

New Molecular Charge-Transfer Salts of TM-TTF and BMDT-TTF with Thiocyanate and Selenocyanate Complex Anions [TMTTF = Tetramethyltetrathiafulvalene; BMDT-TTF = Bis(methylenedithio)tetrathiafulvalene]

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Three new charge-transfer salts of tetrathiafulvalene (TTF)-based donors with thiocyanato- or selenocyanato-metal complex anions have been synthesised. The salts isolated were [BMDT-TTF]₄[Cr(NCS)₆] (**1**), [TM-TTF]₄[Cr(NCS)₆]·2CH₃CN (**2**) and [TM-TTF]₄[Cr(NCSe)₆]·2CH₃CN (**3**) [BMDT-TTF = bis-(methylenedithio)tetrathiafulvalene and TM-TTF = tetramethyltetrathiafulvalene]. Single crystals of compound **1** crystallise in the monoclinic *C2/c* space group with *a* = 37.286(3), *b* = 10.0539(6), *c* = 21.069(2) Å, β = 124.348(4)°, *V* = 6520.9(9) Å³ and *Z* = 4. Compound **3** was also suitable for an X-ray diffraction study, however the anionic part, [Cr(NCSe)₆][−] was highly disordered and the best solution gave a final *R* factor of 16.4%. A solution was found for the monoclinic space group *C2/m* with *a* = 13.787(3), *b* = 19.507(3), *c* = 14.735(5) Å, β = 102.90(3)°, *V* = 3862.9(17) Å³ and *Z* = 2. For compound **1** there are several S...S close

atomic contacts between the donors and acceptors, but there is no discernible magnetic exchange between ions. Such an interaction was previously observed in related salts such as [TTF][Cr(NCS)₄(phenanthroline)₂] and [donor][M(NCS)₄(isoquinoline)₂] [*M* = Cr, Fe and donor = TTF, BEDT-TTF or TM-TTF (tetramethyltetrathiafulvalene)]. Compounds **1** to **3** are all paramagnetic semiconductors in which the magnetic susceptibility is dominated by the Cr-containing anions. The structure-function relationship, along with a comparison with related compounds, indicates that there is no long-range magnetic order because there are no π-stacking interactions between donor and acceptor; these types of interactions are seen in all of the bulk magnets of this type in which the donor spin is magnetically coupled to the anion.

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Introduction

With the discovery of metallic properties in molecular organic compounds,^[1] large efforts have been devoted to the development of new organic conductors based on π-electron donors. Tetrathiafulvalene (TTF) and its analogues have to date provided the largest number of organic metals and superconductors.^[2] Until relatively recently interest in this class of compounds was focused on their transport properties, whereas current synthetic efforts are aimed towards bringing together combinations of physical proper-

ties. Since the majority of TTF-based salts consist of discrete layers of cationic and anionic components, it should be possible to prepare new molecular-based materials in which electrical, optical and magnetic properties can coexist, by including different properties into the different layers. Components with magnetic properties can be introduced by anionic complexes with paramagnetic centres.^[3–8] Of special interest to us is to establish electrical transport, even superconductivity, in a crystal lattice containing localised magnetic moments.^[3,4] With the aim of obtaining salts with long-range magnetic ordering, together with conductivity properties, some research groups have been using bimetallic complexes as counterions to the TTF-based molecule.^[4,5b] Some of us recently embarked on a different approach that consists of promoting strong interactions between the cationic and anionic sub-lattices so the electronic systems in the different networks can be coupled to achieve interesting magnetic properties.^[7] For example, we prepared a range of TTF-based salts with strong donor-acceptor interactions and subsequently long-range ferrimagnetic order.^[7] This was achieved by using anions of the type [Cr(NCS)₄(N-donor)_{*x*}][−], where N-donor = 1,10'-phenanthroline (*x* = 1)

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or isoquinoline ($x = 2$). The anions were designed to provide the opportunity for both π -stacking and close S...S contacts between the anion containing localised magnetic moments and the radical donor; the resulting ferrimagnetic compounds display both of these interactions. The question still remains, however, as to what role each of these interactions plays in promoting long-range magnetic ordering. Looking at this point we prepared salts using hexathiocyanato complexes, which can only have short S...S contacts between anions and cations. No magnetic order was observed.^[8] However, the empirical conclusion that S...S contacts are less important than π -stacking for magnetic exchange interactions was preliminary, since other factors, such as the angle of overlap of S...S short contacts and the donor charge could, of course, be significant in promoting certain physical properties.

