Structure of Trimethyltelluronium Bis(4,5-dimercapto-1,3-dithiole-2-thionato)aurate(III)

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Abstract. $[Te(CH_3)_3][Au(C_6S_{10})]$, $M_r = 762.38$, triclinic, $P\bar{1}$, $a = 9.878$ (1), $b = 12.326$ (1), $c = 16.512$ (3) Å, $\alpha = 102.37$ (1), $\beta = 91.05$ (2), $\gamma = 94.22$ (1)°, $V = 1957.2$ Å^3, $Z = 4$, D_m(flotation) = 2.591, $D_x = 2.587$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 99.86$ cm^{-1}, $F(000) = 1416$, $T = 295$ K, $R = 0.061$, $wR = 0.075$ for 6401 unique reflections. The two independent anions in the asymmetric unit are planar and the planes are nearly parallel to each other. The anions and cations are involved in short intermolecular Au⋯S, S⋯S and Te⋯S contacts.

Introduction. Planar metal complexes with the 4,5-dimercapto-1,3-dithiole-2-thionate ligand (dmit) have recently attracted much attention due to their metallic and superconducting properties (Cassoux, Valade, Kobayashi, Kobayashi, Clark & Underhill, 1991; Shklover, Nagapetyan, & Struchkov, 1990). The structure and properties of a series of gold(III) complexes of the type $[cat^+][Au(dmit)_2]$, where $[cat^+]$ can be a closed shell cation like $(CH_3)_4N^+$, $(CH_3)_3S^+$, *etc.* (Kotov, Kushch, Laukhina, Khomenko, Zvarykina, Shibaeva, Yagubskii, Nagapetyan & Struchkov, 1991), have been published. The salt, $[Au(dmit)_2][(CH_3)_3S]$, whose crystal structure has been determined (Nagapetyan, Arakelova, Belousova, Struchkov, Ukhin & Shklover, 1988), is an insulator and on oxidation in the presence of iodine gives a highly conducting polycrystalline material with $\sigma_{300} \simeq 30$ Ω^{-1}cm^{-1}. Since tellurium has more spatially extended and diffused orbitals than sulfur and selenium, it is expected that the incorporation of tellurium in these complexes may give rise to new and stronger intermolecular interactions. This should lead to an increase in dimensionality. It has been suggested that increasing dimensionality can suppress the Peierl's instability and preserve the metallic state down to low temperature (Wudl, 1981). The crystal structure

of the title compound, which is also an insulator, is the first salt of a metal-dmit complex with a tellurium-containing cation.

Experimental. Potassium tetrachloroaurate(III) and a methanolic solution of trimethyltelluronium chloride were added to 4,5-dimercapto-1,3-dithiole-2-thione disodium salt. The resulting black precipitate was filtered, washed with methanol and dried *in vacuo*. Black needle-shaped crystals were obtained by slow evaporation of an acetonitrile solution of the complex. A crystal of dimensions $0.15 \times 0.3 \times 0.4$ mm was chosen for data collection on an Enraf–Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation, ω–2θ scan. Unit-cell parameters were determined by the least-squares method using 25 accurately centered reflections in the range $6 < \theta < 16°$. Intensities of three standard reflections collected every hour showed no intensity decay over the course of data collection. 9383 reflections were measured in the range $-12 \leq h \leq 12$, $-15 \leq k \leq 0$, $-21 \leq l \leq 21$ ($d_{max} = 0.76$ Å, $2\theta_{max} = 55.75°$) of which 8967 reflections are unique. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction using nine reflections with 37 observations for each reflection varying φ (minimum and maximum transmission factors 0.853 and 0.999) was applied ($R_{int} = 0.030$). The structure was solved by Patterson methods followed by weighted Fourier syntheses and was refined by the full-matrix least-squares method based on F values to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F)$, using anisotropic thermal parameters for non-H atoms. H atoms located from difference Fourier maps were included as constant contributions to the structure factors and were not refined. In the final refinement, 6401 reflections with $F^2 > 3.0\sigma(F^2)$ were used for 380 parameters. $(\Delta/\sigma)_{max} = 0.33$ for the scale factor, $(\Delta\rho)_{max} = 3.3$ e Å^{-3} at 0.905 Å from Au(1) and $(\Delta\rho)_{min} = -0.6$ e Å^{-3}, $R = 0.061$, $wR = 0.075$. *SDP*

