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Structure of Dimethyltetramethylenetetrathiafulvalene Hexafluoroarsenate: $(C_{12}H_{14}S_4)_2AsF_6$

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Abstract. Bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-4,5,6,7-tetrahydro-1,3-benzodithiol]ium hexafluoroarsenate, $(DMCTTF)_2AsF_6$, $M_r = 761{\cdot}89$, triclinic, $P\bar{1}$, $a = 7{\cdot}8665\,(28)$, $b = 7{\cdot}8575\,(14)$, $c = 13{\cdot}4458\,(21)$ Å, $\alpha = 95{\cdot}67\,(1)$, $\beta = 101{\cdot}36\,(2)$, $\gamma = 111{\cdot}08\,(2)$°, $V = 747{\cdot}1$ Å^3, $Z = 2$, $D_x = 1{\cdot}6934$ g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1{\cdot}54178$ Å, $\mu = 68{\cdot}02$ cm^{-1}, $F(000) = 387$, $T = 298$ K, $R = 0{\cdot}0489$ for 2743 observed reflections $[I > 3\sigma(I)]$. $DMCTTF^+$ organic cations stack in a zigzag type mode along the *a* axis and build weakly dimerized conducting columns. AsF_6^- anions are located in cavities left by the organic molecules. The As atom lies on the inversion center.

Introduction. The title compound belongs to a novel series of organic conductors which have been extensively studied recently (Vaca, Granier, Gallois, Coulon, Gouasmia & Fabre, 1988; Vaca, Coulon, Ducasse, Granier, Gallois, Fabre & Gouasmia, 1989). These compounds are based on the new unsymmetrical π donor derived from the tetrathiafulvalene (TTF) backbone: dimethyltetramethylenetetrathiafulvalene (DMCTTF) and its selenium analogue (DMCTSeF) (Giral, Fabre & Gouasmia, 1986). All sulfur compounds [*i.e.* $(DMCTTF)_2X$ where X is a diamagnetic anion such as AsF_6^-, PF_6^-, BF_4^-, ClO_4^- and ReO_4^-] exhibit an antiferromagnetic ground state at low temperature ($T \simeq 10$–30 K), the properties of which are well understood through the structural organization of these compounds. The latter depends on the anion geometry: salts of tetrahedral anions present two organic stacks in the unit cell (Granier, Gallois & Fabre, 1989) while salts of octahedral anions present only one single DMCTTF stack. We discuss here the detailed structure of one of the latter salts: $(DMCTTF)_2AsF_6$.

Experimental. The salt studied was prepared in tetrahydrofuran using oxidative electrocrystallization at constant current (10 μA), in the presence of tetrabutylammonium hexafluoroarsenate and $DMCTTF^+$ (Giral, Fabre & Gouasmia, 1986). The crystals obtained were thin black needles: dimensions $0{\cdot}50 \times 0{\cdot}08 \times 0{\cdot}02$ mm. All measurements were carried out on an Enraf–Nonius CAD-4 diffractometer, determination of the unit-cell parameters was by least-squares refinement of the setting angles of 22 reflections ($10 < \theta < 65$°). 2971 [2743 with $I > 3\sigma(I)$] unique reflections; graphite-monochromated Cu $K\alpha$ radiation, ω–2θ scan, scan angle $(1{\cdot}2 + 0{\cdot}15\tan\theta)$°, $1 < \theta < 73$°; ranges of h, k and l: -9 to 9, -9 to 9, 0 to 16 respectively. Three standard reflections were measured every 100 reflections, small random variation was observed (±3%). Data corrected for Lorentz and polarization factors, and empirical absorption correction applied (North, Phillips & Mathews, 1968), max. and min. transmission factors 0·63 and 0·99. All non-hydrogen atoms were positioned by a Patterson map analysis. Full-matrix least-squares refinement achieved on F, using *SHELX*76 (Sheldrick, 1976), atomic scattering factors inlaid. Methylene and methyl groups were refined as rigid groups with a C—H bond length of

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Table 1. $(DMCTTF)_2AsF_6$ *fractional atomic coordinates*

$U_{eq} = \frac{1}{3}(\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j U_{ij})$.

	x	y	z	$U_{eq}(\times 10^3\ Å^2)$
S1	2543 (1)	7475 (1)	4626 (1)	48 (1)
S11	4395 (1)	6128 (1)	6626 (1)	48 (1)
S2	873 (1)	3663 (1)	3500 (1)	47 (1)
S12	2673 (1)	2308 (1)	5487 (1)	47 (1)
C1	1180 (5)	7081 (5)	3368 (2)	49 (3)
C11	4629 (5)	4412 (5)	7305 (2)	46 (3)
C2	399 (5)	5321 (4)	2853 (2)	46 (3)
C12	3845 (5)	2653 (5)	6788 (2)	47 (3)
C3	2236 (5)	5177 (4)	4641 (2)	43 (3)
C13	3017 (5)	4618 (4)	5483 (2)	44 (3)
C4	−846 (6)	4623 (5)	1771 (3)	59 (4)
C14	3920 (6)	1015 (5)	7244 (3)	61 (4)
C5	998 (6)	8750 (5)	2981 (3)	64 (4)
C15	5704 (6)	4963 (6)	8420 (3)	62 (4)
C16	4962 (12)	1564 (8)	8355 (4)	128 (10)
C17	5620 (14)	3330 (9)	8892 (4)	146 (12)
As	0	0	0	54 (1)
F1	2261 (5)	409 (5)	495 (4)	150 (6)
F2	−74 (7)	820 (4)	1190 (2)	154 (7)
F3	604 (4)	2183 (3)	−270 (2)	88 (3)

