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'Core and sheath' structure of a TTF complex forming a square grid

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The crystal structure of the pentakis(methoxycarbonyl)cyclopentadienide salt of tetrathiafulvalene is reported. It is found to have a novel two-dimensional structure in the form of a square grid. The grid is formed out of TTF stacks running in orthogonal directions; the TTF stacks form a core structure with the counterions providing a sheath around them. DC conductivity measurements on single crystals reveal the anisotropy expected of this unusual two-dimensional packing motif.

Introduction

Since the discovery of metallic conductivity in the tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) complex in 1973,[1] several classes of organic charge transfer complexes, ion-radical salts and conjugated polymers have been investigated which show electrical properties ranging from semiconduction to superconductivity. Planar organic molecules possessing delocalised π-electrons with good electron donating or accepting capabilities are the prime candidates for molecular conducting materials. The growth of the number of organic donors and acceptors which form molecular conductors has been phenomenal. However the single largest family of organic conductors is still based on TTF, one of the earliest π-electron donors, its derivatives such as bis(ethylenedithiolato)-TTF (BEDT-TTF) and its heteroatom analogs such as tetramethyltetraselenafulvalene (TMTSF). Several excellent reviews may be consulted for the extensive work published on the TTF family of complexes.[2] The versatility of TTF stems primarily from its unique electronic and structural features such as the electron rich planar π-system, the stability of fractional oxidation states and the d-orbital electrons on the S atoms which enable interstack interactions. A significant factor that has contributed to the singular success of the TTF framework in forming crystalline complexes is the strong tendency it shows towards the formation of stacked structures. Neutral TTF itself has a stacked structure and a second polymorph discovered some years ago has been found to have a chain structure.[3] The exponential growth in the number of structurally characterised complexes in the TTF family is revealed by a search of the Cambridge Crystallographic Database;[4] the recent update records 136 entries involving the parent TTF and 1003 entries for systems based on donors containing the TTF fragment.

TTF forms charge transfer and ion-radical complexes with a wide variety of molecules and counterions. The counterions are simple inorganic anions such as halides,[5–7] nitrate[8] or thiocyanate,[9] transition metal complexes,[10,11] organometallics[12,13] and so on. Charge transfer complexes with a large number of π-electron acceptors have been investigated and structurally characterised; some examples may be found in Refs. 14–17. Examination of the crystal structures of the TTF salts and complexes reveals a wide range of packing motifs with a predilection towards π-stacking. The regular segregated stacked structure found in many systems[9,11,18–20] including the prototypical case of TTF–TCNQ[14] is most conducive to metallic conduction. Effects such as Peierl's distortion[21] often lead to dimerised[22,23] or trimerised[12,24,25] segregated stack structures; there is even an example with a pentamerised stack of TTF.[26] Though uninteresting from the point of view of conducting materials, several TTF complexes show mixed stacking incorporating the counterions in the TTF stack.[27–31] There exist also TTF complexes where isolated monomeric,[11,17] dimeric[13,32] or trimeric[33,34] TTF's are present.

A survey of these structural variations manifested by TTF complexes suggests that TTF based systems provide fertile ground to probe for novel stacking patterns. Strongly one-dimensional structures are prone to low temperature instabilities such as Peierl's distortion that lead to metal–semiconductor phase transition. From the point of view of stabilising the metallic state in molecular conductors two- and three-dimensional structural motifs are important. Hence exploration of the crystal structures of new TTF complexes continues to be a fruitful exercise. Examination of the known structures of TTF complexes indicates that the counterions are mostly either planar organic ion radicals or transition metal complexes which themselves show a tendency to stack. In several cases the counterions are inorganic ions, many of which, especially the linear ones, tend to form polymeric chains. It appeared to us that planar diamagnetic counterions which do not show any stacking tendency of their own might lead to novel stacking patterns in TTF complexes. Cyclopentadienyl anion would be one such case.

