

Tetrathiafulvalinium Bis-*cis*-(1,2-perfluoromethylethylene-1,2-dithiolato)platinum

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Abstract. $C_6S_4H_4 \cdot PtS_4C_4(CF_3)_4$, triclinic, $P\bar{1}$; $M = 851.8$; $a = 7.661$ (3), $b = 13.015$ (5), $c = 7.589$ (3) Å, $\alpha = 105.7$ (4), $\beta = 118.3$ (4), $\gamma = 102.7$ (2)°; $D_c = 2.42$ g cm⁻³ for $Z = 1$. The structure was solved by Patterson methods and refined by least squares to a final R of 0.047. An alternation of the two kinds of molecules occurs along three directions that are close to orthogonal. Disorder of fluorine atoms is present in the $PtS_4C_4(CF_3)_4$ electron-acceptor molecule.

Introduction. This compound is a member of a group of $TTF \cdot MS_4C_4(CF_3)_4$ ($M = Ni, Pt, Cu, Au$) donor-acceptor compounds of interest for their unusual magnetic properties. The structure determination was undertaken to aid the interpretation of the magnetic data. $C_6S_4H_4 \cdot PtS_4C_4(CF_3)_4$ was prepared by the interaction of the neutral tetrathiafulvalene (TTF) and bis-*cis*-(1,2)-perfluoromethylethylenedithioleneplatinum

[$PtS_4C_4(CF_3)_4$] units in benzene solution. Black needles were obtained by recrystallization from acetonitrile solution and one with dimensions $0.037 \times 0.048 \times 0.384$ mm was used for the structure determination. The space group was determined from precession photographs to be $P\bar{1}$ or $P1$ (no systematic absences); the former was assumed and proven to be correct by the successful solution of the structure. The unit-cell parameters and the intensities of 2618 reflections (2θ maximum of 55° with graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å) were measured on a three-circle automatic diffractometer (Ge-490), employing the θ - 2θ scan technique. 1221 independent reflections with $I/\sigma(I) > 3.0$ were accepted as observed for the structure analysis. Corrections were made for Lorentz-polarization factors and for absorption [μ (Mo $K\alpha$) = 70.92 cm⁻¹].

Pt and S positions were obtained from Patterson

Table 1. Positional parameters ($\times 10^3$) and anisotropic temperature parameters ($\times 10^3$), with standard deviations in parentheses

The values B_{ij} refer to the expression $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0	0	0	24.8 (4)	6.1 (1)	26.3 (4)	5.6 (1)	12.4 (3)	6.9 (2)
S(1)	47 (1)	-151 (1)	-172 (1)	39.4 (20)	7.4 (5)	36.4 (20)	8.1 (10)	22.4 (20)	7.7 (10)
S(2)	157 (1)	116 (1)	-102 (1)	41.7 (20)	6.9 (4)	39.7 (20)	7.3 (10)	24.3 (20)	9.4 (10)
S(3)	531 (1)	-157 (1)	358 (1)	47.3 (20)	12.2 (10)	44.1 (20)	12.0 (10)	28.1 (20)	10.6 (10)
S(4)	357 (1)	-102 (1)	615 (1)	38.4 (20)	13.1 (10)	48.5 (30)	10.1 (10)	27.9 (20)	15.1 (10)
C(1)	158 (3)	248 (2)	15 (3)	36.5 (80)	11.1 (20)	31.7 (70)	9.3 (40)	17.0 (60)	12.2 (40)
C(2)	77 (2)	265 (1)	134 (2)	25.4 (60)	6.8 (20)	25.5 (60)	6.0 (30)	14.7 (50)	6.0 (30)
C(3)	65 (3)	377 (1)	246 (3)	39.5 (80)	7.3 (20)	38.3 (80)	6.1 (30)	15.6 (70)	7.9 (30)
C(4)	266 (4)	344 (2)	-22 (4)	54 (11)	7.6 (20)	47 (10)	9.7 (40)	8.8 (90)	9.4 (40)
C(5)	-353 (3)	238 (2)	457 (4)	32.6 (80)	14.1 (30)	53 (11)	3.2 (40)	13.6 (80)	16.8 (50)
C(6)	437 (3)	-264 (1)	-580 (3)	33.8 (80)	7.1 (20)	43.7 (90)	-1.5 (30)	10.7 (70)	8.8 (40)
C(7)	528 (2)	54 (1)	-497 (2)	14.1 (50)	12.1 (20)	29.0 (60)	0.4 (3)	11.2 (50)	11.6 (40)
Set 1									
F(1)	179 (5)	419 (3)	-40 (6)	87 (14)	10 (2)	82 (15)	18 (5)	68 (13)	22 (5)
F(2)	475 (5)	388 (3)	110 (5)	41 (8)	12 (3)	56 (10)	-1 (4)	19 (8)	13 (5)
F(3)	230 (4)	300 (2)	-224 (4)	47 (8)	11 (2)	38 (7)	8 (3)	30 (6)	12 (3)
F(4)	-104 (6)	395 (3)	119 (5)	66 (12)	24 (5)	48 (11)	25 (6)	26 (10)	11 (6)
F(5)	256 (4)	467 (2)	375 (4)	32 (6)	3 (1)	47 (8)	-1 (2)	21 (6)	-6 (2)
F(6)	27 (5)	378 (2)	405 (5)	91 (18)	10 (2)	35 (9)	20 (5)	36 (11)	7 (4)
Set 2									
F(7)	412 (7)	321 (4)	-71 (7)	89 (18)	8 (2)	192 (34)	14 (6)	95 (22)	26 (7)
F(8)	130 (6)	358 (4)	-181 (7)	60 (12)	23 (5)	80 (18)	13 (6)	27 (11)	30 (9)
F(9)	394 (6)	451 (3)	151 (6)	84 (15)	7 (2)	56 (10)	-3 (4)	36 (10)	4 (4)
F(10)	-94 (6)	363 (3)	277 (6)	77 (14)	14 (3)	61 (14)	14 (5)	48 (13)	12 (5)
F(11)	-21 (5)	421 (3)	96 (4)	68 (10)	10 (2)	69 (11)	23 (4)	44 (9)	17 (4)
F(12)	180 (9)	421 (5)	460 (9)	103 (26)	44 (11)	124 (29)	41 (15)	-36 (24)	-25 (15)