The purpose of the present work is to continue building a range of similar compounds for our investigation into the origin of the bulk ferrimagnetism found in this family of salts. We report on the synthesis and characterisation of novel charge-transfer salts based on TM-TTF (tetramethyl-tetrathiafulvalene) and BMDT-TTF [bis(methylenedithio)tetrathiafulvalene] with paramagnetic anions that can only provide S...S or S...Se interactions.^[9]

Results and Discussion

Synthesis

The salts described here were synthesised by electrocrystallisation in conventional H-shaped electrocrystallisation cells with Pt electrodes. Black needle-shaped crystals of [BMDT-TTF]₄[Cr(NCS)₆] (**1**) were obtained with BMDT-TTF as donor and [C₉H₈N][Cr(NCS)₄(C₉H₇N)₂] [(C₉H₇N) = quinoline] as electrolyte in CH₂Cl₂ solution. The fact that the quinoline ligand is not present can only be explained by a ligand exchange during the electrocrystallisation due to the lability of the quinoline.^[9]

The isomeric salts [TM-TTF]₄[Cr(NCS)₆]·2CH₃CN (**2**) and [TM-TTF]₄[Cr(NCSe)₆]·2CH₃CN (**3**) were synthesised with TM-TTF as donor and the anions [(C₂H₅)₄N]₃[Cr(NCS)₆] and [(C₂H₅)₄N]₃[Cr(NCSe)₆], respectively, as electrolytes in a mixture of dichloromethane and acetonitrile.

Description of Crystal Structures

The collection data and crystal parameters for compounds **1** and **3** are given in Table 1. A standard ORTEP^[13] diagram of the asymmetric unit of compound **1**, showing the atom numbering scheme and atoms as 50% thermal ellipsoids, is shown in Figure 1.

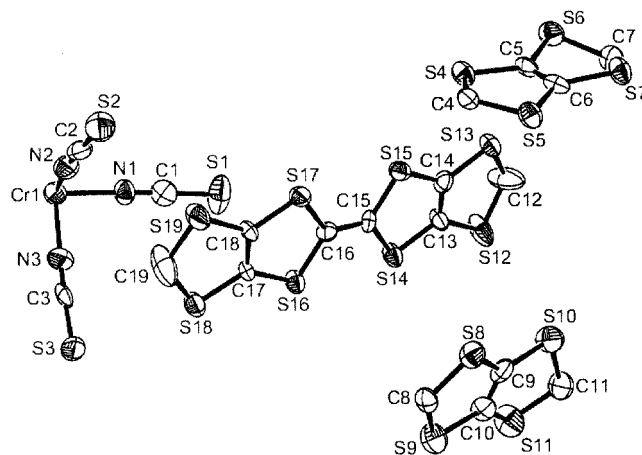


Figure 1. An ORTEP^[13] diagram of the asymmetric unit of **1**, showing the atom numbering scheme and atoms as 50% thermal ellipsoids; the hydrogen atoms have been removed for clarity

As with many charge-transfer salts based on TTF-like donors the overall structure consists of alternating layers of cations and anions, as shown in Figure 2.