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Table 1. Final atomic coordinates ($\times 10^4$, for starred atoms $\times 10^5$) and equivalent isotropic temperature factors (Å^2) of non-H atoms with e.s.d.'s in parentheses

$$B_{eq} = 4/3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha).$$

	x	y	z	B_{eq}
Au(1)*	7962 (6)	24612 (4)	14622 (3)	2.23 (1)
S(11)	−516 (4)	1463 (3)	323 (2)	2.80 (7)
S(21)	−2633 (5)	2269 (3)	−711 (3)	3.53 (8)
S(31)	−4179 (6)	3987 (4)	−1265 (3)	5.20 (10)
S(41)	−2208 (5)	4549 (3)	169 (3)	3.60 (8)
S(51)	−72 (4)	4114 (3)	1341 (3)	3.32 (8)
S(61)	1711 (4)	818 (3)	1567 (3)	3.34 (8)
S(71)	3843 (4)	423 (3)	2761 (2)	2.79 (7)
S(81)	5769 (5)	996 (3)	4212 (3)	3.89 (9)
S(91)	4164 (4)	2690 (3)	3661 (2)	2.90 (8)
S(101)	2101 (5)	3458 (3)	2598 (3)	3.73 (9)
C(11)	−1430 (20)	2540 (10)	113 (8)	2.5 (3)
C(21)	−3070 (20)	3600 (10)	−670 (10)	3.9 (3)
C(31)	−1210 (10)	3630 (10)	518 (8)	2.4 (3)
C(41)	2830 (20)	1320 (10)	2402 (9)	2.5 (3)
C(51)	4660 (20)	1370 (10)	3604 (8)	2.8 (3)
C(61)	2980 (20)	2390 (10)	2820 (10)	2.8 (3)
Te(1)*	22350 (10)	71859 (7)	41442 (7)	2.87 (2)
C(71)	1200 (20)	6210 (10)	3060 (10)	4.3 (4)
C(81)	3510 (20)	5930 (10)	4320 (10)	4.6 (4)
C(91)	3650 (20)	7970 (10)	3470 (10)	3.8 (3)
Au(2)*	22754 (5)	42695 (4)	61551 (3)	1.777 (9)
S(12)	835 (4)	3815 (3)	4986 (2)	2.44 (6)
S(22)	69 (4)	1572 (3)	3848 (2)	2.49 (7)
S(32)	220 (5)	−873 (3)	3249 (3)	3.59 (9)
S(42)	1839 (4)	414 (3)	4708 (3)	2.74 (7)
S(52)	2854 (4)	2453 (3)	5964 (3)	3.12 (7)
S(62)	1714 (4)	6096 (3)	6349 (2)	2.89 (7)
S(72)	2623 (4)	8082 (3)	7674 (2)	2.66 (7)
S(82)	4199 (5)	9328 (3)	9165 (3)	3.45 (8)
S(92)	4396 (4)	6904 (3)	8513 (2)	2.58 (7)
S(102)	3691 (4)	4695 (3)	7333 (2)	2.95 (7)
C(12)	1000 (10)	2383 (9)	4715 (8)	1.9 (2)
C(22)	680 (10)	310 (10)	3894 (9)	2.3 (3)
C(32)	1830 (10)	1830 (10)	5100 (8)	2.1 (3)
C(42)	2690 (10)	6670 (10)	7232 (8)	1.8 (2)
C(52)	3770 (10)	8150 (10)	8516 (9)	2.3 (3)
C(62)	3500 (10)	6110 (10)	7638 (8)	2.1 (3)
Te(2)*	19340 (10)	12406 (7)	87547 (6)	2.67 (2)
C(72)	1040 (20)	2710 (10)	8570 (10)	4.4 (4)
C(82)	3320 (20)	1260 (10)	7810 (10)	4.3 (4)
C(92)	3260 (20)	2120 (10)	9710 (10)	3.6 (4)

Table 2. Bond lengths (Å) and angles (°) for the two molecules of the title compound designated by n

	$n = 1$	$n = 2$		$n = 1$	$n = 2$
Au(n)—S(1n)	2.327 (4)	2.320 (4)	S(7n)—C(4n)	1.731 (16)	1.744 (13)
Au(n)—S(5n)	2.313 (4)	2.309 (4)	S(7n)—C(5n)	1.754 (15)	1.761 (14)
Au(n)—S(6n)	2.316 (4)	2.315 (4)	S(8n)—C(5n)	1.629 (17)	1.632 (14)
Au(n)—S(10n)	2.319 (5)	2.317 (4)	S(9n)—C(5n)	1.717 (14)	1.696 (13)
S(1n)—C(1n)	1.749 (16)	1.746 (12)	S(9n)—C(6n)	1.758 (18)	1.746 (13)
S(2n)—C(1n)	1.750 (17)	1.760 (13)	S(10n)—C(6n)	1.728 (16)	1.734 (13)
S(2n)—C(2n)	1.715 (14)	1.725 (13)	C(1n)—C(3n)	1.366 (18)	1.338 (16)
S(3n)—C(2n)	1.622 (18)	1.639 (14)	C(4n)—C(6n)	1.347 (19)	1.351 (17)
S(4n)—C(2n)	1.769 (17)	1.727 (14)	Te(n)—C(7n)	2.128 (16)	2.148 (15)
S(4n)—C(3n)	1.735 (13)	1.727 (13)	Te(n)—C(8n)	2.129 (16)	2.097 (18)
S(5n)—C(3n)	1.722 (13)	1.735 (13)	Te(n)—C(9n)	2.109 (17)	2.088 (17)
S(6n)—C(4n)	1.727 (17)	1.721 (13)			

