

The structure is built up by a dimeric molecule. Both Cu atoms are bridged by the S atoms of the thiophenolato anions forming a non-planar Cu₂S₂ ring. Although sulfur has a high affinity to copper, the thiocycloheptyne ligands are η^2 -bonded via the alkyne groups. Interestingly, the angles C(10)—C(11)—C(12) of 147.8 (4), C(11)—C(10)—C(17) of 147.1 (4), C(30)—C(31)—C(32) of 145.9 (4) and C(31)—C(30)—C(37) of 147.7 (4)° are not changed much compared to the corresponding angles in the uncomplexed thiacycloheptyne of 145.8° (Krebs & Wilke, 1983). However, the shift of the C≡C stretching frequencies from 2200 and 2170 cm⁻¹ in the uncomplexed alkyne to 1970 and 1950 cm⁻¹ in the Cu—thiophenolate complex shows that a significant interaction between the alkyne and the Cu ligand has taken place.

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Structure of the Organic Superconductor (DMET)₂AuCl₂

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Abstract. 2-(4,5-Dimethyldiselenol-2-ylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiin dichloroaurate(I) (2/1), (C₁₀H₁₀S₄Se₂)₂[AuCl₂], *M_r* = 1100.58, triclinic, *P* $\bar{1}$, *a* = 7.021 (3), *b* = 7.742 (3), *c* = 15.622 (6) Å, α = 108.60 (3), β = 98.27 (3), γ = 70.82 (3)°, *V* = 759.5 (4) Å³, *Z* = 1, *D_x* = 2.41 Mg m⁻³, λ (Mo *K* α) = 0.71068 Å, μ = 10.30 mm⁻¹, *F*(000) = 517, *T* = 297 K, *R* = 0.062 for 2345 reflections. The structure consists of sheets of C₁₀H₁₀S₄Se₂ (DMET) and of AuCl₂. The ordered DMET molecules are stacked in a columnar structure. Some short intermolecular contacts lie not only within a column, but also between columns. The contact mode is similar to that of (DMET)₂Au(CN)₂ and (DMET)₂AuI₂ within a column, but is different between columns.

Introduction. All previously discovered superconductors based on an unsymmetrical donor DMET have

a linear anion as counter anion: Au(CN)₂⁻, AuCl₂⁻, AuBr₂⁻, AuI₂⁻, I₃⁻ and IBr₂⁻ (Kikuchi, Kikuchi, Namiki, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Anzai, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Murata, Honda, Namiki, Saito, Kobayashi, Ishiguro & Ikemoto, 1987; Kikuchi, Honda, Ishikawa, Saito, Ikemoto, Murata, Anzai, Ishiguro & Kobayashi, 1988; Kikuchi, Murata, Honda, Namiki, Saito, Ishiguro, Kobayashi & Ikemoto, 1987). These compounds belong to groups 3, 4 and 5 in the classification according to the low-temperature behavior of conductivity (Murata, Kikuchi, Takahashi, Kobayashi, Honda, Saito, Kanoda, Tokiwa, Anzai, Ishiguro & Ikemoto, 1988; Kikuchi, Saito, Ikemoto, Murata, Ishiguro & Kobayashi, 1988; Kanoda, Takahashi, Kikuchi, Saito, Ikemoto & Kobayashi, 1988). Room-

temperature structures were determined for the radical salts of PF₆, Au(CN)₂, AuBr₂, AuI₂, I₃ and IBr₂ (Kikuchi, Ikemoto & Kobayashi, 1987; Kikuchi, Ishikawa, Saito, Ikemoto & Kobayashi, 1988*a,b*; Ishikawa, Kikuchi, Saito, Ikemoto & Kobayashi, 1989; Aldoshina, Atovmyan, Gol'denberg, Krasochka, Lyubovskaya, Lyubovskii & Khidekel', 1986; Kikuchi, Honda *et al.*, 1988).

At ambient pressure, the title compound has metallic character down to 2.8 K. At 2.8 K, a resistance upturn was observed, similar to Au(CN)₂ and AuI₂ salts (Kikuchi, Murata, Honda, Namiki, Saito, Anzai *et al.*, 1987). According to these observations, (DMET)₂AuCl₂ is classified as group 3. On further cooling, (DMET)₂AuCl₂ undergoes a superconducting transition at 0.83 K (Kikuchi, Murata, Honda, Namiki, Saito, Anzai *et al.*, 1987).

In this paper, we report the crystal structure of (DMET)₂AuCl₂.

