

New Molecular Charge Transfer Salts of BEDT-TTF, Bis(ethylenedithio) Tetrathiafulvalene, with Thiocyanato-Complex Anions: (BEDT-TTF)₄[Fe(NCS)₆] · CH₂Cl₂ and (BEDT-TTF)₂[Cr(NCS)₄(bipym)] · 0.15H₂O

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

Two new charge transfer salts of BEDT-TTF, bis(ethylenedithio) tetrathiafulvalene, with thiocyanato-metal complex anions have been synthesized and characterized as (BEDT-TTF)₄[Fe(NCS)₆] · CH₂Cl₂ and (BEDT-TTF)₂[Cr(NCS)₄(bipym)] · 0.15H₂O, where bipym = 2,2'-bipyrimidine. The Fe salt, I, crystallizes in the *P*-1 (No. 2) space group at 150 K with $a = 10.629(1)$ Å, $b = 12.099(1)$ Å, $c = 16.062(2)$ Å, $\alpha = 99.61(1)^\circ$, $\beta = 90.87(1)^\circ$, $\gamma = 112.92(1)^\circ$, and $V = 1868.5(6)$ Å³. At 150 K the Cr salt, II, crystallizes in the *P*-1 (No. 2) space group with $a = 9.243(2)$, $b = 11.781(2)$, $c = 22.925(5)$ Å, $\alpha = 93.76(3)$, $\beta = 101.51(3)$, $\gamma = 105.45(3)^\circ$, $V = 2339.0(8)$ Å³, and $Z = 2$. Both salts exhibit close S...S contacts between the anion and cation components and in II there is no π -stacking between the bipym group and the BEDT-TTF molecules. Both salts are paramagnetic with $C = 4.926$ I and $C = 1.819$ II with small negative Weiss constants of -0.19 and -0.26 , respectively. Therefore, the S...S contacts alone do not promote correlated magnetic effects as seen in other thiocyanato salts that also contain π -stacking. Each compound is a semiconductor and has two crystallographically independent BEDT-TTF molecules for which bond length analysis give charges of $+0.9 \pm 0.1/+0.6 \pm 0.1$ for I and $+0.3 \pm 0.1/+0.9 \pm 0.1$ for II. © 2001 Academic Press

Key Words: charge transfer salt; magnetic susceptibility; conductivity.

1. INTRODUCTION

Charge transfer salts of organochalcogenide electron donors are characterized by a wide range of transport properties from insulating and semiconducting to metallic and superconducting (1). The transport properties can be correlated with the relative positions of the donors, which are organized, in part, by their spatial relationships with the

counterions and other included molecules such as solvent (2–4). Until relatively recently interest in this class of compounds has focused entirely on their transport properties, although contemporary emphasis has been on preparing materials with mixed properties such as conductivity and magnetism. In addition to the magnetic effects, which arise from the radical donor electrons, paramagnetic centers are typically introduced through the incorporation of a metal complex as the anion component of the salt (5). The vast majority of the paramagnetic systems of this type contain d-block transition metals with unpaired and localized electron density. For example TTF, tetrathiafulvalene, based salts have been made with anions [FeCl₄][−] (6), [Fe(CN)₆]^{3−} (7), Reineckes anion [Cr(NCS)₄(NH₄)₂][−] (8), and [Cr(C₂O₄)₃]^{3−} (9). In these salts the sources of the physical phenomena of conductivity and magnetism are discrete and any magnetic order, such as in salts containing the [M^{II}M^{III}(C₂O₄)₃][−] ion (5), is not mediated by the radical cation. In contrast we have recently prepared a range of TTF-based salts showing long-range ferrimagnetic order that does involve the radical donor. This was realized by promoting close contacts between the anion and cation sublattices. That has been done in the past by exploiting H bonding (3, 9, 10), but to synthesize magnetically ordered materials we focused on promoting S...S or S...Se intermolecular contacts and π -stacking. The ferrimagnetic compounds with anions of the type [Cr(NCS)₄(N–N)_{1,2}][−], where N–N = 1,10 phenanthroline or isoquinoline, displayed both of the anion...cation interactions that we had sought (11, 12). So the question arose as to the origin of the long-range magnetic order, whether it was a consequence of the close chalcogen contacts or the π -stacking, or that both interactions had an effect. The purpose of the present work was to prepare similar salts that only contain close S...S

contacts and to monitor any subsequent deviation from simple paramagnetism.

