

Fig. 1. Cation structure and labeling scheme for $[\text{CrCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$. Symmetry-generated species derived by the transformation $x, 1.5-y, z$.

1986).^{*} Atomic parameters are given in Table 1, bond distances and angles in Table 2. The cation structure is in Fig. 1 and the unit-cell packing is shown in Fig. 2.

Related literature. Methods for the synthesis of the title complex and closely related complexes have been systematically characterized (Kyuno, Kamada & Tanaka, 1967). Solvent interchange (Jackson, Vowles & Fee, 1977) and luminescence (Forster, Rund & Fucaloro, 1984) have been studied. Two reviews are relevant; one on the aqueous chemistry of Cr^{III} complexes (Earley & Cannon, 1965) and the other devoted to ammine complexes of Cr^{III} (Garner & House, 1970). Very few simple Cr^{III} coordination complexes have been crystallographically charac-

^{*} Lists of anisotropic thermal parameters, observed and calculated structure factors and bond distances and angles involving H have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43649 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Low-Temperature Structure of 3,4;3',4'-Bis(ethylenedithio)-2,2',5,5'-tetrathiafulvalene Diiodaurate(I) (2:1), β -(BEDT-TTF)₂AuI₂

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Abstract. $[\text{C}_{10}\text{H}_8\text{S}_8]_2[\text{AuI}_2]$, $M_r = 1220.1$, triclinic, $P\bar{1}$, $a = 6.570$ (1), $b = 8.891$ (1), $c = 15.299$ (3) Å, $\alpha =$

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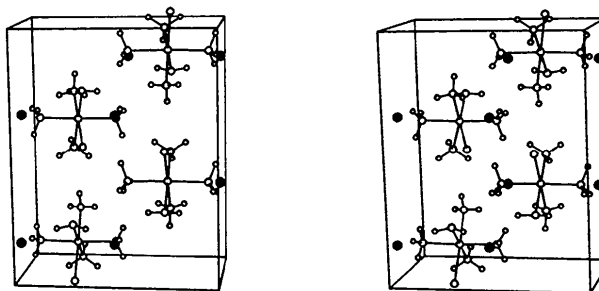


Fig. 2. Unit-cell packing diagram for $[\text{CrCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$. Chloride ions are shown as solid circles.

terized; for $[\text{CrCl}_2(\text{H}_2\text{O})]\text{Cl} \cdot 2\text{H}_2\text{O}$ (Morosin, 1966) a Cr–Cl distance of 2.286 Å and Cr–O distances of 2.002 and 2.013 Å are quoted without e.s.d.'s. $\text{H}_2\text{O} \cdots \text{Cl}(\text{free})$ non-bonded distances of 3.061, 3.112 and 3.197 Å are very similar to those we report.

The crystals were the gift of Dr John V. Rund, University of Arizona.

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consists of layers of partially oxidized BEDT-TTF ($C_{10}H_8S_8$) molecules separated by isolated linear AuI_2^- anions. The donor-radical cations form a two-dimensional network *via* short ($<3.60 \text{ \AA}$) intermolecular $S \cdots S$ contacts, which are substantially reduced from their room-temperature values.

Experimental. Crystals prepared by electrocrystallization of BEDT-TTF and $[n-(C_4H_9)_4N][AuI_2]$ in tetrahydrofuran. Black crystals, size used in diffraction study $0.38 \times 0.28 \times 0.08 \text{ mm}$. Syntex $P2_1$ automated four-circle diffractometer. Unit-cell dimensions determined from a least-squares refinement of the setting angles of 25 reflections ($20 < 2\theta < 29^\circ$). Intensity data collected using the $\theta/2\theta$ -scan technique ($2.0\text{--}2.4^\circ$ width in 2θ) with variable scan rates of 2 to $12^\circ \text{ min}^{-1}$ to $\sin\theta/\lambda = 0.704 \text{ \AA}^{-1}$ ($h = 0$ to 7, $k = -10$ to 9, $l = -18$ to 17). Nitrogen gas-flow cooling system ($T = 120 \text{ K}$). Three standard reflections, measured at an interval of 110 reflections, small (2–3%) random variations. Data corrected for Lorentz and polarization factors, and absorption effects using a Gaussian integration procedure; $T_{\min} = 0.138$, $T_{\max} = 0.577$. 3276 reflections collected, averaged to 2892 unique and allowed reflections, $R_{\text{int}}(F_o) = 0.008$, $wR_{\text{int}}(F_o) = 0.011$. Centrosymmetric space group indicated by intensity statistics, confirmed by successful structure solution and least-squares refinement. Approximate coordinates from room-temperature structure (supplementary material in Wang *et al.*, 1985). H atoms located on difference map. Atomic scattering factors including anomalous 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; H-atom thermal parameters fixed with $U_{\text{iso}} = 0.032 \text{ \AA}^2$; 202 varied parameters. $\sum w(|F_o| - |F_c|)^2$ minimized, where $w = 1/\sigma^2(F_o)$ and $\sigma(F_o) = [\sigma^2(F_o^2) + (0.02F_o^2)^2]^{1/2}/(2F_o)$, with the value of $\sigma(F_o^2)$ based on counting statistics. $\Delta/\sigma \leq 0.03$ for non-hydrogen parameters (≤ 0.14 for H-atom coordinates) in final least-squares cycle which resulted in the agreement factors $R(F_o) = 0.023$, $wR(F_o) = 0.029$ and $S = 2.06$, using all unique reflections. No extinction correction applied. Difference Fourier synthesis based on the structure factors derived from the final parameter values produced random variations of $\pm 0.3 \text{ e \AA}^{-3}$ with the largest peaks ($1.0\text{--}1.8 \text{ e \AA}^{-3}$) near the gold and iodine atoms.

