DALTON
FULL PAPER

TTF based charge transfer salts of $[M(NCS)_4(C_9H_7N)_2]^-$ where $M = Cr$, Fe and C_9H_7N = isoquinoline; observation of bulk ferrimagnetic order

Scott S. Turner,*[a] Cecile Michaut,[a] Stephanie Durot,[a] Peter Day,*[a] Thomas Gelbrich[b] and Michael B. Hursthouse[b]

[a] *Davy-Faraday Research Laboratory, Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS. E-mail: sst@ri.ac.uk, pday@ri.ac.uk*
[b] *Department of Chemistry, University of Southampton, Southampton, UK SO17 1BJ*

Received 22nd December 1999, Accepted 10th February 2000

Three new charge transfer salts of BEDT-TTF and TTF with the counter ions $[M(NCS)_4(C_9H_7N)_2]^-$ (M = Cr, Fe; C_9H_7N = isoquinoline) are described. The materials are prepared by standard electrocrystallisation techniques. The nature of the anion is verified in the crystal structure of the salt $[C_9H_8N][Cr(NCS)_4(C_9H_7N)]\cdot C_{12}H_{24}O_6\cdot H_2O$ which is used as the electrolyte when M = Cr. All of the charge transfer salts display long range ferrimagnetic order originating from the interaction between M ($S = 3/2$ or $S = 5/2$) and the donor ($S = 1/2$). The measured critical temperatures are 4.2 K (BEDT-TTF, M = Cr), 4.5 K (BEDT-TTF, M = Fe) and 8.9 K (TTF, M = Cr). Each of the compounds also shows a modest magnetic hysteresis of 338, 18 and 75 Oe for BEDT-TTF salts of M = Cr, Fe and the TTF salt of Cr, respectively.

Introduction

Charge transfer salts of organic donors are characterised by having a wide range of conducting properties from insulating through semi-conducting to metallic and superconducting.[1] The transport properties can be correlated with the relative orientation of donors in the crystal which are arranged, in part, by the spatial organisation of the counter ions and other included molecules.[2–4] Bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF, has thus far been proved to be the most flexible organochalcogenide electron donor for such salts, being a component in a large number of highly conducting compounds.[1] Until relatively recently the focus of research has been concerned with the transport properties of salts although emphasis has now moved towards the possibility of preparing materials with mixed physical properties such as high conductivity and magnetism. The magnetic properties are typically introduced *via* anionic complexes which have paramagnetic centres distinct from any magnetic effects due to the radical donors,[5] which are usually minor. The vast majority of systems of this type contain d-block metals and display simple paramagnetism together with varying transport properties. For example TTF based salts have been made of anions $[FeCl_4]^-$,[6] $[Fe(CN)_6]^{3-}$,[7] Reineckes anion, $[Cr(NCS)_4(NH_4)_2]^-$ [8] and $[Cr(C_2O_4)_3]^{3-}$.[9]

Charge transfer salts with $[M^{III}(C_2O_4)_3]^{3-}$ include the first molecular superconductor containing paramagnetic metal ions, β″-$(BEDT\text{-}TTF)_4[(H_3O)Fe(C_2O_4)]\cdot C_6H_5CN$.[10] We have prepared and characterised many variations of this material by, for example, replacing Fe with other M(III) ions which controls the magnitude of paramagnetism.[9] Many groups, including ours, have been engaged in trying to replace H_3O^+ with M(II) which in principle could produce a material that exhibited simultaneous molecular long range magnetic ordering and molecular conductivity.[11] The sources of the magnetism and conductivity would be distinct in this case and the magnetic order would not be mediated by the radical donor. The aim of the work described here is to prepare TTF based salts which exhibit long range magnetic order arising in part from the radical donor. This is with a view to making materials in which the donor participates both in the magnetism and conductivity.

Experimental

Two probe DC transport measurements were made on several crystals of the title compound and since they had high intrinsic resistance any contact resistance was assumed to be negligible. Gold wire electrodes (0.025 mm diameter) were attached directly to the crystals using Pt paint (Degussa) and measurements taken using an Oxford Instruments Mag Lab 2000 equipped with an EP probe. AC magnetisation measurements were also made using the Mag Lab 2000 at frequencies of 10 Hz–10 kHz and a drive field of 1 Oe. DC magnetisation experiments were made with a Quantum Design MPSM7 SQUID magnetometer using randomly orientated polycrystalline material encased in a gel capsule. Magnetisation was recorded from 2 to 300 K at 100 G and at 2 K between 0 and 7 T. The crystallographic study was performed at 150(2) K using an Enraf-Nonius Kappa CCD area detector with Mo-Kα radiation (0.71073 Å). The structure was solved using DIRDIF-96[12] and refined by full matrix least squares on F^2 using SHELXL97.[13] The absorption correction was achieved with SORTAV.[14] Crystal parameters and collection data are listed in Table 1.