|	$n = 1$	$n = 2$
S(1n)—Au(n)—S(5n)	91.8 (1)	91.2 (1)
S(6n)—Au(n)—S(10n)	91.7 (2)	91.5 (1)
Au(n)—S(1n)—C(1n)	99.0 (5)	99.3 (4)
C(1n)—S(2n)—C(2n)	99.2 (8)	97.3 (6)
C(2n)—S(4n)—C(3n)	98.6 (7)	97.8 (6)
Au(n)—S(5n)—C(3n)	100.0 (4)	100.5 (4)
Au(n)—S(6n)—C(4n)	99.4 (6)	99.4 (4)
C(4n)—S(7n)—C(5n)	98.9 (8)	97.4 (6)
C(5n)—S(9n)—C(6n)	98.5 (8)	98.7 (6)
Au(n)—S(10n)—C(6n)	99.0 (6)	99.6 (4)
S(1n)—C(1n)—C(3n)	124.3 (11)	125.2 (9)
S(2n)—C(1n)—C(3n)	115.6 (11)	115.4 (9)
S(2n)—C(2n)—S(3n)	126.9 (10)	124.6 (8)
S(2n)—C(2n)—S(4n)	111.0 (9)	112.7 (7)
S(4n)—C(3n)—C(1n)	115.5 (10)	116.9 (9)
S(5n)—C(3n)—C(1n)	124.7 (10)	123.7 (9)
S(6n)—C(4n)—C(6n)	124.5 (13)	125.4 (10)
S(7n)—C(4n)—C(6n)	115.5 (12)	115.7 (9)
S(7n)—C(5n)—S(8n)	122.2 (9)	121.1 (8)
S(7n)—C(5n)—S(9n)	111.1 (9)	112.2 (7)
S(9n)—C(6n)—C(4n)	115.9 (13)	115.9 (9)
S(10n)—C(6n)—C(4n)	125.3 (13)	124.0 (9)
C(7n)—Te(n)—C(8n)	95.3 (6)	93.6 (6)
C(7n)—Te(n)—C(9n)	93.8 (6)	93.7 (6)
C(8n)—Te(n)—C(9n)	95.1 (6)	95.3 (6)

(a)

(b)
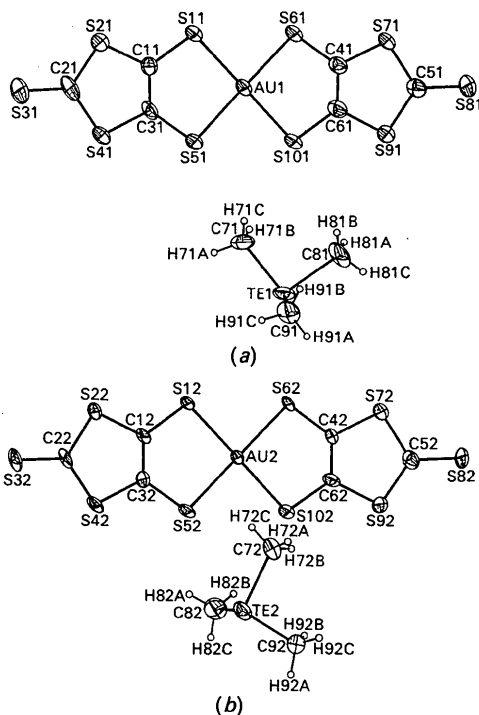
Fig. 1. The two molecules (a) and (b) (with 50% probability ellipsoids) in the asymmetric unit.

software (Enraf-Nonius, 1981) on a VAX 11/750 computer was used for all calculations, *ORTEP* and *PLUTO* drawings and the source of atomic scattering factors.

Discussion. The atomic coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table 1* and important bond lengths and bond angles are given in Table 2. Fig. 1 depicts the *ORTEP* drawings of the two symmetry-independent anions and cations. Figs. 2 and 3 are the *PLUTO* drawings of the unit-cell packing projected on the *bc* and *ac* planes, respectively.