maps and the C and F positions from Fourier maps. A full-matrix least-squares refinement with individual anisotropic thermal parameters led to an R of 0.047 [$R = \sum(|F_o| - |F_c|) / \sum |F_o|$]. The scattering factors were those of Cromer & Waber (1965). The weighting scheme used corresponded to $w = (9.4 + |F_o| + 0.02|F_o|^2)^{-1}$. Anomalous dispersion corrections for Pt were made with the values given by Cromer (1965).*

Disorder of F atoms was indicated in the Fourier plots. It appeared possible to select two sets of F positions for the surroundings of the terminal C atoms in the bisdithiolate molecule. Each set yields reasonable C–F distances. Accordingly, each of the F positions was given one-half weight in the least-squares refinement.

The structural parameters are given in Table 1 and the bond distances and angles in Table 2.

It is convenient to consider the structure in terms of a face-centered cell, space group $F\bar{1}$ and $Z=4$, since then the alternation of the molecules along three almost orthogonal directions is readily apparent with the planes of the molecules close to parallel to one of the basal planes. The relevant transformations to the face-centered cell are $\mathbf{a}_F = \mathbf{a} + 2\mathbf{b} + \mathbf{c}$, $\mathbf{b}_F = -\mathbf{a} + \mathbf{c}$ and $\mathbf{c}_F = \mathbf{a} + \mathbf{c}$. The cell parameters of the face-centered cell are $a = 23.34$ (8), $b = 13.10$ (4), $c = 7.82$ (2) Å, $\alpha = 90.6$ (4), $\beta = 101.4$ (5), $\gamma = 92.0$ (4)°. Fig. 1 illustrates the molec-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31841 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

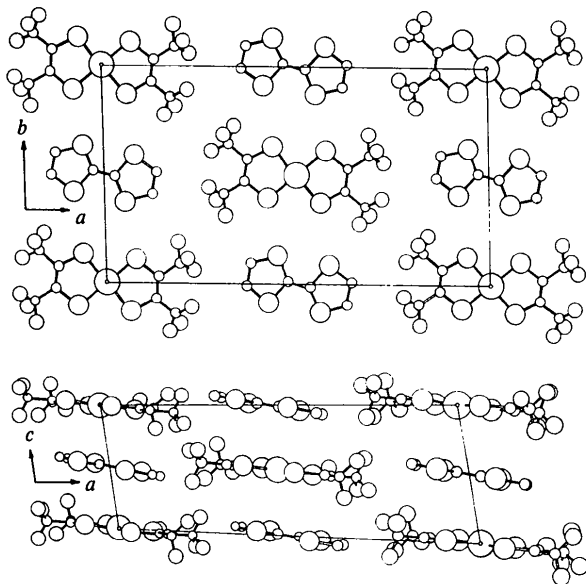
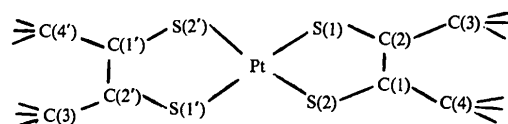


