ratio was less than 0·01. In the final difference map, the highest peak was 0·27 (4) and the lowest peak was −0·24 (4) e Å^{-3}. The atomic coordinates are listed in Table 1 and bond distances and angles in Table 2.*

Discussion. The geometry and atom labeling for the asymmetric unit of triphenyltin 3-pyridinecarboxylate are shown in Fig. 1. The coordination polyhedron around the Sn atom is trigonal bipyramidal, with the *ipso*-carbons of the phenyl groups forming the trigonal plane. The apical positions are occupied by the O of the carboxylate group and the N of the neighbouring pyridyl ring (symmetry transformation: 1−*x*, −*y*, *z*−0·5). The Sn atom is displaced by 0·118 (1) Å out of the trigonal plane towards the O atom. The Sn—N′ bond is 2·568 (7) Å and the intramolecular Sn···O(2) contact is 3·271 (6) Å. The plane of the carboxylate group is twisted by 13·7 (5)° with respect to that of the pyridyl ring. The Sn—O—C(=O)—C_5H_4N fragment is virtually flat, so that the polymer appears to be propagating on the plane that is passing through the pyridyl rings.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51525 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of the Organic Superconductor $(DMET)_2AuI_2$

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Abstract. 2-(4,5-Dimethyldiselenol-2-ylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin diiodoaurate(I) (2:1), $(C_{10}H_{10}S_4Se_2)_2.[AuI_2]$, $M_r = 1283·48$, triclinic, $P\bar{1}$, $a = 6·722$ (1), $b = 7·724$ (3), $c = 15·776$ (2) Å, $\alpha = 90·02$ (2), $\beta = 98·35$ (1), $\gamma = 75·71$ (2)°, $V = 784·7$ (4) Å^3, $Z = 1$, $D_x = 2·72$ Mg m^{-3}, μ(Mo $K\alpha$) = 11·75 mm^{-1}, $F(000) = 589$, $T = 297$ K, $R = 0·049$ for 2574 reflections. The structure consists of sheets of DMET ($C_{10}H_{10}S_4Se_2$) and of AuI_2. The DMET molecules form ordered stacks within the sheet. There are some short intermolecular contacts not only within the stacks but also between the stacks. The structure is very similar to that of $(DMET)_2I_3$, but is different from that of $(DMET)_2Au(CN)_2$ in the relative position of anions with respect to DMET molecules.

Introduction. We have recently discovered some superconductors based on an unsymmetrical donor DMET (Kikuchi, Kikuchi, Namiki, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Ishiguro, Kobayashi & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Anzai, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Honda, Ishikawa, Saito, Ikemoto, Murata, Anzai, Ishiguro & Kobayashi, 1988). Besides superconductivity, DMET salts exhibit a variety of properties depending on the anions and can be classified into five groups on the basis of temperature-dependence of resistivity (Murata, Kikuchi, Takahashi, Kobayashi, Honda, Saito, Kanoda, Tokiwa, Anzai, Ishiguro &

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Ikemoto, 1988; Kikuchi, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1988). As is well known, crystal structures are indispensable as basic information for the investigation of physical properties of systems. We thus undertook a series of structural determinations of DMET salts, some of which have been published elsewhere (Kikuchi, Ikemoto & Kobayashi, 1987; Kikuchi, Ishikawa, Saito, Ikemoto & Kobayashi, 1988*a*; Kikuchi, Honda *et al.*, 1988; Kikuchi, Ishikawa, Saito, Ikemoto & Kobayashi, 1988*b*).

The title compound is, at ambient pressure, metallic at room temperature and, on cooling, undergoes a metal–insulator transition at about 20K. The metal–insulator transition is due to the formation of SDW (Nogami, Tanaka, Kagoshima, Kikuchi, Saito, Ikemoto & Kobayashi, 1987). Below 5 kbar, the transition is suppressed and superconductivity appears below 0·55 K (Kikuchi, Murata, Honda, Namiki, Saito, Anzai *et al.*, 1987). Thus $(DMET)_2AuI_2$ belongs to group 3 (Murata *et al.*, 1988; Kikuchi, Saito *et al.*, 1988). In this paper, the structure of $(DMET)_2AuI_2$ is described and compared with those of $(DMET)_2$-$Au(CN)_2$ (Kikuchi *et al.*, 1988*a*) and $(DMET)_2I_3$ (Aldoshina, Atovmyan, Gol'denberg, Krasochka, Lyubovskaya, Lyubovskii & Khidekel', 1986).

