

# TTF based charge transfer salts of $[\text{Cr}(\text{NCS})_4(\text{phen})]^-$ : bulk magnetic order and crystal structures of the TTF, TMTTF (tetramethyltetraethiafulvalene) and TMTSF (tetramethyltetraselenafulvalene) derivatives<sup>†</sup>

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A series of new charge transfer salts of electron donors based on tetrathiafulvalene, TTF, with the anion  $[\text{Cr}(\text{NCS})_4(\text{phen})]^-$  (phen = 1,10-phenanthroline) have been prepared. Single crystal X-ray diffraction provided structures for salts with donors TTF, TMTTF, tetramethyltetraethiafulvalene, and TMTSF, tetramethyltetraselenafulvalene. The salts were found to be  $[\text{TTF}][\text{Cr}(\text{NCS})_4(\text{phen})]$  at 293 K,  $[\text{TMTTF}][\text{Cr}(\text{NCS})_4(\text{phen})]\cdot\text{CH}_2\text{Cl}_2$  at 250 K and  $[\text{TMTSF}]_3[\text{Cr}(\text{NCS})_4(\text{phen})]_2\cdot 0.5\text{CH}_2\text{Cl}_2$  at 293 K. For the TMTSF compound the solvent is disordered at 293 K so the structure was also solved at 120 K when the solvent becomes ordered. All of the salts have multiple  $\text{S}\cdots\text{S}$  or  $\text{S}\cdots\text{Se}$  close contacts between the anions and cations. The TTF salt is a bulk ferrimagnet with  $T_c = 9$  K and is an insulator whereas the TMTTF salt is an antiferromagnetic ( $T_N = 3.0$  K) insulator. Both have close atomic interactions of the phen-donor  $\pi$ -stacking type, but the TMTTF salt also contains close anion-anion contacts and dimerised cations whereas the TTF salt consists of stacks of alternating cations and anions. The TMTSF salt is a paramagnetic semiconductor and does not display  $\pi$  stacking but has close inter-donor  $\text{Se}\cdots\text{Se}$  contacts and isolated anions which afford the magnetic and transport properties.

## Introduction

Charge transfer salts of organochalcogenide electron donors are characterised by a wide range of transport properties from insulating and semiconducting to metallic and superconducting.<sup>1</sup> The transport properties can be correlated to the relative positions of the donors which are organised, in part, by their spatial relationships with the counter ions and other included molecules such as solvent.<sup>2-4</sup> Until relatively recently the focus was on their transport properties although contemporary emphasis has been in preparing materials with mixed properties such as conductivity and magnetism. In addition to magnetic effects which arise from the electrons associated with the radical donors, paramagnetic centres are typically introduced *via* a metal complex as the anion component of the salt.<sup>5</sup> The vast majority of the paramagnetic systems of this type contain d-block transition metals with unpaired and localised electron density. For example TTF based salts have been made of anions  $[\text{FeCl}_4]^-$ ,<sup>6</sup>  $[\text{Fe}(\text{CN})_6]^{3-}$ ,<sup>7</sup> Reineckes anion,  $[\text{Cr}(\text{NCS})_4(\text{NH}_4)_2]^{8-}$  and  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ .<sup>9</sup> Charge transfer salts with  $[\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]^{3-}$  include the first molecular superconductor containing paramagnetic transition metal ions,  $\beta''$ -[BEDT-TTF]<sub>4</sub>[H<sub>3</sub>O][Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] $\cdot\text{C}_6\text{H}_5\text{CN}$ <sup>10</sup> where BEDT-TTF = bis(ethylene-dithio)tetrathiafulvalene. We have prepared many variations of this material by, for example, replacing Fe with other metal(III) centres which introduces different magnitudes of paramagnetism.<sup>9</sup> Many groups, including ours, have been engaged in trying to replace  $\text{H}_3\text{O}^+$  with  $\text{M}^{\text{II}}$  which would in theory produce a material that exhibited simultaneous molecular long range

magnetic order and appreciable conductivity.<sup>11</sup> It is expected that the sources of the two physical phenomena would be discrete and the magnetic order would not be mediated by the radical cation. One aim of this work was to prepare TTF based salts which exhibit long range magnetic order that involves the radical donor. This is realised by promoting close contacts between the anion and cation, which we have done in the past with hydrogen bonding,<sup>3,9,10</sup> but here focus on  $\text{S}\cdots\text{S}$  or  $\text{S}\cdots\text{Se}$  atomic contacts and  $\pi$  stacking. With this in mind we present a series of salts with an anion having ligands that bear both terminal S groups and  $\pi$  rings,  $[\text{Cr}(\text{NCS})_4(\text{phen})]^-$ , where phen = 1,10-phenanthroline.

