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Structure of 4,5-Dimethyl-9,10-ethylenedithio-1,3-diselena-6,8-dithiafulvalene* Dicyanoaurate(I) (2:1), $(DMET)_2Au(CN)_2$

By Koichi Kikuchi, Yoshimitsu Ishikawa, Kazuya Saito and Isao Ikemoto

Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, *Japan*

and Keiji Kobayashi

Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, *Japan*

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Abstract. $(C_{10}H_{10}S_4Se_2)_2.[Au(CN)_2]$, $M_r = 1081.72$, triclinic, $P\bar{1}$, $a = 6.763$ (3), $b = 7.710$ (3), $c = 15.314$ (7) Å, $\alpha = 91.29$ (2), $\beta = 96.81$ (2), $\gamma = 75.04$ (2)°, $V = 765.9$ (9) Å^3, $Z = 1$, $D_x = 2.35$ Mg m^{-3}, μ(Mo $K\alpha$) = 5.33 mm^{-1}, $F(000) = 509$, $T = 297$ K, $R = 0.057$ for 2390 reflections. The structure consists of ordered stacks of DMET $(C_{10}H_{10}S_4Se_2)$ molecules. There are some short intermolecular contacts not only within the stacks, but also between the stacks, which may give this salt some two-dimensional character.

Introduction. We have recently discovered that $(DMET)_2Au(CN)_2$ exhibits superconductivity below 0.80 K under a pressure of 5 kbar (Kikuchi, Kikuchi, Namiki, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1987). After this discovery, some salts of DMET were found to undergo a superconducting transition (Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Ishiguro, Kobayashi & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Anzai, Ishiguro, Kobayashi & Ikemoto, 1987). This is the first series of organic superconductors based on an unsymmetrical donor. The organic superconductors, such as TMTSF and BEDT-TTF salts, for which structures have so far been determined (Thorup, Rindorf, Soling & Bechgaard, 1981; Kaminskii, Prokhoroea, Shibaeva & Yagubskii, 1984), have fairly high two-dimensional character. It is important to investigate whether new organic superconductors also have high two-dimensionality or not. In this communication, we report the crystal structure of $(DMET)_2$-$Au(CN)_2$ at ambient pressure.

Experimental. Crystals of $(DMET)_2Au(CN)_2$ prepared by electrochemical oxidation of DMET in chloro-

* Systematic name: 2-(4,5-dimethyldiselenol-2-ylidene)dithiolo-[4,5-*b*]dithiin.

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}
Se(1)	2392 (1)	2357 (1)	5792 (1)	2.52 (3)
Se(2)	7266 (1)	1221 (1)	6138 (1)	2.57 (3)
S(1)	2859 (3)	3774 (4)	3805 (2)	2.7 (1)
S(2)	7378 (3)	2744 (4)	4148 (2)	2.7 (1)
S(3)	2668 (4)	4958 (4)	1976 (2)	3.3 (1)
S(4)	8082 (4)	3769 (4)	2389 (2)	3.5 (1)
C(1)	4911 (12)	2246 (12)	5350 (6)	2.1 (2)
C(2)	5030 (13)	2852 (12)	4538 (6)	2.3 (3)
C(3)	3645 (14)	1383 (13)	6902 (6)	2.3 (3)
C(4)	5738 (14)	895 (12)	7061 (6)	2.4 (3)
C(5)	4210 (13)	4084 (13)	2940 (6)	2.6 (3)
C(6)	6292 (13)	3615 (13)	3099 (6)	2.4 (3)
C(7)	2169 (14)	1197 (15)	7550 (7)	3.4 (3)
C(8)	7030 (14)	95 (13)	7899 (6)	2.8 (3)
C(9)	4534 (16)	5281 (16)	1261 (7)	4.0 (4)
C(10)	6511 (16)	3772 (17)	1337 (7)	4.0 (4)
Au(1)	0	0	0	5.09 (3)
C(11)	1479 (29)	1807 (23)	−132 (9)	8.4 (7)
N(1)	2407 (31)	2823 (25)	−237 (9)	13.9 (10)