Experimental. Crystals of $(DMET)_2AuI_2$ prepared by electrochemical oxidation of DMET in chlorobenzene solution in the presence of $(n\text{-}Bu_4N)AuI_2$ at a constant current (1 μA). D_m not determined. A black plate-like crystal 0·4 × 0·2 × 0·03 mm. Rigaku RASA-5 automated four-circle diffractometer. Unit-cell dimensions determined from 20 selected reflections ($25 < 2\theta < 32°$). Intensity data collected using the ω–2θ scan technique ($\Delta\omega = 1{\cdot}00° + 0{\cdot}14°\tan\theta$) with a scan rate 4° min^{-1} in ω to $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1} ($0 \leq h \leq 8$, $-8 \leq k \leq 10$, $-20 \leq l \leq 20$). Three standard reflections measured at an interval of 100 reflections, small (<2%) random variations. Data corrected for absorption effects using a Gaussian integration procedure; $T_{\min} = 0{\cdot}20$, $T_{\max} = 0{\cdot}76$. 3917 independent reflections collected; 2574 reflections $[|F_o| > 3\sigma(F_o)]$ used in the structure refinement. Intensity statistics indicated space group $P\bar{1}$ rather than $P1$ and this choice was later confirmed by the successful structure solution and least-squares refinement. Structure solved by the heavy-atom method and refined by the block-diagonal least-squares method. Atomic and anomalous scattering factors from *International Tables for X-ray Crystallography* (1974). All computations carried out using *UNICS*III program (Sakurai & Kobayashi, 1979). H atoms not located. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = \{\sigma^2(|F_o|) + 0{\cdot}0004|F_o|^2\}^{-1}$, with $\sigma(|F_o|)$ based on counting statistics. $\Delta/\sigma \leq 0{\cdot}22$ in final least-squares cycle which resulted in the agreement factors $R = 0{\cdot}049$, $wR = 0{\cdot}050$ and $S = 1{\cdot}71$. No correction for secondary extinction. A difference synthesis based on the structure factors derived from the final parameter values showed some peaks of density ($-1{\cdot}2$–$1{\cdot}3$ e Å^{-3}). *ORTEP*II (Johnson, 1971) was used to produce crystal structure illustrations.

Table 1. *Fractional atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \tfrac{4}{3}(B_{11}\mathbf{a}.\mathbf{a} + B_{12}\mathbf{a}.\mathbf{b} + B_{13}\mathbf{a}.\mathbf{c} + \ldots).$$

	x	*y*	*z*	B_{eq}
Au(1)	5000	0	0	3·79 (2)
I(1)	8439 (1)	−2366 (1)	162 (1)	4·90 (3)
Se(1)	2504 (1)	2272 (1)	5765 (1)	2·28 (2)
Se(2)	7410 (1)	1174 (1)	6101 (1)	2·33 (2)
S(1)	2825 (3)	3830 (3)	3828 (1)	2·4 (1)
S(2)	7370 (3)	2813 (3)	4172 (1)	2·5 (1)
S(3)	2518 (3)	5184 (3)	2062 (2)	3·0 (1)
S(4)	7970 (3)	3974 (3)	2470 (2)	3·0 (1)
C(1)	4987 (11)	2218 (11)	5337 (5)	2·0 (2)
C(2)	5040 (12)	2912 (11)	4553 (5)	2·1 (2)
C(3)	3870 (12)	1251 (11)	6844 (5)	2·1 (2)
C(4)	5955 (12)	766 (11)	6997 (5)	2·1 (2)
C(5)	4136 (12)	4227 (11)	2993 (5)	2·2 (2)
C(6)	6224 (12)	3768 (12)	3164 (6)	2·4 (2)
C(7)	2446 (14)	955 (13)	7484 (6)	3·0 (3)
C(8)	7314 (14)	−86 (12)	7810 (6)	2·8 (2)
C(9)	4382 (15)	5522 (14)	1372 (6)	3·6 (3)
C(10)	6323 (15)	4029 (14)	1441 (6)	3·5 (3)