## Experimental

DC magnetisation experiments were made with a Quantum Design MPSM7 SQUID magnetometer using randomly orientated polycrystalline material in a gelatine capsule. Magnetisation was recorded from 2 to 300 K at 100 G (all salts) and 5 kG (TMTTF, tetramethyltetraethiafulvalene, salt) and at 2 K between 0 and 7 T.

The X-ray diffraction measurements were either performed on a CAD4 diffractometer with graphite monochromated Cu-K $\alpha$  radiation and a linear detector (TTF and TMTSF, tetramethyltetraselenafulvalene, salts) or an Enraf-Nonius Dip2020 with imaging plate detector and graphite monochromated Mo-K $\alpha$  radiation (TMTTF salt). All structures were determined by direct methods using SIR 97<sup>12</sup> and refined using CRYSTALS 2000.<sup>13</sup>

Raman spectra were measured with a Reninshaw System 1000 Ramascope using a He-Ne laser ( $\lambda = 632.81$  nm) with 10  $\mu\text{m}$  slits and  $\times 50$  objective lens. The laser power was reduced

<sup>†</sup> Electronic supplementary information (ESI) available: Raman spectrum of compound I. See <http://www.rsc.org/suppdata/dt/b0/b004140h/>

until the sample did not burn and then scans were accumulated until the noise: signal ratio did not change. Two and four probe DC transport measurements were made with an Oxford instruments Mag Lab 2000 equipped with an EP probe. Gold wire electrodes (0.025 mm diameter) were attached directly to the crystals using platinum paste (Degussa).

CCDC reference number 186/2083.

See <http://www.rsc.org/suppdata/dt/b0/b004140h/> for crystallographic files in .cif format.

## Synthesis

$[(C_2H_5)_4N][Cr(NCS)_6]$  was prepared by the published method.<sup>14</sup> Dichloromethane and MeCN were purified by standard methods.<sup>15</sup> All of the donors were obtained commercially and recrystallised several times from distilled dichloromethane before use.

$[(C_2H_5)_4N][Cr(NCS)_4(phen)]$ . The method previously described for the 2,2'-bipyrimidine derivative was adapted.<sup>16</sup> 2 mmol (0.360 g) of 1,10-phenanthroline and 2 mmol (1.582 g)  $[(C_2H_5)_4N][Cr(NCS)_6]$  were dissolved in 40 ml MeCN and refluxed for 12 hours at 80 °C. The resulting mixture was separated by filtration and the filtrate cooled to room temperature followed by crystallisation at -20 °C which gave large purple block shaped crystals. Found: C 48.69, H 4.69, Cr 8.8, N 16.59, S 21.77. Calc. for  $C_{14}H_{20}CrN_7S_6$ , C 48.4, H 4.74, Cr 8.73, N 16.54, S 21.55%.

**Charge transfer salts.** Each salt was prepared by *in situ* oxidation of the relevant donor in an H-shaped electrochemical cell in the presence of a solution of  $[(C_2H_5)_4N][Cr(NCS)_4(phen)]$ . The cell had two glass frits separating platinum electrodes which protected the anode from reduction products. 10 mg of TTF, TMTTF or TMTSF were placed in the anode arm of the cell and the remainder of the cell was filled with a solution of  $[(C_2H_5)_4N][Cr(NCS)_4(phen)]$  (100 mg) in dichloromethane (50 ml). 1  $\mu$ A was applied across the cell for up to 1 week after which crystals suitable for X-ray diffraction studies for each salt grew on the anode. TTF gave a large number of well formed black needles which were found to be  $[TTF][Cr(NCS)_4(phen)]$ , **I**; TMTTF gave a very small number of dark blocks of  $[TMTTF][Cr(NCS)_4(phen)] \cdot CH_2Cl_2$ , **II**; the TMTSF donor gave a large number of narrow black plates, the structure of which was solved as  $[TMTSF]_3[Cr(NCS)_4(phen)]_2 \cdot 0.5CH_2Cl_2$ , **III**. Insufficient material was obtained for elemental analysis.