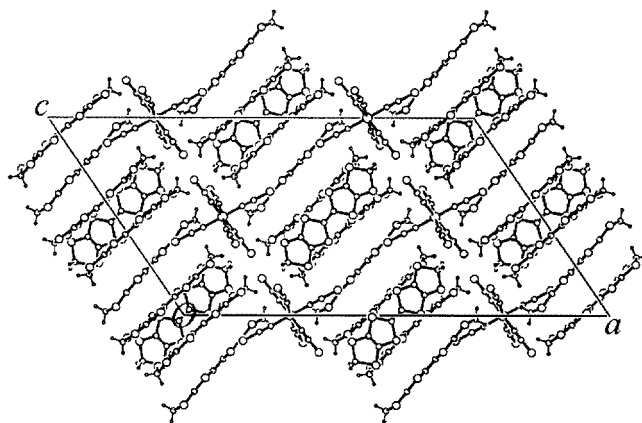


Figure 2. Unit cell diagram showing the overall molecular packing arrangement for **1**

Furthermore, in this salt the cationic BMDT-TTF layers are interpenetrated by two NCS ligands per anion. The packing arrangement for the donor molecules within each cationic layer in Figure 3 can be described in terms of two

Table 1. The collection and crystal-structure parameters for **1** and **3**

Compound	1	3
Chem. formula	C ₃₈ H ₁₆ CrN ₆ S ₃₈	C ₅₀ H ₅₄ CrN ₈ S ₁₆ Se ₆
<i>a</i> (Å)	37.286(3)	13.787(3)
<i>b</i> (Å)	10.0539(6)	19.507(3)
<i>c</i> (Å)	21.069(2)	14.735(5)
α (°)	90.00	90.0
β (°)	124.348(4)	102.90(3)
γ (°)	90.00	90.0
<i>V</i> (Å ³)	6520.9(9)	3862.9(17)
<i>Z</i>	4	2
Molecular weight	1826.85	1805.73
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/m
<i>T</i> (K)	223(2)	223(2)
Reflections [<i>I</i> > 2σ(<i>I</i>)]	2549	1234
$\rho_{\text{calcd.}}$ (g cm ⁻³)	1.861	1.552
μ (mm ⁻¹)	1.433	3.444
<i>R</i> (<i>F</i> _o)	0.0371	0.1639
<i>Rw</i> (<i>F</i> _o ²)	0.0731	0.4066

types of rows. Row A, as marked in Figure 3, consists of a face-to-face BMDT-TTF dimer that alternates with a single donor molecule arranged perpendicular to the dimer. Row B, which lies between each type-A row, consists of single BMDT-TTF molecules that lie parallel to the dimers of row A, but are translated along the crystallographic *b* axis with respect to the dimers.

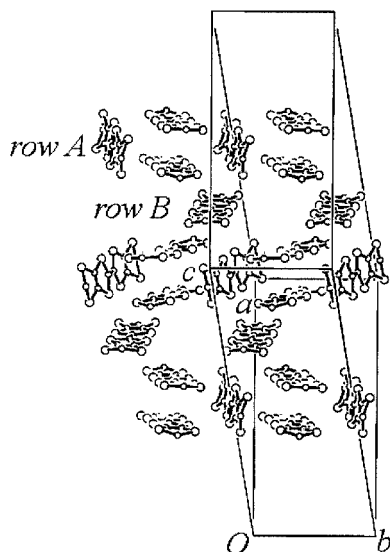


Figure 3. Packing motif of BMDT-TTF donors in compound **1**; the labels for rows A and B are described in the text

Furthermore, in successive instances of row A, the C=C central bonds of the donors are twisted by an angle of approximately 31° with respect to each other. Any close S...S intermolecular contacts are almost all in rows of type A and for the inter-dimer distances these range from 3.38 Å (S12...S6) to 3.50 Å (S15...S16). Between molecules of a dimer and the neighbouring perpendicular BMDT-TTF molecule in the same row they range from 3.43 Å (S14...S17) to 3.56 Å (S13...S4). There are only two close atomic contacts between rows A and B of 3.50 Å (S19...S10) and 3.57 Å (S17...S10). In addition there are a few atomic S...S contacts between the anions and cations even though an NCS ligand (with terminal S1) penetrates the cation layer. Each of these contacts is close to the sum of the van de Waals radii of two sulfur atoms, with values of 3.55, 3.57 and 3.60 Å for contacts S18...S3, S19...S2 and S7...S3, respectively. There are no significant atomic contacts between the anions, as the shortest distance between the terminal S atoms on neighbouring Cr complexes is just 4.06 Å.