We present in this paper, analysis of the crystal structure of the pentakis(methoxycarbonyl)cyclopentadienide (PMC^-) salt of TTF^+. $(TTF)_3(PMC)_2$ complex was originally prepared in connection with the superexchange model for organic ferromagnetism.[35] This complex is found to have an unusual two-dimensional structure wherein trimerised segregated stacks of TTF run in orthogonal directions forming a square grid. The counterions form a sheath structure around the core of TTF stacks. The trimerisation leads to low conductivity; however, the grid structure gives rise to the interesting conductivity anisotropy, $\sigma_{\parallel} \sim \sigma_{\parallel}' > \sigma_{\perp}$.

Experimental

Synthesis

The potassium salt of pentakis(methoxycarbonyl)cyclopentadienide (PMC^-) was prepared following the procedure reported in Ref. 36. The silver salt of PMC^- was formed by treating the potassium salt with excess of silver nitrate in aqueous solution, evaporating off the water and extracting in chloroform followed by precipitation with hexane addition. TTF was reacted with AgPMC in hot acetonitrile. The solution turned dark reddish, indicating the formation of TTF^+, and a black precipitate of silver formed. The silver was carefully filtered out and the solution cooled. Black platelets of $(TTF)_3(PMC)_2$ which separated out were filtered, washed with cold acetonitrile and dried under vacuum. Elemental analysis (calculated for $C_{48}H_{42}S_{12}O_{20}$): C 43.49 (43.56), H 2.85 (3.19)%.

Conductivity measurement

DC conductivity of single crystals of $(TTF)_3(PMC)_2$ was measured at room temperature using the two-probe method. Thin wires were attached to single crystals of approximate dimensions $1.5 \times 0.8 \times 0.3$ mm using silver paint, along the appropriate axes. Constant current in the range 0.1–1.0 μA was passed using a Keithly Model 224 Constant Current Source and the voltage drop was measured using a Keithly Model 175 Multimeter. The ohmic nature of the conductivity was verified.

Crystal structure analysis

Crystal structure data were collected on an Enraf–Nonius MACH3 diffractometer. MoKα ($\lambda = 0.71073$ Å) radiation with a graphite crystal monochromator in the incident beam was used. Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found using the direct method analysis in SHELX-97.[37] The S and O atoms were refined anisotropically whereas the C atoms were refined isotropically. After several cycles of refinements the positions of the hydrogen atoms were calculated and added to the refinement process. Refinement proceeded to convergence by minimising the function, $\Sigma w\,(|F_o| - |F_c|)^2$. Experimental crystal density was determined by the flotation method.

Results and discussion

The composition of the complex was found to be $(TTF)_3(PMC)_2$ based on elemental analysis. Stoichiometries like $(TTF)_3X_2$ with X being a monoanion[38,39] and $(TTF)_3X$ with X being a dianion[24,32–34] are quite well known among TTF complexes. The stoichiometry implies an average partial ionicity of +0.67 on TTF which leads to metallic conductivity as in the case of $TTFCl_{0.67}$[5] and $TTF(SCN)_{0.67}$.[39] However, in several cases trimerised TTF stacks are formed with concomitant localisation of charge and reduced conductivity. The crystal structure analysis of $(TTF)_3(PMC)_2$ indicates that it belongs to the latter case. The crystallographic data are collected in Table 1. The significant bond lengths and angles are presented in Table 2. The asymmetric unit consists of three TTF molecules shown in Fig. 1(a) and two PMC^- shown in Fig. 1(b). The TTF molecules **A** and **B** almost eclipse each other and **B** and **C** are nearly in the 'ring-over-bond' conformation. The molecules are almost flat and parallel with an average interplanar angle of 2.4° between **A** and **B** and 2.8° between **B** and **C**. The average interplanar distance between **A** and **B** is 3.435 Å and that between **B** and **C** is 3.427 Å; these distances are slightly shorter than the interplanar distance of 3.47 Å in TTF-TCNQ.[14] The shortest S···S distance between **A** and **B** is 3.335 Å and that between **B** and **C** is 3.659 Å. The