Final coordinates* of the non-hydrogen atomic coordinates are given in Table 1, and Table 2 contains bond lengths and angles based on the labelling scheme shown in Fig. 1.

*Lists of structure factors, anisotropic thermal parameters and H-atom positions have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43644 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters

The complete temperature factor is $\exp[-8\pi^2 U_{\text{eq}}(\sin^2\theta)/\lambda^2]$, where $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ in units of \AA^2 .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} (\times 10^4)$
Au	0.00000	0.00000	0.00000	225 (1)
I	0.34137 (4)	0.23388 (3)	-0.02493 (2)	270 (1)
S1	0.46268 (14)	-0.26096 (10)	0.44936 (6)	175 (3)
S2	0.09201 (15)	-0.14812 (10)	0.42990 (6)	192 (3)
S3	0.28688 (14)	-0.42381 (10)	0.62186 (6)	165 (3)
S4	-0.08297 (15)	-0.30891 (11)	0.59855 (6)	186 (3)
S5	0.63473 (15)	-0.14590 (11)	0.28831 (6)	209 (3)
S6	0.19673 (16)	-0.00197 (12)	0.26814 (7)	252 (3)
S7	0.20490 (16)	-0.52836 (11)	0.79691 (6)	238 (3)
S8	-0.23926 (15)	-0.39093 (11)	0.76667 (6)	213 (3)
C1	0.2263 (6)	-0.2539 (4)	0.4884 (3)	151 (11)
C2	0.1512 (6)	-0.3233 (4)	0.5597 (2)	148 (11)
C3	0.4341 (6)	-0.1639 (4)	0.3575 (2)	156 (11)
C4	0.2640 (6)	-0.1108 (4)	0.3481 (3)	162 (11)
C5	0.1225 (6)	-0.4450 (4)	0.7071 (3)	141 (11)
C6	-0.0475 (6)	-0.3921 (4)	0.6955 (3)	136 (11)
C7	0.6189 (6)	0.0253 (4)	0.2366 (3)	202 (12)
C8	0.3900 (7)	-0.0009 (5)	0.1915 (3)	213 (13)
C9	0.0622 (7)	-0.4641 (5)	0.8795 (3)	251 (14)
C10	-0.1812 (7)	-0.5109 (5)	0.8479 (3)	222 (13)

Table 2. Interatomic distances (\AA) and angles ($^\circ$) with *e.s.d.*'s in parentheses

