Structure of the Organic Semiconducting Radical Cation Salt [2,3;7,8-Bis(ethylenedioxy)thianthrene] Hexafluoroarsenate

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Abstract. 2,3,9,10-Tetrahydrothianthreno[2,3-*b*:7,8-*b*']didioxinium hexafluoroarsenate, $C_{16}H_{12}O_4S_2^+$.-AsF_6^-, $M_r = 521.30$, monoclinic, $C2/m$, $a = 17.992$ (2), $b = 10.612$ (1), $c = 9.373$ (1) Å, $\beta = 94.22$ (2)°, $V = 1784.9$ (3) Å^3, $Z = 4$, $D_x = 1.94$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 22.0$ cm^{-1}, $F(000) = 1036$, $T = 295$ K, final $R(F) = 0.052$ for 2252 unique observed reflections. Dimers consisting of $[(bEDOT)_2]^{2+}$ molecules ($C_{16}H_{12}O_4S_2$ = bEDOT) form stacks along the *c* axis and are surrounded by the AsF_6^- ions. The nonplanar bEDOT molecules have a dihedral angle of about 11° between the planes defined by each half of the thianthrene molecule and are tilted about 48° relative to the stacking axis. The pronounced dimerization and the 1:1 stoichiometry give rise to semiconducting electronic properties. The ethylene groups of the bEDOT molecules, as well as all the F atoms in the AsF_6^- ions, are found to be disordered. The intermolecular S···S distance in the dimer is unusually short: 3.061 (2) Å.

Introduction. This work is part of a series of studies into the structure and physical properties of electrochemically prepared radical cation salts with chalcogen-substituted aromatic hydrocarbons as donors. Such compounds often exhibit unique electronic and magnetic properties and are relatively simple to prepare (Hellberg, 1987). However, in many cases the crystals are of poor quality. Solvent molecules are often found to be incorporated along with the anions in the channels between the cation stacks. A solvent-free structure is reported here.

Experimental. Black crystals of $[bEDOT]^+$.AsF_6^- with a reddish metallic lustre were prepared by electrolytic oxidation of bEDOT in CH_2Cl_2 solution in the presence of $(nBu_4N)AsF_6$ at a constant current density of a few μA cm^{-2} and a temperature of around 280 K. For details on the synthesis see Engman, Hellberg, Ishag & Söderholm (1988). A somewhat irregularly shaped crystal of maximum dimensions $0.21 \times 0.18 \times 0.10$ mm was chosen for measurements on a PDP8/*a*-controlled Enraf–Nonius CAD-4F diffractometer using graphite-monochromatized Mo $K\alpha$ radiation in ω-scan mode [scan width = 1° (2° for $\theta \le 10°$), scan speed varied to maintain constant $\sigma(I)/I = 0.01$; max. scan time 300 s]. The range of *h*, *k*, *l* was $0 \le h \le 27$, $0 \le k \le 16$, $-14 \le l \le 14$ with $(\sin\theta/\lambda)_{max} = 0.827$ Å^{-1}. Unit-cell dimensions were determined from a least-squares refinement of the setting angles of 25 reflections in the 2θ range 29–48°. Five standard reflections were measured every 200 min of X-ray exposure time; their intensities decreased by less than 6% during the data collection. A scaling function derived from the standard reflections was used to correct the measured intensities; a contribution taking account of instability in the measurement and of uncertainty in the scaling was added to the standard deviations estimated on the basis of counting statistics (McCandlish, Stout & Andrews, 1975). The raw intensities were corrected for background using the profile-analysis method of Lehmann & Larsen (1974). Absorption correction was performed by the Gaussian integration method using a $10 \times 10 \times 12$ grid. The crystal was described by eight faces. Transmission factors were in the range 0.63 to 0.84 for the 4956 collected intensities. Averaging symmetry-equivalent reflections ($R_{int} = 0.026$) and deleting space-group extinctions left 4400 unique intensities.