2. EXPERIMENTAL METHODS

2.1. Synthesis

2.1.1. Synthesis of starting materials. $[(C_4H_9)_4N][Fe(NCS)_6]$ was prepared by a slight variation of the published method for $[(CH_3)_4N][Fe(NCS)_6]$ (13) in that $[(C_4H_9)_4N]SCN$ was used to precipitate the product rather than $[(CH_3)_4N]SCN$. $[(C_2H_5)_4N][Cr(NCS)_6]$ and subsequently $[(C_2H_5)_4N][Cr(NCS)_4(bipym)]$, bipym = 2,2'-bipyrimidine, were prepared by the published methods (14, 15). Dichloromethane was freshly purified by standard methods (16) immediately before use. The electrochemical cell and electrodes were washed with nitric acid followed by distilled water or methanol and thoroughly dried at 160°C.

2.1.2. Synthesis of BEDT-TTF charge transfer salts. Both charge transfer salts were prepared by *in situ* oxidation of BEDT-TTF (10 mg), which was placed in the anode arm of an H-shaped electrochemical cell (max. volume 50 ml). The cell contained a glass frit in the cross-bar of the "H" cell and a second frit in the cathode side that prevented contamination of the anode by reduction products. The remainder of the cell was filled with a filtered solution of either $[(C_4H_9)_4N][Fe(NCS)_6]$ (80 mg) or $[(C_2H_5)_4N][Cr(NCS)_4(bipym)]$ (100 mg) in CH_2Cl_2 (50 ml). A drop of water was added to the cells prior to saturating the solutions and sealing the cells under dry dinitrogen. A constant current of 1 μA was applied across the cells for two weeks, giving either 3 mg of dark blocks for the Fe salt or 4 mg of dark brown plates for the Cr salt. Both sets of crystals were suitable for structure solution by X-ray single-crystal diffraction and were found to have stoichiometries $(BEDT-TTF)_4[Fe(NCS)_6] \cdot CH_2Cl_2$, **I** and $(BEDT-TTF)_2[Cr(NCS)_4(bipym)] \cdot 0.15H_2O$, **II**. Compound **I**: Found C, 27.8; H, 1.5; N, 3.7; S, 60.5; Fe, 2.4; Cl, 3.5; Calc for $C_{46}H_{32}N_6FeS_{38} \cdot CH_2Cl_2$, C, 27.8; H, 1.7; N, 3.5; S, 60.1; Fe, 2.75; Cl, 3.5. Compound **II**: Found C, 31.2; H, 1.7; N, 9.0; S, 51.9; Cr, 4.5; Calc for $C_{32}H_{22}N_8S_{20}Cr \cdot 0.15H_2O$, C, 31.6; H, 1.9; N, 9.2; S, 52.8; Cr, 4.2.

2.2. Physical Measurements

DC magnetization experiments were made with a Quantum Design MPMS7 SQUID magnetometer using randomly orientated polycrystalline samples in a gelatin capsule at an external field of 1 kG. Reflective Raman spectra were measured with a Reninshaw System 1000 Ramascope using a He-Ne laser ($\lambda = 632.81$ nm) with 10- μm slits and $\times 50$ objective lens. The laser power was adjusted downward until the sample did not burn and scans were then accumulated until the signal:noise ratio was static. Single-crystal

X-ray diffraction data were collected on an Enraf-Nonius diffractometer with a KappaCCD area detector and graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using SHELX97 (17). Absorption correction was achieved with SORTAV (18). Two probe DC transport measurements were made with an Oxford instruments Mag Lab 2000 equipped with an EP probe. Gold wire electrodes of 0.025 mm diameter were attached directly to the crystals using Pt paste (Degussa).

3. RESULTS AND DISCUSSION

3.1. Crystal Structures

Standard ORTEP (19) diagrams of compounds **I** and **II**, which show the atom numbering scheme and 50% thermal ellipsoids are shown in Figs. 1 and 2, respectively. Crystallographic data for both compounds can be found in Table 1. For compound **I**, containing the $[Fe(NCS)_6]^{3-}$ anion, the overall structure has a layered motif with alternating layers that exclusively contain anions or cations, which is a common pattern in charge transfer salts with BEDT-TTF. This layering is shown in Fig. 3, which is a packing diagram for compound **I** viewed along the crystallographic *a* direction. Figure 3 also shows that the cationic layer is penetrated to some extent by NCS^- ligands of the anion. However, the terminal S atom of the penetrating ligand (S9) is fairly well isolated from the S atoms of the donors since the closest S9-to-S(cation) distance is just 3.77 Å (compared to the sum of the S atoms' van de Waals distance of 3.6 Å). Nevertheless there is a close cation-to-anion contact $S11 \cdots S1'$ of 3.41 Å.