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

Se(1)–C(1)	1.888 (9)	S(4)–C(6)	1.748 (10)
Se(1)–C(3)	1.886 (10)	S(4)–C(10)	1.821 (13)
Se(2)–C(1)	1.885 (9)	C(1)–C(2)	1.356 (13)
Se(2)–C(4)	1.905 (9)	C(3)–C(4)	1.361 (14)
S(1)–C(2)	1.740 (10)	C(3)–C(7)	1.522 (15)
S(1)–C(5)	1.750 (10)	C(4)–C(8)	1.512 (14)
S(2)–C(2)	1.743 (10)	C(5)–C(6)	1.353 (14)
S(2)–C(6)	1.756 (10)	C(9)–C(10)	1.523 (18)
S(3)–C(5)	1.742 (10)	Au(1)–C(11)	1.939 (19)
S(3)–C(9)	1.832 (12)	N(1)–C(11)	1.148 (29)
C(1)–Se(1)–C(3)	94.5 (4)	C(4)–C(3)–C(7)	125.4 (9)
C(1)–Se(2)–C(4)	94.5 (4)	Se(2)–C(4)–C(3)	117.8 (7)
C(2)–S(1)–C(5)	95.8 (5)	Se(2)–C(4)–C(8)	114.9 (7)
C(2)–S(2)–C(6)	95.3 (5)	C(3)–C(4)–C(8)	127.3 (9)
C(5)–S(3)–C(9)	103.2 (5)	S(1)–C(5)–S(3)	114.9 (6)
C(6)–S(4)–C(10)	99.7 (5)	S(1)–C(5)–C(6)	116.6 (8)
Se(1)–C(1)–Se(2)	114.1 (5)	S(3)–C(5)–C(6)	128.5 (8)
Se(1)–C(1)–C(2)	123.3 (7)	S(2)–C(6)–S(4)	114.7 (6)
Se(2)–C(1)–C(2)	122.6 (7)	S(2)–C(6)–C(5)	117.1 (8)
S(1)–C(2)–S(2)	115.1 (5)	S(4)–C(6)–C(5)	128.2 (8)
S(1)–C(2)–C(1)	122.6 (7)	S(3)–C(9)–C(10)	113.3 (9)
S(2)–C(2)–C(1)	122.3 (7)	S(4)–C(10)–C(9)	112.5 (9)
Se(1)–C(3)–C(4)	119.1 (7)	Au(1)–C(11)–N(1)	176.8 (19)
Se(1)–C(3)–C(7)	115.5 (7)		

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benzene solution in the presence of $(n\text{-}Bu_4N)Au(CN)_2$ at a constant current (1 μA). D_m not determined. Black plate-like crystal 0·6 × 0·1 × 0·02 mm. Rigaku AFC-M automated four-circle diffractometer. Unit-cell dimensions determined from 40 selected reflections ($17 < 2\theta < 27°$). Intensity data collected using the ω-scan technique ($2\theta < 30°$) and 2θ–ω scan technique ($2\theta > 30°$) with a scan rate 3·75° min^{-1} to $(\sin\theta)/\lambda = 0{\cdot}65$ Å^{-1} ($-8 < h < 8$, $-9 < k < 0$, $-19 < l < 19$) because of the rather poor quality of the sample. Two standard reflections measured at an interval of 100 reflections, small (< 1%) random variations. Data corrected for absorption effects using a Gaussian integration procedure; $T_{min} = 0{\cdot}386$, $T_{max} = 0{\cdot}770$.