From the diffraction symmetry the space groups $C2$, Cm or $C2/m$ were possible. The structure was solved and refined in $C2/m$. The As and S atoms were located in a Patterson synthesis using the integrated Patterson search and direct methods program *PATSEE* (Egert & Sheldrick, 1985); the rest of the structure (except for H atoms) was found in successive Fourier syntheses. All H-atom positions were calculated; the C—H distance was fixed at 1.08 Å. Reflections with $F_o^2 \le 0$ were excluded in refinements. Neutral atomic and anomalous-scattering factors were taken from *International Tables for X-ray Crystallography* (1974, pp. 99–100, 102, 149). For H atoms the spherical bonded scattering factor was used. The function minimized in the full-matrix least-squares program *DUPALS* (Lundgren, 1982) was $\Sigma w(|F_o|^2 - |F_c|^2)^2$ where $w^{-1} = \sigma^2_{count}(F_o^2) + (0.070F_o^2)^2$.

After conventional refinements the distances between the C atoms in the two terminal ethylene groups (C1—C1' and C8—C8' respectively) were found to be abnormally short, 1.30 (2) and 1.27 (2) Å. The atomic displacement ellipsoids were also very elongated. In the ordered structure assumed so far, atoms C1 and C1' (C8 and C8') are located on the same side of the molecular plane. The resulting conformation in the ethylenedioxy group is not consistent with normal valence angles. It was quite evident that the ethylene groups could have two possible conformations relative to the rest of the molecule. A disordered model was therefore introduced with two alternative positions for C1 and C8 (C1A, C1B and C8A, C8B, respectively). The final stages of refinement were performed using geometrical constraints for H atoms in *SHELX76* (Sheldrick, 1976). The C—H distances were then fixed to 1.08 Å. The ethylene-H atoms were restricted to have identical isotropic temperature factors. Similarly, the temperature factors of hydrogen for the two C—H groups were kept the same. The disordered atoms were refined at two positions with fixed occupancies of 0.5.

The AsF$_6^-$ ion was also found to be disordered and was treated in a similar way, *i.e.* the F atoms were refined at two positions with fixed occupancies of 0.5, as was clearly indicated in a difference Fourier map.

Lowering the symmetry to $C2$ or Cm gave no significant improvement in the structure description; therefore space group $C2/m$ was chosen. In the final cycle, 2148 reflections with $F_o^2 < \sigma(F_o^2)$ were excluded, leaving 2252 reflections for the refinement of 180 parameters. These were one scale factor, 59 positional parameters, 118 anisotropic displacement parameters (non-hydrogens) and two groups of isotropic displacement parameters (hydrogens). Final agreement factors: $R(F) = 0.052$, $R(F^2) = 0.068$, $wR(F^2) = 0.12$, $S(F^2) = 1.35$. $(\Delta/\sigma)_{max} < 0.1$ in the final cycle. A final $\Delta\rho$ map gave a max. peak height of 0.8 e Å^{-3} and min. of -0.5 e Å^{-3}; both values close to the As atom. No secondary-extinction correction was necessary. The molecular plots were made using *ORTEP*II (Johnson, 1976); other computer programs used are described by Lundgren (1982).

Discussion. Final atomic parameters are given in Table 1.* A stereoview of the crystal packing is shown in Fig. 1 whereas bond distances, thermal