## Results and discussion

### Crystal structures

Single crystals of salts **I**, **II** and **III** were found to be suitable for structural determination by single crystal X-ray diffraction. Standard ORTEP<sup>17</sup> diagrams of each salt are shown in Figs. 1, 2 and 3 with the atom numbering scheme and 50% thermal ellipsoids. Table 1 shows the crystal parameters and collection data for each compound. Compound **I** consists of stacks of alternating TTF cations and  $[Cr(NCS)_4(phen)]^-$  anions in the *c* direction (Fig. 4). The closest contacts in the *c* direction are between the donor and acceptor, in particular  $S(TTF) \cdots S(NCS)$  atomic contacts and  $\pi$  stacking between TTF and the phen ligand. The donor and phen ligand are almost coplanar; the plane bounded by S5, S6 and S8 makes an angle of just 0.52° to the plane C14–C5–C9 and the shortest distance between the planes is 3.49 Å. The same cation–anion pair have contacts  $S5 \cdots S4$  at 3.835(2) Å and  $S7 \cdots S4$  at 3.682(2) Å, where the  $S \cdots S$  van der Waals distance is 3.6 Å. Furthermore, there is a close contact between a donor and the anion on the other side, in the *c* direction, of 3.486(2) Å between S1 and S8. There are no close contacts in either *a* or *b* directions and in particular there are no inter-anion or inter-donor  $S \cdots S$  close

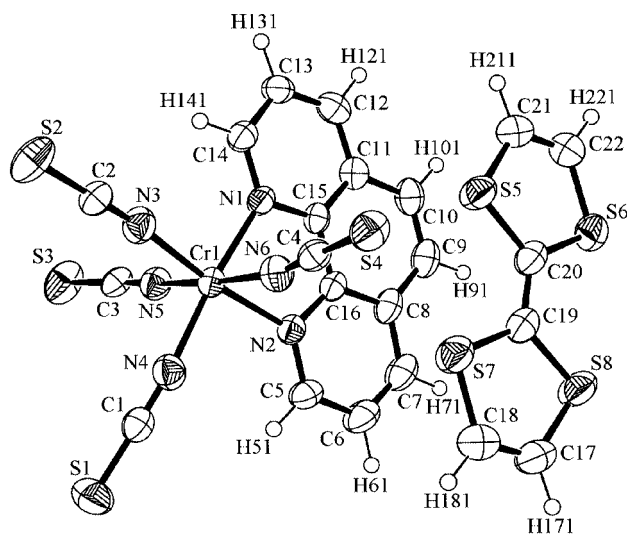


Fig. 1 An ORTEP<sup>17</sup> diagram of compound **I**.

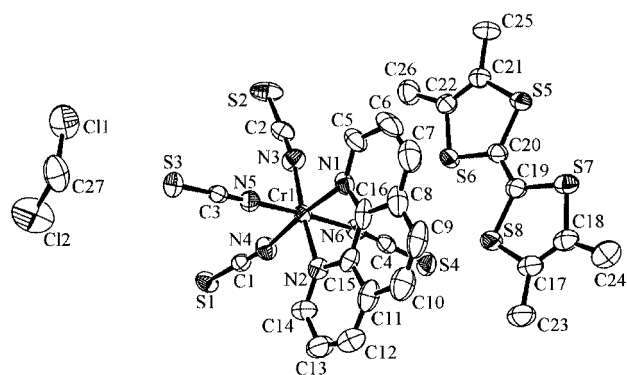


Fig. 2 An ORTEP<sup>17</sup> diagram of compound **II**. Hydrogen atoms have not been included for clarity.

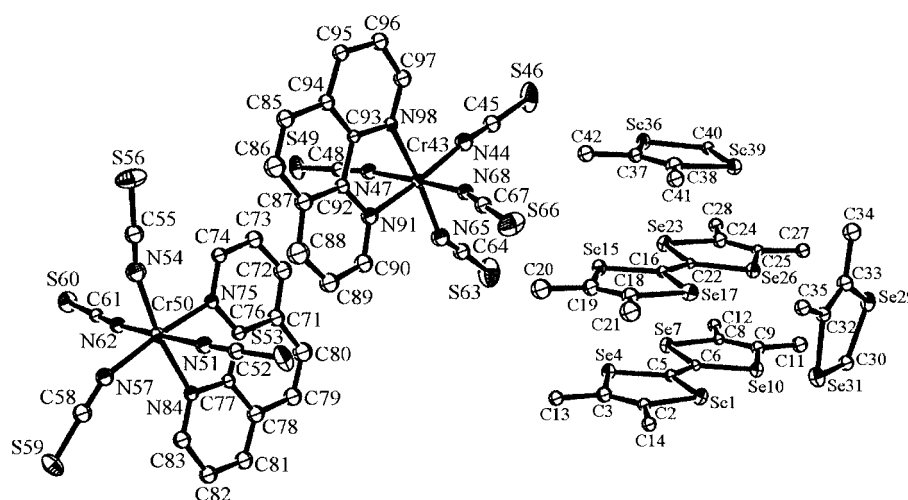
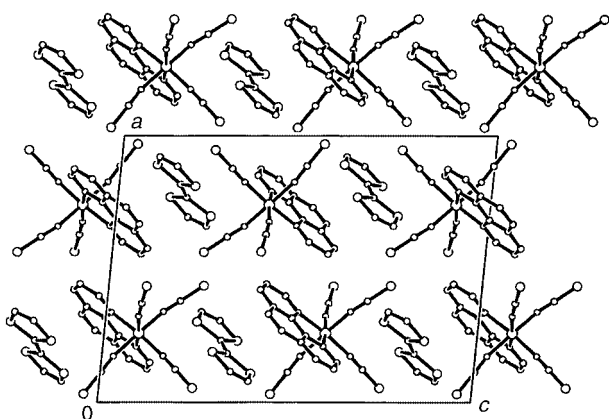
contacts as typically seen in highly conducting charge transfer salts. Using the empirical correlation between C–S and C=C bond lengths and the donor charges for BEDT-TTF salts,<sup>18</sup> **I** has a TTF charge of  $+0.9 \pm 0.1$  which agrees well with the stoichiometry and Raman data (see below). This indicates that the correlation could be valid not only for BEDT-TTF but for other donors with the TTF central backbone. The bond lengths used in the analysis are given Table 2.