The title compound is isomorphous with [Au(dmit)$_2$][(CH$_3$)$_3$S] (Nagapetyan *et al.*, 1988). Both Au atoms exhibit square-planar coordination. The anions [*A*1, containing atoms Au(1), S(11) *etc.* and *A*2, containing atoms Au(2), S(12) *etc.*] are planar with the maximum deviation of an atom from its own plane being 0.139 (5) Å. The planes of *A*1 and *A*2 are almost parallel to one another with a dihedral angle of 3.0 (10)°. The Au—S distances are in the range 2.309 (4)–2.327 (4) Å, which are comparable to similar structures (Shklover *et al.*, 1990; Kotov *et al.*, 1991). The maximum deviation of the S—Au—S angles from the ideal 90° value is 1.8 (1)°. The S—C,
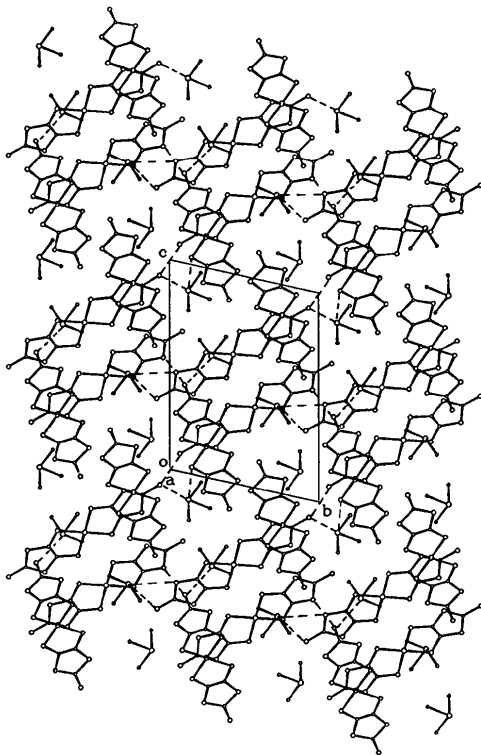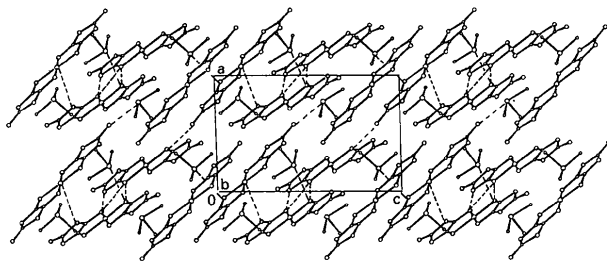
Table 3. *Important intermolecular distances* (Å) *with e.s.d.'s in parentheses*

Au(1)···S(72)^i	3.761 (4)	S(12)···S(62)^i	3.339 (5)
S(81)···Te(1)^{ii}	3.581 (5)	S(22)···S(62)^i	3.549 (5)
S(81)···S(42)^{iii}	3.683 (6)	S(32)···Te(2)^v	3.826 (5)
Te(1)···S(12)^i	3.626 (4)	S(82)···S(82)^{vi}	3.217 (7)
Te(1)···S(32)^{iv}	3.739 (4)	S(82)···Te(2)^{iv}	3.525 (5)
Te(1)···S(42)^{iv}	3.938 (4)	S(102)···S(31)^{vii}	3.392 (6)
S(12)···S(12)^i	3.451 (5)	Te(2)···S(11)^{vii}	3.558 (4)

Symmetry code: (i) $-x$, $1-y$, $1-z$; (ii) $1-x$, $1-y$, $1-z$; (iii) $1-x$, $-y$, $1-z$; (iv) x, $1+y$, z; (v) $-x$, $-y$, $1-z$; (vi) $1-x$, $2-y$, $2-z$; (vii) $1+x$, y, $1+z$; (viii) x, y, $1+z$.

S=C, C=C bond lengths and bond angles are nearly equal to the corresponding values reported for the isomorphous structure. The cation has a tetrahedral geometry with Te—C distances in the range 2.088 (17)–2.148 (15) Å. The C—Te—C angles lie between 93.6 (6) and 95.3 (6)°. In a reported trimethyltellurium cation structure (Einstein, Trotter & Williston, 1967) the Te—C bond lengths are 2.01, 2.08 and 2.13 Å while the C—Te—C angles are 91, 95 and 97°. Table 3 gives some important intermolecular distances.

