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Non-Superconducting Phase of Bis(3,4;3′,4′-ethylenedithio)-2,2′,5,5′-tetrathiafulvalene–Tetrakis(trifluoromethyl)argentate(III) (2/1), (BEDT-TTF)$_2$[Ag(CF$_3$)$_4$]

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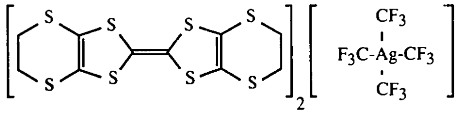
Abstract

The semiconductive phase in the system BEDT-TTF:[Ag(CF$_3$)$_4$]$^-$, where BEDT-TTF is 3,4;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene {alternative IUPAC name: 5,5′,6,6′-tetrahydro-2,2′-bi(1,3-dithiolo-[4,5-*b*][1,4]dithiinylidene), $C_{10}H_8S_8$} contains θ-packing motif type layers of the electron-donor molecules. The anion has a planar AgC$_4$ core and its trifluoromethyl groups are crystallographically ordered.

Comment

The electron-donor molecule BEDT-TTF has yielded approximately 30 superconductors to date (for a review see Williams, Ferraro, Thorn, Carlson, Geiser, Wang, Kini & Whangbo, 1992). Recently, we reported superconductivity in three distinct crystallographic phases of the BEDT-TTF:[Ag(CF$_3$)$_4$]$^-$:TCE (TCE = 1,1,2-trichloroethane) system, *i.e.* plate-like κ_L-(BEDT-TTF)$_2$[Ag(CF$_3$)$_4$].TCE, with superconducting transition temperature T_c = 2.6 K, and two separate needle phases (BEDT-TTF)$_2$[Ag(CF$_3$)$_4$].TCE$_x$ ($x \simeq 1$), with T_c = 9.4 and 11.1 K, respectively (Schlueter, Carlson, Geiser, Wang, Williams, Kwok, Fendrich, Welp, Keane, Dudek, Komosa, Naumann, Roy, Schirber, Bayless & Dodrill, 1994). The κ_L-phase is isostructural (Geiser, Schlueter, Williams, Naumann & Roy, 1995) with the superconductor κ_L-(BEDT-TTF)$_2$[Cu(CF$_3$)$_4$].TCE, with T_c = 4 K (Schlueter, Geiser, Williams, Wang, Kwok, Fendrich, Carlson, Achenbach, Dudek, Naumann, Roy, Schirber & Bayless, 1994), whereas the small crystal size and intergrowth problems have prevented the determination of the structures of needle phases. Superconducting needle-phase crystals with T_c = 9.2 K were also found in the BEDT-TTF:[Cu(CF$_3$)$_4$]$^-$:TCE system (Schlueter, Carlson, Williams, Geiser, Wang, Welp, Kwok, Fendrich, Dudek, Achenbach, Naumann, Roy, Schirber & Bayless, 1994).

As reported previously (Schlueter, Carlson, Geiser *et al.*, 1994), semiconducting (activation energy 0.19 eV) rod-shaped crystals of a fourth phase grow simultaneously with the superconductors during electrocrystallization of solutions of BEDT-TTF and PPN[Ag(CF$_3$)$_4$] [PPN = bis(triphenylphosphoranylidene)ammonium] in TCE on a platinum anode. An irregular fragment of these rod-shaped crystals, cut to proper size for the X-ray crystallographic analysis, is the subject of the present study. The atomic labelling scheme and the molecular structure of the individual components of the title compound, (I), are shown in Figs. 1 and 2 for the BEDT-TTF molecule and the [Ag(CF$_3$)$_4$]$^-$ anion, respectively.



(I)

As is frequently the case in BEDT-TTF-containing salts, one of the ethylene end groups of the electron-donor molecule was found to be conformationally disordered. The core of the anion was found to be planar because of the $\bar{1}$ site symmetry, and the trifluoromethyl groups were ordered. In contrast, in the structure of κ_L-(BEDT-TTF)$_2$[Ag(CF$_3$)$_4$].TCE, the AgC$_4$ moiety was found to be bent, and the CF$_3$ groups were modelled with two disordered conformations (Geiser *et al.*, 1995).

