The compound $UCl_4.3\cdot3dmf$ is formed by two U^{IV} complex ions $[UCl_3(dmf)_5]^+$ (Fig. 1) and $[UCl_6]^{2-}$. In the cation, the U atom has no imposed crystallographic symmetry while in the anion the U atom lies on an inversion centre. The anion $[UCl_6]^{2-}$ is a nearly regular octahedron, the U—Cl distances ranging from 2·59 (2) to 2·64 (1) Å. The U atom of the cation is eight coordinated by three Cl atoms [U—Cl 2·66 (2)–2·68 (1) Å] and five dmf ligands [U—O 2·29 (3)–2·45 (2) Å]. This eight coordination (Fig. 2) does not fall into the idealized geometries of dodecahedron, bicapped trigonal prism or square antiprism. The three Cl and O(3) atoms are coplanar, plane 1 [deviations of Cl(11), Cl(12), Cl(13) and O(3) from least-squares plane: −0·05 (1), 0·043 (1), −0·05 (1), 0·06 (3) Å respectively] and parallel to the O(1)O(2)O(4) plane (plane 2). The U atom lies at 0·69 (1) Å above plane 1 and 1·78 (2) Å below plane 2; the U—O(5) bond is perpendicular to these planes.

The average U—Cl bond lengths are 2·67 (1) Å in the cation and 2·62 (2) Å in the anion, values which are similar to those reported for $[UCl_3(depa)_4]^+$ [2·65 (3) Å].$[UCl_5(depa)]^-$ [2·58 (3) Å] (Bagnall *et al.*, 1982), $[UCl_3(dcc)]^+$ (dcc = dicyclohexyl-18-crown-6) [2·6512(Å)].UCl_6^{2-} [2·61 (4) Å] (de Villardi, Charpin, Costes, Folcher, Plurien, Rigny & de Rango, 1978): the significantly shorter values in the anion may result from less hindrance around the U atom. The three structures show that $[UCl_3]^+$ is not a rigid cation, its conformation depends on the total U coordination: $[UCl_3]^+$ is planar in $[UCl_3(depa)_4]^+$ with Cl—U—Cl angles 177, 89 and 93° (heptacoordinated U) and in $[UCl_3(dcc)]^+$ with Cl—U—Cl angles 141, 141 and 77° (nonacoordinated U) while in $[UCl_3(dmf)_5]^+$ described here, the U atom is out of the Cl plane with Cl—U—Cl angles of 93, 92 and 149° (octacoordinated U).

The mean U—O distance [2·37 (5) Å] is in good agreement with those found for $2[UCl(dmf)_7]^{3+}$.-$3[UO_2Cl_4]^{2-}$ [2·35 (3) Å: Kepert, Patrick & White (1983)]. However, one dmf ligand seems to be differently attached judging from the U—O—C angle: the value of 144 (3)° for ligand 5, which occupies the apical position in the U coordination sphere, is slightly higher than the mean value of the others, 134 (3)°.

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Structure of Tetrathiafulvalenium Bis(5,6-dihydro-1,4-dithiin-2,3-dithiolato)aurate(III), (TTF)[Au(DDDT)$_2$]

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Abstract. $[C_6H_4S_4][Au(C_4H_4S_4)_2]$, $M_r = 761\cdot9$, triclinic, $P\bar{1}$, $a = 8\cdot7247$ (8), $b = 9\cdot5089$ (10), $c = 14\cdot7007$ (19) Å, $\alpha = 107\cdot179$ (10), $\beta = 102\cdot372$ (9), $\gamma = 95\cdot934$ (8)°, $V = 1119\cdot8$ (2) Å^3, $Z = 2$, $D_x = 2\cdot26$ Mg m^{-3}, μ(Mo $K\alpha$, $\lambda = 0\cdot71073$ Å) = 7·63 mm^{-1}, $F(000) = 734$, $T = 298$ K, $R(F) = 0\cdot082$ for 2306 observed reflections ($F_o > 2\sigma$). The structure contains two inequivalent, centrosymmetric $[Au(DDDT)_2]^-$ complexes. One of these is located in the same molecular layer as the dimerized TTF$^+$ cations, whereas the other lies between these layers. The dimerization of the TTF$^+$ cations and the molecular packing arrangement do not favor high electrical conductivity in the title compound.