Experimental. Crystals of (DMET)₂AuCl₂ prepared by electrochemical oxidation of DMET in chlorobenzene solution in the presence of (*n*-Bu₄N)AuCl₂ at a constant current (1 μA). *D_m* not determined. A black plate-like crystal 0.5 × 0.05 × 0.03 mm. Rigaku AFC-M automated four-circle diffractometer. Unit-cell dimensions determined from 35 selected reflections (18 < 2θ < 31°). Intensity data collected using the ω-scan technique (2θ < 30°) and the ω-2θ scan technique (2θ > 30°) with a scan rate 3.75° min⁻¹ [Δω = (1.40 + 0.50 tan θ)°] in ω to (sin θ)/λ = 0.65 Å⁻¹ (0 ≤ *h* ≤ 8, -9 ≤ *k* ≤ 9, -19 ≤ *l* ≤ 19). Two standard reflections measured at an interval of 100 reflections, small (< 1.2%) random variations. Data corrected for absorption effects using a Gaussian integration procedure; *T*_{min} = 0.58, *T*_{max} = 0.78. 3350 independent reflections collected; 2345 reflections [|*F*_o| > 3σ(|*F*_o|)] used in the structure refinement. Intensity statistics indicated space group *P* $\bar{1}$ rather than *P*1 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 UNICSIII (Sakurai & Kobayashi, 1979). H atoms not located. Σ*w*(|*F*_o| - |*F*_c|)² minimized, where *w* = [σ²(|*F*_o|) + 0.0001|*F*_o|²]⁻¹, with σ(|*F*_o|) based on counting statistics. Δσ ≤ 0.08 in final least-squares cycle which resulted in the agreement factors *R* = 0.062, *wR* = 0.055 and *S* = 1.83. No correction for secondary extinction. A difference synthesis based on the structure factors derived from the final parameter values showed some peaks of density -1.6-1.4 e Å⁻³. ORTEPII (Johnson, 1971) was used to produce crystal structure illustrations.

Table 1. Fractional atomic coordinates (× 10⁴) and equivalent isotropic temperature factors (Å²)

$$B_{eq} = (4/3)(a \cdot a B_{11} + a \cdot b B_{12} + a \cdot c B_{13} + \dots).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Au(1)	0	0	0	3.77 (3)
Cl(1)	-2066 (6)	2957 (6)	35 (2)	5.1 (2)
Se(1)	3161 (2)	3017 (2)	6197 (1)	2.44 (4)
Se(2)	7805 (2)	1372 (2)	5788 (1)	2.51 (4)
S(1)	2308 (4)	3640 (5)	4130 (2)	2.6 (1)
S(2)	6634 (4)	2117 (5)	3797 (2)	2.6 (1)
S(3)	1015 (5)	4040 (5)	2307 (2)	3.5 (1)
S(4)	6228 (5)	2259 (5)	1916 (2)	3.1 (1)
C(1)	5145 (16)	2400 (16)	5368 (7)	2.4 (4)
C(2)	4747 (17)	2691 (17)	4558 (8)	2.4 (4)
C(3)	5044 (17)	2281 (17)	7119 (7)	2.5 (4)
C(4)	6988 (17)	1550 (16)	6924 (7)	2.5 (4)
C(5)	3015 (16)	3343 (16)	3042 (7)	2.3 (4)
C(6)	5003 (17)	2668 (16)	2901 (7)	2.3 (4)
C(7)	4098 (18)	2540 (20)	7990 (8)	3.2 (5)
C(8)	8772 (17)	828 (18)	7543 (7)	2.9 (4)
C(9)	2354 (18)	4056 (20)	1374 (8)	3.3 (5)
C(10)	4094 (19)	2252 (21)	1086 (8)	3.7 (5)