A crystal packing diagram for compound **II**, showing the *bc* plane and viewed in the *a* direction, is given in Fig. 5. Corresponding anion–cation interactions as described for **I** are also present although they are much weaker; the  $\pi$ -stacking angle between the planes S5–S6–S8 and C14–C5–C9 is 10.16° and the planes are closest at 3.48 Å; within this cation–anion unit  $S4 \cdots S6$  is 3.841(2) Å and  $S4 \cdots S8$  is 4.054(10) Å. Furthermore, the donors are isolated as dimers with inter-donor distances  $S6 \cdots S7$  of 3.411(2) Å and  $S5 \cdots S8$  of 3.449(2) Å. There are also close contacts  $S4 \cdots S5$  and  $S4 \cdots S7$  between a donor and acceptor not involved in  $\pi$  stacking of 3.594(2) and 3.575(2) Å, respectively, which is a consequence of the N6–C4–S4 ligand slightly overhanging the nearest donor towards its dimer neighbour. Finally, anion–anion interactions are present in the form of  $\pi$  stacking where nearest neighbour phen ligands are just 3.48 Å apart and their planes are at an angle of just 0.11°. The  $CH_2Cl_2$  solvent sits in a cavity bounded by anions and cations. Bond length analysis of **II** using the bonds in Table 2 gives a donor charge of  $+1.0 \pm 0.1$  which again is consistent with the stoichiometry and Raman data.

For compound **III** the solvent was highly disordered at 293 K so the structure was solved at 120 K and unless otherwise stated the close contact distances reported below are measured at the lower temperature. The TMTSF salt has a more conventional

**Table 1** Crystallographic data for compounds **I**, **II** and **III**

	<b>I</b>	<b>II</b>	<b>III</b>
Empirical formula	C <sub>22</sub> H <sub>12</sub> CrN <sub>6</sub> S <sub>8</sub>	C <sub>27</sub> H <sub>22</sub> Cl <sub>2</sub> CrN <sub>6</sub> S <sub>8</sub>	C <sub>62.5</sub> H <sub>53</sub> ClCr <sub>2</sub> N <sub>12</sub> S <sub>8</sub> Se <sub>12</sub>
Formula weight	668.86	809.90	2315.64
<i>T</i> /K	293	250	293, 120
Radiation, $\lambda/\text{\AA}$	1.54180	0.71073 (Mo-K $\alpha$ )	1.54180 (Cu-K $\alpha$ )
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 1 (no. 2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)
<i>a</i> /Å	15.289(2)	8.858(1)	11.576(3), 11.505(2)
<i>b</i> /Å	8.466(3)	12.905(1)	43.097(2), 43.00(2)
<i>c</i> /Å	21.015(4)	16.341(1)	15.918(3), 15.632(3)
$\alpha/^\circ$		71.756(4)	
$\beta/^\circ$	95.713(11)	80.504(3)	99.816(17), 100.033(15)
$\gamma/^\circ$		80.119(4)	
<i>V</i> /Å <sup>3</sup>	2706(1)	1735(2)	7825(4), 7615(4)
<i>Z</i>	4	2	4
$\mu/\text{mm}^{-1}$	9.47	1.00	11.05, 11.68
Reflections collected	5995	6607	14718, 5972
Independent reflections	4067	3882	8402, 4621
Final <i>R</i> 1, <i>wR</i> 2	0.0394, 0.0448 [ <i>I</i> < 3 $\sigma$ ( <i>I</i> )]	0.0522, 0.0427 [ <i>I</i> < 5 $\sigma$ ( <i>I</i> )]	0.0542, 0.0509, 0.0605, 0.0573 [ <i>I</i> < 3 $\sigma$ ( <i>I</i> )]

