Preparation and X-ray crystal structures of the first radical cation salts of 4-iodotetrathiafulvalene: $[\mathrm{ITTF}^{\cdot +}]_2\cdot\{\mathrm{Pd}[\mathrm{S_2C_2(CN)_2}]_2\}^{2-}$ and $\mathrm{ITTF}^{\cdot +}\mathrm{HSO_4}^{-}$

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The title radical ion salts of 4-iodotetrathiafulvalene **1** have been prepared and their X-ray crystal structures determined at 150 K. The 2:1 salt $[\mathrm{ITTF}^{\cdot +}]_2\cdot\{\mathrm{Pd}[\mathrm{S_2C_2(CN)_2}]_2\}^{2-}$ **3** forms a mixed stack structure in which the $\mathrm{Pd(mnt)_2}$ anions intermingle with pairs of iodo-TTF radical cations, *i.e.* a DDADDA stacking arrangement. The structure of the 1:1 salt $\mathrm{ITTF}^{\cdot +}\ \mathrm{HSO_4}^{-}$ **4** comprises stepped stacks of ITTF cations with two alternating modes of overlap. Between the cation stacks there are infinite chains of hydrogensulfate anions, linked by hydrogen bonds. Both structures are characterised by short intermolecular contacts involving the iodine substituent.

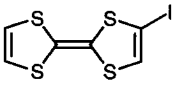
Within the field of molecular conductors,[1] the control of intermolecular interactions in the solid state by chemical modification is a challenging topic, and the pivotal role played by chalcogen atoms is well established. It is widely recognised within solid-state chemistry that halogen atoms can participate in relatively strong and directional intermolecular interactions, thereby providing an effective means of 'crystal engineering'.[2] In this context, halogenated derivatives of tetrathiafulvalene (TTF), ethylenedithio-TTF (EDT-TTF) and ethylenedithio-diselenadithiafulvalene (EDT-DSDTF) are emerging as new π-electron donors in the search for TTF-based radical cation salts and charge-transfer complexes which possess increased dimensionality.[3]

Although a range of halogenated derivatives of TTF have been synthesised in several laboratories,[4] to date, only one radical cation salt has been well characterised, *viz.* an insulating 1:1 iodide salt of tetraiodo-TTF, the X-ray crystal structure of which has been reported recently.[4e] The X-ray crystal structures of a few radical ion salts of halogenated EDT-TTF and EDT-DSDTF derivatives are known,[5] and some are molecular semiconductors {*e.g.* a $[\mathrm{Pd(dmit)_2}]$[5a] and a $\mathrm{ClO_4}$ salt}[5c] and these structures are characterised by relatively strong interactions between the halogen substituent and the anions.

It is known that halogenation of the TTF skeleton raises the oxidation potential significantly[4] (as would be expected for the attachment of electron-withdrawing substituents). Therefore, we directed our attention to monohalogeno-TTFs,[4b] and we considered iodine to be the most promising substituent for participating in intermolecular interactions, as it is more polarisable than the other halogens. Herein we report the preparation and X-ray crystal structures of the first radical cation salts of 4-iodo-TTF **1**.

Results and Discussion

4-Iodo-TTF **1** was synthesised by halogenation of 4-tetrathiafulvalenyllithium using perfluorohexyl iodide, as reported by Becker *et al.*[4c] This halogenating reagent is more efficient than tosyl iodide which we had used previously.[4b] The 2:1 salt $[\mathrm{ITTF}^{\cdot +}]_2\cdot\{\mathrm{Pd}[\mathrm{S_2C_2(CN)_2}]_2\}^{2-}$ **3** was obtained as black crystals by mixing compound **1** and $\mathrm{K}^{+}\{\mathrm{Pd}[\mathrm{S_2C_2(CN)_2}]_2\}^{-}$ **2** in acetone. The 1:1 salt $\mathrm{ITTF}^{\cdot +}\mathrm{HSO_4}^{-}$ **4** was obtained by electrochemical oxidation of donor **1** under constant current in acetonitrile containing sulfuric acid. Remarkably, the same hydrogensulfate salt **4** was obtained during attempts to obtain a perchlorate salt by electrocrystallisation in acetonitrile in the presence of tetrabutylammonium perchlorate as supporting electrolyte. In these experiments the $\mathrm{HSO_4}^{-}$ anion must be derived from residual sulfuric acid which had been used for washing the electrodes prior to the electrocrystallisation.