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

Au(1)—Cl(1)	2.260 (4)	S(3)—C(5)	1.736 (11)
Se(1)—Se(2)	3.165 (2)	S(3)—C(9)	1.850 (16)
Se(1)—C(1)	1.880 (12)	S(4)—C(6)	1.761 (13)
Se(1)—C(3)	1.905 (11)	S(4)—C(10)	1.836 (13)
Se(2)—C(1)	1.886 (10)	C(1)—C(2)	1.330 (18)
Se(2)—C(4)	1.892 (12)	C(3)—C(4)	1.333 (16)
S(1)—C(2)	1.754 (11)	C(3)—C(7)	1.526 (19)
S(1)—C(5)	1.763 (13)	C(4)—C(8)	1.534 (16)
S(2)—C(2)	1.760 (13)	C(5)—C(6)	1.344 (15)
S(2)—C(6)	1.746 (11)	C(9)—C(10)	1.511 (16)
Se(2)—Se(1)—C(1)	32.9 (3)	S(2)—C(2)—C(1)	123.0 (8)
Se(2)—Se(1)—C(3)	61.6 (4)	Se(1)—C(3)—C(4)	117.4 (9)
C(1)—Se(1)—C(3)	94.4 (5)	Se(1)—C(3)—C(7)	114.6 (8)
Se(1)—Se(2)—C(1)	32.8 (4)	C(4)—C(3)—C(7)	128.0 (11)
Se(1)—Se(2)—C(4)	60.7 (3)	Se(2)—C(4)—C(3)	120.3 (9)
C(1)—Se(2)—C(4)	93.5 (5)	Se(2)—C(4)—C(8)	112.6 (8)
C(2)—S(1)—C(5)	96.4 (5)	C(3)—C(4)—C(8)	127.1 (11)
C(2)—S(2)—C(6)	96.4 (6)	S(1)—C(5)—S(3)	114.6 (6)
C(5)—S(3)—C(9)	101.4 (6)	S(1)—C(5)—C(6)	116.4 (9)
C(6)—S(4)—C(10)	100.0 (6)	S(3)—C(5)—C(6)	129.0 (10)
Se(1)—C(1)—Se(2)	114.4 (6)	S(2)—C(6)—S(4)	114.2 (6)
Se(1)—C(1)—C(2)	123.8 (8)	S(2)—C(6)—C(5)	117.4 (10)
Se(2)—C(1)—C(2)	121.8 (9)	S(4)—C(6)—C(5)	128.4 (9)
S(1)—C(2)—S(2)	113.1 (7)	S(3)—C(9)—C(10)	111.6 (11)
S(1)—C(2)—C(1)	123.9 (10)	S(4)—C(10)—C(9)	111.2 (8)

Discussion. Final positional and thermal parameters are tabulated in Table 1.* Bond lengths and angles are given in Table 2, and are reasonable compared to those for the compounds reported so far (Kikuchi, Ikemoto & Kobayashi, 1987; Kikuchi, Ishikawa *et al.*, 1988*a*; Ishikawa *et al.*, 1989). The DMET molecule is almost planar except for the C(10) atom. It is about 0.9 Å away from the DMET molecular plane determined by the Se(1), Se(2), S(1), S(2), C(1)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52934 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and C(2) atoms; the other atoms are within 0.26 Å from the plane. The anion $AuCl_2$ is completely linear because the Au atom is at an inversion center.

As seen in Fig. 1, the ordered DMET molecules are stacked along the direction of the b axis and form a column. In the column, the DMET molecules are stacked with an alternate molecular orientation related by an inversion center. The normal to the molecular plane is tilted by 23.2° from the b axis. There exist two different types of overlap between the neighboring molecules within the column. 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 [3.933 (4) and 3.949 (4) Å]. The two independent interplanar spacings are 3.52 and 3.59 Å, respectively. Therefore two DMET molecules in a unit cell interact rather strongly. The ethylenedithio group is not responsible for shorter contacts in both types of overlap of DMET molecules within the column.

The interplanar distance in $(DMET)_2Au_2$ is intermediate (3.57 Å; Ishikawa *et al.*, 1989) between those in $(DMET)_2AuCl_2$. This will be related to the shorter Se—S contacts [3.814 (4) and 3.798 (4) Å] observed in $(DMET)_2AuCl_2$ compared with those in other DMET compounds reported (Aldoshina *et al.*, 1986; Kikuchi, Ikemoto & Kobayashi, 1987; Kikuchi, Ishikawa *et al.*, 1988a; Ishikawa *et al.*, 1989).

There also exist intercolumn contacts as shown in Fig. 2. The interatomic distances indicated in the figure (one Se—Se and two Se—S contacts) are

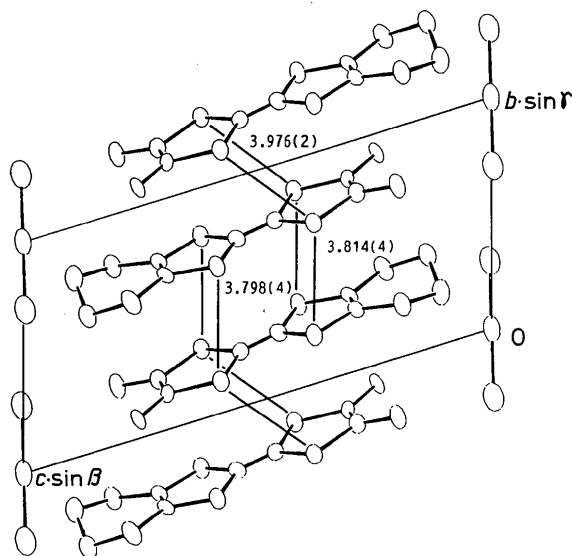


Fig. 1. Crystal structure viewed along the a axis. The thermal ellipsoids indicate the region of 50% probability. The inter-molecular contacts (Å) shorter than the sum of van der Waals radii are drawn with thick lines.