CCDC reference number 186/1855.

See http://www.rsc.org/suppdata/dt/a9/a910259k/ for crystallographic files in .cif format.

Synthesis

Reineckes salt, $NH_4[Cr(NCS)_4(NH_3)_2]\cdot H_2O$ and isoquinoline (C_9H_7N) were purchased from Aldrich and used as received. 18-crown-6 (Aldrich) was dried over acetonitrile and CH_2Cl_2 was distilled over P_2O_5 immediately before use. $[N(C_4H_9)_4]$-$[Fe(SCN)_6]$ was prepared by a slight variation of the published method[15] by using $[N(C_4H_9)_4]SCN$ rather than $[N(CH_3)_4]SCN$ to precipitate the product.

DOI: 10.1039/a910259k

Table 1 Crystallographic data for **II**

Empirical formula	$C_{43}H_{48}CrN_7O_7S_4$
Formula weight	955.12
T/K	150(2)
Radiation	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å	8.2051(5)
b/Å	9.5548(7)
c/Å	16.1340(11)
α/°	75.502(3)
β/°	78.898(4)
γ/°	74.485(4)
V/Å^3	1169.23(14)
Z	1
μ/mm^{-1}	0.479
Reflections collected	12540
Independent reflections	4554 [R(int) = 0.0565]
R values (all data)	$R1 = 0.0653$, $wR2 = 0.1062$
Final R values [$I > 2\sigma(I)$]	$R1 = 0.0418$, $wR2 = 0.0975$

$[C_9H_8N][Cr(NCS)_4(C_9H_7N)_2]\cdot 3H_2O$. Isoquinoline (3.87 g, 30 mmol) and Reineckes salt (3.54 g, 10 mmol) were refluxed at 70 °C in 100 ml absolute ethanol for three hours. During this time all solids dissolved and the mixture became deep red. The clear solution was refluxed for a further twelve hours until the red product precipitated. After cooling the solid was isolated by filtration and washed with cold absolute ethanol. The solid was found to be sparingly soluble in common organic solvents and was not recrystallised. Yield 74% based on Cr. Found C 51.10, H 3.67, N 13.70, S 16.09, Cr 7.12. Calc. for $C_{31}H_{28}N_7S_4O_3Cr$, C 51.23, H 3.88, N 13.49, S 17.64, Cr 7.15%.

BEDT-TTF$[Cr(NCS)_4(C_9H_7N)_2]$, I. The charge transfer salt was prepared by *in situ* oxidation of BEDT-TTF (10 mg), placed in the anode arm of an H-shaped electrochemical cell. The remainder of the cell was filled with a filtered solution of $[C_9H_8N][Cr(NCS)_4(C_9H_7N)_2]\cdot 3H_2O$ (80 mg) and 18-crown-6 (100 mg) in CH_2Cl_2 (50 ml). 1 μA was applied across the cell for 1 week giving 3 mg of dark brown plates which grew on the anode. The crystals were found to be unsuitable for structure solution by X-ray single crystal diffraction due to excessive twinning. Found C 41.52, H 2.33, N 9.04, S 41.49, Cr 5.61, Cl 0.0. Calc. for $C_{32}H_{22}N_6S_{12}Cr$, C 41.45, H 2.39, N 9.06, S 41.49, Cr 5.61, Cl 0.0%.

A portion (2 ml) of the electrolyte solution was removed and the solvent allowed to slowly evaporate giving red prisms containing the anion which were suitable for X-ray single crystal structure determination. The crystals were identified from their structure as $[C_9H_8N][Cr(NCS)_4(C_9H_7N)]\cdot C_{12}H_{24}O_6\cdot H_2O$, **II**.

TTF$[Cr(NCS)_4(C_9H_7N)_2]$, III. The TTF charge transfer salt was prepared using an identical method to that which gave the BEDT-TTF salt. 4 mg of a dark brown amorphous powder grew on the anode after two weeks. Found C 41.20, H 2.7, N 8.99, S 42.00, Cr 5.42. Calc. for $C_{32}H_{22}S_{12}N_6Cr$, C 41.45, H 2.39, N 9.06, S 41.49, Cr 5.50%.