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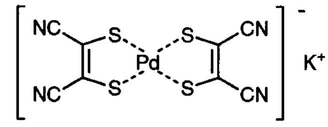

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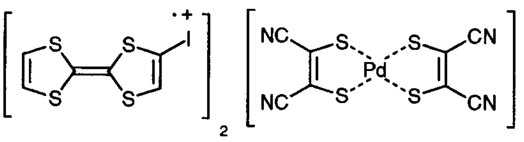

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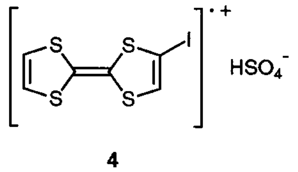

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The asymmetric unit of the crystal structure of salt **3** comprises one $\mathrm{ITTF}^{\cdot +}$ radical cation (in a general position) and a half of a $[\mathrm{Pd(mnt)_2}]^{2-}$ anion located at an inversion centre (Fig. 1, Table 1); both moieties are nearly planar. The

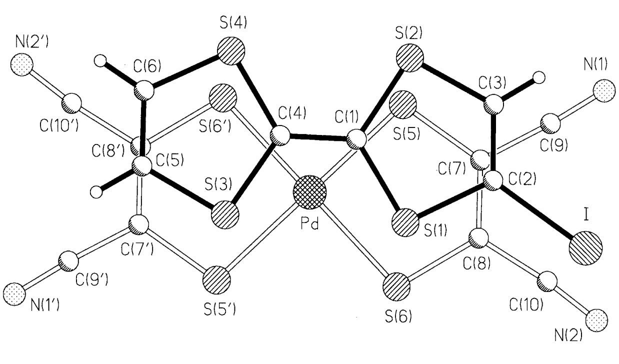

Fig. 1 ITTF and $\mathrm{Pd(mnt)_2}$ ions in the crystal structure of **3**, projected on their planes

Table 1 Selected bond distances (Å) in the structures of **3** and **4**

	3		**3**	**4**
Pd—S(5)	2.302(4)	C(1)—C(4)	1.38(2)	1.392(7)
Pd—S(6)	2.288(4)	C(1)—S(1)	1.72(1)	1.731(5)
S(5)—C(7)	1.72(2)	C(1)—S(2)	1.74(2)	1.735(5)
S(6)—C(8)	1.73(2)	S(1)—C(2)	1.77(2)	1.738(5)
C(7)—C(8)	1.39(2)	S(2)—C(3)	1.73(2)	1.735(5)
	4	C(2)—C(3)	1.35(2)	1.344(7)
S(5)—O(1)	1.443(4)	C(2)—I	2.06(2)	2.083(5)
S(5)—O(2)	1.519(4)	C(4)—S(3)	1.72(2)	1.723(5)
S(5)—O(3)	1.521(3)	C(4)—S(4)	1.737(14)	1.724(5)
S(5)—O(4)	1.444(3)	S(3)—C(5)	1.74(2)	1.724(5)
		C(5)—C(6)	1.34(2)	1.337(8)

radical cations form a dimer with an interplanar separation of 3.4 Å. These dimers intermingle with $[\mathrm{Pd(mnt)_2}]^{2-}$ anions to form a mixed DDADDA stack parallel to the $[1\ \bar{1}\ 0]$ crystallographic direction (Fig. 2). The cation and anion planes in the stack form a dihedral angle of 9° with an average interplanar separation of 3.6 Å. Short contacts (S···S 3.67–3.73 Å and S···I 3.81 Å) between cations and anions of different stacks join the stacks into layers parallel to the (0 0 1) plane (Fig. 3). A nearly linear C—I···N—C interlayer contact [I···N(2) 3.04 Å] is remarkably shorter than the sum of van der Waals radii (3.65 Å),[6] even after the correction for asphericity of the iodine atom (3.36 Å).[7]