**Fig. 3** An ORTEP<sup>17</sup> diagram of compound **III**. To aid clarity the TMTSF molecules containing C30 and C40 are not fully generated and the solvent molecules are excluded.**Fig. 4** Crystal packing diagram of compound **I** viewed along the 010 direction.

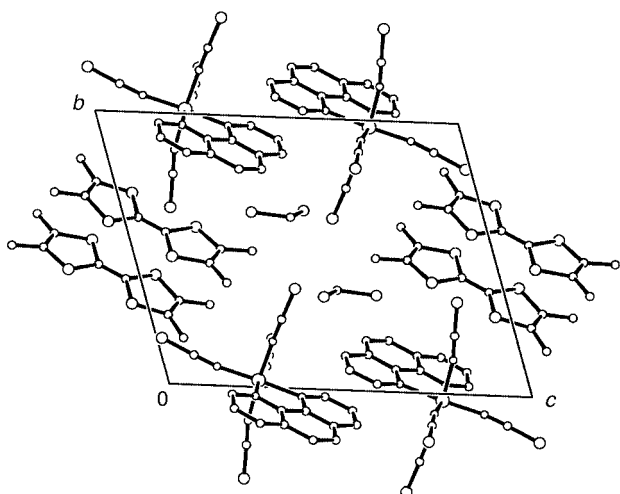
gross structure in which the donors and acceptors are segregated into layers as shown in the packing diagram in Fig. 6. The asymmetric unit (Fig. 3) consists of two anions, two donors and two donor halves which can fully be generated by the crystal symmetry, plus a solvent molecule (not shown). The donor layer viewed in the direction of the C5–C6 bond (corresponding to approximately to the unit cell *b* axis), Fig. 7, consists of stacks of TMTSF molecules interleaved with a row which con-

**Table 2** Bond lengths (Å) used for the donor charge calculation for compounds **I** and **II** together with the charge calculated<sup>18</sup>

	<b>I</b>	<b>II</b>
C19–C20	1.374(5)	1.390(6)
C19–S8	1.730(3)	1.726(5)
C19–S7	1.714(3)	1.714(5)
C20–S6	1.722(4)	1.715(5)
C20–S5	1.726(3)	1.714(5)
S8–C17	1.716(4)	1.737(5)
C7–C18	1.716(4)	1.745(5)
S5–C21	1.719(4)	1.736(5)
S6–C22	1.720(4)	1.744(5)
C21–C22	1.333(5)	1.344(7)
C17–C18	1.332(5)	1.336(7)
Charge <sup>18</sup>	+0.9 ± 0.1	+1.0 ± 0.1

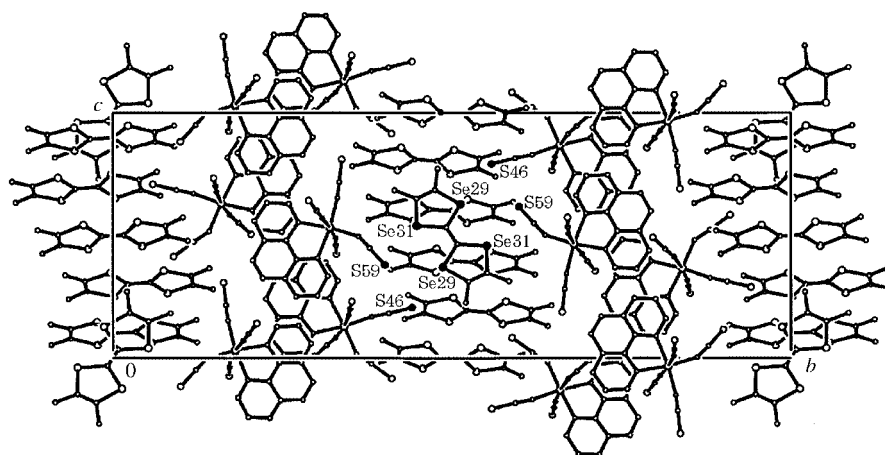
tains alternating solvent molecules and a TMTSF molecule which lies orthogonal to the stack. This packing motif is similar to that observed in [TMTSF]<sub>5</sub>[Nb<sub>6</sub>Cl<sub>18</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub><sup>19</sup> although in this case the stacks are interleaved with other donors only and the stack has a pronounced zigzag pattern, similar to that seen for the (TMTSF)<sub>2</sub>X salts (X = ClO<sub>4</sub>, PF<sub>6</sub>, Br, etc.).<sup>20</sup> The donors in a stack have numerous Se...Se close contacts below the van der Waals distance of 3.8 Å. For example those which contain atoms C5 (molecule A in Fig. 7) and C16 (B in Fig. 7) have very short contacts Se1...Se17 at 3.656(2) Å,