Au—I	2.5599 (5)	C4—S6	1.748 (4)
C1—C2	1.362 (5)	C5—C6	1.358 (5)
C3—S1	1.749 (4)	C7—S5	1.814 (4)
C4—S2	1.754 (4)	C9—S7	1.813 (4)
C5—S7	1.749 (4)	C1—S2	1.746 (4)
C6—S8	1.754 (4)	C2—S4	1.748 (4)
C8—S6	1.817 (4)	C3—C4	1.358 (5)
C10—S8	1.812 (4)	C5—S3	1.765 (4)
C1—S1	1.742 (4)	C6—S4	1.752 (4)
C2—S3	1.746 (4)	C7—C8	1.512 (5)
C3—S5	1.753 (4)	C9—C10	1.512 (6)
S1—C1—S2	115.0 (2)	S3—C5—S7	115.1 (2)
C1—S1—C3	95.3 (2)	S4—C6—S8	113.8 (2)
C1—C2—S3	122.9 (3)	C3—S5—C7	99.4 (2)
C2—S4—C6	95.1 (2)	C6—S8—C10	101.4 (2)
C4—C3—S5	127.7 (3)	S7—C9—C10	113.4 (3)
C3—C4—S6	129.2 (3)	C2—C1—S2	121.8 (3)
C6—C5—S7	128.6 (3)	S3—C2—S4	115.3 (2)
C5—C6—S8	128.6 (3)	C2—S3—C5	95.3 (2)
C5—S7—C9	99.6 (2)	C4—C3—S1	117.5 (3)
S6—C8—C7	114.0 (3)	C3—C4—S2	116.2 (3)
C2—C1—S1	123.1 (3)	C6—C5—S3	116.3 (3)
C1—S2—C4	95.7 (2)	C5—C6—S4	117.6 (3)
C1—C2—S4	121.7 (3)	C4—S6—C8	102.4 (2)
S1—C3—S5	114.7 (2)	S5—C7—C8	113.6 (3)
S2—C4—S6	114.6 (2)	S8—C10—C9	113.1 (3)
Intermolecular S...S distances (less than 3.8 \AA)			
S1—S4 ⁱ	3.699 (1)	S5—S6 ⁱⁱ	3.515 (1)
S2—S3 ⁱ	3.685 (1)	S7—S8 ⁱⁱ	3.517 (1)
S4—S6 ^{iv}	3.606 (1)	S2—S5 ⁱⁱⁱ	3.515 (2)
S6—S8 ^{iv}	3.505 (1)	S3—S4 ⁱ	3.736 (2)
S1—S4 ⁱⁱ	3.731 (1)	S5—S7 ^v	3.589 (1)
S3—S8 ⁱⁱ	3.524 (1)		

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

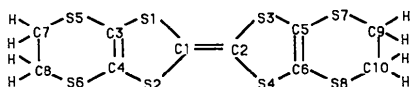


Fig. 1. Atomic labelling in the BEDT-TTF molecule.

Related literature. β -(BEDT-TTF)₂AuI₂ is an ambient-pressure superconductor with $T_c \approx 5$ K (Wang *et al.*, 1985; Carlson *et al.*, 1986; Amberger, Fuchs & Polborn, 1985; Heidmann, Veith, Andres, Fuchs, Polborn & Amberger, 1986; Talham, Kurmoo, Day, Obertelli, Parker & Friend, 1986; Schwenk, Parkin, Lee & Greene, 1986). For a review of superconductivity in organic compounds, see Williams, Beno, Wang, Leung, Emge, Geiser & Carlson (1985). Organic conductors very often exhibit low-temperature phase transitions, *i.e.* the modulated structure of the superconductor β -(BEDT-TTF)₂I₃ [which at room temperature is isostructural to β -(BEDT-TTF)₂AuI₂] below 175 K (Leung, Emge, Beno, Wang, Williams, Petricek & Coppens, 1985). Since the interesting physical properties in these materials appear at low temperatures, it is essential to know their crystal structures at such temperatures. In addition, the detailed analysis of structure-properties relationships (*e.g.* band electronic structures, non-bonded donor-to-anion interactions, electron-phonon coupling) require accurate positional parameters which, because of reduced thermal motion, can only be obtained at low temperatures and for this reason this low-temperature study was carried out. In the title compound we find no evidence of any structural change except for a lattice contraction between 298 K (Wang *et al.*, 1985) and 120 K. The present structure determination is more accurate than the room-temperature study, as evidenced by the better

agreement factors ($R = 0.043$, $wR = 0.033$ at 298 K) and a reduction in the bond length and angle e.s.d.'s by *ca* 25%. The major difference is found in the intermolecular S...S contacts which are important for electrical conduction. The S...S distances listed in Table 2 are reduced by 0.046–0.087 Å from their room-temperature values.

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Structure of 3,4;3',4'-Bis(propylenedithio)-2,2',5,5'-tetrathiafulvalene (BPDT-TTF)

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Abstract. C₁₂H₁₂S₈, $M_r = 412.7$, monoclinic, $P2_1/c$, $a = 10.484$ (1), $b = 12.308$ (1), $c = 13.040$ (2) Å, $\beta = 96.553$ (9)°, $V = 1671.7$ (3) Å³, $Z = 4$, $D_x = 1.64$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.013$ mm⁻¹, $F(000) = 848$, $T = 298$ K. The structure of the neutral organic electron donor molecule, BPDT-

TTF, is reported. The overall structure of this product is that of a twisted chair containing fused five- and seven-atom heterocyclic rings. The molecules are arranged in sheets in the lattice and do not display any unusual intermolecular contacts. Convergence to conventional R values of $R = 0.060$ and $wR = 0.036$ was obtained using 2952 averaged reflections with $F_o > 0.0$ and 354 variable parameters.

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