The asymmetric unit of salt **4** comprises an ITTF$^{\cdot+}$ radical cation and a $\mathrm{HSO_4}^-$ anion (Fig. 4, Table 1). Almost planar cations form a stair-like stack with two alternating kinds of overlap: (i) between two TTF moieties with a lateral shift of *ca.* 0.5 Å, and (ii) between substituted dithiole rings only; the interplanar separations are 3.33 and 3.40 Å, respectively. Parallel to this stack, *i.e.* in the direction of the crystallographic axis *y*, runs a chain of hydrogensulfate anions, linked by strong hydrogen bonds O(2)···O(2′) 2.555(7) and O(3)···O(3′) 2.627(7) Å. Both of these bonds are crystallographically centrosymmeric. In the former bond the hydrogen atom was found to be disordered over two positions, corresponding to (asymmetric) distances O—H 0.8(1) and H···O 1.9(1) Å. In the latter bond the only peak of electron density was located at the inversion centre, implying a truly symmetrical bond. Although both H atoms were successfully refined, the reliability of this result is limited. The anion–cation contacts I···O(4) 2.92 (C—I—O 168°) and S(3)···O(2) 2.82 Å are substantially shorter than the sums of the van der Waals radii (3.5 and 3.2 Å, or if corrected for ellipsoidal shape of the I and S atoms, 3.16 and 3.00 Å, respectively),[6,7] and imply significant polarisation of the 'soft' I or S atoms. On the other hand, the H(3)···O(1) and H(6)···O(1) contacts of 2.19(5) and 2.24(6) Å can be regarded as hydrogen bonds. Thus, the anionic chain contributes significantly to the close packing of cations.

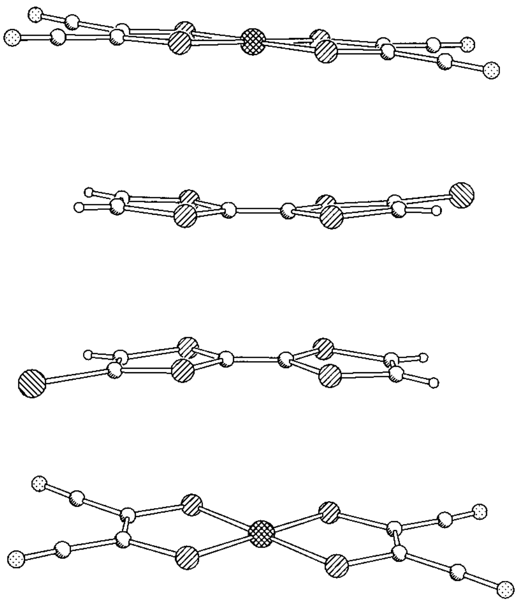

Fig. 2 Stack of ions in the structure of **3**

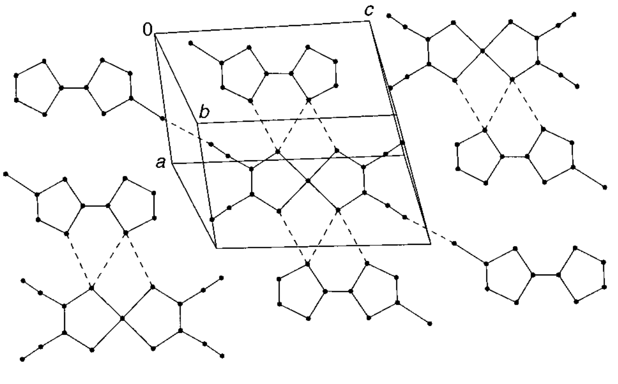

Fig. 3 Interstack contacts in the structure of **3**; projection on the (1 $\bar{1}$ 0) plane