Table 1 Crystallographic data for $(TTF)_3(PMC)_2$

Chemical formula	$C_{48}H_{42}O_{20}S_{12}$
Formula weight	1323.54
Crystal system	Monoclinic
Space group	*Cc*
a/Å	16.017(10)
b/Å	14.307(12)
c/Å	25.091(8)
α/°	90.0
β/°	92.11(3)
γ/°	90.0
$V/Å^3$	5746(6)
T/K	293
Z	4
μ/cm^{-1}	5.3 (MoKα)
ρ_{calc}/g cm^{-3}	1.530
ρ_{meas}/g cm^{-3}	1.559
Number of reflections measured	5029
Number of independent reflections	5029
Number of reflections with $I > 2\sigma_I$	2562
Number of parameters	490
R	0.0514
wR^2	0.1247

Table 2 Significant bond lengths and bond angles in $(TTF)_3(PMC)_2$ from single crystal X-ray analysis (atom labelling is shown in Fig. 1)

Bond	Length/Å	Bond	Length/Å
S(1)–C(13)	1.728(12)	C(19)–C(20)	1.34(2)
S(1)–C(19)	1.733(15)	C(21)–C(22)	1.329(19)
S(2)–C(20)	1.704(15)	C(23)–C(24)	1.30(2)
S(2)–C(13)	1.721(12)	C(25)–C(26)	1.32(2)
S(3)–C(14)	1.704(14)	C(27)–C(28)	1.33(2)
S(3)–C(21)	1.721(14)	C(29)–C(30)	1.34(2)
S(4)–C(14)	1.723(13)	C(31)–C(32)	1.397(17)
S(4)–C(22)	1.734(15)	C(31)–C(35)	1.417(17)
S(5)–C(23)	1.717(16)	C(31)–C(41)	1.460(18)
S(5)–C(15)	1.755(14)	C(32)–C(33)	1.406(17)
S(6)–C(24)	1.716(17)	C(32)–C(42)	1.452(18)
S(6)–C(15)	1.758(14)	C(33)–C(34)	1.416(17)
S(7)–C(25)	1.721(15)	C(33)–C(43)	1.488(18)
S(7)–C(16)	1.764(14)	C(34)–C(35)	1.396(18)
S(8)–C(16)	1.728(14)	C(34)–C(44)	1.477(19)
S(8)–C(26)	1.725(17)	C(35)–C(45)	1.508(19)
S(9)–C(27)	1.702(17)	C(36)–C(40)	1.390(16)
S(9)–C(17)	1.730(14)	C(36)–C(37)	1.391(16)
S(10)–C(17)	1.709(15)	C(36)–C(46)	1.498(16)
S(10)–C(28)	1.720(17)	C(37)–C(38)	1.395(18)
S(11)–C(18)	1.725(14)	C(37)–C(47)	1.434(19)
S(11)–C(29)	1.735(17)	C(38)–C(39)	1.431(17)
S(12)–C(30)	1.707(15)	C(38)–C(48)	1.497(19)
S(12)–C(18)	1.703(14)	C(39)–C(40)	1.411(16)
C(13)–C(14)	1.389(17)	C(39)–C(49)	1.438(17)
C(15)–C(16)	1.345(17)	C(40)–C(50)	1.512(16)
C(17)–C(18)	1.385(18)		