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* Lists of structure factors, anisotropic displacement parameters, H-atom parameters and details of the TLS analysis have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54412 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic fractional coordinates and displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
As	0.39802 (3)	0.00000	0.78509 (6)	0.0422 (3)
S	0.05843 (4)	0.16206 (7)	0.88928 (8)	0.0353 (4)
C(1)A	0.3545 (5)	0.0424 (10)	1.2627 (12)	0.053 (5)
C(1)B	0.3345 (6)	0.0805 (10)	1.3110 (11)	0.054 (5)
C(2)	0.23470 (15)	0.0660 (3)	1.1386 (3)	0.0389 (15)
C(3)	0.1796 (2)	0.1317 (3)	1.0617 (3)	0.0374 (15)
C(4)	0.12325 (13)	0.0663 (3)	0.9804 (3)	0.0294 (12)
C(5)	0.00479 (15)	0.0659 (3)	0.7744 (3)	0.0352 (14)
C(6)	−0.0437 (2)	0.1309 (4)	0.6759 (4)	0.056 (2)
C(7)	−0.0921 (2)	0.0662 (5)	0.5832 (3)	0.059 (2)
C(8)A	−0.1837 (4)	0.0340 (7)	0.3887 (7)	0.042 (4)
C(8)B	−0.1982 (4)	0.0980 (9)	0.4307 (9)	0.048 (4)
O(1)	0.28855 (13)	0.1338 (3)	1.2131 (3)	0.0582 (15)
O(2)	−0.1388 (2)	0.1330 (5)	0.4933 (3)	0.103 (3)
F(1)A	0.3732 (6)	0.0878 (9)	0.6440 (9)	0.096 (7)
F(1)B	0.3523 (4)	0.1261 (7)	0.6992 (10)	0.075 (5)
F(2)A	0.3169 (3)	0.0380 (6)	0.8545 (7)	0.093 (5)
F(2)B	0.4776 (3)	0.0474 (8)	0.7162 (11)	0.131 (8)
F(3)A	0.4420 (8)	0.1155 (10)	0.8690 (11)	0.092 (6)
F(3)B	0.4202 (9)	0.0996 (11)	0.9264 (13)	0.129 (10)

Disordered atoms (marked A and B) have fixed occupancies of 0.5.

ellipsoids and bond angles are given in Fig. 2 (bond angles in the AsF$_6^-$ ion are 87.4–93.2° with standard deviations 0.4–0.6°). The asymmetric unit consists of half a bEDOT molecule and half an AsF$_6^-$ ion. The mirror plane is parallel to the long molecular axis and perpendicular to the molecular plane (Fig. 2). The bEDOT molecules within a dimer are related by the twofold axis. The As atom lies in the mirror plane. The intermolecular S···S distance within the bEDOT dimer is only 3.061 (2) Å (van der Waals contact distance 3.6 Å; Bondi, 1964). From the stoichiometry it follows that each bEDOT molecule has a charge of +1. The bEDOT molecule is somewhat bent around the S—S axis (*cf.* Fig. 3); the dihedral angle between the planes defined by each half of the thianthrene molecule is about 11°.

Stacking arrangement. The nonplanar bEDOT molecules are packed in stacks along the c axis, with the AsF$_6^-$ ions surrounding them (Figs. 1 and 3). Within a stack, the bEDOT molecules form dimers. These are tilted about 48° relative to the stacking axis, thus displacing the adjacent dimers. This gives rise to two different modes of molecular overlap (Figs. 3 and 4). Because of the strong S···S interaction and the symmetry properties, there is an almost perfect overlap between the molecules within the dimer when viewed perpendicular to the mean molecular plane (*cf.* Figs. 3 and 4).

The interstack arrangement is shown in Fig. 4. The detailed contacts are not straightforward to analyze owing to the disorder. The bEDOT dimers are surrounded by six AsF$_6^-$ ions on four sides (Figs. 3 and 4). This arrangement is similar to that found in (bMDODBF)$_2$AsF$_6$ [bMDODBF = 2,3;7,8-bis-