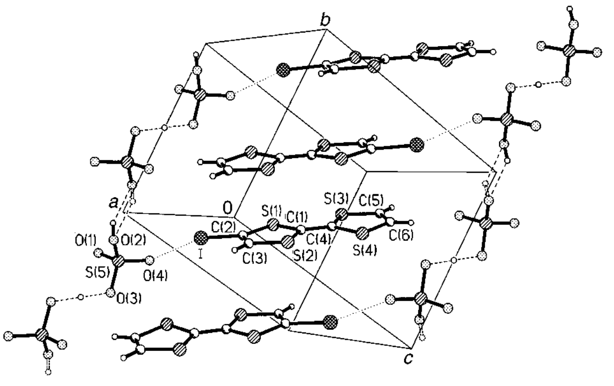

Fig. 4 Crystal structure of **4**, showing hydrogen bonds (dashes), the disorder of the H atom in the O(2)HO(2′) bond, and short contacts (dots)

The geometry of the ITTF moieties in **3** and **4** clearly characterises them as radical cations. The elongation of the central C=C bond distance is usually the most sensitive indicator of the degree of charge transfer. These bonds in **3** [1.38(2) Å] and **4** [1.392(7) Å] are significantly longer than in neutral **1** [1.34(1) Å][4c] and in two polymorphs of pure TTF [1.349(3)[8a] and 1.337(4)[8b] Å]. They are also marginally longer than in radical cation salts with 'soft' anions, such as $\mathrm{I_4TTF^{\cdot+}I^-}$ [1.369(4) Å],[4e] and close to the distances in the salts with strongly electronegative counter ions and complete charge transfer (1.39–1.40 Å).[9] A linear relation $b = 1.757 - 0.0385\delta$ has been suggested recently[10] between the mean length (*b*) of the four C—S bonds adjacent to the central C=C bond and the degree of charge transfer δ. For $b = 1.730(8)$ Å in **3** and 1.728(5) Å in **4**, this formula gives $\delta = 0.7(2)$ and 0.75(13), respectively.

Both salts **3** and **4** exhibit low conductivity values [$\sigma_{\mathrm{rt}} = 2\times10^{-6}$ S cm^{-1} (four-probe compressed pellet measurement) and 5×10^{-7} S cm^{-1} (two-probe, single-crystal measurement) respectively]. Preliminary static susceptibility data on a small polycrystalline sample of salt **3** over the temperature range 300–4 K suggest that the material behaves as a one-dimensional Heisenberg antiferromagnet with an isotropic nearest neighbour exchange interaction, $J \approx 50$ K, consistent with the Bonner–Fischer model.[11] These magnetic data are qualitatively similar to those of many linear chain charge-transfer compounds studied previously,[12] including the salt $\mathrm{I_4TTF^{\cdot+}\cdot I^-}$.[4e]

Conclusions

The first radical ion salts of the electron donor molecule ITTF **1** have been prepared, and the X-ray crystal structures of the title salts establish that the iodine substituent participates to a significant extent in intermolecular interactions. These results, combined with those recently obtained by other workers,[4e,5a–c] auger well for the use of halogenated TTF derivatives in the synthesis of new charge-transfer materials, in which the solid state structure can be modified by intermolecular and interstack interactions involving polarisable halogen atoms.