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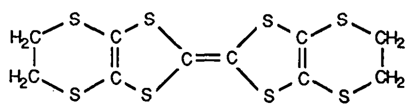
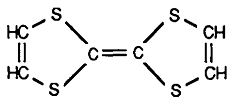
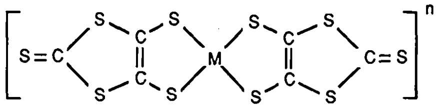
Introduction. The β-phase 2:1 salts of bis(ethylenedithio)tetrathiafulvalene, β-(BEDT-TTF)$_2X$, where $X^- = I_3^-$, IBr_2^-, and AuI_2^-, are ambient-pressure superconductors with critical temperatures, T_c, of 1·5, 2·8, and 5·0 K, respectively (for a review, see Williams, Beno, Wang, Leung, Emge, Geiser & Carlson, 1985). Under an applied pressure of 0·5 kbar (50 M Pa), β-(BEDT-TTF)$_2$I$_3$ transforms into the β^*-phase (Schultz, Wang, Williams & Filhol, 1986) with T_c = 7–8 K (Laukhin, Kostyuchenko, Sushko, Shchegolev & Yagubskii, 1985; Murata, Tokumoto, Anzai, Bando, Saito, Kajimura & Ishiguro, 1985; Creuzet, Creuzet, Jérome, Schweitzer & Keller, 1985; Schirber, Azevedo, Kwak, Venturini, Leung, Beno, Wang & Williams, 1986). All of these salts are built from layers of BEDT-TTF molecules which contain two-dimensional networks of S···S contacts, equal to or slightly less than the sum of the van der Waals radii, 3·60 Å (Bondi, 1964), which provide the conduction pathways for the electrons.



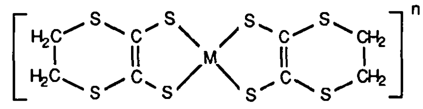
BEDT-TTF



TTF



[M(dmit)$_2$]^n



[M(DDDT)$_2$]^n

Transition-metal dithiolene complexes with S atoms in the periphery of the molecules have been investigated as possible analogues of BEDT-TTF. Superconductivity has been observed in the compound (TTF)[Ni(dmit)$_2$]$_2$ (dmit = 4,5-dimercapto-1,3-dithiole-2-dithione) at 1·62 K under a hydrostatic pressure of 7 kbar (0·7 GPa) (Brossard, Ribault, Bousseau, Valade & Cassoux, 1986). Recently, the compound (Et$_4$N)[Ni(DDDT)$_2$] (DDDT = 5,6-dihydro-1,4-dithiin-2,3-dithiolato) was synthesized and structurally characterized, but it does not contain any S···S contacts of less than 3·98 Å (Vance, Bereman, Bordner, Hatfield & Helms, 1985). In this paper we describe the synthesis and structure of (TTF)[Au(DDDT)$_2$] (TTF = tetrathiafulvalenium cation).