For compound **3** the structure could only be refined to an *R* factor of 16%, mainly due to one-dimensional disorder of the anion layers and therefore this structure will not be discussed in detail. Nevertheless, the donor molecules are well ordered and are stacked along the *a* axis with intermolecular S...S distances of between 3.65 and 3.81 Å (Figure 4). The donor molecules between neighbouring stacks along the *c* axis have alternate distances due to the insertion of NCSe ligands. A simplified layout showing only Cr and Se

atoms of the anionic layer, parallel to the crystallographic *ab* plane, is shown in Figure 5. The CrSe₆ units with filled bonds form a regular anionic sheet, although in this refinement all the positions have an occupancy factor of 0.5 except for the overlying Se(1) atoms along the *b* axis, which have a factor of 1.0. The one-dimensional disorder is caused by displacement of the regular layer with a half-lattice constant along the *a* direction.

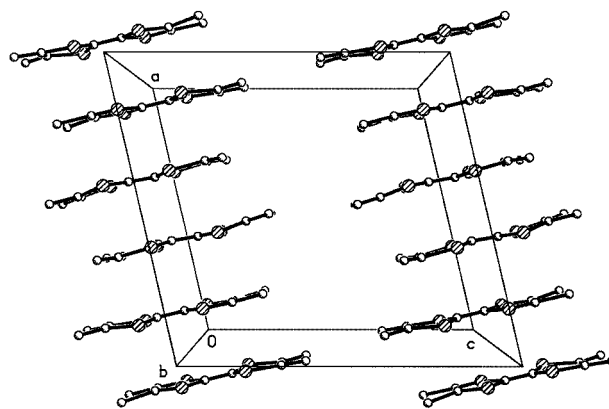


Figure 4. Packing motif of TM-TTF donors in compound **2** and **3**

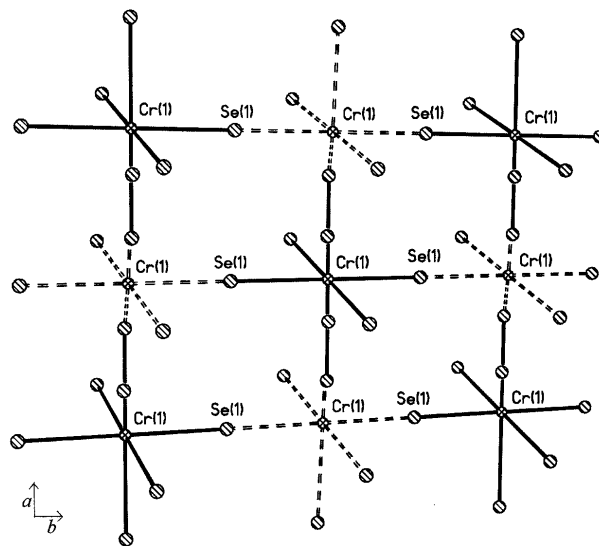


Figure 5. Two overlying Cr(NCSe)₆³⁻ sheets showing one-dimensional disorder (see text)

Compound **2** crystallises in the same space group with nearly identical coordinates for all atoms and a similar one-dimensional disorder. The *R* value is about 18.5%, with unit cell parameters *a* = 13.806(7), *b* = 19.41(1), *c* = 14.63(1) Å, β = 103.03(4)° and *V* = 3818.7(4) Å³ at 223 K.