Table 2. *Bond lengths* (Å) *and angles* (°)

Au(1)–I(1)	2·548 (1)	Se(1)–C(1)	1·881 (8)
Se(1)–C(3)	1·885 (8)	Se(2)–C(1)	1·881 (7)
Se(2)–C(4)	1·900 (9)	S(1)–C(2)	1·736 (7)
S(1)–C(5)	1·754 (9)	S(2)–C(2)	1·742 (9)
S(2)–C(6)	1·741 (9)	S(3)–C(5)	1·740 (8)
S(3)–C(9)	1·838 (11)	S(4)–C(6)	1·750 (10)
S(4)–C(10)	1·822 (10)	C(1)–C(2)	1·357 (12)
C(3)–C(4)	1·343 (11)	C(3)–C(7)	1·542 (14)
C(4)–C(8)	1·508 (11)	C(5)–C(6)	1·346 (11)
C(9)–C(10)	1·504 (13)		

C(1)–Se(1)–C(3)	93·9 (4)	C(1)–Se(2)–C(4)	94·3 (3)
C(2)–S(1)–C(5)	96·0 (4)	C(2)–S(2)–C(6)	95·4 (4)
C(5)–S(3)–C(9)	102·3 (4)	C(6)–S(4)–C(10)	100·0 (5)
Se(1)–C(1)–Se(2)	114·3 (4)	Se(1)–C(1)–C(2)	123·2 (5)
Se(2)–C(1)–C(2)	122·5 (6)	S(1)–C(2)–S(2)	114·7 (5)
S(1)–C(2)–C(1)	123·2 (6)	S(2)–C(2)–C(1)	121·9 (6)
Se(1)–C(3)–C(4)	119·8 (7)	Se(1)–C(3)–C(7)	115·6 (5)
C(4)–C(3)–C(7)	124·6 (7)	Se(2)–C(4)–C(3)	117·6 (6)
Se(2)–C(4)–C(8)	115·0 (6)	C(3)–C(4)–C(8)	127·4 (8)
S(1)–C(5)–S(3)	114·4 (5)	S(1)–C(5)–C(6)	116·0 (6)
S(3)–C(5)–C(6)	129·6 (7)	S(2)–C(6)–S(4)	114·9 (4)
S(2)–C(6)–C(5)	117·8 (7)	S(4)–C(6)–C(5)	127·2 (7)
S(3)–C(9)–C(10)	114·1 (8)	S(4)–C(10)–C(9)	111·8 (7)

Discussion. Final positional and thermal parameters are tabulated in Table 1.* Bond lengths and angles are given in Table 2. The molecular geometry of DMET is in reasonable agreement with those observed in other DMET salts (Kikuchi, Ikemoto & Kobayashi, 1987; Kikuchi, Honda *et al.*, 1988; Kikuchi *et al.*, 1988*a*;

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Kikuchi *et al.*, 1988*b*). The DMET molecule is almost planar except for the ethylenedithio group. The C(10) atom is about 0·9 Å away from the DMET molecular plane determined by the Se(1), Se(2), S(1), S(2), C(1) and C(2) atoms; the other atoms are within about 0·1 Å from the plane. The anion AuI$_2$ is exactly linear because of the inversion symmetry.