$[N(C_4H_9)_4][Fe(NCS)_4(C_9H_7N)_2]$. $[N(C_4H_9)_4]_3[Fe(SCN)_6]$ (2 g, 1.7 mmol) and isoquinoline (0.684 g, 5.3 mmol) were refluxed in 50 ml absolute methanol for four hours over which time the solution changed colour from deep red to black. The clear solution was left at −10 °C for one week giving a black powder and light yellow solution. The product was isolated by filtration and washed with cold methanol followed by diethyl ether. Upon drying the powder proved to be very deep purple in colour. Yield 69% based on Fe. Found C 58.17, H 6.25, N 12.39, S 17.08, Fe 6.84. Calc. for $C_{38}H_{50}N_7S_4Fe$, C 57.84, H 6.39, N 12.43, S 16.26, Fe 7.07%.

BEDT-TTF$[Fe(NCS)_4(C_9H_7N)_2]$, IV. A method identical to that used for the Cr derivative was used to synthesise this salt on replacing $[C_9H_8N][Cr(NCS)_4(C_9H_7N)_2]\cdot 3H_2O$ with $[N(C_4H_9)_4][Fe(NCS)_4(C_9H_7N)_2]$ as electrolyte. 3 mg of a dark brown microcrystalline powder grew on the anode after one week. Found C 40.96, H 2.78, N 9.22, S 40.67, Fe 6.30. Calc. for $C_{32}H_{22}N_6S_{12}Fe$, C 41.27, H 2.38, N 9.02, S 41.32, Fe 6.00%.

A similar route to the TTF derivative was attempted without success.

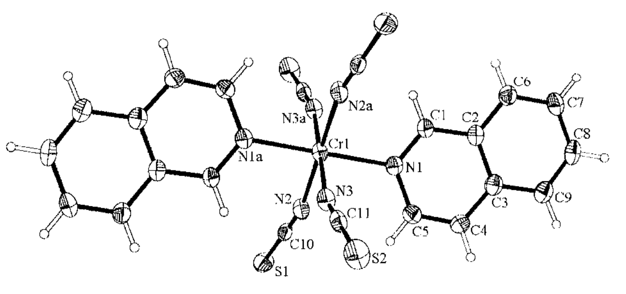

Fig. 1 ORTEP[22] diagram of $[Cr(NCS)_4(C_9H_7N)]^-$ in **II** showing 50% thermal ellipsoids and the atom numbering scheme.

Results and discussion

Since crystals of **I** were unsuitable for X-ray structure determination, the structure of the anion found in **I** was confirmed by solving the structure of the salt employed as the electrolyte in the electrochemical cells. As anticipated the unit cell of **II** contains the isoquinolinium cation, $[C_9H_8N]^+$, and $[Cr(NCS)_4(C_9H_7N)_2]^-$, together with one molecule of H_2O and a molecule of 18-crown-6, which was added to aid solubility. A standard ORTEP diagram of the anion is given in Fig. 1 showing 50% thermal ellipsoids and the atom numbering scheme. The anion presents octahedral co-ordination about Cr with two *trans* co-ordinated C_9H_7N ligands. The metal atom is on an inversion centre with the Cr–N (of NCS) distances slightly shorter than those to N of isoquinoline (*i.e.* Cr1–N1 is 2.077(2) as compared to 1.984(2) and 1.991(2) for Cr1–N2 and Cr1–N3, respectively). Fig. 2 shows the crystal packing in **II**. The water molecule, which has been located in the cavity of the crown ether, is disordered equally over two positions related by an inversion centre and is hydrogen bonded to the macrocycle. The cation $[C_9H_8N]^+$ is disordered in the same manner and is hydrogen bonded, through N–H, to the water molecule. During the refinement twenty-two restraints for chemically equivalent bond distances were used for the disordered cation.