Se4...Se15 at 3.592(2) Å, Se7...Se23 at 3.666(2) Å and Se10...Se26 at 3.650(2) Å. These distances are much shorter than those observed either in the Bechgaard salts<sup>21</sup> or in [TMTSF]<sub>5</sub>[Nb<sub>6</sub>Cl<sub>18</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub> (3.74–3.98 Å). The third crys-

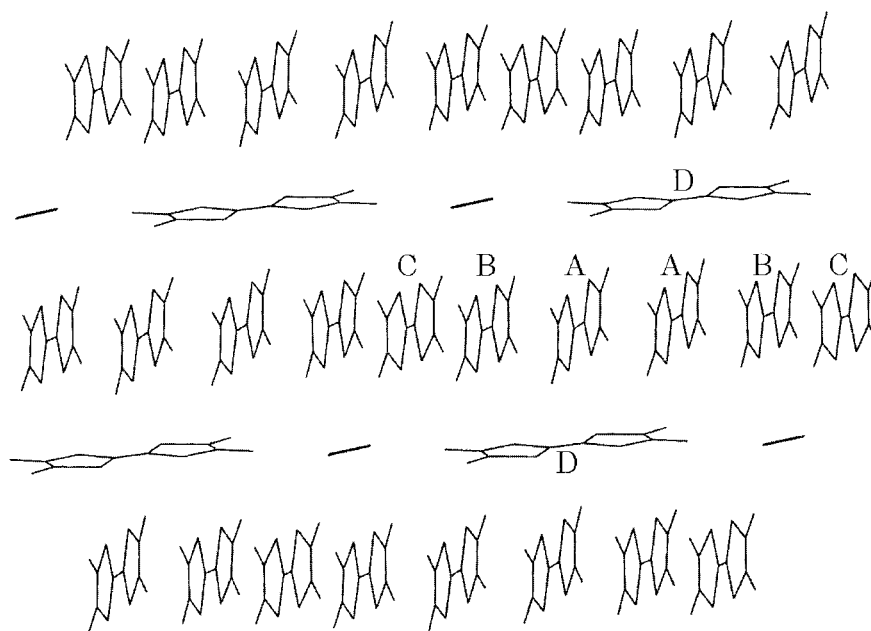


**Fig. 5** Crystal packing diagram of compound **II** viewed along the 100 direction.

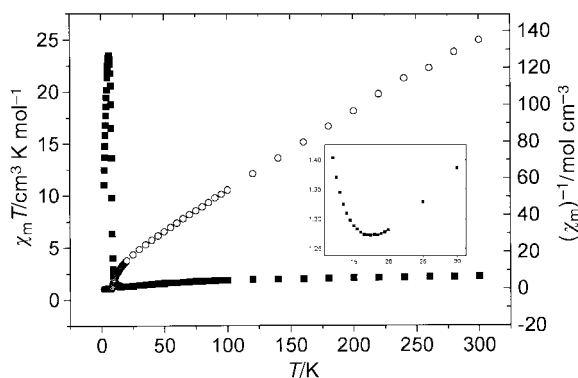
tallographically independent donor in the stack, molecule C, which contains atom C40, is further apart from its neighbours with Se15...Se36 at 3.914(2) Å, Se17...Se39 at 3.804(3) Å, Se23...Se39 at 3.928(3) Å and Se26...Se39 at 3.999(2) Å. There are also three close inter-TMTSF contacts between the stack and row Se10(molecule A)...Se29(D) at 3.935(2) Å, Se10(A)...Se31(D) at 3.673(2) Å and Se26(B)...Se29(D) with a distance of 3.534(2) Å. Unlike **I** and **II** the donor–acceptor contacts do not involve  $\pi$  stacking, only S(NCS)...Se(TMTSF) close contacts. The TMTSF molecule D, perpendicular to the stack, has six such contacts which are highlighted in Fig. 6 (the atoms involved are labelled and coloured black), Se29...S59 is 3.713(4), Se31...S59 3.539(2) and Se29...S46 3.595(2) Å. Selected donor–acceptor contacts between the stacked TMTSF and NCS ligands are Se7...S46 at 3.640(5), Se15...S63 at 3.547(4) and Se36...S46 at 3.655(5) Å. The bond length to charge correlation, as used above for TTF and TMTTF, and originally investigated for BEDT-TTF, is invalid for TMTSF because the central section of the donor is different. However, from the central C=C bonds lengths, two of the donors clearly have similar charges since at 120/293 K C5–C6 is 1.448(16)/1.419(11) Å and C16–C22 is 1.447(12)/1.418(11) Å with the remaining donor in the stack having C40–C40 of 1.400(12)/1.377(12) Å. The TMTSF molecule orthogonal to the stack has a smaller C30–C30 distance of