Bond–bond	Angle/°	Bond–bond	Angle/°
C(13)–S(1)–C(19)	95.1(7)	C(26)–C(25)–S(7)	116.7(13)
C(20)–S(2)–C(13)	96.0(7)	C(25)–C(26)–S(8)	119.6(13)
C(14)–S(3)–C(21)	95.0(6)	C(28)–C(27)–S(9)	116.8(14)
C(14)–S(4)–C(22)	94.7(7)	C(27)–C(28)–S(10)	117.8(14)
C(23)–S(5)–C(15)	94.1(7)	C(30)–C(29)–S(11)	116.4(13)
C(24)–S(6)–C(15)	93.6(8)	C(29)–C(30)–S(12)	117.5(13)
C(25)–S(7)–C(16)	94.7(7)	C(32)–C(31)–C(35)	107.3(11)
C(16)–S(8)–C(26)	94.0(7)	C(32)–C(31)–C(41)	127.3(11)
C(27)–S(9)–C(17)	95.5(8)	C(35)–C(31)–C(41)	125.4(12)
C(17)–S(10)–C(28)	94.9(8)	C(33)–C(32)–C(31)	108.5(11)
C(18)–S(11)–C(29)	94.8(7)	C(33)–C(32)–C(42)	124.3(11)
C(30)–S(12)–C(18)	95.7(7)	C(31)–C(32)–C(42)	127.1(11)
C(14)–C(13)–S(2)	122.7(9)	C(32)–C(33)–C(34)	108.0(11)
C(14)–C(13)–S(1)	122.6(9)	C(32)–C(33)–C(43)	125.3(11)
S(2)–C(13)–S(1)	114.6(7)	C(34)–C(33)–C(43)	126.4(11)
C(13)–C(14)–S(3)	123.5(10)	C(35)–C(34)–C(33)	107.3(11)
C(13)–C(14)–S(4)	120.4(10)	C(35)–C(34)–C(44)	126.8(12)
S(3)–C(14)–S(4)	115.9(7)	C(33)–C(34)–C(44)	125.9(12)
C(16)–C(15)–S(5)	123.5(10)	C(34)–C(35)–C(31)	108.9(11)
C(16)–C(15)–S(6)	122.2(10)	C(34)–C(35)–C(45)	122.2(12)
S(5)–C(15)–S(6)	114.2(8)	C(31)–C(35)–C(45)	128.9(12)
C(15)–C(16)–S(8)	124.4(10)	C(40)–C(36)–C(37)	109.5(10)
C(15)–C(16)–S(7)	120.6(10)	C(40)–C(36)–C(46)	123.8(10)
S(8)–C(16)–S(7)	115.0(8)	C(37)–C(36)–C(46)	125.9(11)
C(18)–C(17)–S(10)	123.4(11)	C(38)–C(37)–C(36)	108.0(11)
C(18)–C(17)–S(9)	121.5(11)	C(38)–C(37)–C(47)	124.9(12)
S(10)–C(17)–S(9)	115.0(8)	C(36)–C(37)–C(47)	127.0(12)
C(17)–C(18)–S(12)	122.6(11)	C(37)–C(38)–C(39)	107.7(11)
C(17)–C(18)–S(11)	121.7(10)	C(37)–C(38)–C(48)	123.7(12)
S(12)–C(18)–S(11)	115.7(8)	C(39)–C(38)–C(48)	128.3(12)
C(20)–C(19)–S(1)	116.8(12)	C(40)–C(39)–C(38)	107.1(11)
C(19)–C(20)–S(2)	117.4(12)	C(40)–C(39)–C(49)	128.0(11)
C(22)–C(21)–S(3)	117.7(12)	C(38)–C(39)–C(49)	124.8(11)
C(21)–C(22)–S(4)	116.5(12)	C(36)–C(40)–C(39)	107.6(10)
C(24)–C(23)–S(5)	118.2(14)	C(36)–C(40)–C(50)	125.6(10)
C(23)–C(24)–S(6)	119.4(14)	C(39)–C(40)–C(50)	126.7(10)