Experimental. Crystals of (TTF)[Au(DDDT)$_2$] prepared by slow diffusion of a 1·7 mM solution of (TTF)$_3$(BF$_4$)$_2$ (Wudl, 1975) in acetonitrile into a 3·2 mM solution of [N(C$_4$H$_9$)$_4$][Au(DDDT)$_2$] (Schultz, Wang, Soderholm, Sifter, Beno, Williams, Bechgaard & Whangbo, 1987) in acetonitrile. Small black plate-shaped needle, 0·28 × 0·02 × 0·06 mm. Nicolet $P3/F$ automated four-circle diffractometer. Unit-cell dimensions determined from a least-squares refinement of the setting angles of 24 reflections ($20° < 2\theta < 29°$). Intensity data collected using the $\theta/2\theta$-scan technique (2·5–2·8° width) with variable scan rates of 2 to 12° min^{-1} to $(\sin\theta)/\lambda = 0{\cdot}538$ Å^{-1} ($h = 0$ to 9, $k = -10$ to 10, $l = -15$ to 15). Three standard reflections, measured at an interval of 100 reflections, small (±3%) random variations. Data corrected for Lorentz and polarization factors, and absorption effects using a Gaussian integration procedure; $T_{\min} = 0{\cdot}586$, $T_{\max} = 0{\cdot}818$. 3278 reflections collected, averaged to 2942 unique reflections, $R_{\rm int}(F_o) = 0{\cdot}033$, $R_{\rm int}(wF_o) = 0{\cdot}015$. Centrosymmetric space group indicated by intensity statistics, confirmed by successful structure solution and least-squares refinement. Structure solved by Patterson method which provided positions for the Au and the coordinated S atoms. Structure completed by use of Fourier methods. Atomic scattering factors including anomalous-dispersion contributions from *International Tables for X-ray Crystallography* (1974). All computations carried out with a modified version of the *UCLA Crystallographic Program Package* (Strouse, 1978). All non-hydrogen atoms refined with anisotropic thermal parameters. 247 parameters varied. H atoms of TTF molecule included with fixed, idealized positions; not included for DDDT ligands, because of conformational disorder. $\sum w(|F_o|-|F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0{\cdot}02F_o^2)^2]^{1/2}/(2F_o)$, with the value of $\sigma(F_o^2)$ based on counting statistics. $\Delta/\sigma \le 0{\cdot}05$ in final least-squares cycle which resulted in the agreement factors $R(F_o) = 0{\cdot}082$, $wR(F_o) = 0{\cdot}080$, and $S = 3{\cdot}10$ for 2306 observed reflections ($F_o > 2\sigma$). $R(F_o) = 0{\cdot}134$ for all 2942 unique reflections. No evidence of secondary extinction. A difference Fourier synthesis based on the structure factors derived from the final parameter values produced random variations of ±0·1 e Å^{-3} with the largest peaks 3–3·5 e Å^{-3} in the vicinity of the Au atoms. The high agreement factors, and resulting high standard deviations in the refined parameters, are due

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters for* (TTF)$[\mathrm{Au(DDDT)}_2]$

The complete temperature factor is $\exp(-8\pi^2U_{\rm eq}\sin^2\theta/\lambda^2)$, where $U_{\rm eq} = \frac{1}{3}\sum_i\sum_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ in units of Å^2.

	x	y	z	$U_{\rm eq}$
Au1	0·0000	0·0000	0·0000	0·0268 (8)
Au2	0·5000	0·0000	0·5000	0·0393 (9)
S11	0·2462 (9)	0·0130 (9)	0·1010 (7)	0·040 (3)
S12	−0·0223 (9)	0·2270 (8)	0·1056 (6)	0·038 (3)
S13	0·4725 (10)	0·2411 (11)	0·2624 (8)	0·072 (4)
S14	0·1961 (11)	0·4633 (9)	0·2706 (7)	0·062 (4)
C11	0·280 (3)	0·189 (3)	0·184 (2)	0·035 (12)
C12	0·168 (3)	0·280 (3)	0·188 (2)	0·044 (13)
C13	0·482 (5)	0·398 (6)	0·355 (3)	0·14 (3)
C14	0·340 (4)	0·454 (4)	0·377 (2)	0·06 (2)
S21	0·7259 (11)	0·0624 (11)	0·6285 (7)	0·052 (4)
S22	0·6070 (11)	−0·1902 (10)	0·4110 (7)	0·057 (4)
S23	1·0099 (11)	−0·0601 (12)	0·6770 (7)	0·074 (5)
S24	0·8829 (11)	−0·3269 (10)	0·4441 (7)	0·067 (4)
C21	0·834 (4)	−0·081 (3)	0·584 (3)	0·054 (14)
C22	0·786 (3)	−0·180 (3)	0·498 (2)	0·040 (12)
C23	1·102 (5)	−0·208 (6)	0·636 (4)	0·13 (3)
C24	1·094 (4)	−0·246 (7)	0·530 (4)	0·16 (3)
S1	0·1818 (8)	0·4255 (9)	0·0013 (6)	0·045 (3)
S2	0·2618 (9)	0·4933 (9)	−0·1647 (6)	0·046 (3)
S3	0·4419 (9)	0·7079 (9)	0·1515 (6)	0·046 (3)
S4	0·5233 (9)	0·7805 (8)	−0·0136 (6)	0·043 (3)
C1	0·293 (3)	0·535 (3)	−0·045 (2)	0·041 (12)
C2	0·410 (3)	0·666 (3)	0·030 (2)	0·050 (14)
C3	0·076 (3)	0·320 (3)	−0·114 (3)	0·06 (2)
C4	0·108 (3)	0·341 (3)	−0·194 (2)	0·044 (13)
C5	0·583 (4)	0·870 (3)	0·181 (3)	0·055 (15)
C6	0·622 (3)	0·895 (3)	0·102 (2)	0·035 (12)

