

# Synthesis, Crystal Structures and Physical Properties of TTF-Based Conducting Charge Transfer Salts with Anions Containing Selenocyanate Ligands

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Three new charge transfer salts of tetrathiafulvalene (TTF)-based donors with selenocyanate-metal complex anions have been synthesized. The salts have been characterized as BEDT-TTF<sub>4</sub>[Cr(NCSe)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, II, TTF<sub>3</sub>[Cr(NCSe)<sub>4</sub>phen]<sub>2</sub>, III and BEDT-TTF<sub>2</sub>[Cr(NCSe)<sub>4</sub>phen]·CH<sub>2</sub>Cl<sub>2</sub>, IV, where phen = 1,10'-phenanthroline and BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene. At 120 K, II crystallizes in the *P2<sub>1</sub>/m* space group with  $a = 10.454(1)$ ,  $b = 31.990(1)$ ,  $c = 12.339(1)$  Å,  $\beta = 113.163(2)^\circ$ ,  $V = 3793.8$  Å<sup>3</sup>,  $Z = 4$  and at 240 K in the same space group with  $a = 10.530(1)$ ,  $b = 32.122(1)$ ,  $c = 12.396(1)$  Å,  $\beta = 113.186(3)^\circ$ ,  $V = 3854.2$  Å<sup>3</sup>,  $Z = 4$ . At 240 K III crystallizes in the *C2/c* space group,  $a = 38.9272(5)$ ,  $b = 11.2992(1)$ ,  $c = 15.2540(3)$  Å,  $\beta = 106.8877(6)^\circ$ ,  $V = 6420.1$  Å<sup>3</sup>,  $Z = 8$ . The structure of IV has been solved in the *P1* space group with  $a = 8.7629(3)$ ,  $b = 11.7977(4)$ ,  $c = 26.6031(9)$ ,  $\alpha = 81.697(2)$ ,  $\beta = 87.858(3)$ ,  $\gamma = 74.8471(14)$ ,  $V = 2626.8$  Å<sup>3</sup>,  $Z = 2$ . All of the salts have numerous S...Se close atomic contacts between donors and acceptors but there is no magnetic exchange between ions, as previously seen in closely related salts such as TTF[Cr(NCS)<sub>4</sub>phen] and (donor)[M(NCS)<sub>4</sub>(isoquinoline)<sub>2</sub>], where  $M = \text{Cr, Fe and donor} = \text{TTF, BEDT-TTF or TMTTF}$  (tetramethyltetrathiafulvalene). Indeed, II and IV are paramagnetic semiconductors whereas III is a paramagnetic insulator. The absence of long-range magnetic order is discussed in terms of structure-function relations since there are no  $\pi$ -stacking interactions between donor and acceptor, which are seen in all of the bulk magnets of this type where the donor spin is magnetically coupled to the anion. The synthesis and crystal structure of the starting material, [(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3</sub>[Cr(NCSe)<sub>6</sub>], I, is also reported; it crystallizes in the *P1* space group with  $a = 12.220(1)$ ,  $b = 12.814(1)$ ,  $c = 13.008(1)$  Å,  $\alpha = 99.608(6)$ ,  $\beta = 114.028(5)$ ,  $\gamma = 92.637(6)^\circ$ ,  $V = 1819.5$  Å<sup>3</sup>,  $Z = 2$ . © 2002 Elsevier Science (USA)

**Key Words:** BEDT-TTF; TTF; selenocyanate complex; chromium; magnetism; conductivity; charge transfer salts.

## INTRODUCTION

Understanding the chemistry and physics of organic conductors has progressed greatly since the discovery of the first one-dimensional metal, a tetrathiafulvalene-tetracyano-*p*-quinodimethane (TTF·TCNQ) complex, in 1973 (1). In particular there has been a recent focus on synthesizing molecular organic ferromagnetic metals, although to date there is only one published example, BEDT-TTF<sub>3</sub>[MnCr(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>] (2–4), where BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene. This charge transfer salt shows metallic behavior down to low temperatures and is also ferromagnetic below 5.5 K. One of the features of this salt is that the unpaired electrons associated with TTF, which are involved in the conduction process and those associated with the anion, which provide the magnetic properties, are entirely discrete. That is, interactions between the cationic conducting component and the anionic magnetic component are weak. Several groups have tried to promote electronic interactions between the two ions, notably in  $\gamma$ -(BETS)<sub>2</sub>FeCl<sub>4</sub> (5), where BETS = bis(ethylenedithio) tetraselenafulvalene, and its mixed anion derivatives such as  $\lambda$ -(BETS)<sub>2</sub>GaY<sub>x</sub>Z<sub>4-x</sub> ( $Y, Z = \text{F, Br, Cl}$ ) (6) and  $\lambda$ -(BETS)<sub>2</sub>[Fe<sub>x</sub>Ga<sub>1-x</sub>]Cl<sub>4</sub> (7). These salts show a range of electronic behavior, often mediated by  $\pi$ -*d* interactions. For example, the series  $\lambda$ -(BETS)<sub>2</sub>FeBr<sub>x</sub>Cl<sub>4-x</sub> (8) exhibits a range of  $\pi$ -*d* coupled metal-insulator transitions where the temperature of the phase change increases linearly with  $x$ .