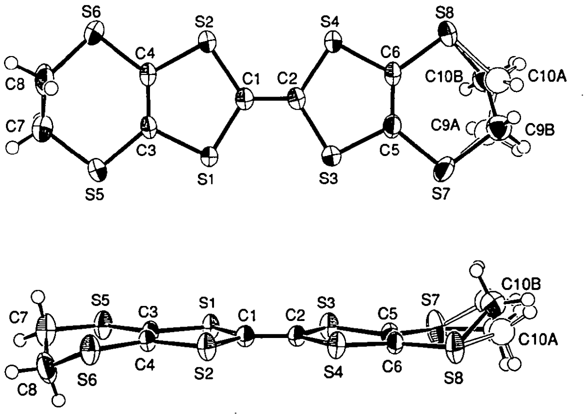


Fig. 1. Molecular structure and atomic labelling of the BEDT-TTF electron-donor molecule in (BEDT-TTF)$_2$[Ag(CF$_3$)$_4$]. The major conformation [occupancy 0.645 (7)] of the disordered ethylene group, C9–C10, is drawn with shaded atoms and bonds, whereas the minor conformation is shown with open atoms and bonds. Displacement ellipsoids are drawn at the 50% probability level.

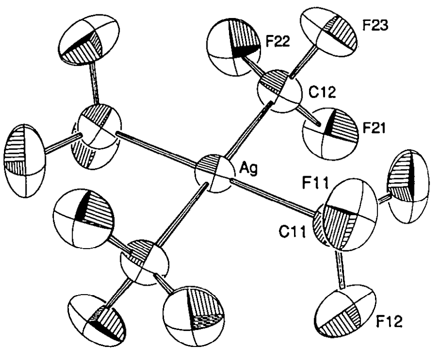


Fig. 2. View of the anion in $(BEDT\text{-}TTF)_2[Ag(CF_3)_4]$ with atomic labels. The Ag atom is located on an inversion centre. Displacement ellipsoids are drawn at the 50% probability level.

As in the majority of BEDT-TTF-based charge-transfer salts (Williams *et al.*, 1992), the crystal structure contains layers of electron-donor molecules alternating with anionic layers (parallel to the *ab* plane) (Fig. 3). Two layers of each comprise one unit cell (Fig. 4). Within each BEDT-TTF layer there are two uniform stacks of donor molecules, related to each other by screw rotations. Since the normal to the plane through the molecule is inclined by 60.36 (3)° with respect to the *b* axis, the screw-rotation operation causes molecules on adjacent stacks to form a dihedral angle of $180 - 2 \times 60.36 = 59.28\,(6)°$ with each other (Fig. 3). Such molecular packing is characteristic of both α and θ phases in BEDT-TTF salts (Williams *et al.*, 1992).

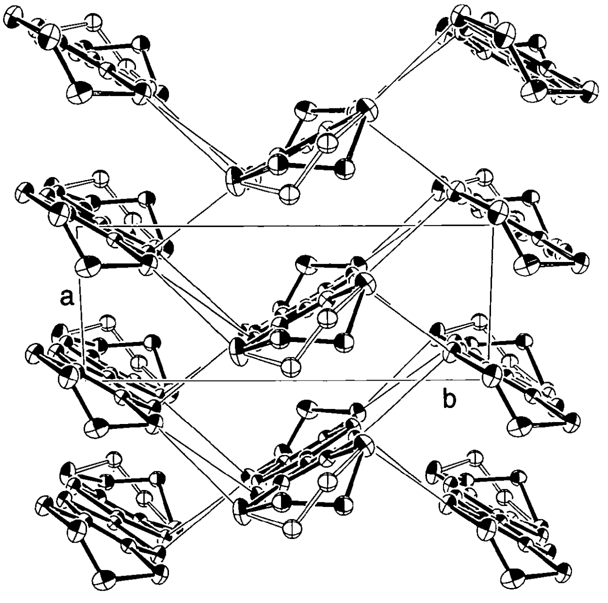


Fig. 3 Projection of the electron-donor layer in the title compound approximately along the long molecular axis. H atoms have been omitted for clarity. Intermolecular S···S contacts shorter than 3.60 Å (sum of van der Waals radii; Bondi, 1964) are drawn as thin lines.

Because of the uniform stacking and the existence of two donor-molecule layers per unit cell, the structure of the title compound qualifies as a θ phase (Kobayashi, Kato, Kobayashi, Nishio, Kajita & Sasaki, 1986). One difference between this salt and other θ phases is the angle between the long molecular axis (approximately along the C1—C2 bond direction) and the *b* axis, which is 90° within experimental error in the title compound compared to *ca* 70° in other θ-phase salts (Kobayashi *et al.*, 1986).