The magnetic properties of **I** are characteristic of a bulk ferrimagnet exhibiting long range magnetic order below the critical temperature, T_c, of 4.2 K. The temperature dependencies of $\chi_m T$ and χ_m^{-1} in a field of 100 G are given in Fig. 3 where χ_m is the molar magnetic susceptibility and T the temperature measured. The value of $\chi_m T$ at 300 K is 2.26 emu K mol^{-1} which is very close to the spin only value of 2.251 emu K mol^{-1} for an uncorrelated spin system with an acceptor ion spin $S_A = 3/2$ (from Cr^{3+}) and a donor spin $S_D = 1/2$ (from BEDT-TTF$^+$), assuming $g = 2$ for both magnetic centres. This indicates that at this temperature short range order is low and there is minimal orbital contribution to the g factor. As the temperature is lowered the value of $\chi_m T$ decreases and there is a rounded minimum of 1.7 emu K mol^{-1} at 10 K (inset Fig. 3). Below 10 K the value of $\chi_m T$ increases rapidly up to a maximum of 56.6 emu K mol^{-1} at 2.7 K at which point the salt is saturated. Below the saturation point χ_m is roughly constant and so $\chi_m T$ decreases linearly with T. This behaviour confirms that **I** is a ferrimagnet.[16] At high temperature $\chi_m T$ approaches the paramagnetic limit and as T is lowered the decrease in $\chi_m T$ corresponds to a short range order where local spins S_A and S_D are aligned antiparallel but have no correlation with neighbouring Cr–BEDT-TTF units. As T is lowered beyond the minimum the correlation length increases which leads to spontaneous

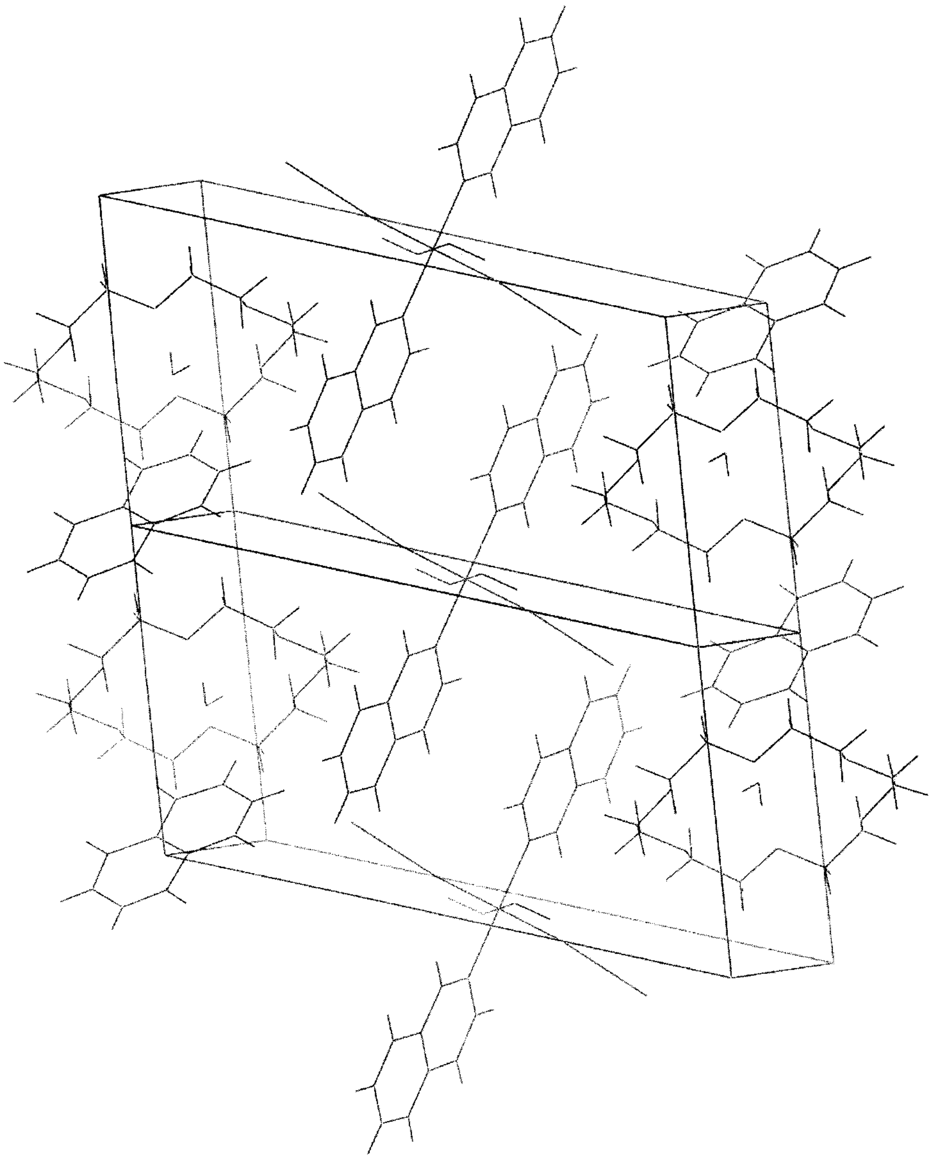

Fig. 2 Crystal packing in **II**. For clarity the disorder in $[C_9H_8N]^+$ and H_2O is not shown.