Experimental

Preparation of $[\mathrm{ITTF}^{\cdot +}]_2\cdot\{\mathrm{Pd}[\mathrm{S_2C_2(CN)_2}]_2\}^{2-}$ 3

Method 1. 4-Iodo-TTF **1**[4c] (7 mg, 0.021 mmol) and $K^+\{Pd[S_2C_2(CN)_2]_2\}^-$ **2** (15 mg, 0.035 mmol) were each dissolved in separate portions of dry acetone (10 ml) and placed in the outer compartments of a three-compartment diffusion cell. The central section was filled with dry acetone (10 ml) and separated from the outer compartments by porous glass frits. After 13 days, black crystals of complex **3** (2 mg, 18%) suitable for X-ray analysis were collected from the central compartment and washed with acetone.

Method 2. 4-Iodo-TTF **1** (13 mg, 0.038 mmol) and $K[Pd(mnt)_2]$ (28 mg, 0.068 mmol) were each dissolved in dry acetone (10 ml) and the solutions mixed, affording immediately a black precipitate which was collected by filtration, washed with cold acetone and dried to afford complex **3** (8 mg, 40%) as a fine black powder. Analysis: found C, 22.80; H, 0.90; N, 5.38; S, 36.51; $C_{20}H_6I_2N_4PdS_{12}$ requires C, 22.84; H, 0.57; N, 5.35; S, 36.71%.

Preparation of $\mathrm{ITTF}^{\cdot +}\mathrm{HSO_4}^-$ 4

4-Iodo-TTF **1** (11 mg, 0.033 mmol) was dissolved in dry, degassed acetonitrile (25 ml) containing 0.02 ml of concentrated sulfuric acid and placed in the anode compartment of a 50 ml H-shaped electrocrystallisation cell. In the cathode compartment, separated from the anode compartment by a porous glass frit, was placed dry, degassed acetonitrile (25 ml) containing 0.02 ml of concentrated sulfuric acid. A constant current of 1 μA was passed through the cell for 10 days. Black crystals of complex **4** (10 mg, 71%) were harvested from the anode, and were also collected from the walls of the anode compartment. Analysis: found C, 17.01; H, 0.85; S, 35.32; $C_{20}H_6N_4S_{12}I_2$ requires C, 16.86; H, 0.94; S, 37.47%.

X-Ray crystallography

Single-crystal X-ray diffraction experiments for **3** and **4** were carried out at $T = 150$ K on a Siemens three-circle diffractometer, equipped with a CCD area detector (graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, ω-scan mode, semi-empirical absorption correction on Laue equivalents) and an Oxford Cryosystems open-flow N_2 gas cryostat. The structures were solved by Patterson (**3**) and direct (**4**) methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[13] Non-H atoms were refined anisotropically; all H atoms in **4** were refined in isotropic approximation, in **3** were treated as 'riding'. Crystal data and experimental details are listed in Table 2; atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/27.

Table 2 Crystal data

compound	**3**	**4**
formula	$C_{20}H_6I_2N_4PdS_{12}$	$C_6H_4IO_4S_5$
M	1047.21	427.29
symmetry	triclinic	triclinic
a/Å	7.667(1)	8.145(1)
b/Å	8.577(1)	8.242(1)
c/Å	11.638(2)	9.916(1)
α/degrees	74.42(1)	99.17(1)
β/degrees	88.38(1)	100.98(1)
γ/degrees	86.64(1)	104.75(1)
U/Å^3	735.9(2)	616.5(1)
space group	$P\bar{1}$	$P\bar{1}$
Z	1	2
μ/cm^{-1}	36.0	34.4
D_c/g cm^{-3}	2.36	2.30
crystal size/mm	0.02 × 0.2 × 0.25	0.11 × 0.2 × 0.3
$2\theta_{max}$/degrees	50.5	51
data total	3126	2718
data unique	2227	1948
data observed, $I > 2\sigma(I)$	1745	1909
R_{int}[a]	0.101, 0.060	0.092, 0.027
transmission min, max	0.67, 1.00	0.46, 0.85
no. of variables	178	162
$wR(F^2)$, all data	0.223	0.081
goodness-of-fit	1.56	1.12
$R(F)$, obs. data	0.078	0.029
$\Delta\rho_{max}$/e Å^{-3}	2.4	0.79
$\Delta\rho_{min}$/e Å^{-3}	−2.2	−1.03

[a] Before and after the absorption correction.