Table 2. $DMCTTF^+$ *and* AsF_6^- *bond lengths* (Å) *and angles* (°)

C5—C1	1·500 (5)	S12—C13	1·738 (3)
C4—C2	1·507 (5)	S11—C11	1·744 (3)
C2—C1	1·343 (5)	S12—C12	1·753 (3)
S2—C2	1·743 (4)	C11—C12	1·342 (5)
S1—C1	1·747 (3)	C11—C15	1·503 (5)
S1—C3	1·736 (3)	C12—C14	1·494 (5)
S2—C3	1·730 (3)	C15—C17	1·473 (8)
C3—C13	1·367 (5)	C14—C16	1·491 (7)
S11—C13	1·733 (3)	C16—C17	1·362 (9)
S1—C1—C5	116·3 (3)	S12—C13—S11	114·7 (2)
S2—C2—C4	116·4 (3)	C13—S11—C11	95·6 (2)
C5—C1—C2	127·0 (3)	C12—S12—C13	95·7 (2)
C4—C2—C1	126·8 (3)	S11—C11—C12	117·4 (3)
S1—C1—C2	116·7 (3)	S12—C12—C11	116·4 (3)
S2—C2—C1	116·8 (3)	S11—C11—C15	119·1 (3)
C3—S1—C1	96·0 (2)	S12—C12—C14	119·1 (3)
C3—S2—C2	96·2 (2)	C12—C11—C15	123·5 (3)
S1—C3—S2	114·3 (2)	C11—C12—C14	124·6 (3)
S1—C3—C13	122·7 (3)	C11—C15—C17	111·7 (4)
S2—C3—C13	123·0 (3)	C12—C14—C16	111·8 (4)
S11—C13—C3	123·3 (3)	C14—C16—C17	123·0 (6)
S12—C13—C3	122·0 (3)	C15—C17—C16	124·5 (7)
As—F1	1·670 (4)	F1—As—F2	87·6 (2)
As—F2	1·685 (3)	F1—As—F3	90·7 (2)
As—F3	1·705 (2)	F2—As—F3	89·6 (2)

1·08 Å and an H—C—H bond angle of 109·5°. Function minimized $\sum w(|F_o| - |F_c|)^2$, optimized weighting scheme $\{w = 1/[\sigma^2(F_o) + gF_o^2];\ g = 0{\cdot}00001\}$. Final $wR = 0{\cdot}0604$, $S = 0{\cdot}84$, $(\Delta/\sigma)_{max} = 0{\cdot}77$, residual maximum height in final Fourier map $0{\cdot}5\ e\ Å^{-3}$. Final atomic positional and thermal parameters are given in Table 1.*

Discussion. Bond lengths and angles of both the $DMCTTF^+$ cation and the AsF_6^- anion are given in Table 2. It appears that the values for the $DMCTTF^+$ cation are very similar to those found in the tetrahedral salts $(DMCTTF)_2ClO_4$ and $(DMCTTF)_2BF_4$ (Granier, Gallois & Fabre, 1989). More precisely, the cyclohexene moiety adopts here the boat-like conformation (C16 and C17 are located on the same side of the mean molecular plane) observed in the α phases of the monoclinic ClO_4^-