As seen in Fig. 1, the DMET molecules form an ordered stack in the direction of the *b* axis. The normal to the molecular plane is tilted by 22·4° from the stacking axis. The DMET molecules are stacked with an alternate molecular orientation related by an inversion center. Although two interplanar distances are almost equal (3·57 Å) to each other within the experimental accuracy, there are two different types of overlap between the neighboring molecules within the stack. One type of overlap has four Se—S contacts shorter than the sum of the van der Waals radii. The other has two shorter Se—Se contacts and two slightly longer Se—S contacts [3·909 (3) and 3·909 (3) Å]. The ethylenedithio group is not responsible for shorter contacts in either type of overlap of DMET molecules within the stack.

There also exist interstack contacts as shown in Fig. 2. The interatomic distances indicated in the figure (one Se—Se and two S—S contacts) are shorter than the sum of the van der Waals radii. These contacts lie between the molecules related by a translation of *a* along the *a* axis. In the interstack contacts, the ethylenedithio group contributes to the S—S contacts. The pattern of the intra- and interstack contacts is exactly the same as those reported in (DMET)$_2$Au(CN)$_2$ (Kikuchi *et al.*, 1988*a*) and (DMET)$_2$I$_3$ (Aldoshina *et al.*, 1986).

The relative position of anions with respect to DMET molecules in (DMET)$_2$AuI$_2$ is similar not to that in (DMET)$_2$Au(CN)$_2$, which belongs to the same group (group 3) as (DMET)$_2$AuI$_2$, but to that in (DMET)$_2$I$_3$ (group 4). The AuI$_2$ anion lies nearly in the direction of the long axis of the DMET molecule. Conversely, in (DMET)$_2$Au(CN)$_2$ the anion lies in between the long axes of two adjacent molecules. These facts clearly demonstrate that the location of the anions is not essential for the electrical properties of (DMET)$_2$*X* crystals.

A quantitative comparison of the stacking geometry of DMET molecules is now made between (DMET)$_2$AuI$_2$, (DMET)$_2$Au(CN)$_2$ and (DMET)$_2$I$_3$. While the intrastack distances are nearly the same as each other, the interstack contacts in (DMET)$_2$I$_3$ (3·77, 3·59 and 3·48 Å; Aldoshina *et al.*, 1986) are shorter by *ca* 0·06 Å than those in (DMET)$_2$AuI$_2$ (3·832, 3·611 and 3·552 Å) and in (DMET)$_2$Au(CN)$_2$ (3·884, 3·672 and 3·580 Å; Kikuchi *et al.*, 1988*a*). The longer interstack contacts in (DMET)$_2$AuI$_2$ and in (DMET)$_2$Au(CN)$_2$ give the crystal less two-dimensionality (Murata *et al.*, 1988; Kikuchi, Saito *et al.*, 1988; Kanoda, Takahashi, Kikuchi, Saito, Ikemoto & Kobayashi, 1988).

Among the group 3 superconductors [(DMET)$_2$Au(CN)$_2$, (DMET)$_2$AuCl$_2$ and (DMET)$_2$AuI$_2$], it is observed that the smaller the molar volume, the lower the critical pressure for the appearance of superconductivity (Kikuchi, Murata, Honda, Namiki, Saito, Anzai *et al.*, 1987). Thus it is natural to expect that the interstack contacts in (DMET)$_2$Au(CN)$_2$, which has smaller molar volume, are shorter than those in (DMET)$_2$AuI$_2$. However, this is not the case. The

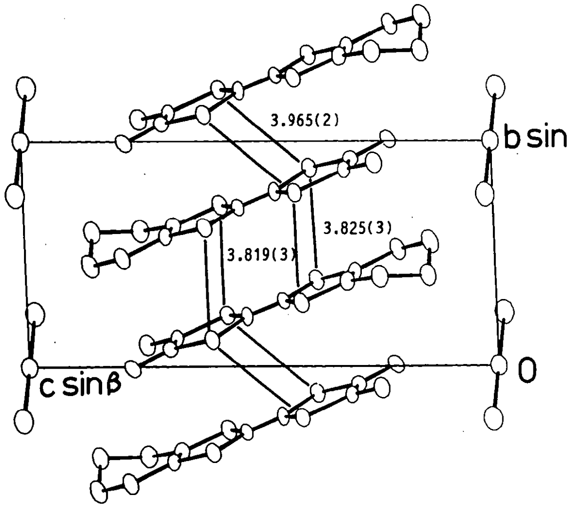

Fig. 1. Crystal structure viewed along the *a* axis. The thermal ellipsoids indicate the region of 50% probability. The intermolecular contacts (Å) shorter than the sum of van der Waals radii are drawn with thick lines.