(methylenedioxy)dibenzofuran] (Olovsson, 1987), although there is only half the number of AsF_6^- ions per donor molecule in that structure.
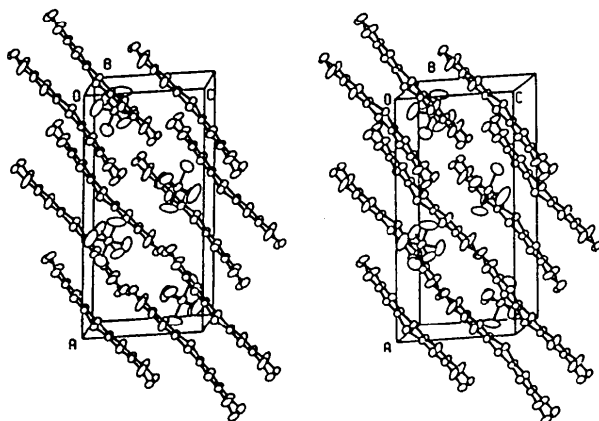

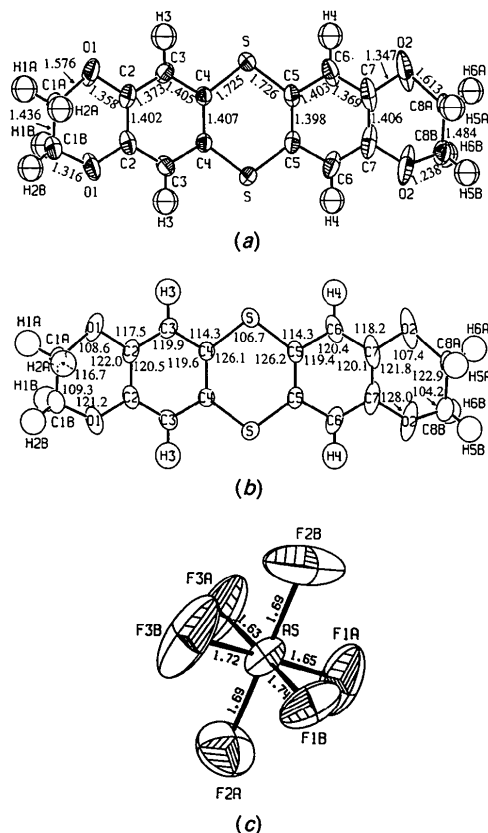Fig. 1. A stereoscopic view of the molecular packing. H atoms have been omitted for clarity.

Rigid-body analysis. The rigid-body analysis of Schomaker & Trueblood (1968) was used to fit the T, L and S tensors to the observed anisotropic displacement parameters (ADP's) for the S and C atoms of the thianthrene part of the bEDOT molecule. It was not possible to include the ethylenedioxy groups owing to the disorder. The approximation of Dunitz & White (1973) was used for the libration of the non-rigid groups of the molecule. Analysis of the disordered AsF_6^- ion was not attempted.

The rigid model is described by non-intersecting librational axes. The translation tensor is the reduced T after diagonalizing S. The rigid model resulted in a principal librational motion around an axis close to the stacking axis. This is in agreement with what would be expected, since the interactions between molecules are strong along the stack. The detailed results of the TLS analysis have been deposited.*
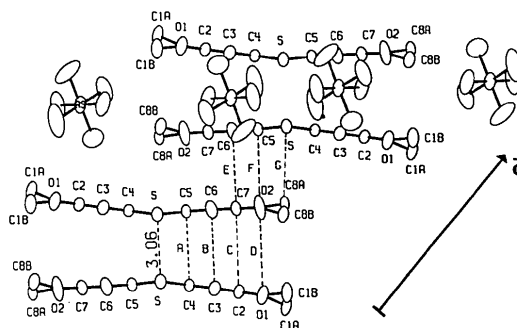
* See deposition footnote.

Fig. 3. Stacking along the c axis. The shortest intermolecular distances in the stack are marked as dotted lines [S···S = 3.061 (2), A = 3.372 (4), B = 3.594 (5), C = 3.790 (4), D = 3.990 (4), E = 3.635 (5), F = 3.675 (4), G = 3.818 (7) Å]. The AsF_6^- ions surrounding the lower dimer have been omitted for clarity.