Molecular interactions through S···S contacts form effective intermolecular orbital overlap establishing electrical conduction pathways. Intermolecular S···S distances less than 3.70 Å (twice the Pauling value for the van der Waals radius of the S atom) are important for the conductivity of sulfur-containing compounds with planar molecules. The shortest distance is S(82)···S(82) with a value of 3.217 (7) Å. The intermediate distances are S(12)···S(62) 3.339 (5), S(102)···S(31) 3.392 (6), S(12)···S(12) 3.451 (5) and S(22)···S(62) 3.549 (5) Å, while the longest distance is S(81)···S(42) 3.683 (6) Å. The shortest S···S distance is longer than its counterpart found in the isomorphous structure. The Au(1)···S(72) distance is 3.761 (4) Å while the Au(2)···S distance is greater than 4.0 Å. The cations play an important role in determining the packing within [*M*(dmit)$_2$], where *M* is a metal, and hence the physical properties of the salt. The anion–cation interactions are also important for the conductivity of the crystal. In the isomorphous structure, the anion–cation interactions are established through the S$_{cat}$···S distances, 3.654 (4) and 3.688 (4) Å. However, in the present study tellurium is involved in more Te···S-type interactions. The Te···S distances are in the range 3.525 (5)–3.938 (4) Å. The packing of anions and cations within various dmit compounds (Shklover *et al.*, 1990) and superconductors with high transition temperatures (*T$_c$*) (Saito & Kagoshima, 1990) has been reviewed. In some of the dmit structures the anions are arranged in a stack. In the isomorphous structure the two symmetry-independent anions and three atoms of each cation lie in the same plane within 0.1 Å and form a two-dimensional layer struc-

Fig. 2. Unit-cell packing projected on the *bc* plane (dashed lines show the intermolecular contacts).

Fig. 3. Unit-cell packing projected on the *ac* plane (dashed lines show the intermolecular contacts).

ture corresponding to the (21$\bar{3}$) plane with an inter-planar spacing of 3.59 Å and within the layer the cations form rows along the [2$\bar{1}$1] direction. Even in the present study, the anions are arranged in two-dimensional layers and three atoms of the tetrahedral cations [Te(1), C(71) and C(81) for cation K1 and Te(2), C(72) and C(92) translated along the b axis for cation K2]·lie in the anion layer plane. In fact, the layers correspond to a (21$\bar{3}$) plane with an interlayer distance of 3.623 Å and within the anion plane the cations are arranged in rows along the [2$\bar{1}$1] directions.

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Structure of a Platinum(II) Complex of Levamisole

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Abstract. Chloro(ethylenediamine){(−)-2,3,5,6-tetra-hydro-6-phenylimidazo[2,1-b]thiazole}platinum(II) chloride, [PtCl(C₂H₈N₂)(C₁₁H₁₂N₂S)]Cl, M_r = 530.39, orthorhombic, $P2_12_12_1$, a = 31.676 (11), b = 8.190 (2), c = 6.6242 (6) Å, V = 1718.5 (7) Å³, Z = 4, D_x = 2.050 g cm⁻³, λ(Mo $K\alpha$) = 0.71069 Å, μ = 86.8 cm⁻¹, F(000) = 1016, T = 296 K, final R = 0.030 for 1646 unique observed reflections [$F > 4\sigma(F)$]. The Pt coordination is square planar, bonded to three N atoms (one from the levamisole and two from the ethylenediamine moiety) and to one Cl atom.

Introduction. The antitumor activity of platinum(II) triamine complexes has been reported recently (Hollis, Amundsen & Stern, 1989) and implies that the criteria established for the design of platinum-containing cancer drugs be re-evaluated to include an investigation of this class of compounds so as to provide additional structure–activity relationships. This and the promising leads afforded by Pt imidazole and thiazole compounds (van Kralingen, de Ridder & Reedijk, 1979; Graves, Hodgson, van Kralingen & Reedijk, 1978; Hacker, Douple & Krafkoff, 1984; van Beusichem & Farrel, 1992) prompted us to a study of Pt triamine species coordinated to a series of imidazo[2,1-b]thiazoles which themselves possess relevant biological activity (Bhargava, Lee, Huang, Cunningham, Agrawal & Sartorelli, 1977; Preston, 1986). We describe the structure of one such complex here.

Experimental. To 2.18 g (6.7 mmol) PtCl₂(C₂H₈N₂) in 15 ml of dimethylformamide (DMF) was added 1.19 g (7 mmol) AgNO₃. The mixture was stirred in the dark for 12 h and then filtered. To the filtrate was added 1.63 g (8 mmol) of (−)-2,3,5,6-tetrahydro-6-phenylimidazo[2,1-b]thiazole in 10 ml DMF. After