The organic layer consists of two distinct rows of donors: a row of dimers (molecules i and ii in Fig. 4) that are interleaved by the penetrating NCS^- ligand, as described

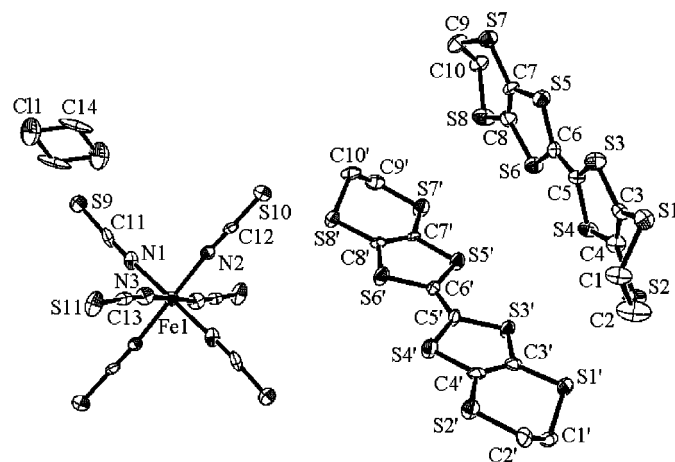


FIG. 1. ORTEP (19) diagram for compound **I** showing the atom numbering scheme and 50% thermal ellipsoids. H atoms are excluded for clarity.

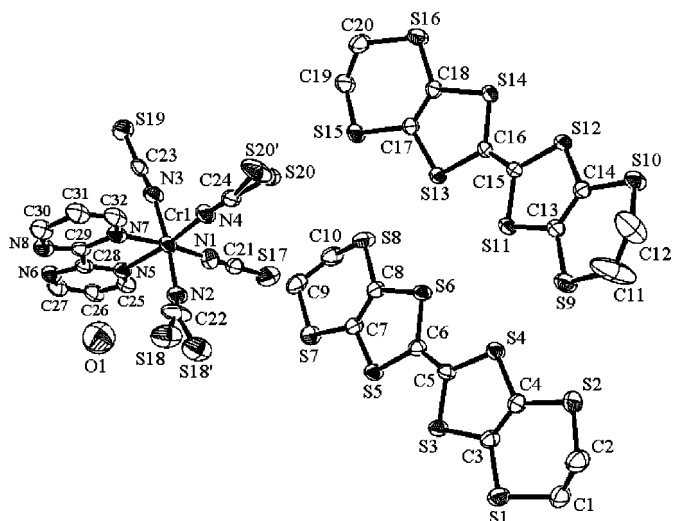


FIG. 2. ORTEP (19) diagram for compound **II** showing the atom numbering scheme and 50% thermal ellipsoids. H atoms are excluded for clarity.

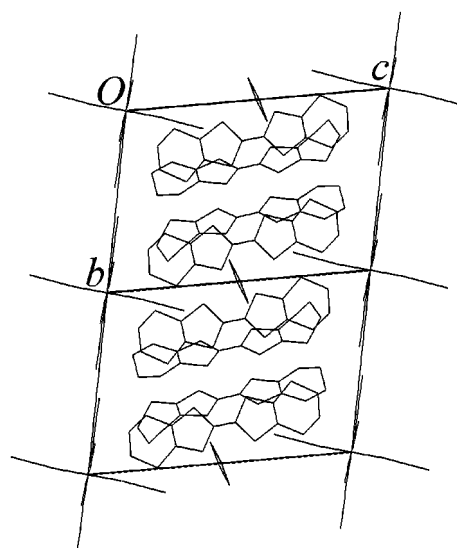


FIG. 3. The crystal packing for compound **I** viewed along the crystallographic *a* direction.

above, and a row of donors perpendicular to the dimers. Table 2 gives a list of the short S...S contacts within the cationic layer. Furthermore, there is an interanion short S...S contact of 3.45 Å that occurs between the S11 atoms