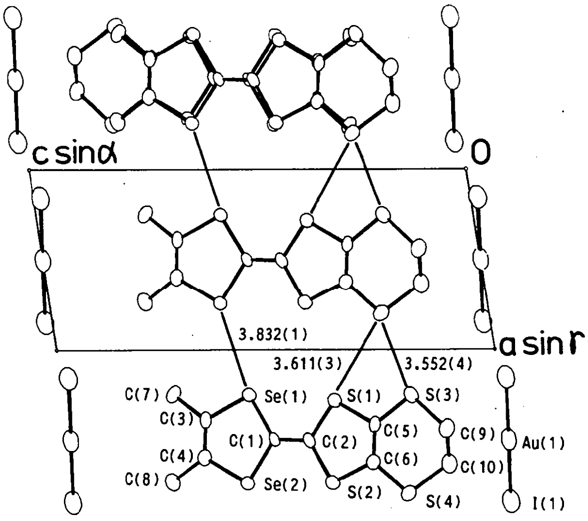

Fig. 2. Crystal structure viewed along the *b* axis. The thermal ellipsoids indicate the region of 50% probability. The intermolecular overlap is shown uppermost. Only two molecules related by the translation *a* are drawn in the lower part for clarity in showing the interstack contacts (Å). The numbering scheme is also given.

structure determination of $(DMET)_2AuCl_2$ and the variable temperature studies will help to solve the apparent inconsistency.

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Structures of Two Fe—S Cluster Complexes and Comparisons of Structures of Eight Fe—S Cluster Complexes $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$

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Abstract. (1) μ-1,4-Butanedithio-bis(μ-methylthio-hexacarbonyldiiron), $[(CH_3S)Fe_2(CO)_6S]_2C_4H_8$, $M_r = 773·95$, monoclinic, $P2_1/a$, $a = 7·910\,(1)$, $b = 12·564\,(2)$, $c = 14·644\,(2)$ Å, $\beta = 101·28\,(1)°$, $V = 1427·2$ Å^3, $Z = 2$, $D_x = 1·801$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 23·286$ cm^{-1}, $F(000) = 772$, $T = 296$ K, $R = 0·035$ for 890 reflections. (2) μ-Phenylvinyl-μ-*tert*-butylthio-hexacarbonyldiiron, $[(C_4H_9S)\text{-}Fe_2(C_2H_2C_6H_5)(CO)_6]$, $M_r = 472·08$, monoclinic, $P2_1/n$, $a = 15·145\,(2)$, $b = 9·151\,(1)$, $c = 16·198\,(2)$ Å, $\beta = 113·45\,(1)°$, $V = 2057·8$ Å^3, $Z = 4$, $D_x = 1·52$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15·350$ cm^{-1}, $F(000) = 960$, $T = 296$ K, $R = 0·075$ for 1337 reflections. The influences of the different substituents R^1 and R^2 on the structures of eight Fe—S cluster complexes, $(\mu\text{-}R^1S)(\mu\text{-}R^2S)Fe_2(CO)_6$, were studied. The Fe—Fe distances are almost constant (2·505–2·542 Å). The average Fe—S distances in these complexes are also close to each other (2·250–2·270 Å). Mössbauer spectroscopy of (2) has established that two Fe atoms in this compound have the same coordination environment, so probably one of the Fe atoms is bonded to the π-electrons of the ethylene. In each complex, Fe atoms keep a six-coordinate geometry. The conformations of R^1 and R^2 are (a,e) type for the majority of these complexes.

Introduction. Iron–sulfur proteins play an important role in the life sciences, and therefore the investigation of Fe—S cluster complexes is an active field in inorganic

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