Stronger interactions between ions are known although in these salts any conductive network tends to be compromised, since the nearest molecular neighbors are then likely to be cation and anion, rather than cations as in the conducting salts. Examples of this type of material are TTF[Cr(NCS)<sub>4</sub>phen] (9), where phen = 1,10'-phenanthroline and (donor)[M(NCS)<sub>4</sub>(isoquinoline)<sub>2</sub>] (10), donor = TTF, BEDT-TTF, tetramethyltetrathiafulvalene

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(TMTTF) (11) and  $M = \text{Cr, Fe}$ . There are two types of donor–acceptor interactions in these salts, namely  $\pi$ -stacking between the donor and the phen or isoquinoline ligands and  $\text{S}\cdots\text{S}$  close contacts between the terminal atoms of the NCS ligands and the cation. Despite their insulating behavior, these are unique TTF-based salts because they display long-range magnetic order with  $T_c$ 's up to 8.9 K. The present work expands on this series and in particular looks at the effect of using the  $\text{NCSe}^-$  ligand in the anionic metal complex. This will provide valuable information on the interplay of structure and function for these materials and will give some indications of the best strategies towards novel TTF-based salts that exhibit long-range magnetic order, with or without electronic conductivity.

## EXPERIMENTAL

### Synthesis

All solvents were purified by standard methods (12). The donors, TTF and BEDT-TTF were obtained commercially and were recrystallized several times from distilled dichloromethane before use.

$[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$ , **I**. The method previously described for the preparation of  $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}(\text{NCS})_6]$  was adapted (13).  $[(\text{C}_4\text{H}_9)_4\text{N}]\text{Br}$  (10.6554 g, 33 mmol),  $\text{KSeCN}$  (9.572 g, 66 mmol) and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (2.9347 g, 11 mmol) were refluxed in acetone (30 ml) for 2 h. The resulting mixture was separated by filtration and the filtrate was cooled to room temperature followed by crystallization at  $-5^\circ\text{C}$ . Large thin purple/red plates (12.1 g, 8.6 mmol, 78% yield), found to be **I**, were suitable for single crystal structure X-ray diffraction. Found C 45.8, H 5.9, N 8.7, Se 33.4, Cr 3.9; Calcd. for  $\text{C}_{54}\text{H}_{108}\text{N}_9\text{Se}_6\text{Cr}$ , C 46.0, H 7.7, N 8.95, S 33.6, Cr 3.7.

$[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{NCSe})_4(\text{phen})]$ . The method described for  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{Cr}(\text{NCS})_4(\text{bipym})]$ , where bipym = 2,2'-bipyrimidine was adapted (14). 1,10'-Phenanthroline (0.360 g, 2 mmol) and  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$  (2.8185 g, 2 mmol) were refluxed in MeCN (40 mL) over 12 h at  $80^\circ\text{C}$ . The resulting yellow/brown mixture was separated by filtration and the filtrate was cooled to room temperature followed by cooling at  $-20^\circ\text{C}$  for 1 day. The resulting fine orange/yellow powder was recrystallized twice from MeCN giving an orange/yellow microcrystalline product (1.12 g, 1.3 mmol, 65% yield). Found C 43.1, H 5.3, N 11.3, Se 35.2, Cr 5.5; Calcd. for  $\text{C}_{32}\text{H}_{35}\text{N}_7\text{Se}_4\text{Cr}$ , C 43.4, H 4.0, N 11.1, Se 35.7, Cr 5.8.

*Charge transfer salts.* All charge transfer salts were prepared by *in situ* oxidation of the relevant organic donor

in an H-shaped electrochemical cell in the presence of a solution of either  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$  or  $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Cr}(\text{NCSe})_4(\text{phen})]$ . The cell consisted of two Pt electrodes separated by a glass frit in the cross-arm. Ten milligrams of TTF or BEDT-TTF was placed in the base of the anode arm side of the cell and the remainder filled with a solution of the relevant Cr complex (100 mg) in dichloromethane (50 mL). A current of  $1\ \mu\text{A}$  was applied across the cells for up to 2 weeks after which crystals had grown on the anode. Crystals suitable for X-ray single crystal structure were obtained:  $\text{BEDT-TTF}_4[\text{Cr}(\text{NCSe})_6] \cdot \text{CH}_2\text{Cl}_2$ , **II**, as long thin dark black plates;  $\text{TTF}_3[\text{Cr}(\text{NCSe})_4(\text{phen})]_2$ , **III**, as brown plates;  $\text{BEDT-TTF}_2[\text{Cr}(\text{NCSe})_4(\text{phen})] \cdot \text{CH}_2\text{Cl}_2$ , **IV**, also as dark plates. As is usual from this type of experiment, insufficient material was obtained to prove bulk stoichiometry by, for example, elemental analysis or powder diffraction measurements. The stoichiometry of compounds **II–IV** were identified by X-ray single crystal structure diffraction. Nevertheless, using the results to interpret magnetic measurements (see below) indicates that the single crystal data are well representative of the bulk.

### Physical Measurements

Variable temperature DC magnetization experiments were made with a Quantum Design MPMS7 SQUID magnetometer using randomly orientated polycrystalline material in a gelatin capsule. Magnetization was recorded from 2 to 300 K with an externally applied field of 5 kG. The X-ray diffraction measurements were performed with an Enraf-Nonius Dip2020 diffractometer with imaging plate detector for compounds **I** and **II**, and an Enraf-Nonius  $\kappa$ -CCD for compounds **III** and **IV**, both with graphite monochromated  $\text{MoK}\alpha$  radiation. All structures were solved using direct methods with CRYSTALS 2000 (version 11.3) (15). 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 diam.) were attached directly to the crystals using Au paste.