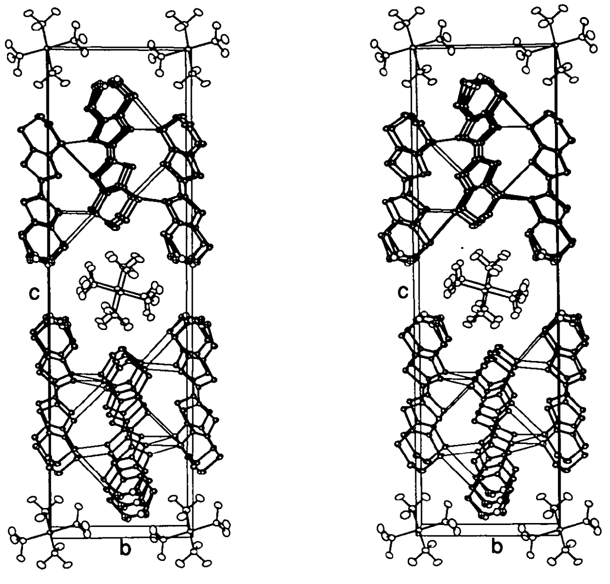


Fig. 4. Stereoview of the unit cell of $(BEDT\text{-}TTF)_2[Ag(CF_3)_4]$. H atoms are omitted for clarity. Intermolecular S···S contacts shorter than 3.60 Å (sum of van der Waals radii; Bondi, 1964) are drawn as thin lines.

Experimental

Crystals were obtained by electrocrystallization (Schlueter, Carlson, Geiser *et al.*, 1994).

Crystal data

$(C_{10}H_8S_8)_2[Ag(CF_3)_4]$
$M_r = 1153.2$
Monoclinic
$P2_1/n$
$a = 5.0037\,(7)$ Å
$b = 10.5940\,(14)$ Å
$c = 35.728\,(5)$ Å
$\beta = 93.689\,(11)°$
$V = 1890.0\,(5)$ Å^3
$Z = 2$
$D_x = 2.026$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 43 reflections
$\theta = 12.9\text{–}17.2°$
$\mu = 1.459$ mm^{-1}
$T = 298$ K
Irregular fragment
$0.45 \times 0.26 \times 0.19$ mm
Black

Data collection

Syntex $P2_1$ diffractometer
ω scans

$R_{\text{int}} = 0.016$
$\theta_{\text{max}} = 27.5°$

Absorption correction:
spherical and six ψ scans
$T_{\min} = 0.701$, $T_{\max} = 0.853$
5387 measured reflections
4360 independent reflections
3542 observed reflections
$[I > 2\sigma(I)]$

$h = -6 \rightarrow 0$
$k = 0 \rightarrow 13$
$l = -46 \rightarrow 46$
3 standard reflections
monitored every 58 reflections
intensity decay: 2% (random)

Refinement

Refinement on F
$R = 0.039$
$wR = 0.038$
$S = 1.85$
3542 reflections
238 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max} = 0.16$

$\Delta\rho_{\max} = 0.85$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}
Extinction correction: Larson (1967)
Extinction coefficient: 0.33 (2) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
S1	0.3631 (2)	0.42809 (9)	0.23940 (2)	0.0336 (3)
S2	0.6146 (2)	0.66751 (9)	0.26379 (2)	0.0359 (3)
S3	0.6817 (2)	0.43004 (9)	0.16490 (2)	0.0371 (3)
S4	0.9381 (2)	0.67052 (9)	0.18644 (2)	0.0348 (3)
S5	0.0431 (2)	0.39849 (10)	0.30497 (3)	0.0411 (3)
S6	0.3458 (2)	0.68366 (10)	0.33473 (3)	0.0422 (3)
S7	0.9596 (3)	0.39583 (11)	0.09602 (3)	0.0579 (4)
S8	1.2558 (2)	0.68566 (10)	0.11914 (3)	0.0462 (3)
C1	0.5826 (6)	0.5504 (3)	0.22966 (9)	0.0292 (10)
C2	0.7180 (6)	0.5511 (3)	0.19781 (9)	0.0286 (10)
C3	0.2717 (6)	0.4905 (3)	0.28218 (8)	0.0289 (9)
C4	0.3868 (6)	0.6002 (3)	0.29324 (8)	0.0288 (10)
C5	0.9198 (7)	0.4885 (4)	0.13563 (9)	0.0344 (10)
C6	1.0342 (7)	0.5993 (3)	0.14532 (9)	0.0309 (10)
C7	−0.0132 (8)	0.4881 (4)	0.34603 (11)	0.0512 (14)
C8	0.2217 (9)	0.5532 (5)	0.36290 (10)	0.0544 (15)
C9*A*†	1.033 (3)	0.5154 (12)	0.0629 (3)	0.0458 (10)
C9*B*†	1.1750 (15)	0.4916 (7)	0.0682 (2)	0.0458
C10*A*†	1.258 (3)	0.5984 (12)	0.0759 (3)	0.0458
C10*B*†	1.1298 (15)	0.6351 (7)	0.0726 (2)	0.0458
Ag	1/2	0	0	0.0315 (1)
C11	0.4689 (8)	0.1908 (4)	0.01565 (11)	0.0462 (13)
F11	0.3674 (6)	0.2066 (3)	0.04926 (7)	0.0721 (11)
F12	0.7080 (6)	0.2494 (3)	0.01835 (8)	0.0787 (11)
F13	0.3164 (7)	0.2671 (3)	−0.00739 (8)	0.0872 (13)
C12	0.2560 (8)	0.0362 (4)	−0.04869 (10)	0.0450 (13)
F21	0.3545 (5)	0.1279 (3)	−0.07036 (6)	0.0681 (10)
F22	0.2150 (6)	−0.0606 (3)	−0.07324 (7)	0.0785 (11)
F23	0.0088 (5)	0.0746 (3)	−0.04148 (7)	0.0689 (10)

