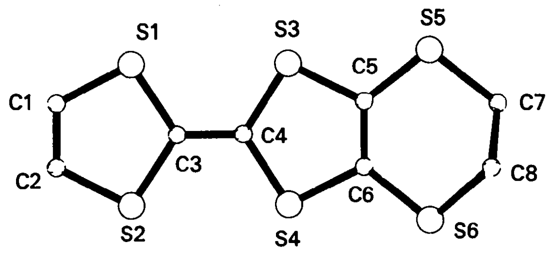
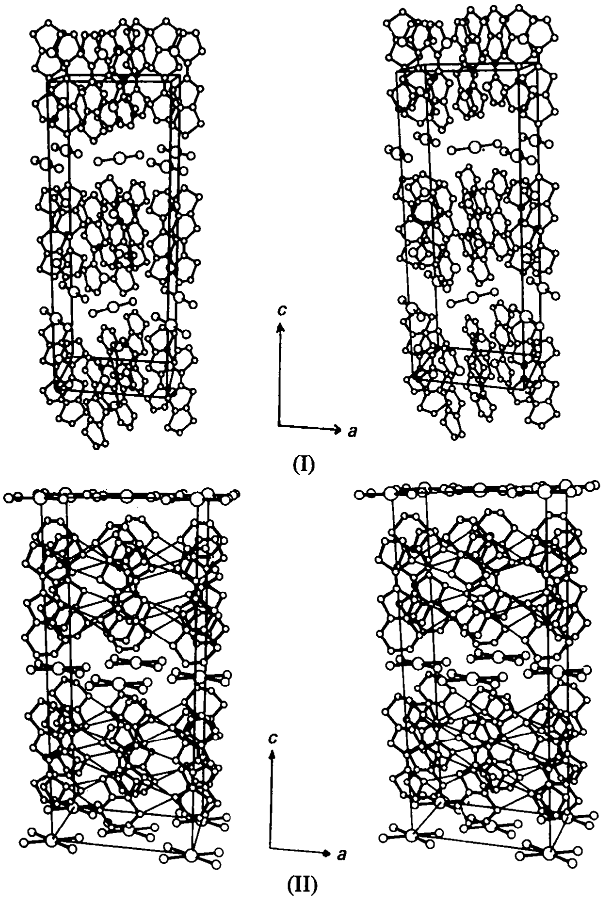


Fig. 2. Atom numbering for (II). For (I) substitute the ethylene C(7)—C(8) group by a methylene C(7).



(I)

(II)

Fig. 3. Stereoviews of the molecular packing. For (II) S···S contacts (< 3·6 Å) are indicated by thin lines and the average structure of the disordered AuI_2^- ion is shown.

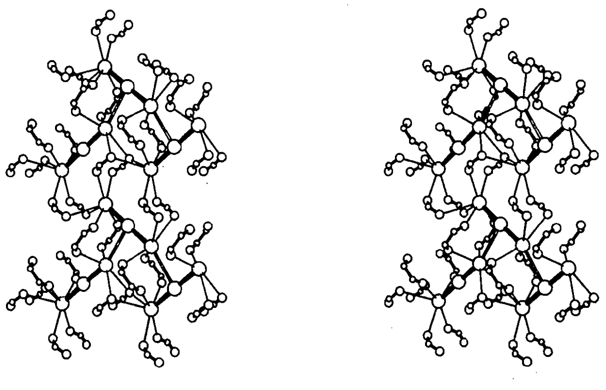


Fig. 4. Stereoview of (I) showing the Au···I interactions (3·703 Å) with double lines and the interactions between the terminal methylene and vinylene groups of the donor and the AuI_2 anions. Thin lines indicate H···I (< 3·35 Å) interactions.

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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.

1987) as in the $(EDTTTF)_2X$ salts and the superconducting $(ET)_2X$ 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).

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Structures of Tetraaquabis(hydroxymethanesulfonato)magnesium(II) and Hexaaquaaluminium(III) Hydroxymethanesulfonate

BY T. STANLEY CAMERON, WALTER J. CHUTE, GORDON OWEN, JACK AHERNE AND ANTHONY LINDEN

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, B3H 4J3, Canada

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Abstract. (I) $C_2H_{14}MgO_{12}S_2$, $[Mg(CH_3O_4S)_2(H_2O)_4]$, M_r = 318·55, monoclinic, $P2_1/c$, a = 10·658 (2), b = 7·717 (1), c = 21·449 (3) Å, β = 92·02 (2)°, V = 1763 Å^3, Z = 6, D_x = 1·800 g cm^{-3}, Mo $K\alpha$ (graphite-monochromated), λ = 0·70926 Å, μ = 5·56 cm^{-1}, $F(000)$ = 996, T = 295 K, 3102 unique reflections, 2382 with $I > 3\sigma(I)$, final R = 0·039 for 2364 reflections. (II) $C_3H_{21}AlO_{18}S_3$, $[Al(H_2O)_6]^{3+}.3CH_3O_4S^-$, M_r = 468·34, monoclinic, $P2_1/n$, a = 10·821 (1), b = 22·503 (4), c = 14·439 (3) Å, β = 91·58 (2)°, V = 3514 Å^3, Z = 8, D_x = 1·770 g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, μ = 5·54 cm^{-1}, $F(000)$ = 1952, T = 295 K, 4850 unique reflections, 1170 with $I > 2\sigma(I)$, final R = 0·080. The structures are similar in that they contain water coordinated to the metal, but they are distinctly different from the corresponding hydroxymethanesulfonate salts of the remaining Group I and Group II metals which contain no coordinated water.

Introduction. The structures of the hydroxymethanesulfonate salts of the cations Li^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and NH_4^+ have recently been determined (Owen, 1982). In order to complete this series of Group I and Group II salts, the structure of the Mg^{II} salt has now been determined. In addition, the structure of the Al^{III} salt has also been determined for comparison. There have been only a few reports of crystal-structure determinations of organometallic compounds that contain both aluminium and oxygen and which involve relatively simple organic ligands (Hon & Pfluger, 1973; McClelland, 1975; Taylor, 1978; Boardman, Small & Worall, 1983; Simonsen & Bechtel, 1980; Bulc, Golic & Siftar, 1976, 1982; Mooy, Krieger, Heijdenrijk & Stam, 1974). All of these reported compounds have the organic ligand hexacoordinated to Al^{III} and were similar to the expected compounds of Cr^{III} and Fe^{III}. In the hydroxymethanesulfonate salt of Al^{III}, however, the organic ligand is not coordinated to the metal.

Experimental. A crystalline sample of the Mg^{II} salt (I) was prepared by routine methods, but the preparation of the Al^{III} salt (II) proved more difficult. A single large crystal (0·5 × 0·5 × 1·5 cm) of the

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