## RESULTS AND DISCUSSION

### Description of Crystal Structures

The crystal and collection parameters for all the structures, described within, are listed in Table 1. Compound **I**,  $[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$ , is of interest because the structure of the anion has not been previously reported and it provides a useful comparison with the charge transfer salts. A standard ORTEP (16) diagram of the asymmetric unit of **I**, with the atom numbering scheme and 50% thermal ellipsoids, is in Fig. 1. The bond lengths

TABLE 1  
Crystallographic Data for Compounds I–IV

Compound	I	II	II	III	IV
Chemical formula	C <sub>54</sub> H <sub>108</sub> CrN <sub>9</sub> Se <sub>6</sub>	C <sub>47</sub> H <sub>34</sub> CrCl <sub>2</sub> N <sub>6</sub> Se <sub>6</sub> S <sub>32</sub>	C <sub>47</sub> H <sub>34</sub> CrCl <sub>2</sub> N <sub>6</sub> Se <sub>6</sub> S <sub>32</sub>	C <sub>50</sub> H <sub>28</sub> Cr <sub>2</sub> N <sub>12</sub> Se <sub>8</sub> S <sub>12</sub>	C <sub>37</sub> H <sub>26</sub> CrN <sub>6</sub> S <sub>16</sub> Se <sub>4</sub> Cl <sub>2</sub>
<i>a</i> (Å)	12.2200(14)	10.4540(5)	10.5300(5)	38.9272(5)	8.7629(3)
<i>b</i> (Å)	12.8140(12)	31.9900(13)	32.1220(15)	11.2992(1)	11.7977(4)
<i>c</i> (Å)	13.0080(15)	12.3390(3)	12.3960(3)	15.2540(3)	26.6031(9)
$\alpha$ (deg)	99.608(6)	90.0	90.0	90.0	81.697(2)
$\beta$ (deg)	114.028(5)	113.163(2)	113.186(3)	106.8877(6)	87.697(2)
$\gamma$ (deg)	92.637(6)	90.0	90.0	90.0	74.8471(14)
<i>V</i> (Å <sup>3</sup> )	1819.5	3793.8	3854.2	6420.1	2626.8
<i>Z</i>	2	4	4	8	2
Formula weight	681.45	1151.70	1151.70	958.62	1506.36
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> 21/ <i>m</i>	<i>P</i> 21/ <i>m</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> -1
<i>T</i> (K)	293	120	240	240	240
$\lambda$ (Å)	0.71069 (MoK $\alpha$ )	0.71069	0.71069	0.71069	0.71069
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.24	2.02	1.98	1.98	1.90
$\mu$ (mm <sup>-1</sup> )	3.19	4.02	3.96	5.31	3.76
<i>R</i> ( <i>F</i> <sub>o</sub> ) <sup>a</sup>	0.0812	0.0615	0.0446	0.0336	0.1166
	[ <i>I</i> < 5 $\sigma$ ( <i>I</i> )]	[ <i>I</i> < 3 $\sigma$ ( <i>I</i> )]	[ <i>I</i> < 3 $\sigma$ ( <i>I</i> )]	[ <i>I</i> < 3 $\sigma$ ( <i>I</i> )]	[ <i>I</i> < 4 $\sigma$ ( <i>I</i> )]
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>o</sub> ) <sup>b</sup>	0.0659	0.0342	0.0467	0.0275	0.0925

$$^a R = \sum(F_o - F_c) / \sum F_o.$$

$$^b R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

about the Cr atom are as expected for Cr–NCSe bonds (17); the average Cr–N bond length is 1.998 Å; the average N–C bond length is 1.125 Å; the average C–Se bond is 1.794 Å. The tetrabutylammonium ion is disordered over two positions related by a non-crystallographic mirror plane passing through the atom N29.

The ORTEP diagram at 120 K for compound **II**, BEDT-TTF<sub>4</sub>[Cr(NCSe)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>, as shown in Fig. 2, reveals two

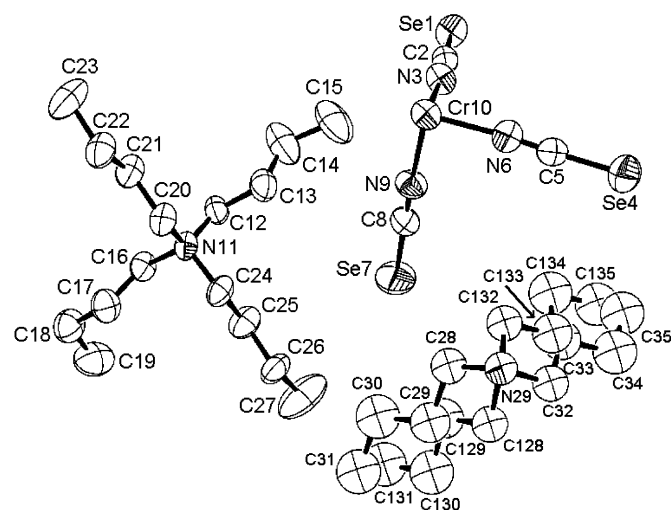


FIG. 1. ORTEP (16) diagram of **I** showing 50% thermal ellipsoids and the atom numbering scheme.