Electrical Transport and Magnetic Properties

The conductivity behaviour for compound **1** was measured from 300 to 120 K. This compound shows a semiconducting behaviour with a modest room temperature conductivity ($\sigma_{300\text{K}}$) of $4 \times 10^{-3} \text{ S cm}^{-1}$ and an Arrhenius-like behaviour on decreasing the temperature with an activation energy (*E*_a) of 0.1 eV. For compound **2**, due to the crystal

morphology (elongated hexagonal plates), we were able to measure the electrical transport in three mutually perpendicular directions, although because of the small crystal size only two probe measurements were possible. For all three directions a plot of $\ln(\text{resistance})$ vs. $1/T$ gave a straight line, i.e. the Arrhenius behaviour of a semiconductor. Perpendicular to the plane of the plate $\sigma_{300\text{K}} = 2.26 \times 10^{-3} \text{ S cm}^{-1}$ and $E_a = 0.05 \text{ eV}$; in the plane of the plate, across the long direction of the elongated hexagon $\sigma_{300\text{K}} = 3.07 \times 10^{-3} \text{ S cm}^{-1}$ and $E_a = 0.04 \text{ eV}$; in the plane of the plate across the shorter direction $\sigma_{300\text{K}} = 6.02 \times 10^{-3} \text{ S cm}^{-1}$ and $E_a = 0.04 \text{ eV}$. For compound **3** it was only possible to measure along the needles long axis by standard four-probe methods and although a large $\sigma_{300\text{K}}$ of 454.1 S cm^{-1} was found, the variation with temperature indicated semiconducting behaviour, with $E_a = 0.06 \text{ eV}$ (Figure 6).

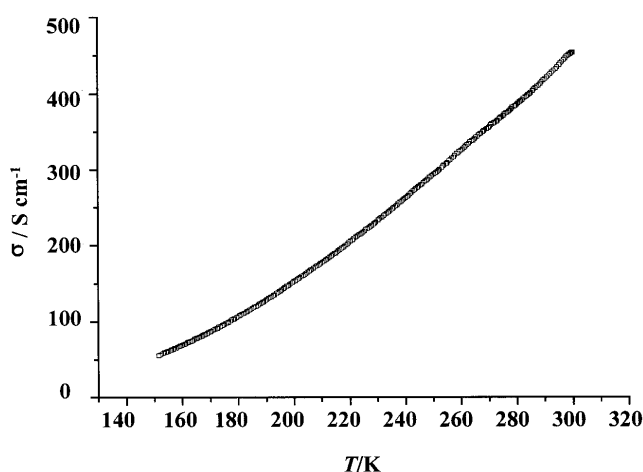


Figure 6. Plot of conductivity vs. temperature for compound **3**

The magnetic properties of **1** resemble a paramagnetic material in which the magnetic susceptibility is dominated by the metal complex. A plot of susceptibility vs. temperature was fitted well to the Curie–Weiss law and gave a Curie constant C of $2.49 \text{ emu K mol}^{-1}$ and a small negative Weiss constant of $\theta = -1.1 \text{ K}$. For compound **2** a similar fit gave $C = 2.10 \text{ emu K mol}^{-1}$ and $\theta = -0.05 \text{ K}$; for compound **3** the values are $C = 1.94 \text{ emu K mol}^{-1}$ and $\theta = -0.28 \text{ K}$. All of the salts gave a Curie constant greater than expected for a Cr^{III} spin $3/2$ centre alone, for which a value of $1.875 \text{ emu K mol}^{-1}$ is expected, indicating that the donor radical contributes to the measured susceptibility to some extent. The salts each show small negative Weiss values, which indicate that they all have a small number of short range antiferromagnetic interactions.

Spectroscopic Properties

The mixed-valence character of compounds **1–3** was confirmed by the presence of the characteristic broad A band in the IR and NIR-visible spectra, corresponding to the mixed-valence states of low-dimensional conducting organic solids, centred at 3300 , 2400 and 2350 cm^{-1} , respectively.^[14]

Since the size of the crystals for compound **1** was suitable, the degree of ionicity of the donor could be studied by Raman reflection spectrometry. It has been reported previously that there is an approximately linear dependence between the donor charge and the Raman-active $\text{C}=\text{C}$ stretching frequencies in salts of the electron-donor molecule BEDT-TTF.^[15] Raman spectra of the BMDT-TTF neutral donor shows two bands at 1501.9 and 1549.7 cm^{-1} in the $\text{C}=\text{C}$ stretching region, while in salt **1** we can observe one band at 1438.6 cm^{-1} . Fitting this data to the equations used for BEDT-TTF, for salt **1** the donor charge was found to be 0.75 , which is in agreement with the compound stoichiometry found by single crystal X-ray diffraction and elemental analysis. The Raman data further show that the charge is the same for each of the donor molecules, rather than being distributed unevenly.