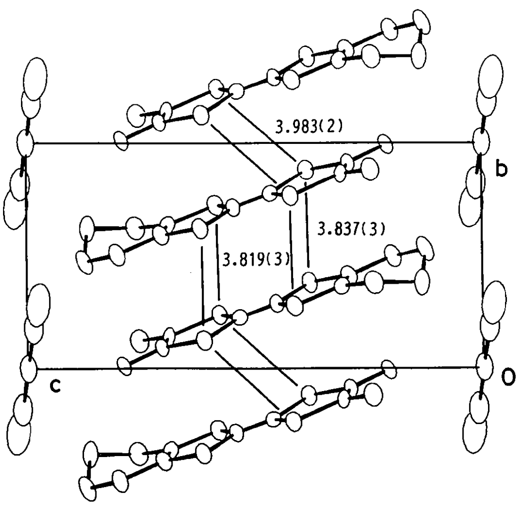

Fig. 1. Crystal structure viewed along the *a* axis. The thermal ellipsoids indicate the region of 50% probability.

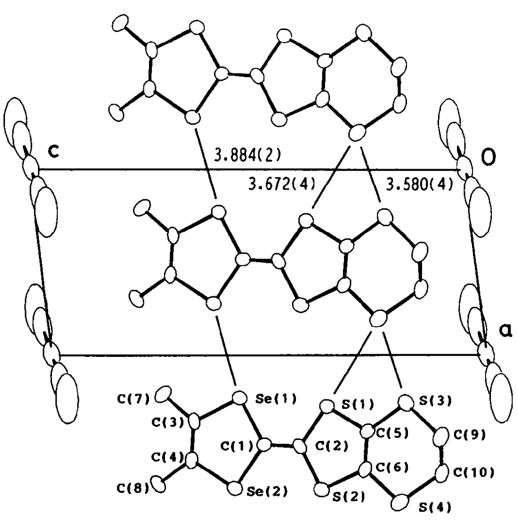

Fig. 2. Crystal structure viewed along the *b* axis. The thermal ellipsoids indicate the region of 50% probability. The numbering scheme is also given.

3493 independent reflections collected. 2390 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 Patterson 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 $w = \{\sigma^2(|F_o|) + 0{\cdot}0001|F_o|^2\}^{-1}$, with $\sigma(|F_o|)$ based on counting statistics. $\Delta/\sigma \leq 0{\cdot}014$ in final least-squares cycle which resulted in the agreement factors $R = 0{\cdot}057$, $wR = 0{\cdot}046$ and $S = 1{\cdot}94$. No correction for secondary extinction. A difference synthesis based on the structure factors derived from the final parameter values showed some peaks of density (−1·4 to 1·2 e Å^{-3}), but no manifestation of disorder in the orientation and/or the position of $Au(CN)_2$. *ORTEP*II (Johnson, 1971) was used to produce the crystal-structure illustrations.

Discussion. Final positional and thermal parameters are presented in Table 1.* Bond lengths and angles are given in Table 2. These values are consistent with corresponding values for TMTSF and BEDT-TTF salts, *e.g.* $(TMTSF)_2PF_6$ (Thorup, Rindorf, Soling & Bechgaard, 1981) and β-$(BEDT\text{-}TTF)_2I_3$ (Mori, Kobayashi, Sasaki, Kobayashi, Saito & Inokuchi, 1984). The DMET molecule is almost planar except for the ethylenedithio group. The C(10) atom of the ethylenedithio group is about 0·9 Å apart from the DMET molecular plane determined by the Se(1), Se(2), S(1), S(2), C(1) and C(2) atoms. As is shown in Fig. 1, the DMET molecules form an ordered stack along the *b* axis. The angle is 22·2° between the normal to the molecular plane and the stacking axis. The stacking mode is the classical 'ring double bond' type. The DMET molecules are stacked with an alternate molecular orientation related by an inversion center. Although two independent interplanar distances are almost equal (3·54 and 3·56 Å), there are two different types of overlap between the neighboring molecules. One type of overlap has two Se–Se contacts shorter than the sum of the van der Waals radii. The other has four shorter Se–S contacts. It is noted that the ethylenedithio group is not responsible for shorter contacts in both types of overlap of DMET molecules within the stack.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44544 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The interstack contacts are shown in Fig. 2. There exist one Se—Se and two S—S contacts shorter than the sum of the van der Waals radii. These contacts lie between molecules related by a translation of *a* along the *a* axis, in contrast to TMTSF salts (Thorup, Rindorf, Soling & Bechgaard, 1981). The ethylenedithio group contributes to the S—S interstack contacts. The interstack contacts in $(DMET)_2Au(CN)_2$ are related to the appearance of superconductivity. The detailed comparison of crystal structures will be helpful in clarifying this point. The crystal structures of other DMET salts will be published shortly.