crystallographically distinct BEDT-TTF molecules. At 240 K the BEDT-TTF molecule that contains atom C43 has both terminal ethylene groups with a twisted conformation eclipsed with respect to the other end of the molecule. The second BEDT-TTF molecule also has a twisted conformation at one end but the other end has a boat conformation with a torsion angle S23–C24–C25–S26 of 14.1°, which is associated with disorder in the molecule (18). In view of this, the structure was solved at 120 K, but no further resolution of the disordered C24–C25 ethylene group could be achieved. From bond length analysis (19), the estimated charges on the donor molecules are 0.5 ± 0.1 and 0.8 ± 0.1 at 240 K and are hardly changed at 120 K, being 0.6 ± 0.1 and 0.8 ± 0.1, respectively. **II** is isostructural with BEDT-TTF<sub>4</sub>[Fe(NCS)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub> (20) in which the overall crystal packing consists of alternating layers that contain exclusively anions or cations (Fig. 3). The donor layers consist of two distinct rows of BEDT-TTF molecules (Fig. 4). Firstly, a row of dimers which are interleaved by a penetrating NCSe ligand and a solvent molecule, and secondly, a row that consists of donor molecules perpendicular to the dimers. However, there are small differences in the S...S contact networks within the cation layers (Table 2), which likely accounts for the differences in transport properties (see below). In the crystallographic *c* direction, there is a single close contact between terminal Se atoms of the NCSe ligands on neighboring anions of 3.41 Å (120 K) and 3.43 Å (240 K). This contact is spatially equivalent to a contact between terminal S atoms in

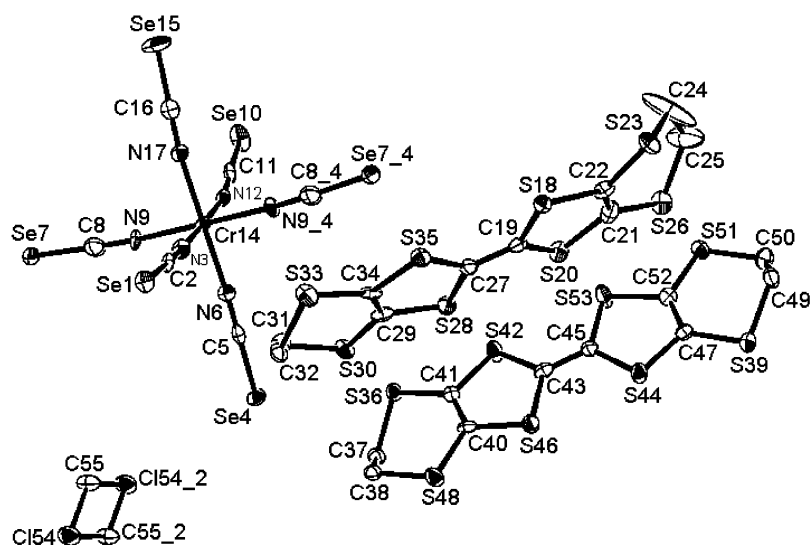


FIG. 2. ORTEP (16) diagram of **II** at 120 K showing 50% thermal ellipsoids and the atom numbering scheme.

BEDT-TTF<sub>4</sub>[Fe(NCS)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub> (3.45 Å). Cation-to-anion contacts are limited to Se4...S30 at 3.76 Å and Se7...S35 at 3.88 Å, where Se7 is the terminal atom of the penetrating ligand mentioned above.

The ORTEP diagram for compound **III** is shown in Fig. 5 and an overall packing diagram with the TTF packing motif is shown in Figs. 6a and 6b, respectively. This structure contains two crystallographically distinct TTF molecules, one of which is located on an inversion center. Bond length analysis, using a scheme devised for TTF (21), gives charges of  $0.5 \pm 0.1$  for the TTF molecule containing atom C38 and  $0.6 \pm 0.1$  for that containing C33. The crystal packing, as with compound **II**, is composed of discrete anionic and cationic alternating layers. However,

there is no discernable continuous network of S...S contacts in the cationic layer since the donors are organized into isolated stacks of TTF trimers, neighboring trimers being arranged perpendicular to each other (Fig. 6b). Within stack A (as marked on Fig. 6b), there are several very close S...S distances, namely S39...S34 at 3.39 Å, S37...S32 at 3.49 Å, S43...S32 at 3.40 Å and S46...S34 at 3.54 Å. And within stack B the short contacts are S34...S46 at 3.54 Å, S37...S32 at 3.49 Å, S39...S34 at 3.39 Å and S32...S43 at 3.40 Å. However, no short contacts exist between stacks of types A and B. However, there is a group of Se...Se close contacts between anions spanning a TTF layer, in particular between symmetrically equivalent atoms Se28...Se28 at 3.54 Å and between Se28...Se12 at

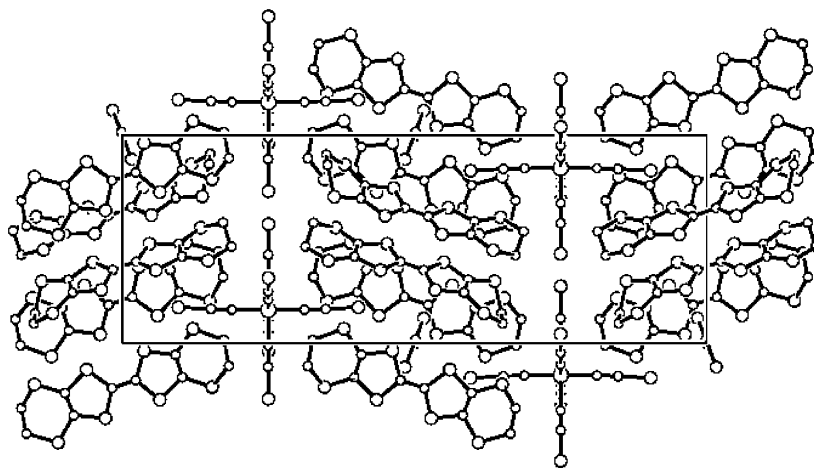


FIG. 3. Unit-cell packing diagram for **II**, at 120 K, viewed along the crystallographic *c* direction.