TABLE 1
Crystallographic Data for Compounds **I** and **II**

	Compound	
	I	II
Empirical formula	C ₄₇ H ₃₄ Cl ₂ FeN ₆ S ₃₈	C ₃₂ H ₂₀ CrN ₈ O _{0.15} S ₂₀
Formula weight	2027.83	1212.28
Temperature (K)	150(2)	150(2)
Wavelength (Å)	0.71073 (MoK α)	0.71073
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
Unit cell dimensions	<i>a</i> = 10.629(1) Å <i>b</i> = 12.099(1) Å <i>c</i> = 16.062(2) Å α = 99.61(1)° β = 90.87(1)° γ = 112.92(1)°	<i>a</i> = 9.243(2) Å <i>b</i> = 11.781(2) Å <i>c</i> = 22.925(5) Å α = 93.76(3)° β = 101.51(3)° γ = 105.45(3)°
Volume (Å ³)	1868.5(6)	2339.0(8)
<i>Z</i>	1	2
Density (calc.) (Mg/m ³)	1.802	1.812
Absorption coefficient (mm ⁻¹)	1.378	1.268
Reflections collected	10835	42657
Independent reflections	5265 [<i>R</i> _{int} = 0.0861]	12731 [<i>R</i> _{int} = 0.0573]
Final <i>R</i> indices [<i>F</i> ² > 2 σ (<i>F</i> ²)]	<i>R</i> ₁ = 0.0788, <i>wR</i> ₂ = 0.1367	<i>R</i> ₁ = 0.0538, <i>wR</i> ₂ = 0.1528
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1523, <i>wR</i> ₂ = 0.1546	<i>R</i> ₁ = 0.0861, <i>wR</i> ₂ = 0.1728

of neighboring [Fe(NCS)₆]³⁻ groups, for example, across the gap between donor molecules *iv* and *iii* in Fig. 4. The donor layer is composed of two crystallographically discrete BEDT-TTF molecules that are arranged approximately perpendicular to each other (Fig. 4). Using the empirical correlation between C-S and C=C bond lengths and the donor charges in BEDT-TTF salts (20) the calculated charges in compound **I** are consistent with the stoichiometry. The donor molecule with central bond C5-C6 has a calculated charge of 0.9 ± 0.1 (exemplified by molecules *i* or *ii* in Fig. 4) and the other molecule has a charge of 0.6 ± 0.1.

Compound **II** also has segregation of anionic and cationic layers in the packing diagram (Fig. 5) in which the relationship between the layers is similar to that displayed by the related compound [TMTSF]₃[Cr(NCS)₄

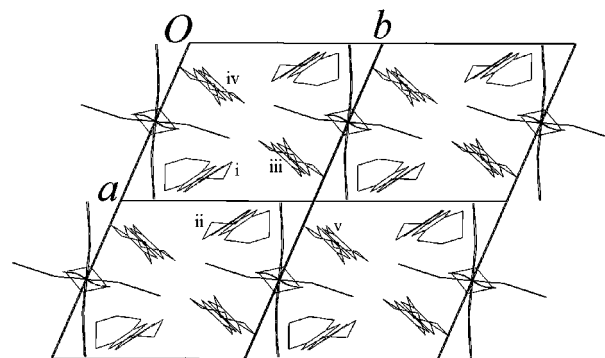


FIG. 4. The crystal packing for compound **I** viewed along the crystallographic *c* direction.

TABLE 2
S...S Close Contacts in Compound I

S...S	Distance (Å)	S...S	Distance (Å)
S4(i) ... S5(ii)	3.42	S7(iv)-S3'(iii)	3.43
S6(i) ... S3(ii)	3.44	S7'(iv)-S1'(iii)	3.56
S2(i) ... S7'(iii)	3.46	S2'(iii)-S8'(v)	3.35
S4(i) ... S7'(iii)	3.55	S6'(iii)-S4'(v)	3.53
S8(i) ... S3'(iii)	3.54	S2'(iii)-S6'(v)	3.54
S1(ii) ... S6'(v)	3.59	S8'(iii)-S2'(v)	3.59

Note. The notations i to v refer to the labeled molecules in Fig. 4.

(phen)₂·0.5CH₂Cl₂, where phen = 1,10'-phenanthroline (11). The ORTEP diagram (Fig. 2) shows that two of the terminal S atoms on the anion are disordered onto two sites, each S20'/S20 and S18'/S18. There are close S...S contacts between anion and cation but no suggestion of interion π -stacking as inferred for the ferrimagnetic TTF-based salts BEDT-TTF[*M*(NCS)₄(isoquinoline)₂] (*M* = Cr, Fe) (12) and TTF[Cr(NCS)₄(isoquinoline)₂] (12) and as seen in the structure of TTF[Cr(NCS)₄(phen)] (11). In fact the bipym ligands face toward the center of the anionic layers and are isolated from the donors by the NCS⁻ ligands. Notable S...S, anion...cation short contacts are S15-S20 at 3.35 Å, S15-S20' at 3.46 Å, and S8-S20 at 3.60 Å. The structure contains two crystallographically independent donor molecules, both of which have a twisted conformation with eclipsed terminal ethylene groups. The donor molecule with the C15-C16 central bond is bent in the same manner as found for BEDT-TTF molecules in the crystal structure of the neutral compound.