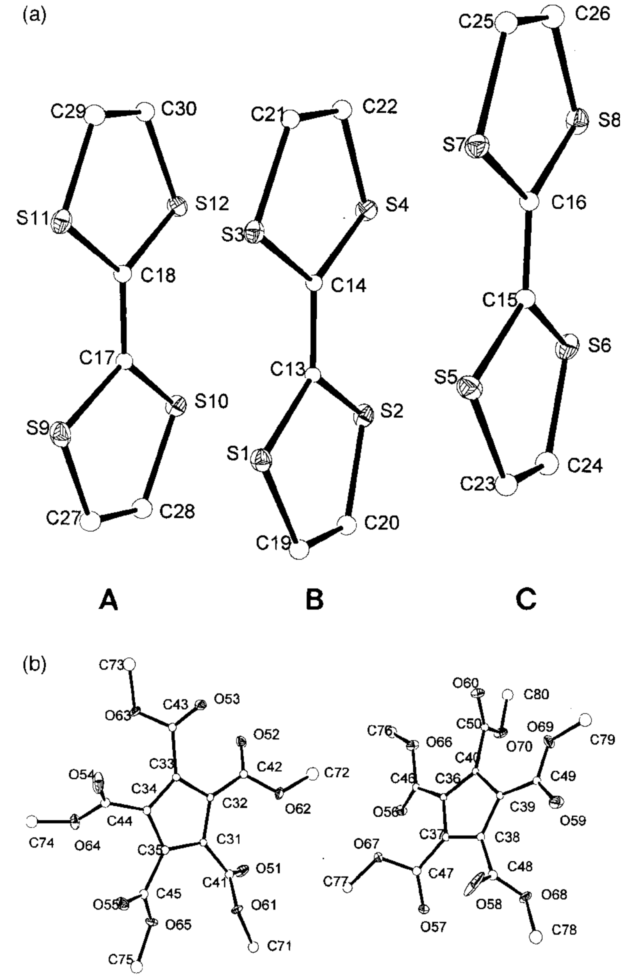


Fig. 1 (a) Molecular structure of the TTF trimer unit in $(TTF)_3(PMC)_2$ from single crystal X-ray analysis showing 10% probability ellipsoids on S atoms which were refined anisotropically. (b) Molecular structure of the PMC dimer unit in $(TTF)_3(PMC)_2$ from single crystal X-ray analysis showing 10% probability ellipsoids on O atoms which were refined anisotropically; H atoms are omitted for clarity.

average interplanar distance between **C** and its neighbouring **A** in the stack is 3.402 Å. The three interplanar distances indicate that the stack deviates only slightly from a regular segregated stacking motif; it is probably best described as a weakly alternating stack of **C**–**A** dimers and **B** (Fig. 2).

The stacking clearly suggests the possibility of localisation of charge along the TTF stack. The lengths of the bridging C–C bond (p), the C–S bond between the bridge C and the S atom (q) and the other C–S bond in the ring (r) found in the three TTF molecules **A**, **B** and **C** in the asymmetric unit are presented in Table 3, along with similar data from several reported crystal structures. By a simple process of minimising the square deviations, it is found that the previous compounds having the closest structural resemblance to **A**, **B** and **C** are TTF-ClO_4, TTF-OCNAQ and TTF respectively. Based on the ionicities of these compounds, we conclude that **A** and **B** are fully ionic with a charge of +1 and **C** is nearly neutral. This charge distribution between the TTF molecules is well accommodated by the stacking pattern (Fig. 2) where the ionic **B** alternates with a dimer formed from ionic **A** and neutral **C**. It is interesting to note that the charge distribution in this trimeric system is different from that found in $(TTF)_3(BF_4)_2$ where the dimerised TTF shares +2 charge and the intervening TTF is neutral.[38]

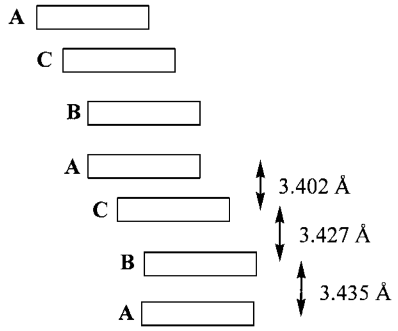
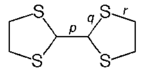


Fig. 2 Schematic representation of the TTF stack in $(TTF)_3(PMC)_2$.

Table 3 Comparison of mean bond lengths[a] p, q and r of TTF in $(TTF)_3(PMC)_2$ with those in some known structures and the ionicity, ρ of TTF in the latter

Complex	p/Å	q/Å	r/Å	ρ	Ref.
TTF	1.349	1.757	1.730	0	3
TTF–CA	1.354	1.751	1.740	~0	31
TTF–FA	1.359	1.750	1.738	~0	31
TTF–TCNQ	1.369	1.743	1.736	0.59	14
TTF–ATO	1.371	1.740	1.729	0.60	40
$(TTF)_3SnCl_6$	1.360	1.735	1.726	0.67	41
TTF–$HgCl_3$	1.41	1.72	1.71	1.0	42
TTF–ClO_4	1.404	1.713	1.725	1.0	43
TTF–OCNAQ	1.392	1.730	1.733	1.0	44
A (Fig. 1)	1.385	1.717	1.716	[b]	This work
B (Fig. 1)	1.389	1.719	1.723	[b]	This work
C (Fig. 1)	1.345	1.751	1.720	[b]	This work

[a] p, q and r are shown in the figure below; values of q and r are the averages over the four symmetry related bonds.