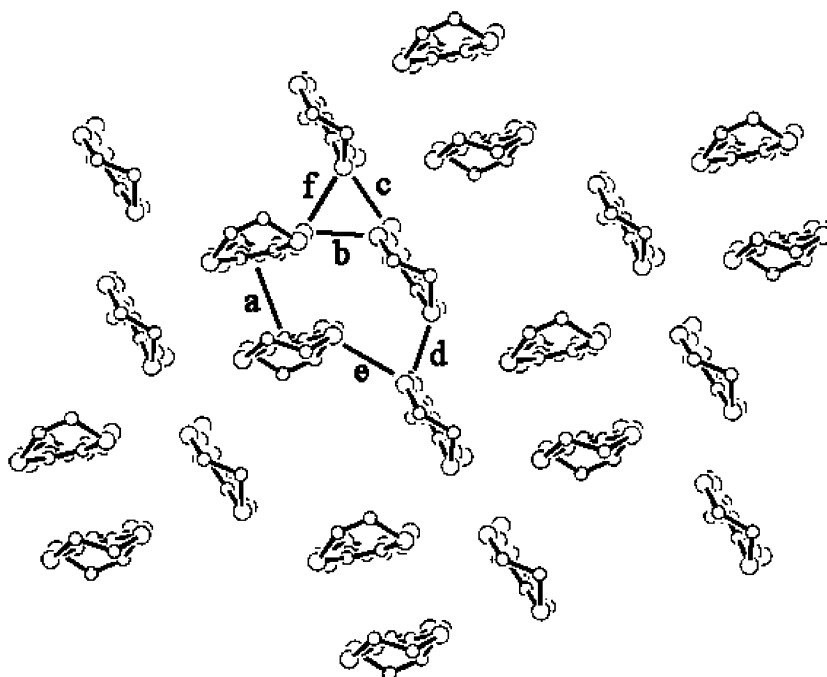


FIG. 4. Packing motif of the ET layer for **II**, at 120 K, labels a–f refer to those in Table 2.

TABLE 2  
Close S...S Contacts in Compound **II** Compared to Isostructural BEDT-TTF<sub>4</sub>[Fe(NCS)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub>  
(see Fig. 4 for Definitions of a–f)

S...S distance	Compound <b>II</b> , 240 K	Compound <b>II</b> , 120 K	Fe salt, 150 K
a	3.43, 3.51	3.41, 3.50	3.42, 3.44
b	3.50, 3.56	3.47, 3.53	3.46, 3.55, 3.54
c	3.42	3.38	3.43, 3.56
d	3.37, 3.48, 3.48, 3.59	3.34, 3.43, 3.45, 3.54	3.35, 3.53, 3.54, 3.59
e	No short contacts	No short contacts	3.59
f	3.52	3.45	3.51