shorter than the sum of the van der Waals radii. These contacts lie between the molecules related by the inversion center between columns, and do not exist between molecules related by a translation along the a axis, in contrast to other compounds in groups 3 and 4 (Kikuchi, Ishikawa *et al.*, 1988a; Ishikawa *et al.*, 1989; Aldoshina *et al.*, 1986). Fig. 3 clearly shows the situation. In $(DMET)_2AuCl_2$, the symmetry operation that relates the closest molecule is not a translation (*e.g.* molecule \bar{A} vs C) but an inversion (*i.e.* molecule A vs B , or C). For the molecules A and B there exist two Se—S contacts, and for A and C one Se—Se contact, as seen in Fig. 2. It is also noted that the location of the $AuCl_2$

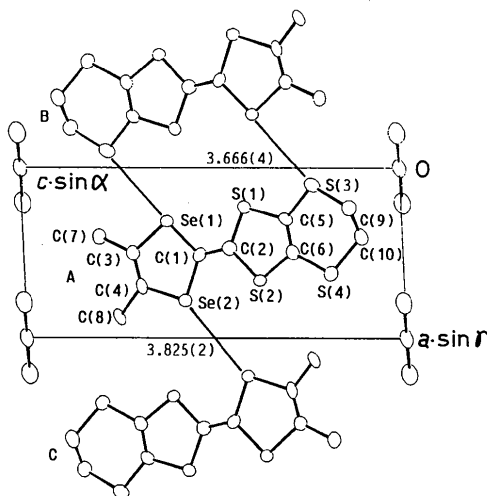


Fig. 2. Crystal structure viewed along the b axis. The thermal ellipsoids indicate the region of 50% probability. The inter-molecular overlap is shown for the central cell. The molecules having intermolecular contacts (Å) shorter than the sum of van der Waals radii are drawn for clarity in showing the interstack contacts. Letters (A , B , etc.) refer to the same molecules as in Fig. 3. The numbering scheme is also given.

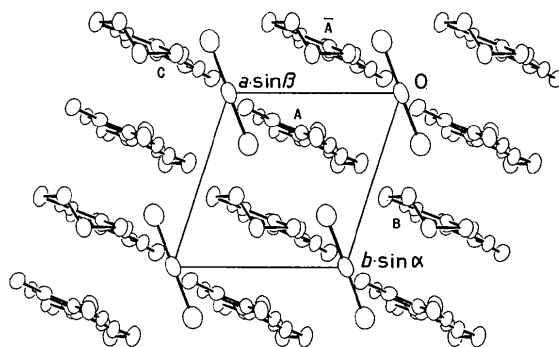


Fig. 3. Crystal structure viewed along the c axis. The thermal ellipsoids indicate the region of 50% probability. Letters (A , B , etc.) refer to the same molecules as in Fig. 2.

anion with respect to the DMET stack is different from that of anions in other compounds. The AuCl₂ anion is located among eight DMET molecules.

Between the DMET columns, the Se—Se distance in (DMET)₂AuCl₂ is shorter than that in (DMET)₂-AuI₂. The contact mode is quite different in (DMET)₂AuCl₂ and (DMET)₂AuI₂; a comparison of the dimensionality is rather difficult. Similar electrical properties of the two compounds, however, suggest that the dimensionality is almost equal.

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Structure of 6-Chloro-10-oxabicyclo[5.2.1]decane-2,3-diol

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Abstract. C₉H₁₅ClO₃, *M_r* = 206.7, monoclinic, *P*2₁/*a*, *a* = 11.627 (2), *b* = 7.486 (4), *c* = 11.625 (5) Å, β = 109.5 (1)°, *V* = 954 (1) Å³, *Z* = 4, *D_x* = 1.44 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 33.8 cm⁻¹, *F*(000) = 440, room temperature, *R* = 0.074 for 1123 reflections with *I* ≥ 2σ(*I*). The crystal structure is stabilized by extensive intermolecular hydrogen bonding, with a specific interaction between the hydroxyl (O3H) group of one molecule and the hydroxyl (O2H) group of another, forming hydrogen-bonded chains along the *b* axis. There is also an intramolecular hydrogen bond O2—H1...O3.

Introduction. Medium-size cyclic ethers are becoming increasingly recognized as common structural units

in naturally occurring compounds, such as toxins (Shimizu, Chou, Bando, Duyne & Clardy, 1986; Murata, Kumagai, Soo Lee & Yasumoto, 1987) and marine natural products (Moore, 1978). Owing to the biological interest in these substances and the well recognized problems in building midsize rings, we are involved in the development of new synthetic methodologies for such molecules. Single-crystal X-ray analysis is a useful tool for solving structure-related problems. In this work we wish to report the molecular and crystal structure of the title compound synthesized in our laboratories (Alvarez, Manta, Martín, Rodríguez & Ruiz-Pérez, 1988; Alvarez, Manta, Martín, Rodríguez, Ruiz-Pérez & Zurita, 1988).