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References

1 Reviews: (*a*) M. R. Bryce, *Chem. Soc. Rev.*, 1991, **20**, 355; (*b*) A. E. Underhill, *J. Mater. Chem.*, 1992, **2**, 1; (*c*) *J. Mater. Chem.*, Special Issue on Molecular Conductors, 1995, **5**(**10**), 1469–1760.

2 G. R. Desiraju, *Crystal Engineering, The Design of Organic Solids*, Elsevier, Amsterdam, 1989, ch. 6.

3 For reviews which focus on increased dimensionality in TTF materials, see: (*a*) M. Adam and K. Müllen, *Adv. Mater.*, 1994, **6**, 439; (*b*) M. R. Bryce, *J. Mater. Chem.*, 1995, **5**, 1481.

4 For leading references, see: (*a*) M. Jorgensen and K. Bechgaard, *Synthesis*, 1989, 207; (*b*) M. R. Bryce and G. Cooke, *Synthesis*, 1991, 263; (*c*) C. Wang, A. Ellern, V. Khodorkovsky, J. Bernstein and J. Y. Becker, *J. Chem. Soc., Chem. Commun.*, 1994, 983; (*d*) C. Wang, J. Y. Becker, J. Bernstein, A. Ellern and V. Khodorkovsky, *J. Mater. Chem.*, 1995, **5**, 1559; (*e*) R. Gompper, J. Hock, K. Polborn, E. Dormann and H. Winter, *Adv. Mater.*, 1995, **7**, 41.

5 (*a*) T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1995, 1097; (*b*) T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1995, 1667; (*c*) M. Iyoda, H. Suzuki, S. Sasaki, H. Yoshino, K. Kikuchi, K. Saito, I. Ikemoto, H. Matsuyama and T. Mori, *J. Mater. Chem.*, 1996, **6**, 501.

6 A. Gavezzotti, *J. Am. Chem. Soc.*, 1983, **105**, 5220.

7 S. C. Nyburg and C. H. Faerman, *Acta Crystallogr., Sect. B*, 1985, **41**, 274.

8 (*a*) W. F. Cooper, J. W. Edmonds, F. Wudl and P. Coppens, *Cryst. Struct. Commun.*, 1974, **3**, 23; (*b*) A. Ellern, J. Bernstein, J. Y. Becker, S. Zamir, L. Shahal and S. Cohen, *Chem. Mater.*, 1994, **6**, 1378.

9 (*a*) P. Batail, C. Livage, S. S. P. Parkin, C. Coulon, J. D. Martin and E. Canadell, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1498; (*b*) P. Erk, S. Hünig, G. Klebe, M. Krebs and J. U. von Schütz, *Chem. Ber.*, 1991, **124**, 2005; (*c*) G. Matsubayashi, K. Ueyama and T. Tanaka, *J. Chem. Soc., Dalton Trans.*, 1985, 465; (*d*) T. Iamakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.*, 1995, 1097.

10 D. A. Clemente and A. Marzotto, *J. Mater. Chem.*, 1996, **6**, 941.

11 J. C. Bonner and M. E. Fischer, *Phys. Rev. A*, 1964, **135**, 640.

12 (*a*) J. B. Torrance in *Low-Dimensional Conductors and Superconductors*, ed. D. Jérome and L. G. Caron, *NATO ASI Ser. B*, 1987, **165**, 113; (*b*) S. D. Obertelli, R. H. Friend, D. R. Talham, M. Kurmoo and P. Day, *J. Phys., Condens. Matter*, 1989, **1**, 5671.

13 G. M. Sheldrick, SHELXTL, Version 5, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA, 1995.

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