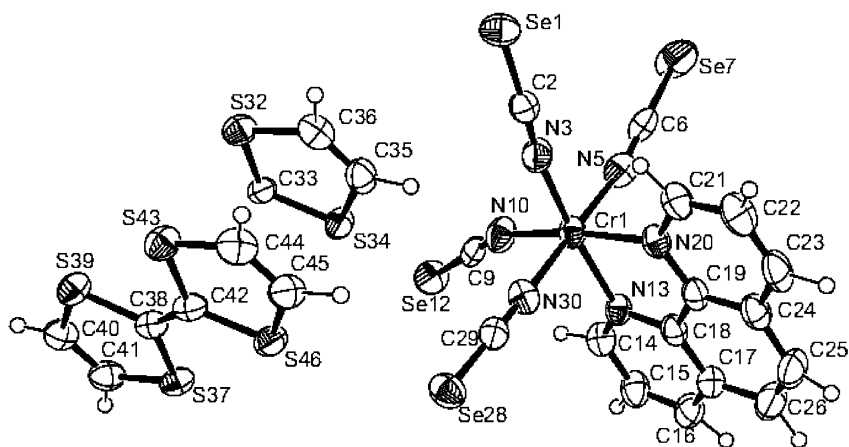
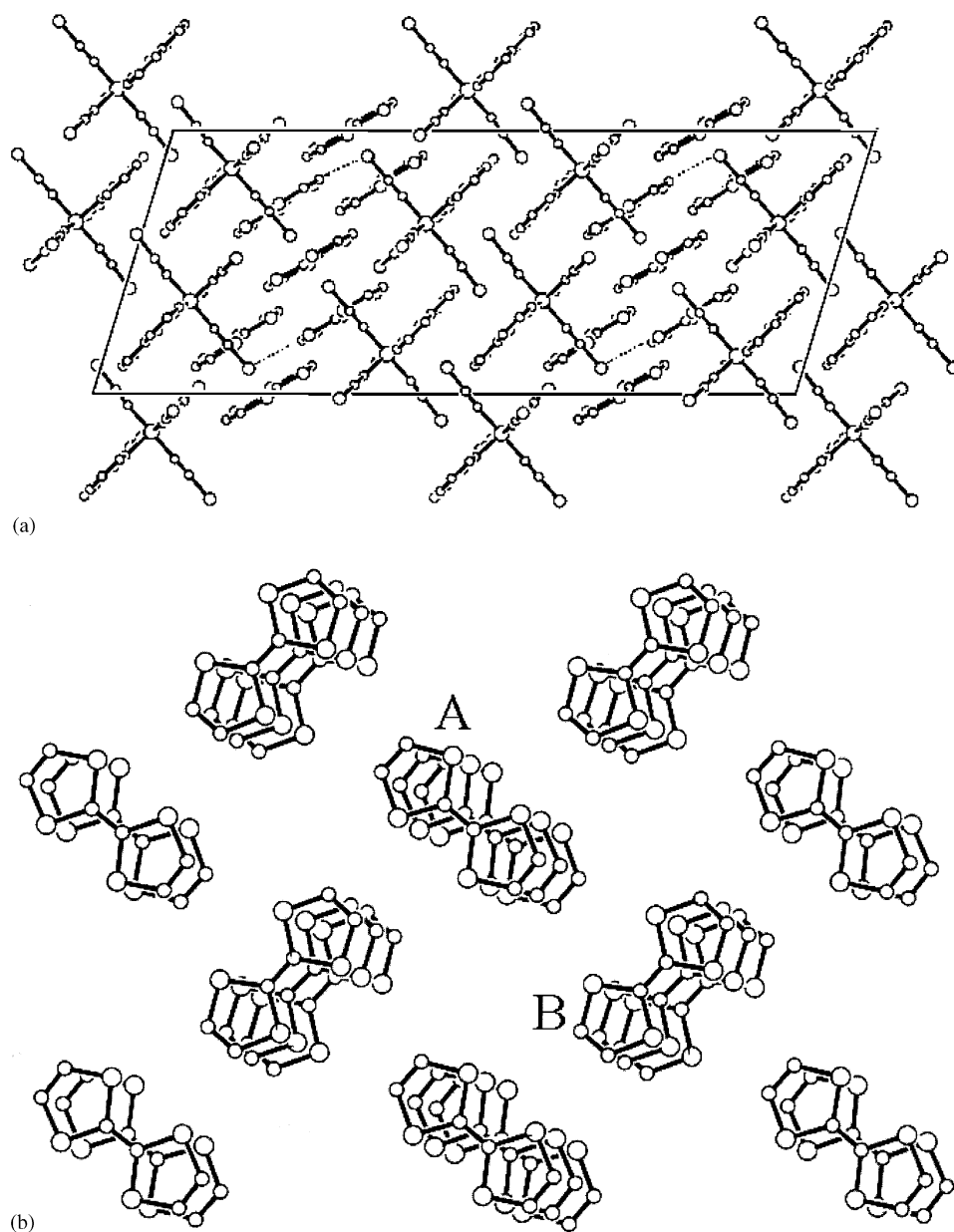


FIG. 5. ORTEP (16) diagram of **III** showing 50% thermal ellipsoids and the atom numbering scheme. Labels for hydrogen atoms have been omitted for clarity.



**FIG. 6.** (a) Unit-cell packing diagram for **III** as viewed along the crystallographic *b* direction. (b) The packing motif for the TTF cations in compound **III**.

3.78 Å. Finally, between anion and cation are a number of significant contacts; Se12...S39 is 3.80 Å, Se12...S43 is 3.82 Å and Se28...S46 is 3.65 Å. The contents of the asymmetric unit of the ferrimagnetic compound TTF[Cr(NCS)<sub>4</sub>(phen)] (**9**) differ from compound **III** by only five non-hydrogen atoms but, despite this, it has a substantially different structure; the ferrimagnet contains alternating cations and anions between which are found the strongest interactions. In particular,  $\pi$ -stacking between the phen group and TTF is prevalent. On changing the

NCS ligand to NCSe, the anion...cation interactions that involve this ligand are more accentuated since Se has a more diffuse valence orbitals and a higher van der Waals radius. It can be noted that the shortest Se...S contact in **III** (3.65 Å), as marked by dotted lines in Fig. 6a, is slightly longer than would be accepted for a S...S close contact (minimum 3.6 Å). In fact, two [Cr(NCSe)<sub>4</sub>(phen)]<sup>-</sup> anions make a cavity, bounded by Se28...S46 contacts, which has an ideal size and shape to fit the unit of three stacked TTF molecules. And so, there seems to be a competition

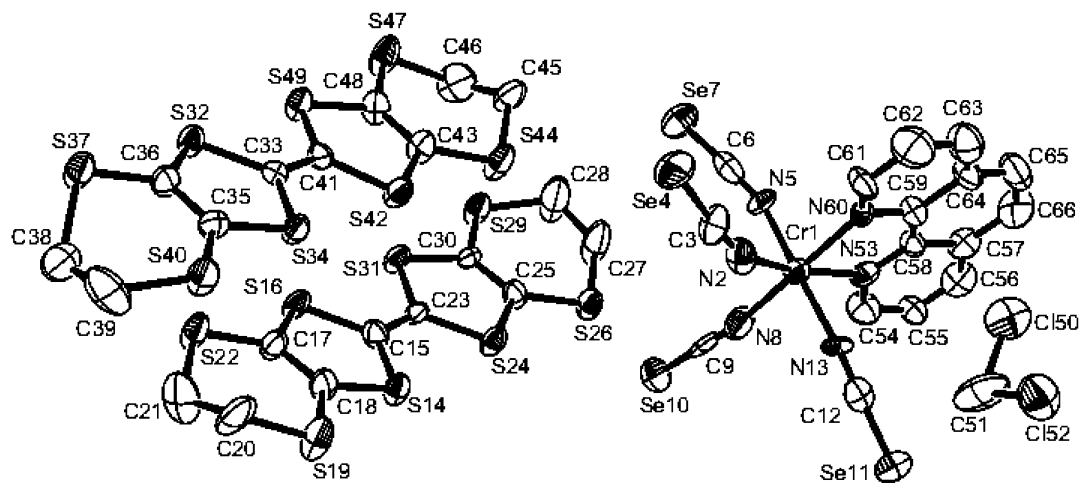


FIG. 7. ORTEP (16) diagram of IV showing 50% thermal ellipsoids and the atom numbering scheme.