Fig. 1. Projections of the TTF·PtS₄C₄(CF₃)₄ crystal structure on the (001) and (010) planes (face-centered cell). Only one set of F positions (set 1) is shown.

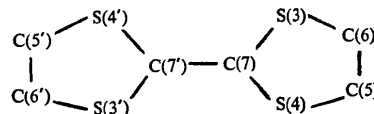
Table 2. Bond distances (Å) and angles (°)

PtS₄C₄(CF₃)₄



Pt—S(1)	2.256 (8)	C(1)—C(2)	1.33 (3)																								
Pt—S(2)	2.253 (8)	C(1)—C(4)	1.51 (3)																								
S(1)—C(2)	1.74 (2)	C(2)—C(3)	1.52 (3)																								
S(2)—C(1)	1.69 (3)																										
Set 1	<table border="0"> <tbody> <tr><td>C(4)—F(2)</td><td>1.30 (4)</td></tr> <tr><td>C(4)—F(3)</td><td>1.29 (4)</td></tr> <tr><td>C(4)—F(7)</td><td>1.34 (4)</td></tr> <tr><td>C(3)—F(4)</td><td>1.32 (4)</td></tr> <tr><td>C(3)—F(5)</td><td>1.32 (4)</td></tr> <tr><td>C(3)—F(6)</td><td>1.37 (4)</td></tr> </tbody> </table>	C(4)—F(2)	1.30 (4)	C(4)—F(3)	1.29 (4)	C(4)—F(7)	1.34 (4)	C(3)—F(4)	1.32 (4)	C(3)—F(5)	1.32 (4)	C(3)—F(6)	1.37 (4)	Set 2	<table border="0"> <tbody> <tr><td>C(4)—F(1)</td><td>1.40 (4)</td></tr> <tr><td>C(4)—F(8)</td><td>1.27 (4)</td></tr> <tr><td>C(4)—F(9)</td><td>1.35 (4)</td></tr> <tr><td>C(3)—F(10)</td><td>1.33 (4)</td></tr> <tr><td>C(3)—F(11)</td><td>1.36 (4)</td></tr> <tr><td>C(3)—F(12)</td><td>1.28 (4)</td></tr> </tbody> </table>	C(4)—F(1)	1.40 (4)	C(4)—F(8)	1.27 (4)	C(4)—F(9)	1.35 (4)	C(3)—F(10)	1.33 (4)	C(3)—F(11)	1.36 (4)	C(3)—F(12)	1.28 (4)
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C(3)—F(12)	1.28 (4)																										
S(1)—Pt—S(2)	91.5 (5)	S(1)—C(2)—C(1)	121.4 (7)																								
S(1)—Pt—S(2')	88.5 (5)	S(2)—C(1)—C(2)	122.5 (8)																								
Pt—S(1)—C(2)	103.2 (6)	C(1)—C(2)—C(3)	127.9 (8)																								
Pt—S(2)—C(1)	104.3 (6)	C(2)—C(1)—C(4)	122.6 (7)																								

C₆S₄H₄



S(3)—C(7)	1.76 (2)	C(7)—C(7)—S(4)	118 (2)
S(4)—C(7)	1.66 (1)	C(7)—C(7)—S(3)	127 (2)
S(3)—C(6)	1.71 (2)	S(3)—C(7)—S(4)	114.3 (8)
S(4)—C(5)	1.70 (2)	C(7)—S(4)—C(5)	95.3 (9)
C(7)—C(7)	1.36 (3)	C(7)—S(3)—C(6)	99.4 (9)
C(5)—C(6)	1.38 (3)	S(3)—C(6)—C(5)	117 (1)
		S(4)—C(5)—C(6)	115 (1)

ular arrangement in terms of the larger cell, with the Pt atom at the origin.