Table 2. *Interatomic distances* (Å) *and angles* (°); *estimated standard deviations are in parentheses*

$[\mathrm{Au(DDDT)}_2]^-$, complex 1			
Au1–S11	2·303 (8)	Au1–S12	2·311 (7)
S11–C11	1·71 (3)	S12–C12	1·76 (3)
S13–C11	1·75 (3)	S13–C13	1·68 (4)
S14–C12	1·76 (3)	S14–C14	1·81 (3)
C11–C12	1·37 (4)	C13–C14	1·45 (5)
S11–Au1–S12	89·8 (3)	Au1–S11–C11	102·5 (9)
Au1–S12–C12	101 (1)	C11–S13–C13	109 (2)
C12–S14–C14	102 (1)	S11–C11–C12	123 (2)
S13–C11–C12	124 (2)	S11–C11–S13	113 (1)
S12–C12–C11	123 (2)	S14–C12–C11	126 (2)
S12–C12–S14	112 (2)	S13–C13–C14	122 (3)
S14–C14–C13	114 (3)		
$[\mathrm{Au(DDDT)}_2]$, complex 2			
Au2–S21	2·304 (9)	Au2–S22	2·308 (9)
S21–C21	1·78 (3)	S22–C22	1·77 (3)
S23–C21	1·77 (3)	S23–C23	1·71 (4)
S24–C22	1·78 (3)	S24–C24	1·93 (4)
C21–C22	1·29 (4)	C23–C24	1·48 (6)
S21–Au2–S22	89·8 (3)	Au2–S21–C21	101 (1)
Au–S22–C22	101 (1)	C21–S23–C23	108 (2)
C22–S24–C24	98 (2)	S21–C21–C22	123 (3)
S23–C21–C22	128 (2)	S21–C21–S23	109 (2)
S22–C22–C21	124 (2)	S24–C22–C21	128 (2)
S22–C22–S24	108 (2)	S23–C23–C24	112 (3)
S24–C24–C23	114 (3)		
Tetrathiafulvalenium ion			
S1–C1	1·73 (3)	S1–C3	1·69 (4)
S2–C1	1·63 (3)	S2–C4	1·75 (3)
S3–C2	1·66 (3)	S3–C5	1·75 (3)
S4–C2	1·74 (3)	S4–C6	1·70 (3)
C1–C2	1·51 (4)	C3–C4	1·33 (4)
C5–C6	1·36 (4)		
C1–S1–C3	91 (2)	C1–S2–C4	95 (2)
C2–S3–C5	95 (2)	C2–S4–C6	93 (2)
S1–C1–C2	115 (2)	S2–C1–C2	125 (2)
S1–C1–S2	119 (2)	S3–C2–C1	125 (2)
S4–C2–C1	117 (2)	S3–C2–S4	118 (2)
S1–C3–C4	122 (3)	S2–C4–C3	112 (2)
S3–C5–C6	114 (2)	S4 C6 C5	119 (2)
Intermolecular S···S distances less than 3·60 Å			
S11–S4$^{\rm i}$	3·366 (12)	S12–S1	3·358 (11)
S12–S2$^{\rm i}$	3·572 (10)	S22–S3$^{\rm ii}$	3·569 (13)
S1–S4$^{\rm i}$	3·398 (10)	S2–S3$^{\rm i}$	3·377 (10)

Symmetry code: (i) $1-x$, $1-y$, $-z$; (ii) x, $1+y$, z.

to unfavorable counting statistics because of the extremely small sample volume and the ethylene-group disorder. Low $R_{\rm int}$ values reflect the fact that a large number of duplicates were of high intensity (standard reflections).

Discussion. Final positional and thermal parameters are presented in Table 1.* Bond lengths and angles, as well as short intermolecular contact distances, are given in Table 2. The unit cell contains two independent, centrosymmetric $[\mathrm{Au(DDDT)}_2]^-$ complexes, and a pair of tetrathiafulvalenium cations. The constituent molecules and the atomic labeling scheme are shown in Fig. 1.