between anion...cation interactions, between  $\pi$ -stacking or Se...S (or S...S) contacts, which determines the overall crystal packing and whether or not there is an infinitely extended S...S close contact network between cations. Another example of the competition is shown by  $\text{TMTSF}_3[\text{Cr}(\text{NCS})_4(\text{phen})_2] \cdot 0.5\text{CH}_2\text{Cl}_2$  (TMTSF = tetramethyltetraselenafulvalene) (9), which also has several Se...S contacts rather than  $\pi$ -stacking and incidentally has the same donor: Cr ratio as compound III. However, in the TMTSF salts, it is the presence of the Se-containing donor rather than a Se-containing acceptor that gives it

semiconducting rather than ferrimagnetic-insulating properties.

Compound IV, with the ORTEP diagram shown in Fig. 7, also has two crystallographically independent BEDT-TTF molecules, both with a 'twisted-boat' conformation and the calculated charges are  $0.8 \pm 0.1$  and  $0.4 \pm 0.1$ . Again, the structure packs with alternating anion and cation layers. The packing of the donor molecules superficially looks like a  $\beta$  packing motif (Fig. 8), which normally gives highly conducting compounds. However, in this instance the closest S...S contacts are not face-to-

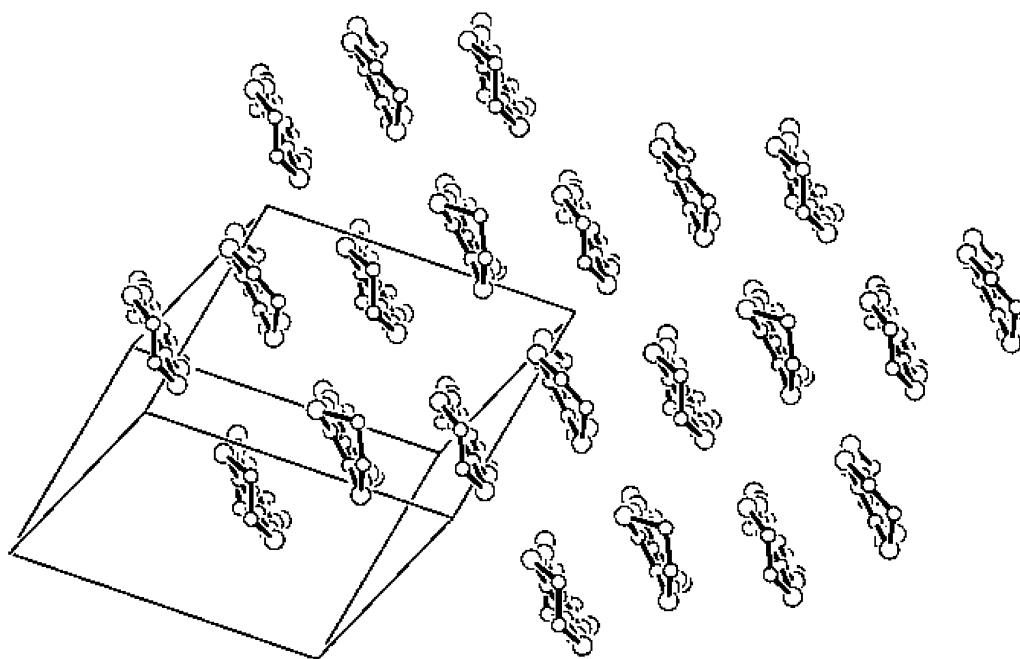


FIG. 8. The BEDT-TTF packing motif in compound IV.

face interactions within the BEDT-TTF stacks, as expected in highly conducting samples, but are between neighboring stacks in the side-to-side mode. The shortest contacts in full are S22...S47 which is 3.34 Å, S44...S19 is 3.30 Å, S40...S26 is 3.36 Å, S42...S19 is 3.38 Å, S22...S49 is 3.39 Å, S29...S37 is 3.43 Å, S40...S24 is 3.46 Å and S31...S37 is 3.51 Å. Indeed, the shortest face-to-face atomic contacts are longer than the sum of sulfur van der Waals distances; the shortest three face-to-face S...S distances are S40...S49 at 3.66 Å, S42...S16 at 3.87 Å and S49...S32 at 3.85 Å. There is also one cation...anion atomic contact between Se10 and S47 of 3.88 Å. The distance between the phen groups of neighboring Cr complexes is close, at 3.61 Å, and even though this contact is only at the edge of the ligands, this is perfectly reasonable as a  $\pi$ - $\pi$  stacking interaction (see comment in Conclusion) (22). As with compound III, the more numerous inter-ion Se...S contacts win over  $\pi$ -stacking, although this time the inter-donor S...S network is not completely removed.