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Structure of Phenylbis[2-pyridinethiolato(1−)]antimony(III)

BY HANS PREUT, FRIEDO HUBER AND KARL-HEINZ HENGSTMANN

Fachbereich Chemie, Universität Dortmund, D-4600 Dortmund 50, Federal Republic of Germany

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Abstract. $[Sb(C_5H_4NS)_2(C_6H_5)]$, $M_r = 419{\cdot}2$, monoclinic, $P2_1/c$, $a = 11{\cdot}123\,(9)$, $b = 15{\cdot}649\,(5)$, $c = 10{\cdot}165\,(14)$ Å, $\beta = 115{\cdot}27\,(9)°$, $V = 1600{\cdot}0$ Å^3, $Z = 4$, $D_x = 1{\cdot}740$ Mg m^{-3}, $F(000) = 824$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}98$ mm^{-1}, $T = 291\,(1)$ K. Final $R = 0{\cdot}016$ for 2279 unique observed $[I \geq 1{\cdot}96\sigma(I)]$ X-ray diffractometer data. In the distorted tetragonal pyramidal (pseudo-octahedral) coordination polyhedron around Sb the two S and the two N atoms [Sb—S 2·503 (1), 2·500 (1) Å; S—Sb—S 85·00 (2)°; Sb—N 2·633 (2), 2·725 (2) Å; N—Sb—N 152·76 (6)°] are in *cis*-position, the phenyl group is in apical position. Intermolecular distances exceed van der Waals distances.

Experimental. The compound was prepared from $C_6H_5SbCl_2$ and sodium 2-pyridinethiolate in ethanol at 343 K. Colorless crystals from DMF. M.p. 443–445 K. Crystal size ~0·3 × 0·4 × 0·4 mm, $\omega/2\theta$ scan, scan speed 1·1–3·3° min^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$; lattice parameters from least-squares fit with 25 reflections up to $2\theta = 26{\cdot}2°$; six standard reflections recorded every 2·5 h, only random deviations; 9293 reflections measured; $1{\cdot}5 \leq \theta \leq 25{\cdot}0°$, $-12 \leq h \leq 12$,

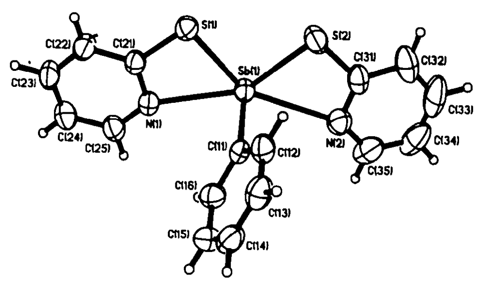

Fig. 1. General view of the molecule, showing the atom-numbering scheme.

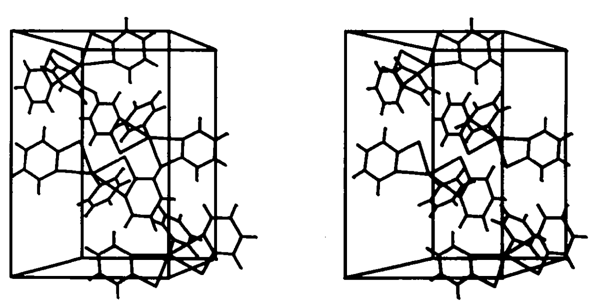

Fig. 2. Stereoscopic view of the unit cell (*b* vertical, *c* horizontal).

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