† The disordered ethylene group C9–C10 was refined in two conformations, *A* and *B*, with occupancy factors 0.355 (7) and 0.645 (= 1.000 − 0.355), and a common isotropic displacement parameter.

Table 2. *Selected geometric parameters* (Å, °)

S1—C1	1.748 (3)	S8—C10*A*	1.802 (12)
S1—C3	1.753 (3)	S8—C10*B*	1.820 (7)
S2—C1	1.740 (3)	C1—C2	1.361 (4)
S2—C4	1.752 (3)	C3—C4	1.344 (5)
S3—C2	1.742 (3)	C5—C6	1.342 (5)
S3—C5	1.748 (3)	C7—C8	1.459 (6)
S4—C2	1.742 (3)	C9*A*—C10*A*	1.48 (2)
S4—C6	1.746 (3)	C9*B*—C10*B*	1.546 (10)
S5—C3	1.745 (3)	Ag—C11	2.106 (4)
S5—C7	1.785 (4)	Ag—C12	2.096 (4)
S6—C4	1.749 (3)	C11—F11	1.344 (4)
S6—C8	1.841 (4)	C11—F12	1.345 (5)
S7—C5	1.744 (3)	C11—F13	1.353 (5)
S7—C9*A*	1.789 (12)	C12—F23	1.342 (4)
S7—C9*B*	1.822 (7)	C12—F21	1.355 (4)
S8—C6	1.753 (3)	C12—F22	1.357 (5)
C1—S1—C3	95.5 (2)	S3—C5—S7	113.8 (2)
C1—S2—C4	95.5 (2)	C5—C6—S4	117.3 (2)
C2—S3—C5	95.6 (2)	C5—C6—S8	126.3 (2)
C2—S4—C6	95.5 (2)	S4—C6—S8	116.2 (2)
C3—S5—C7	103.2 (2)	C8—C7—S5	115.2 (3)
C4—S6—C8	98.4 (2)	C7—C8—S6	114.8 (3)
C5—S7—C9*A*	100.3 (4)	C10*A*—C9*A*—S7	113.4 (9)
C5—S7—C9*B*	103.4 (2)	C10*B*—C9*B*—S7	113.3 (5)
C6—S8—C10*A*	103.3 (4)	C9*A*—C10*A*—S8	121.8 (9)
C6—S8—C10*B*	98.0 (2)	C9*B*—C10*B*—S8	109.8 (5)
C2—C1—S1	121.6 (3)	C11—Ag—C12	89.8 (2)
C2—C1—S2	123.6 (3)	F11—C11—F12	105.3 (3)
S1—C1—S2	114.8 (2)	F11—C11—F13	103.8 (3)
C1—C2—S3	121.6 (3)	F11—C11—Ag	113.3 (3)
C1—C2—S4	123.7 (3)	F12—C11—F13	103.4 (4)
S3—C2—S4	114.7 (2)	F12—C11—Ag	112.4 (3)
C4—C3—S1	116.9 (2)	F13—C11—Ag	117.4 (3)
C4—C3—S5	128.8 (2)	F21—C12—F22	102.6 (3)
S1—C3—S5	114.3 (2)	F21—C12—F23	105.4 (3)
C3—C4—S2	117.3 (2)	F21—C12—Ag	113.1 (3)
C3—C4—S6	127.9 (2)	F22—C12—F23	104.5 (3)
S2—C4—S6	114.8 (2)	F22—C12—Ag	117.0 (3)
C6—C5—S3	116.8 (2)	F23—C12—Ag	113.0 (2)
C6—C5—S7	129.3 (3)		