EPR Spectroscopy

The EPR spectrum of **1** was carried out on a microcrystalline sample. One unique broad signal with a g factor of 2.0134 and a linewidth of 320 G was observed. Since no discrete signals were seen for the cation and anion this indicates that there is some electronic interaction between the spins of the different sites. The temperature dependence of the EPR signal for compound **1** was studied down to 108 K but no significant changes in its parameters were observed, revealing that there are no electronic phase-transitions down to this temperature. Compounds **2** and **3** both display a narrow EPR signal of 7.5 G with a g factor of 2.0076 , which is consistent with the radical donor alone, and also show a very broad signal arising from the Cr^{III} spin, with a g factor of 1.8455 . This shows that there are no electronic interactions between the anion and the radical donor. In order to examine the paramagnetic contribution of the donor network separately, the temperature dependence of the narrow signal was observed down to 4 K . The dependence of the double integral of this signal with temperature follows the Curie–Weiss law, with the rest of the signal parameters not changing to any significant extent.

Conclusions

We have described three new charge-transfer salts, including their synthesis and characterisation by magnetic susceptibility, electrical transport and spectroscopic measurements. One of the salts, $[\text{BMDT-TTF}]_4[\text{Cr}(\text{NCS})_6]$ (**1**), was well characterised by single crystal X-ray diffraction. The remaining two compounds were found to be $[\text{TM-TTF}]_4[\text{Cr}(\text{NCS})_6] \cdot 2\text{CH}_3\text{CN}$ and $[\text{TM-TTF}]_4[\text{Cr}(\text{NCSe})_6] \cdot 2\text{CH}_3\text{CN}$. As observed in the crystal structure of **1** the only close atomic contacts between the anion and cation components are close $\text{S} \cdots \text{S}$ contacts at distances below the sum of the van de Waals radii of two sulfur atoms. It must also be assumed that the TM-TTF salts have either no anion to cation contacts or, more likely, they are also only those between chalcogenides. As a result each of the salts is a paramagnetic semiconductor, since there is no magnetic ex-

change between donor and acceptor molecules. Unlike the related salts based on $[\text{Cr}(\text{NCS})_4\text{phenanthroline}]^-$ or $[\text{Cr}(\text{NCS})_4(\text{isoquinoline})_2]^-$ anions, which show magnetic exchange, the new salts have no mechanism for anion to cation π -stacking. At present we and others have made several salts, with different stoichiometries,^[16] which only have close S...S or S...Se contacts between ions, and none of them show long range-magnetic order. Other salts have been made with other close contacts between ions, such as those involving halogens^[17] or hydrogen bonding,^[18] but so far only our approach with π -stacking has resulted in bulk magnetic materials with TTF-based donor-to-acceptor magnetic exchange. Therefore, our further efforts in this area will focus on the synthesis of TTF-based salts containing paramagnetic anions with aromatic ligands that can increase π -stacking interactions between the ions in an effort to increase magnetic critical temperatures beyond the current highest value of 8.9 K.

Experimental Section

Synthesis

The synthesis of BMDT-TTF was carried out as described previously.^[10] TM-TTF was synthesised by a Wittig-type coupling with triethylamine as reported in the literature.^[11] $[\text{C}_9\text{H}_8\text{N}][\text{Cr}(\text{NCS})_4(\text{C}_9\text{H}_7\text{N})_2]$, where $\text{C}_9\text{H}_7\text{N}$ is quinoline, was prepared as described previously for the isoquinoline derivative,^[7a] by a ligand-exchange reaction with Reinecke's salt, $\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$, on adding the corresponding nitrogen donor ligand and refluxing in ethanol overnight. $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}(\text{NCS})_6]$ and $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$ were prepared by the published methods.^[12]

Electrocrystallisation

The charge-transfer salts were synthesised by electrochemical crystallisation from freshly distilled dichloromethane or acetonitrile solutions (see below for details) in conventional H-shaped electrochemical cells with Pt electrodes at a constant temperature of 295(2) K over one week and at a constant current of 1 μA .