[b] See text.

The packing of the TTF stacks is presented in Fig. 3 and 4. The TTF stacks form layers parallel to the *ab* plane. Fig. 3 shows that the stacks in one layer run along the [110] axis while the stacks in the adjacent layers run in an orthogonal direction, namely [1$\bar{1}$0]. The orthogonality of these stacks

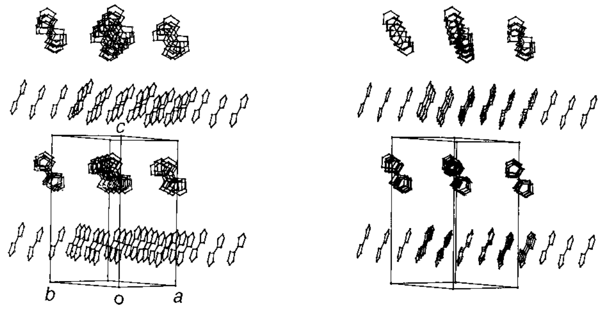


Fig. 3 Stereoview of the TTF stacks in $(TTF)_3(PMC)_2$ along the [110] axis; H atoms are omitted for clarity.

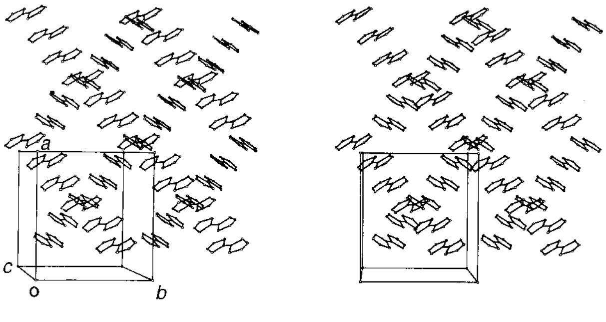


Fig. 4 Stereoview of the TTF stacks in $(TTF)_3(PMC)_2$ along the [001] axis; H atoms are omitted for clarity.

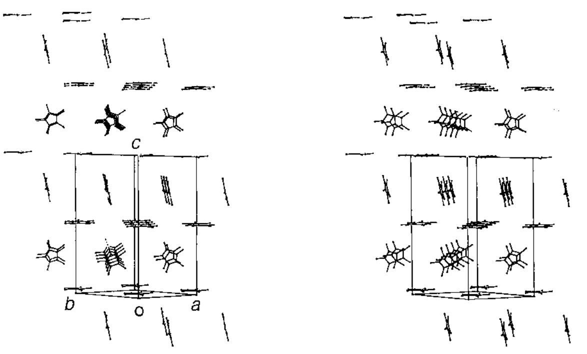


Fig. 5 Stereoview of the packing of PMC ions in $(TTF)_3(PMC)_2$ along the [110] axis; only the pentagonal ring C atoms of PMC ions are shown for clarity.

forming a square grid is clearly revealed by the view along the *c* axis in Fig. 4. The packing of the PMC^- ions is shown in Fig. 5. They form columns running along the [110] and $[1\bar{1}0]$ axes. The spacing between the mean planes of adjacent pentagons within the column is 10.738 Å ruling out any kind of π-stacking. The adjacent columns running in orthogonal directions are separated by a layer of PMC^-. The molecular planes of the PMC^- in the middle layer are oriented perpendicular to the molecular planes of those in the columns. Fig. 5 clearly shows the formation of channels as a result of the packing of PMC^-.