### Magnetic and Electrical Transport Properties

The magnetic properties of compound II, as expected, resemble a paramagnet. In the high-temperature regime ( $> 50$  K), the molar magnetic susceptibility is modeled well by the Curie-Weiss law with a Curie constant of  $2.516 \text{ emu K mol}^{-1}$  and a Weiss temperature of  $-3.2$  K, which indicates that there are some short-range antiferromagnetic interactions. At room temperature, the  $\chi_m T$  value is  $2.488 \text{ emu K mol}^{-1}$  which suggests that the magnetic contribution from each of the BEDT-TTF units average just  $0.153 \text{ emu K mol}^{-1}$ , assuming a normal paramagnetic contribution from the anion. Also for compound II four-probe DC conductivity in the most conductive direction, parallel to the long thin plates, gives semiconducting-like behavior which does not quite follow an Arrhenius manner. A plot of  $\ln(\text{conductivity})$  versus  $(\text{temperature})^{-1}$  gives a slight curve which may correspond to a small change of activation energy ( $E_{\text{act}}$ ) with temperature from 0.13 to 0.22 eV. In the same direction, the conductivity at 300 K ( $\sigma_{300 \text{ K}}$ ) is  $0.43 \text{ S cm}^{-1}$  and is also consistent with the sample being a semiconductor. A two-probe DC measurement made perpendicular to the plate also gave a small gradual change in  $E_{\text{act}}$ ; 0.21 eV from 307 to 280 K and 0.37 eV from 280 to 266 K and with  $\sigma_{300 \text{ K}} = 4.34 \times 10^{-3} \text{ S cm}^{-1}$ . For the isostructural compound, BEDT-TTF<sub>4</sub>[Fe(SCN)<sub>6</sub>]·CH<sub>2</sub>Cl<sub>2</sub> the magnetic and electrical properties are quite similar; it is a paramagnet with small short-range antiferromagnetic interactions (Weiss constant =  $-0.19$  K) and a semiconductor with  $E_{\text{act}} = 0.7$  eV and  $\sigma_{300 \text{ K}} = 7 \times 10^{-3} \text{ S cm}^{-1}$ .

For compound III, four-probe DC measurements in the most conductive direction reveal a low but nevertheless measurable  $\sigma_{300 \text{ K}} = 4.1 \times 10^{-5} \text{ S cm}^{-1}$ , which becomes

immeasurably low at even slightly reduced temperatures. The reason for the highly resistant, insulating behavior is evident from the structure, since the TTF molecules are isolated as trimer stacks and there is no continuous network of S...S contacts throughout the crystal. The magnetic susceptibility of III also follows the Curie-Weiss law at high temperatures ( $> 50$  K) with a larger negative Weiss constant of  $\theta = -11.7$  K and a Curie constant of  $C = 3.23$ . The Weiss constant indicates substantial short-range antiferromagnetic interactions which are confirmed since the value of  $\chi_m T$  at 300 K is 1.566 per Cr center when 1.876 is expected for the Cr centers alone, with no adjusted contribution from the TTF molecules.

In contrast, a four-probe DC transport measurement in the plane of the flat crystal plates of compound IV shows semiconducting behavior with relatively high  $\sigma_{300 \text{ K}} = 1.9 \times 10^{-2} \text{ S cm}^{-1}$  and low  $E_{\text{act}} = 0.05$  eV. Anisotropic behavior is shown since perpendicular to the plate  $\sigma_{300 \text{ K}}$  falls to  $3.3 \times 10^{-4} \text{ S cm}^{-1}$ . Again, the magnetic properties of a polycrystalline sample agree with the Curie-Weiss law, this time with  $C = 1.64$  and  $\theta = -4.0$  K.

### CONCLUSIONS

We have described the synthesis, crystal structures, and the transport and magnetic properties of three new charge transfer salts with the TTF and BEDT-TTF electron donors. The common feature of these salts has been the inclusion of the NCSe ligand in the anionic complexes, namely as  $[\text{Cr}(\text{NCSe})_6]^{3-}$  or  $[\text{Cr}(\text{NCSe})_4(\text{phen})]^-$ . The new compounds provide valuable correlation between structure and physical properties, for our investigation into the supramolecular origins of bulk ferrimagnetism in the related salts (9,10) based on  $[\text{Cr}(\text{NCS})_4(\text{phen})]^-$  and  $[\text{M}(\text{NCS})_4(\text{isoquinoline})]^-$ ,  $M = \text{Cr, Fe}$ . They also provide pointers to those routes best avoided when looking for other examples of long-range magnetic order. Principally, the interactions between anion and cation can be separated into S...S or S...Se contacts and  $\pi$ -stacking, which then compete with each other. If the former plays a larger role than the latter, as occurs in the compounds presented here, then the resulting compounds are essentially paramagnetic with some conducting properties. The fact that S...Se contacts are formed more readily than S...S contacts implies that compounds with both S and Se atoms, where the Se is associated with either the anions or cation, would not be a profitable route to new materials with long-range magnetic order. A more attractive strategy includes totally Se-based salts, such as TMTSF salts of NCSe-based anions, or even removing the interaction altogether by not using S- and Se-based ligands on the anion. It would also be instructive to use modifications of the delocalized  $\pi$ -systems (here the phen ligand) to improve the likelihood of  $\pi$ -stacking. For example, electron withdrawing groups



are well known to improve the strength of the  $\pi$ -stacking interaction (22). Finally, it is worth noting that, since  $\pi$ -stacking can communicate magnetic exchange, a scheme in which this interaction is sufficiently strong between anions in TTF-based salts would open a novel route to conducting materials with long-range magnetic order. Our efforts are continuing in these directions.

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*Supporting Information Available:* All crystallographic data are available as CIF files.

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