A suspension of $[\text{C}_9\text{H}_8\text{N}][\text{Cr}(\text{NCS})_4(\text{C}_9\text{H}_7\text{N})_2]$ (80 mg) in 50 mL of dichloromethane was prepared and, whilst stirring, 18-crown-6-ether was added slowly until the anion dissolved completely. Solid BMDT-TTF (10 mg) was placed on the anode arm and the remainder of the cell was filled with the solution of the Cr complex (total cell volume 60 mL). Black needle-shaped crystals suitable for X-ray diffraction were obtained and found to be $[\text{BMDT-TTF}]_4[\text{Cr}(\text{NCS})_6]$ (**1**).

The compound $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}(\text{NCS})_6]$ or $[(\text{C}_2\text{H}_5)_4\text{N}]_3[\text{Cr}(\text{NCSe})_6]$ (6 mg) was dissolved in 12 mL of a mixture of dichloromethane and acetonitrile (2:1 v/v). TM-TTF (3 mg) was placed in the anode compartment of the electrochemical cell and the remainder was filled with the solution of the anion (total cell volume 15 mL). The product salts are characterised as black elongated hexagonal plates of $[\text{TM-TTF}]_4[\text{Cr}(\text{NCS})_6] \cdot 2\text{CH}_3\text{CN}$ (**2**) and thin dark needles of $[\text{TM-TTF}]_4[\text{Cr}(\text{NCSe})_6] \cdot 2\text{CH}_3\text{CN}$ (**3**).

Physical Measurements

The magnetic measurements of polycrystalline and randomly orientated samples of **1–3**, held in gelatine capsules inside a plastic

tube, were measured using a Quantum Design MPMS7 SQUID magnetometer. The core diamagnetism was estimated for each of the salts by using Pascal's constants.

Conductivity measurements were performed on an Oxford Instruments Maglab System 2000 with an electrical properties (EP) probe. Gold wires (0.0025 mm) were attached directly to the crystals using Au conductive paste, and then connected to the EP probe with an eight-pin integrated circuit plug, allowing simultaneous measurement of two samples by four-electrode techniques.

EPR spectra were obtained with a Bruker X-band ESP 300E spectrometer, equipped with a rectangular cavity, operating in the T102 mode. Spectra were recorded in the 2–400 K range using a Bruker variable-temperature unit and an Oxford Instruments EPR-900 cryostat, a field frequency lock ER 033M system and an NMR gaussmeter ER 035M.

Transmission spectra were measured for finely ground samples as a KBr pellet (about 1 wt.%) with a Nicolet 5ZDX interferometer with Fourier transform (400–4400 cm^{-1}) or a Varian Cary 5 spectrometer (3330–20000 cm^{-1}). The Raman spectrum of **1** was measured at room temperature on a Renishaw Ramascope System 1000 using a He-Ne laser (632.8 nm), a CCD detector, a slit width of 10 μm and a 10% neutral density filter.

X-ray diffraction data were collected at 223 K, on a Nonius Kappa CCD diffractometer with monochromatic $\text{Mo-K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Data were collected via ϕ and ω multiscans and reduced with the program DENZO-SMN without absorption correction. For compounds **2** and **3** several crystals were checked and four or five measurements were made with the best of them. Nevertheless, the refinement of the structures was not good due to one-dimensional disorder of the anionic lattice. This resulted in diffuse stripes being seen in the broad reflections of the diffraction images, which means that some diffuse scattering is included in the diffraction. Further problems with one-dimensional disorder lie in the variability of the diffraction, which usually produces extinction of some of the reflections and hence a change in the Bravais lattice could occur. Since the disorder only exists in the anionic part, the donor molecules are well ordered and the packing can be well established.

CCDC-179735 (**1**) and CCDC-179736 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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