The packing of the donor molecules (Fig. 6) appears to resemble the β packing motif seen in many highly conducting BEDT-TTF salts. However, the shortest S...S contacts between neighboring molecules are relatively long, near to

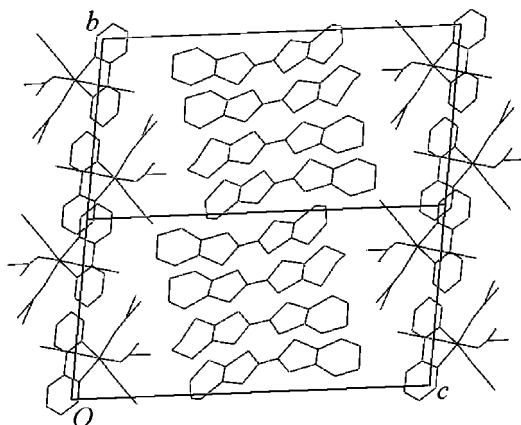


FIG. 5. Packing diagram of compound II viewed along the crystallographic *a* direction.

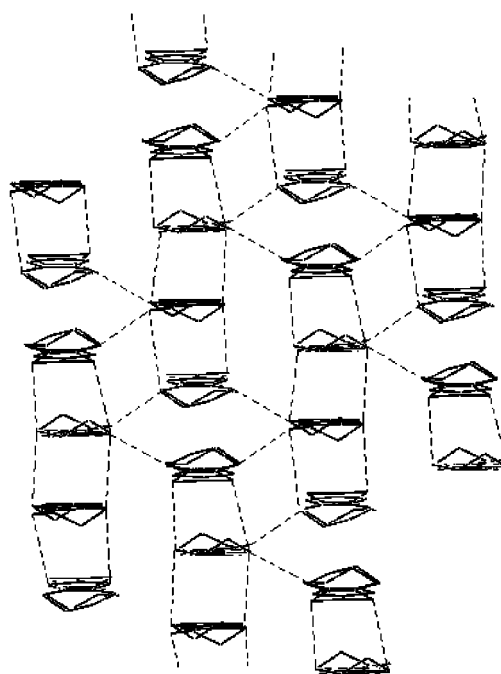


FIG. 6. The BEDT-TTF donor stacking motif in compound II. The dashed lines indicate the network of close S...S contacts below 3.6 Å.

3.6 Å, and closer examination reveals that a better description of the packing would be of stacks that contain a repeating pattern of four donors isolated from the next group of four. The network of closest contacts is shown as dashed lines in Fig. 6. The S...S contacts within a group of four donors are exemplified by S13-S4 at 3.56 Å, S3-S14 at 3.60 Å, and S3-S6 at 3.57 Å, but the closest distance to the next nearest group of four is 4.47 Å. The interstack close contacts are 3.57 Å (S1-S10), 3.53 Å (S7-S16), and 3.55 Å (S5-S9). The irregularity of the spacing found in this packing motif is mirrored by the charges calculated using C-C and C-S bond lengths: the bent donor containing atom C15 has a charge of 0.3 ± 0.1 , whereas the other donor has a charge of 0.9 ± 0.1 . The sum of these charges of $+1.2 \pm 0.2$ is within the limits expected for the compound stoichiometry.

3.2. Magnetic and Transport Properties

Unlike the ferrimagnetic salts mentioned above (11, 12) both I and II are found to be simple paramagnets. Compound I has an experimental Curie constant of 4.926 emu K mol⁻¹, which is higher than expected for a spin-only high-spin Fe(III) (4.377 emu K mol⁻¹). This implies that the remainder is a contribution from the BEDT-TTF radical ions. The Weiss constant for I is -0.19 K, which indicates that there are essentially no magnetic interactions, as expected for the paramagnet. The magnetic susceptibility and inverse