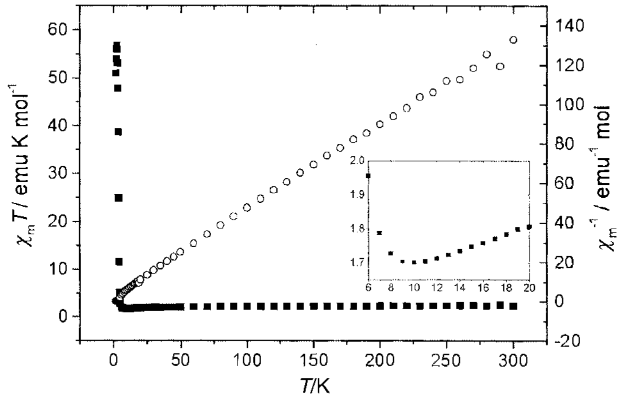

Fig. 3 $\chi_m T$ (filled squares) and χ_m^{-1} (open circles) *versus* T for **I**. The expanded view (inset) shows the minimum in $\chi_m T$ at 10 K.

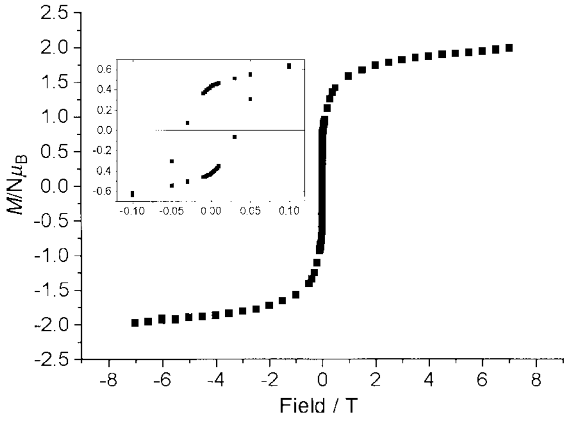

Fig. 4 Magnetisation *versus* field for **I**. Inset shows expanded view about 0 G.

magnetisation below T_c, due to the interaction of non-equivalent spins. Above 50 K the temperature dependence of χ_m^{-1} follows the Curie–Weiss law with a Weiss parameter, corresponding to the T-intercept of χ_m^{-1}, of −12.17 K. The negative sign indicates that antiferromagnetic interactions dominate. Ferrimagnetism was further confirmed by measuring the magnetisation as a function of field (Fig. 4) which reveals saturation at 2 Nμ_B corresponding to all S_A spins aligned with the field direction and the S_D spins aligned in the opposite direction.

Approximately 90% of the saturation magnetisation is reached within a few hundred Oersted and on cycling the field a modest hysteresis (shown inset Fig. 4) is found (338 Oe). Fig. 5a and 5b show the in phase and out of phase AC magnetisation

Table 2 Magnetic parameters for **I**, **III** and **IV**

	I	**III**	**IV**
T_c/K	4.2	8.9	4.5
$\chi_m T$ (at 300 K)/emu K mol^{-1}	2.26	2.18	4.75
Minimum $\chi_m T$/emu K mol^{-1}	1.7	0.99	3.97
Minimum T/K	9.9	16.9	14.8
Coercive field/Oe	338	75	18
Remnant M/Nμ_B	0.42	0.74	0.38
M_{sat} at 7 T/Nμ_B	2.0	2.1	4.3