**Fig. 6** Crystal packing diagram of compound **III** viewed along the 100 direction, showing the donor–acceptor layered structure. See text for labelled atoms.



**Fig. 7** The donor layer of compound **III** without the anionic complex. For labelling see text.



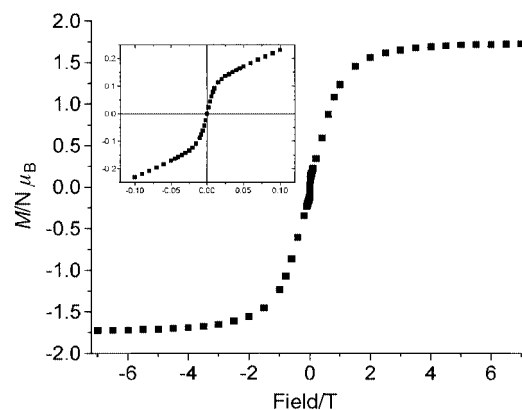
**Fig. 8**  $\chi_m T$  (filled squares) and  $\chi_m^{-1}$  (open circles) versus temperature for compound **I**. The expanded view (inset) shows the minimum in  $\chi_m T$ .

1.377(16)/1.303(13) Å which indicates a smaller positive charge. This bond length pattern is replicated in [TMTSF]<sub>5</sub>[Nb<sub>6</sub>Cl<sub>18</sub>]·0.5CH<sub>2</sub>Cl<sub>2</sub> at 295 K where two stacked molecules have central C=C bonds of 1.393 and 1.400 Å with the third having 1.388 Å and for the non-stacked donor it is 1.306 Å.

### Magnetic properties

The magnetic properties of compound **I** are characteristic of a bulk ferrimagnet exhibiting long range magnetic order below 9.0 K. The  $\chi_m T$  versus  $T$  plot is shown in Fig. 8 where  $T$  is the temperature and  $\chi_m$  the molar magnetic susceptibility measured in an external field of 100 G. The value of  $\chi_m T$  at 300 K is 2.22 cm<sup>3</sup> K mol<sup>-1</sup> which is very close to 2.251 cm<sup>3</sup> K mol<sup>-1</sup> the ideal value for non-interacting spins  $S = 3/2$  (from Cr<sup>3+</sup>, 1.876 cm<sup>3</sup> K mol<sup>-1</sup>) and 1/2 (from radical TTF, 0.375 cm<sup>3</sup> K mol<sup>-1</sup>). Therefore at 300 K short range order is low. As the temperature is decreased the value of  $\chi_m T$  falls and there is a rounded minimum, characteristic of 1-D antiferromagnetic ordering, at 1.2 cm<sup>3</sup> K mol<sup>-1</sup> and 17.5 K (inset Fig. 8). Below 17.5 K the value of  $\chi_m T$  increases rapidly up to a maximum of 23.5 cm<sup>3</sup> K mol<sup>-1</sup> at 6.0 K. This behaviour is indicative of a ferrimagnetic material<sup>22</sup> in which at high temperature  $\chi_m T$  approaches the paramagnetic limit and as  $T$  decreases the decrease in  $\chi_m T$  corresponds to a short range order where local spins  $S_{Cr}$  and  $S_{TTF}$  are aligned antiparallel but have no correlation with neighbouring Cr–TTF units. As  $T$  is lowered beyond the minimum the correlation length increases which leads to spontaneous magnetisation below a critical temperature,  $T_c$  9 K. The plot of  $1/\chi_m$  against  $T$ , above 50 K, gives a straight line from which is extracted a Curie constant of 2.35 K and a Weiss constant of –24.9 K, which confirms that antiferromagnetic interactions dominate. Fig. 9 shows the magnetisation versus field plot which shows saturation at 1.7 N  $\mu_B$  which is less than expected (2 N  $\mu_B$ ) for all chromium spins being aligned along the field direction and the TTF local spins aligned in the opposite direction which implies that the spins are canted. Furthermore, **I** is a very soft magnet since on cycling the field any hysteresis effect is too small to be measured. At both 100 and 5 kG compound **II** displays the overall behaviour of an antiferromagnet with a maximum in the  $\chi_m$  versus  $T$  curve at  $T_N = 3.0$  K. Furthermore there is a very broad minimum in the  $\chi_m T$  versus  $T$  curve at 205 K, which as stated above is found for compounds with 1-D antiferromagnetic interactions. Unfortunately, these results are difficult to interpret since the crystal structure indicates close anion–anion, cation–cation and anion–cation contacts all of which are sure to contribute, with varying degree, to the magnetic properties.