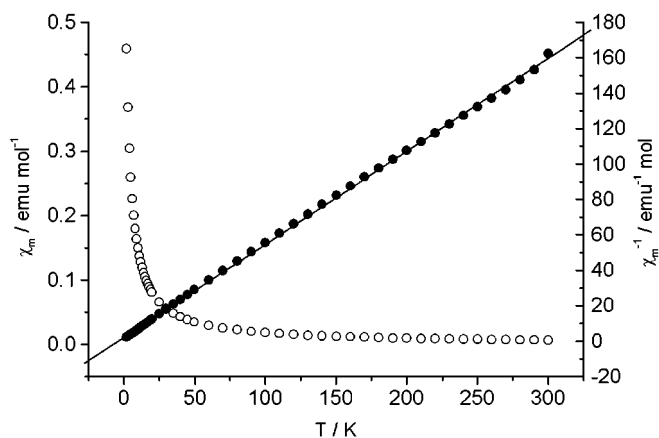


FIG. 7. Plot of magnetic susceptibility (open circles) and inverse susceptibility (closed circles) versus temperature for compound **II**. The straight line is the best least-squares fit to the Curie–Weiss expression.

susceptibility versus temperature curves for compound **II** are shown in Fig 7. The inverse susceptibility curve fits well to the Curie–Weiss expression (filled line in Fig. 7), giving a Curie constant of $1.819 \text{ emu K mol}^{-1}$ ($1.876 \text{ emu K mol}^{-1}$ expected for spin-only Cr(III)) and a small Weiss constant of -0.26 K . These results imply that $\text{S} \cdots \text{S}$ contacts alone do not promote magnetic interactions between the anion and cation subsystems.

As expected neither compound is a particularly strong conductor and are found to be semiconductors. In the most conductive directions compound **I** has a room temperature conductivity of $7 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ and a relatively large activation energy of 0.7 eV , whereas compound **II** has a room temperature conductivity of $1.5 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ with a more typical activation energy of 0.3 eV .

3.3. Raman Spectroscopy

Reflective Raman spectroscopy is used as a rapid means of determining or confirming the charge on the donor molecule by comparing the ν_3 and ν_4 modes of the symmetrical central $\text{C}=\text{C}$ bond in the range $1400\text{--}1480 \text{ cm}^{-1}$ (21). Compound **I** shows two prominent peaks in the spectrum at 1460.4 and 1418.1 cm^{-1} , although the base of the peaks is quite broad from 1557 to 1332 cm^{-1} and could therefore mask other peaks. The prominent peaks corresponds to a charge of $+0.9$, which agrees well with that calculated from bond lengths for the donor molecules that contains central bond $\text{C5}\text{--}\text{C6}$. Peaks for the donor with calculated charge 0.3 ± 0.1 are expected at 1486 (ν_3) and 1454 cm^{-1} (ν_4), well within the broad base. For compound **II** the signal:noise ratio is quite low and the peaks also encompass a broad base from 1591 to 1207 cm^{-1} but never-

theless there is one principal peak at 1433 cm^{-1} and a possible shoulder at 1509 cm^{-1} . The peaks expected from the donor charges calculated from the structure are 1509 (ν_3) and 1477 cm^{-1} (ν_4) for the donor with charge $+0.9 \pm 0.1$ and 1462 and 1429 cm^{-1} for the donor charge $+0.6 \pm 0.1$.

4. CONCLUSIONS

We have described the synthesis, crystal structures, and magnetic properties of two new charge transfer salts with BEDT-TTF donors and the anions $[\text{Fe}(\text{NCS})_6]^{3-}$ and $[\text{Cr}(\text{NCS})_4(2,2'\text{-bipyrimidine})]^-$. The new compounds provide valuable evidence in our search for the supramolecular origins of the bulk ferrimagnetism found for the first time (11, 12) in TTF-based salts with the anions $[\text{Cr}(\text{NCS})_4(\text{N-N})_{1,2}]^-$, $\text{N-N} = 2,2'\text{-phenanthroline}$ or isoquinoline . The ferrimagnetic materials contain two types of interion contacts, namely $\text{S} \cdots \text{S}$ or $\text{S} \cdots \text{Se}$ close contacts and π -stacking. By contrast the compounds reported here have only close $\text{S} \cdots \text{S}$ contacts but no π -stacking and no long-range magnetic order was found. The conclusion, therefore, is that $\text{S} \cdots \text{S}$ contacts act to organize the donor packing and are probably less important than π -stacking for communicating magnetic exchange interactions. However, this preliminary conclusion must bear a caveat since factors such as the angle of overlap of $\text{S} \cdots \text{S}$ contacts and the donor charge are likely to be significant. We will be able to review these details once we have structural data for a larger number of similar salts and with this in mind we are continuing to synthesize compounds of this type.

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