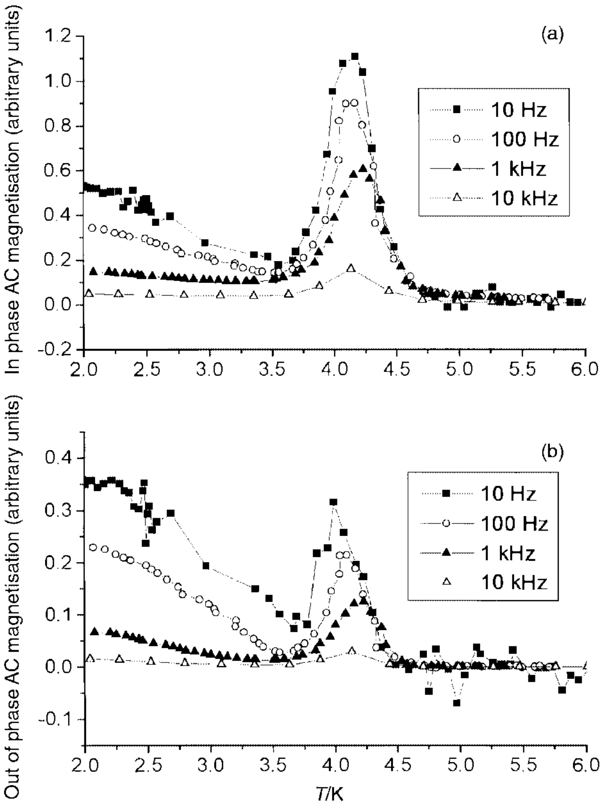

Fig. 5 (a) In phase and (b) out of phase AC magnetisation *versus* T for **I** as a function of frequency at a drive field of 1 Oe.

as a function of frequency. There is no frequency dependence and T_c, taken at the curve peak, is estimated at 4.2 K. Two approaches were used to enhance T_c in **I**. First the number of unpaired electrons was increased by substituting Fe for Cr and secondly a smaller donor was used to increase the electron density. The corresponding curves for **III** and **IV** take the same form as that described above for **I** and the magnetic parameters for all three salts are summarised in Table 2. For the Fe containing salt, **IV**, the room temperature value of $\chi_m T$ of 4.747 emu K mol^{-1} is close to the spin only value of 4.752 emu K mol^{-1} for isolated $S_A = 5/2$ and $S_D = 1/2$ spins. By comparison magnetic data for the starting materials, $[N(C_4H_9)_4][Fe(NCS)_4(C_9H_7N)_2]$ and $[C_9H_8N][Cr(NCS)_4(C_9H_7N)_2]\cdot 3H_2O$ show normal $S = 5/2$ and $S = 3/2$ paramagnetism.

The transport properties for each of the charge transfer salts were measured by both four and two probe conductivity methods on compressed pellets using Au wire electrodes attached by Pt paste (Degussa). At room temperature all of the salts gave resistance values too high to be measured, indicating **I**, **III**, and **IV** are extremely good insulators. The magnetic data indicates that the strongest exchange pathway is between donor and acceptor ions since the major interaction is between S_D and S_A, and the transport data suggests that the donor molecules are isolated from each other. Together with consideration of coulomb interactions, the most likely structure of the salts is therefore stacks of alternating donor and acceptor ions. This structure type is common in other charge transfer molecular magnets such as $[M(C_5(CH_3)_5)_2]^+[TCNQ]^-$ (M = Cr, Mn),[17] $[Fe(C_5(CH_3)_5)_2]^+[TCNE]^-$ [18] and porphyrin based materials.[19] Since other BEDT-TTF salts with Reineckes type anions, $[Cr(NCS)_4(amine)_{1,2}]^-$ with a large range of amines[20] do not show long range magnetic order, the properties described here are consistent with exchange mediated by the isoquinoline ligand. It is well known that isoquinoline derivatives can act as a radical stabiliser or radical trap through charge transfer[21] so it is reasonable to assume the closest anion to cation distances in the donor–acceptor stacks are between the planar donor and planar isoquinoline ligand.

Conclusions

We have described the synthesis of three new charge transfer salts with stoichiometry $[donor][M(NCS)_4(C_9H_7N)_2]$ where M = Cr and Fe for donor = BEDT-TTF and M = Cr for donor = TTF. The salts were grown by standard electrochemical techniques and the configuration of the anion was confirmed from the crystal structure of the isoquinolinium salt. All three salts display bulk ferrimagnetism *via* antiferromagnetic exchange between the donor radical spin and the acceptor spin on the M ion. Small coercive fields were measured for each of the compounds, the largest of 338 Oe being found when M = Cr and donor = BEDT-TTF. The highest T_c of 8.9 K was found for M = Cr and donor = TTF. A combination of magnetic and transport data implies that the magnetic properties are mediated by π stacking of the donor and isoquinolium ligand. Further work will concentrate on preparing new examples of this series in an effort to clarify the mechanism of the exchange, to increase T_c and to obtain single crystal structural information.