Discussion. There is an alternation of the two types of molecules along the three directions with a 'stacking' of the units along c . This alternation, along with the results of physical property measurements (Jacobs, Interrante & Hart, 1975), suggests that this is a fully charge-transferred π -donor-acceptor compound with an unpaired electron on each of the respective TTF⁺ and PtS₄C₄(CF₃)₄⁻ units.

As indicated by EPR measurements (Davison, Edelstein, Holm & Maki, 1964), the unpaired electrons on these units reside in molecular orbitals of π symmetry. These orbitals project along the stacking direction [001] leading to an effective one-dimensional (1-D) exchange pathway. The ferromagnetic character of the interactions within these 1-D chains has been demonstrated by magnetic susceptibility measurements (Jacobs, Interrante & Hart, 1975).

The closest intermolecular separations, not including F, along [001] are S(2)—C(5) and Pt—C(7) at 3.64 and 3.74 Å respectively. Somewhat shorter distances between units are found along [010] [S(1)—S(4) = 3.49 Å]; however, owing to the directional character of the

π molecular orbitals, these are believed to be less effective in establishing a magnetic exchange interaction.

The intramolecular bond lengths and angles correspond well with the results of previous structural studies of compounds containing the TTF⁺ (Kistenmacher, Phillips & Cowan, 1974) and MS₄C₄(CF₃)₄⁻ units (Schmitt, Wing & Maki, 1969) and are generally consistent with the conclusion that complete one-electron charge transfer has occurred in this compound.

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Potassium Hexafluoroantimonate (I)

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Abstract. KSbF₆ (I), tetragonal, $P\bar{4}2m$, $a = 5.16$ (1), $c = 10.07$ (2) Å, $V = 267.86$ Å³, $Z = 2$, $D_c = 3.407$ g cm⁻³. In KSbF₆ (I), which is stable above $\sim 16^\circ\text{C}$, the Sb is surrounded by six F atoms in a slightly distorted octahedral configuration. The average Sb–F distance is 1.844 Å and the mean deviation of the F–Sb–F bond angles from the ideal octahedral values is 3.3° . The F–F distances in the coordination octahedra vary between 2.544 and 2.736 Å, with a mean of 2.605 Å. The K atoms are surrounded by eight F atoms, forming a slightly distorted dodecahedron, at distances between 2.618 and 3.204 Å. The coordination octahedra and dodecahedra are connected by sharing of corners.

Introduction. KNbF₆ and KTaF₆ have been reported to be cubic, space group $Ia\bar{3}$ (Cox, 1956) or tetragonal, space group $P\bar{4}c2$ ($Z = 2$) (Bode & von Döhren, 1958). KSbF₆ has been reported to possess the same structure as cubic KNbF₆ and KTaF₆ (Bode & Voss, 1951). The structures and space groups of these compounds have not been established unambiguously since the reported structures are based primarily on the positions of the heavy atoms. It was also shown that the powder pattern of KSbF₆ (I), which is stable above $\sim 16^\circ\text{C}$, can be fully indexed on the basis of a tetragonal unit cell, but the correct space group could

not be convincingly established (Heyns & Pistorius, 1976). In the same study, low-temperature KSbF₆ (II) was reported to be cubic.

Crystals of KSbF₆ (I) were obtained by recrystallization of a commercial sample of KSbF₆ from a methanol solution at 30°C . A multi-faceted, roughly spherical crystal with a diameter of 0.28 mm was used. Accurate cell parameters were determined and intensities collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The intensities were collected in the ω – 2θ scan mode over a scan width of 1.5° in θ and at a scan rate of 0.05° s^{-1} . A unique set of 282 reflexions with a maximum $\sin \theta/\lambda$ of 0.7 was measured of which 53 were considered to be unobserved with $I < 1.650\sigma(I)$. The background was counted for half the total scanning time on each side of a reflexion. Lorentz–polarization and absorption corrections for a spherical crystal were applied.

The apparent systematic absences: $0kl$ for $l = 2n + 1$ indicated space groups $P\bar{4}c2$, $P4cm$ and $P4_2/mcm$. Closer inspection of the $0kl$ reflexions revealed, however, that they are definitely not systematically absent when l is odd. Several $0kl$ and $00l$ reflexions, although very weak, were clearly discernible above background, especially when the scans were traced on a recorder. The possible space groups with Laue symmetry $4/mmm$ and no systematic absences are: $P4/mmm$, $P422$, $P4mm$, $P\bar{4}m2$ and $P\bar{4}2m$.

Crystal-packing considerations were used to deter-

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