The PMC^- columns running parallel to the TTF stacks and the layer of PMC^- with their molecular planes in a perpendicular orientation together provide a sheath structure around the TTF stacks. Superposition of the core structure of TTF and the sheath structure of PMC^- ions leads to the 'core and sheath' architecture of the $(TTF)_3(PMC)_2$ crystal shown in Fig. 6. Some of the short interatomic distances observed between the core and sheath structures are the following: S1···O68 = 3.117 Å, C19···O68 = 3.122 Å, C22···O58 = 3.200 Å, C26···O60 = 3.264 Å, C24···O70 = 3.266 Å and C21···O58 = 3.275 Å. The sheath of counterions around the TTF stack precludes interstack interactions and the two-dimensional character which normally supports the formation of a metallic state. However, the novel case of TTF stacks running in orthogonal directions in $(TTF)_3(PMC)_2$ leads to a new kind of two-dimensional structural motif.

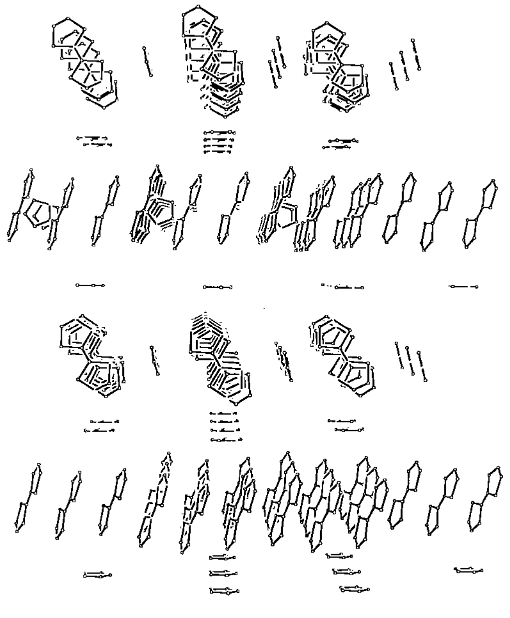


Fig. 6 View of the 'core and sheath' structure of $(TTF)_3(PMC)_2$ along the [110] axis; only the pentagonal ring C atoms of PMC ions are shown for clarity.

The two-dimensional character of the grid network is reflected in the unusual conductivity anisotropy. DC conductivity measurements were carried out on single crystals in the form of rectangular plates. Measurements were made in the $[1\bar{1}0]$ and [110] directions which were found to be along the long and short axes of the rectangular face respectively and in the [001] direction, perpendicular to the rectangular face. The measured values are $\sigma\,[1\bar{1}0] = 1.5\times10^{-5}\ \Omega^{-1}\,cm^{-1}$, $\sigma\,[110] = 4.3\times10^{-6}\ \Omega^{-1}\,cm^{-1}$ and $\sigma\,[001] = 4.1\times10^{-7}\ \Omega^{-1}\,cm^{-1}$. The conductivity anisotropy in the orthogonal directions in the *ab* plane is about 3.5 whereas the anisotropy between the axes in the *ab* plane and the *c* axis are respectively 10 and 36. The semiconducting nature of $(TTF)_3(PMC)_2$ results from the small but definite trimerisation present in the stack. An ESR experiment carried out on a microcrystalline sample of $(TTF)_3(PMC)_2$ showed weak triplet exciton signals. This is consistent with the presence of neighbouring localised TTF^+ radicals in the stack. Since the signals are very weak we have not investigated this further.

Conclusion

We have presented in this paper the unusual square grid structure of $(TTF)_3(PMC)_2$ formed from the TTF stack cores and the PMC^- sheaths. The flat structure of the anions and their non-stacking nature have led to this new packing motif in the TTF complex. The trimerisation observed in the TTF stacks is not very strong. Incorporation of suitable derivatives of Cp^- which support interaction between the cores of TTF stacks, could lead to complexes with similar architecture exhibiting novel two-dimensional metallic conductivity. Investigation of other Cp^- derivatives as counterions for TTF is under consideration.

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Supporting information

Details of crystal structure analysis of $(TTF)_3(PMC)_2$; full listing of atomic coordinates, thermal parameters, bond distances and angles.†

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