Fig. 2. (a) Bond distances (Å) and atomic notations for the bEDOT molecule. (b) Bond angles (°) for the bEDOT molecule. (c) Bond distances (Å) for the AsF_6^- ion. All thermal ellipsoids plotted at 50% probability. Standard deviations for As—F distances are 0.003 Å; for C—C (non-disordered) and C—O distances they are 0.005–0.006 Å and for corresponding angles 0.2–0.3°.
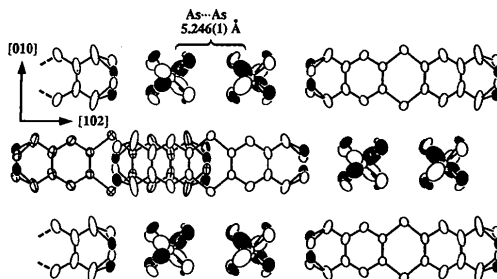

Fig. 4. Arrangements around the bEDOT dimers viewed approximately perpendicular to the mean molecular plane. Both positions of the disordered F atoms and ethylene groups are shown. The bEDOT molecules in the dimer have an almost perfect overlap and are therefore practically indistinguishable from a single molecule. The overlap between two bEDOT molecules in adjacent dimers is shown in the middle of the figure.

Physical properties. The [bEDOT]$^+$.AsF$_6^-$ salt is semiconducting with a room-temperature conductivity of $2(1) \times 10^{-6}$ S m^{-1}. Basic low-dimensional physics (*cf.* Söderholm, 1987) shows that a compound with 1:1 stoichiometry cannot be more than semiconducting. In this case every donor has a charge of $+1$, and in order to move an electron along the stack the repulsive energy between two electrons on the same bEDOT molecule has to be overcome. The electrical, optical and magnetic properties are reported by Söderholm, Noreland, Olovsson, Olovsson, Hellberg & Engman (1989). (In that paper a slightly erroneous X-ray wavelength was used for the lattice parameter refinement, giving rise to a small systematic error in the lattice-parameter values.)

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Di-μ-chloro-bis[(4-hydroxy-4'-methylazobenzenato-C^2,N^2)palladium(II)] Ethanol Solvate

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Abstract. C$_{26}$H$_{22}$Cl$_2$N$_4$O$_2$Pd$_2$.C$_2$H$_5$OH, $M_r = 752.2$, triclinic, $P\bar{1}$, $a = 9.354$ (2), $b = 11.926$ (3), $c = 13.417$ (3) Å, $\alpha = 90.30$ (2), $\beta = 105.04$ (2), $\gamma = 93.00$ (2)°, $V = 1443.3$ (6) Å^3, $Z = 2$, $D_x = 1.731$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 14.52$ cm^{-1}, $F(000) = 748$, $T = 298$ K, $R = 0.037$ for 4755 reflections with $I > 3\sigma(I)$. The dimeric complex has an overall *trans* conformation with bridging Cl atoms and a folded Pd$_2$Cl$_2$ unit. The Cl---Cl hinged dihedral angle is 14.0 (1)°. The Pd···Pd distance is 3.554 (1) Å.

Introduction. Azobenzenes or aromatic imines easily react with the appropriate source of palladium(II)

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chloride to give cyclometallated $\overline{C(sp^2)\text{—}Pd\text{—}N}(sp^2)$ complexes as in (I) (Ryabov, 1990).

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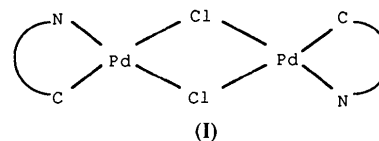
In the solid state the Pd$_2$Cl$_2$ fragment can be either planar (Clark, Dyke, Smith, Kennard & White, 1985) or bent (Ghedini, Armentano, De Munno, Crispini & Neve, 1990). The cyclopalladated μ-Cl dimer obtained from 2',6'-dimethylazobenzene has a strictly planar Pd$_2$Cl$_2$ rhomboid (Armentano, Crispini, De Munno, Ghedini & Neve, 1991). Here