Acknowledgements

This work was supported by the UK Engineering and Physical Sciences Research Council and the European Commission Training and Mobility of Researchers Programme.

References

1 J. M. Williams, J. R. Ferraro, R. J. Thom, K. D. Carlson, U. Gesser, H. H. Wang, A. M. Kini and M.-H. Whangbo, *Organic Superconductors (including Fullerenes) Synthesis, Structure, Properties and Theory*, Prentice-Hall, NY, 1992.

2 H. Yamochi, K. Tokutaro, N. Matsukawa, G. Saito, M. Takehiko, M. Kusunoki and K. Sakaguchi, *J. Am. Chem. Soc.*, 1993, **115**, 11319.

3 S. S. Turner, P. Day, D. E. Hibbs, K. M. A. Malik, M. B. Hursthouse, S. Teat, E. J. MacLean, L. Martin and S. A. French, *Inorg. Chem.*, 1999, **38**, 3543.

4 L. Martin, S. S. Turner and P. Day, *Synth. Met.*, 1999, **102**, 1638; S. S. Turner, L. Martin, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, *Chem. Commun.*, 1999, 513.

5 E. Coronado, J. R. Galan-Mascaros, C. Gimenez-Saiz and C. J. Gomez-Garcia, *Adv. Mater. Opt. Electron.*, 1998, **8**, 61.

6 H. Kobayashi, T. Naito, A. Sato, K. Kawano, A. Kobayashi, H. Tanaka, T. Saito, M. Tokumoto, L. Brossard and P. Cassoux, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1996, **284**, 61.

7 P. LeMagueres, L. Ouahab, N. Conan, D. J. Gomez-Garcia, P. Delhaes, J. Even and M. Bertault, *Solid State Commun.*, 1996, **97**, 27.

8 C. J. Kepert, M. Kurmoo, M. R. Truter and P. Day, *J. Chem. Soc., Dalton Trans.*, 1997, 607.

9 L. Martin, S. S. Turner, P. Day, F. E. Mabbs and E. J. L. McInnes, *Chem. Commun.*, 1997, 1367.

10 M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M. B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209; A. W. Graham, M. Kurmoo and P. Day, *J. Chem. Soc., Chem. Commun.*, 1995, 2061.

11 E. Coronado, J. R. Galan-Mascaros and C. J. Gomez-Garcia, *Synth. Met.*, 1999, **102**, 1459; M. Clement-Leon, E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia, C. Rovira and V. N. Lauhkin, *Synth. Met.*, 1999, **103**, 2339.

12 P. T. Beurskens, G. Beurskens, W. P. Bosman, R. de Gelder, S. Garcia-Granda, R. O. Gould, R. Israël and J. M. M. Smits, DIRDIF-96, Crystallography Laboratory, University of Nijmegen, The Netherlands, 1996.
13 G. M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.
14 R. H. Blessing, *Acta Crystallogr.*, *Sect. A*, 1995, **51**, 33; R. H. Blessing, *J. Appl. Crystallogr.*, 1997, **30**, 421.
15 D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1965, 268.
16 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
17 W. E. Broderick, J. A. Thompson, E. P. Day and B. M. Hoffman, *Science*, 1990, **249**, 401; W. E. Broderick and B. M. Hoffman, *J. Am. Chem. Soc.*, 1991, **113**, 6334.
18 J. S. Miller and A. J. Epstein, *J. Am. Chem. Soc.*, 1987, **109**, 3850; J. S. Miller, A. J. Epstein and W. M. Reiff, *Chem. Rev.*, 1988, **88**, 201.
19 D. K. Rittenberg, K. Sugiura, Y. Sakata, I. A. Guzei, A. L. Rheingold and J. S. Miller, *Chem. Eur. J.*, 1999, **5**, 1874; S. Mikami, K. Sugiura, J. S. Miller and Y. Sakata, *Chem. Lett.*, 1999, 413.
20 S. S. Turner, P. Day, S. Coles and M. B. Hursthouse, in preparation.
21 P. Tsai, S. Pou, R. Straus and G. M. Rosen, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 1759; A. E. A. M. Gaber, *Bull. Pol. Acad. Sci.*, *Chem.*, 1998, **46**, 185; X. Q. Wang and R. Silverman, *J. Org. Chem.*, 1998, **63**, 7357.
22 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

Paper a910259k