Except for the terminal ethylene groups which exhibit considerable conformational disorder, the Au complexes are essentially planar, and no significant differences in chemically equivalent bond lengths or angles are observed. The Au—S distances are equal within the accuracy of the structure determination, at an average of 2·306 (9) Å, to those in the neutral $\mathrm{Au(DDDT)}_2$ complex (Schultz, Wang, Soderholm, Sifter, Beno, Williams, Bechgaard & Whangbo, 1987), and are slightly longer than in the smaller mono-anionic complex $[\mathrm{Au\{S_2C_2(CF_3)_2\}_2}]^-$, where they are 2·289 (8) Å (Enemark & Ibers, 1968). Another mono-anionic gold dithiolato complex, $[\mathrm{Au\{S_2C_2(CN)_2\}_2}]^-$, has Au—S distances between 2·31 and 2·33 Å (Kuppusamy, Venkatalakshmi & Manoharan, 1985). The bond lengths and angles of the tetrathiafulvalenium ion are in their usual ranges. The large standard deviations preclude a detailed analysis of charge *vs* bond-length correlations. Ethylene end-group disorder, such as observed here in the $[\mathrm{Au(DDDT)}_2]^-$ complexes, is

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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 44440 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

extremely common in BEDT-TTF and related compounds (for examples, see Schultz, Emge, Leung, Beno, Wang & Williams, 1986; Geiser, Wang, Hammond, Firestone, Beno, Carlson, Nuñez & Williams, 1987). In the case of β-(BEDT-TTF)$_2$I$_3$, the ethylene-group disorder is responsible for unusual superconducting properties (Schultz, Wang, Williams & Filhol, 1986).

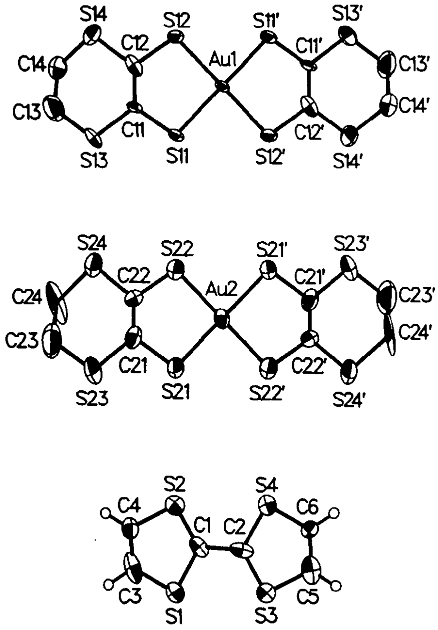

Fig. 1. The constituent molecules and atomic labeling scheme of (TTF)[Au(DDDT)$_2$]. Atoms related by a center of inversion are labeled with a prime. Thermal ellipsoids are drawn at the 50% probability level.

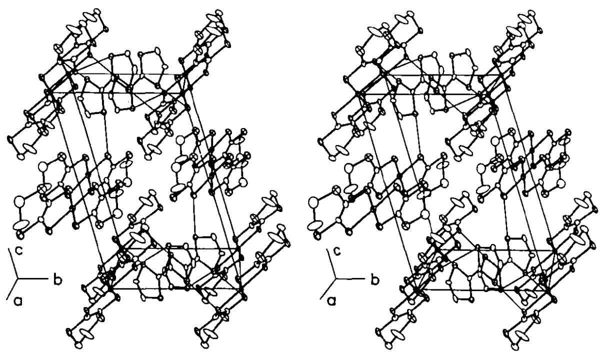

Fig. 2. Stereoview of a unit cell of (TTF)[Au(DDDT)$_2$] as viewed approximately along the a axis. Intermolecular S$\cdots$S distances less than 3·60 Å are indicated with thin lines.

The crystal structure (Fig. 2) contains two independent uniform stacks of very weakly interacting [Au(DDDT)$_2$]$^-$ complexes. The stacks near $z = 0$ are packed in a somewhat more space-filling fashion and allow the interspersion of dimerized TTF$^+$ cations within the ab plane. All intermolecular contacts (S$\cdots$S less than 3·6 Å, the van der Waals radii sum; Bondi, 1964) involve S atoms on the tetrathiafulvalenium unit. The molecular packing arrangement is not particularly favorable for the formation of extended delocalized electronic states for the unpaired electrons of the TTF$^+$ radical cations, and resulting electrical conductivity. Rather, the pronounced face-to-face dimerization of the cations is expected to lead to localized pair states, and insulating behavior.

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