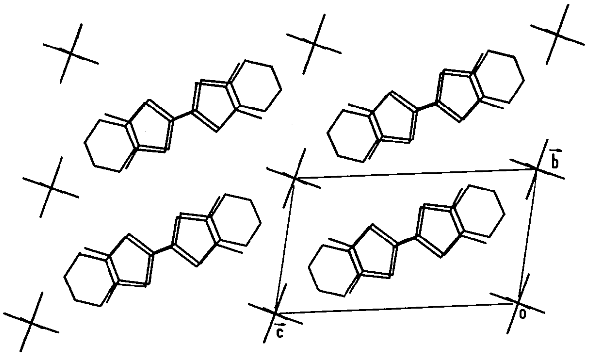
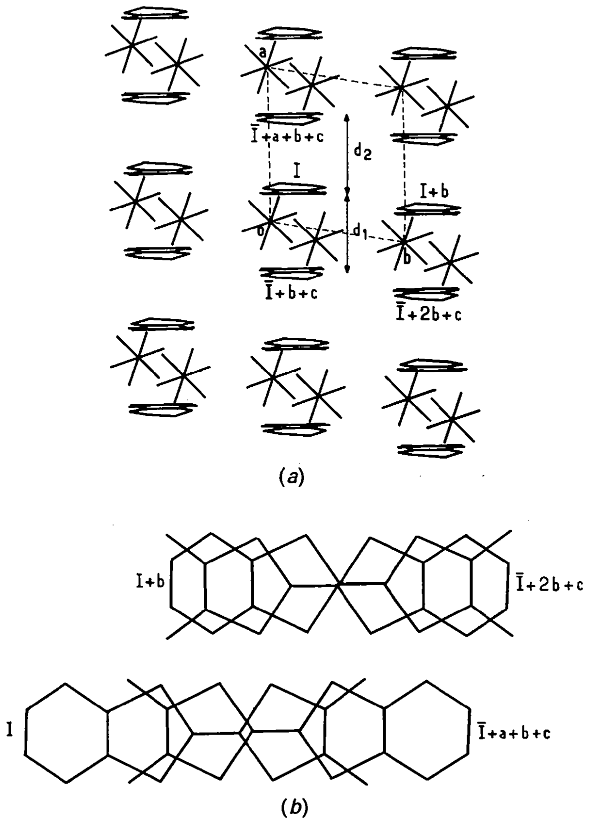


Fig. 1. Projection of the unit cell along the a axis.



(a)

(b)

Fig. 2. Projections of (a) one layer of DMCTTF units and AsF_6 anions along the C3—C13 double bond; (b) consecutive DMCTTF units in their mean molecular plane.

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52662 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and BF$_4^-$ salts, and also in type I (DMCTTF) stacking of the triclinic ClO$_4^-$ salt β phase (for details see Granier, Gallois & Fabre, 1989), as in the latter case C16 and C17 have very high *U* equivalent temperature factors. Fourier map analysis did not provide evidence for two distinct statistical positions. The As atom is on the inversion center and the whole octahedron is generated starting from the positions of three F atoms. Dispersion of bond lengths and bond angles from an ideal regular octahedron is commonly observed in this type of compound. Large temperature factors account for a strong rotational disorder of the anion; this is supported by the fact that no distinct statistical positions of F atoms could be deduced from Fourier map analysis. DMCTTF$^+$ cations build independent columns along the *a* axis; these columns form layers parallel to the *ab* plane, which alternate with AsF$_6^-$ anions (Fig. 1). The DMCTTF columns are weakly dimerized, the interplanar distances within and between dimers being $d_1 = 3\cdot49$ and $d_2 = 3\cdot72$ Å respectively (Fig. 2*a*). The mean molecular plane makes an angle $\delta = 23\cdot42°$ with the stacking *a* axis. The one-dimensional character of the structure is reinforced by the overlapping mode of the DMCTTF$^+$ cations within each stack: the projection of three consecutive DMCTTF units ($\bar{1} + b + c$), (I) and ($\bar{1} + a + b + c$) in the mean molecular plane of molecule I shows very small transverse shifts of their longitudinal axes (Fig. 2*b*), $\Delta t_1 = 0\cdot014$ Å between (I) and ($\bar{1} + b + c$), and $\Delta t_2 = 0\cdot139$ Å between (I) and ($\bar{1} + a + b + c$) (these shifts are calculated relative to the center of the C3=C13 double bond; see Granier, Gallois & Fabre, 1989, for a detailed description). On the other hand, alternate longitudinal shifts, $\Delta l_1 = -1\cdot261$, $\Delta l_2 = +1\cdot864$ Å allow the formation of cavities in which AsF$_6^-$ anions are located. This structural arrangement is very reminiscent to that found in type 1 DMCTTF layers of β-ClO$_4^-$ salts (Vaca, Granier, Gallois, Coulon, Gouasmia & Fabre, 1989).

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Structure of a Palladium(II) Complex with a Non-Symmetrical Tetradentate Schiff Base

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Abstract. (1-Phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-*O*,*N*,*N*′,*N*″)palladium(II) perchlorate, [Pd(C$_{14}$H$_{20}$N$_3$O)]ClO$_4$, $M_r = 452\cdot18$, monoclinic, $P2_1/c$, $a = 10\cdot339$ (1), $b = 19\cdot901$ (1), $c = 8\cdot4629$ (9) Å, $\beta = 98\cdot74$ (1)°, $V = 1721\cdot1$ (3) Å^3, $Z = 4$, $D_m = 1\cdot732$ (3), $D_x = 1\cdot745$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1\cdot247$ mm^{-1}, $F(000) = 912$, $T = 296$ K, $R = 0\cdot034$ for 2656 unique observed reflections. The complex cation which includes the baden ligand, 1-phenyl-3-{2-[(2-aminoethyl)amino]ethylimino}-1-buten-1-olato-*O*,*N*,*N*′,*N*″, contains two five-membered and one six-membered chelate ring, and the phenyl ring. The coordination polyhedron around Pd is a distorted square formed by three N

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