The magnetic susceptibility of compound **III** is typical of a simple paramagnet. The temperature variation with  $\chi_m^{-1}$  follows the Curie–Weiss law over the whole temperature range with a Curie constant of 3.572 K and a small negative Weiss constant of –3.818 K. The Curie constant corresponds to



**Fig. 9** Magnetisation versus field for compound **I**. Inset is an expanded view about zero field showing no hysteresis.

1.786 K per Cr where the expected value is 1.876 K, and so the magnetic response is dominated by the  $S = 3/2$  ion with little contribution from the TMTSF radical. The most significant structure–property relationships here seems to be the fact that the salts with magnetic order, **I** and **II**, differ from **III** in that they have cation–anion interactions which involve  $\pi$  stacking whereas the paramagnetic salt does not. It seems therefore that this type of interaction could be important in promoting long range magnetic order.

### Raman studies

Reflective Raman spectroscopy is used as a rapid means of determining the charge on the donor molecule by comparing the  $\nu_3$  and  $\nu_4$  modes of the symmetrical central C=C bond in the range 1400–1480 cm<sup>-1</sup>.<sup>23</sup> As in the bond length analysis it is assumed that the central TTF portion of the donors can be compared well with those in salts of BEDT–TTF. Comparisons of the charges calculated from the Raman spectra with those calculated from the donor C–S and C=C bond lengths (see above), and indeed the stoichiometry of the salts, confirm that this assumption is valid. Both **I** and **II** show single strong peaks at 1424.5 and 1411.8 cm<sup>-1</sup>, respectively, which correspond to charges of +0.94 and +1.09. The spectrum for **I** is provided as supplementary data. The TMTSF salt does not show this behaviour but has a broad band with a significant noise to signal ratio, which implies that there is a range of charges located on the donor molecules.

### Conductivity studies

Two probe DC resistance measurements were attempted along the needle axis of single crystals of compound **I**. For each one of several crystals the resistance values were too high to be measured by our equipment (full scale deflection 1 G  $\Omega$ ). Therefore **I** is an extremely good insulator which can easily be predicted since the TTF molecules are well isolated. The crystals for **II** were too small for direct transport measurements, although since their structure also shows isolated donors, this time as dimers, the compound is expected to be insulating. By contrast four probe DC transport measurements for **III** were made in the most conductive direction namely the plane of the crystal plate. The room temperature conductivity was  $2.23 \times 10^{-2}$  ohm<sup>-1</sup> cm<sup>-1</sup>, characteristic of a semiconductor. This is confirmed from the exponential growth of conductivity with temperature and a calculated activation energy of 0.16 eV.

### Conclusion

We have described the synthesis, structures and properties of three new charge transfer salts with TTF based organochalcogenide donors and the anion [Cr(NCS)<sub>4</sub>(phen)]<sup>-</sup>, grown by standard electrochemical techniques. The salt of TTF displays

bulk ferrimagnetism which originates from the antiferromagnetic interaction between the donor radical spin and the spin associated with the Cr; the TMTTF salt shows antiferromagnetism and both are ambient temperature insulators. By contrast the TMTSF salt is a  $S = 3/2$  paramagnet and a semiconductor with an activation energy of 0.16 eV. The salts which show magnetic order have both  $S \cdots S$  (donor–acceptor) close contacts and evidence of  $\pi$  stacking. By contrast the paramagnetic semiconductor does not show  $\pi$  stacking and only  $Se \cdots S$  (donor–acceptor) or  $Se \cdots Se$  (donor–donor) atomic contacts are significant. Therefore it seems that  $\pi$  stacking can be used as an important tool when designing long range magnetic order into these systems. This conclusion was also offered for the behaviour of salts of the type  $[donor][Cr(NCS)_4(L)_2]$  ( $L$  = isoquinoline) which were not structurally characterised but showed similar ferrimagnetic behaviour to that described here.<sup>24</sup>

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