The *UCLA Crystallographic Program Package* (Strouse, 1985) was employed for data reduction, structure solution and refinement. 19 reflections were excluded because of instrument problems.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: BK1111). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-Aquacarbonylbis(triphenylarsine)rhodium(I) Tetrafluoroborate Dichloromethane Solvate (1/1)

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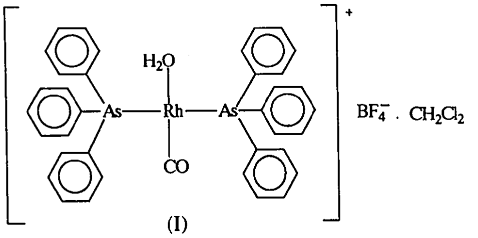
Abstract

The crystal structure of the title compound, $[Rh(C_{18}H_{15}As)_2(CO)(H_2O)]BF_4.CH_2Cl_2$, consists of $[Rh(AsPh_3)_2(CO)(H_2O)]^+$ cations, BF_4^- anions and CH_2Cl_2 solvate molecules held together by hydrogen bonds and van der Waals forces. The cationic complex has a slightly distorted square-planar geometry at the Rh atom, with the two $AsPh_3$ ligands mutually *trans*. The Rh—As(average), Rh—C(CO) and Rh—O(H_2O) bond distances are 2.4256 (5), 1.787 (4) and 2.118 (3) Å, respectively. The coordinated water molecule is involved in hydrogen bonding with the BF_4^- anion.

Comment

Most homogeneous catalytic cycles involve transition metal compounds interacting with weakly coordinating ligands. Often, it is postulated that the solvent coordinates to the transition metal and stabilizes intermediate species (Collman, Hegedus, Norton & Finke, 1987). Recently, there have been two reports of crystal structures of four-coordinate rhodium(I) cationic compounds in which a water molecule is coordinated to the metal centre. Branan *et al.* (1991) reported the isolation and crystal structure of *trans*-$[Rh(PPh_3)_2(CO)(H_2O)]BF_4$, (II), and Stang, Song, Huang & Arif (1991) prepared and characterized the analogous $(CH_3SO_3)^-$ salt, (III). In the present paper, we report the crystal structure of the related triphenylarsine compound (I), which was obtained as described by Evans, Howlader & Atlay (1994).



(I)

The structure, together with atom labelling, is shown in Fig. 1. The geometry around the Rh centre is essentially square-planar with the four bond angles in the range 87.9 (1)–93.7 (1)°, in agreement with the geometry of the analogous phosphine compounds. The Rh—C bond length [1.787 (4) Å] is also similar to those found in the phosphine compounds, while the C═O bond is slightly longer [1.162 (5) Å, *cf.* 1.099 and 1.145 (11) Å for the corresponding $CF_3SO_3^-$ and BF_4^- triphenylphosphine compounds, respectively]. This difference is not statistically significant but appears to be consistent with the reduced back-bonding ability of the triphenylarsine ligands compared with phosphines, between the metal and the carbonyl group. This effect is also consistent with the lowering of the carbonyl stretching frequency to 1990 cm^{-1} [*cf.* 2009 and 1998 cm^{-1} in (II) and (III), respectively].

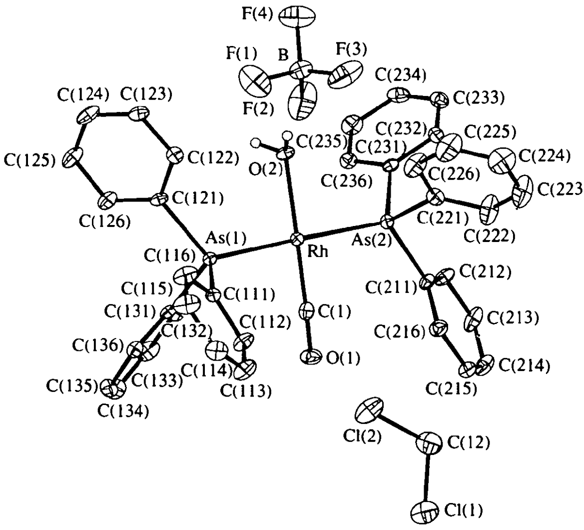


Fig. 1. Structure of (1) showing the atom-numbering scheme. H atoms (except those of the water molecule) have been omitted for clarity. Displacement ellipsoids are plotted at the 40% probability level.