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TTF charge transfer salts containing cyanometallate anions $[M(phen)(CN)_4]^-$ (M = Cr or Fe; phen = 1,10-phenanthroline)

Shi Wang [a], Peter Day [a,*], Luminita Marilena Toma [b], Miguel Julve [b], John D. Wallis [c]

[a] *Davy-Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London W1S 4BS, UK*
[b] *School of Biomedical and Natural Sciences, Nottingham Trent University, Nottingham NG11 8NS, UK*
[c] *Departament de Química Inorgànica/Instituto de Ciencia Molecular, Universitat de Valencia, Dr. Moliner 50, Burjassot 46100, Spain*

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Abstract

Two new charge transfer salts of TTF with the counter anions $[M(phen)(CN)_4]^-$ (phen = 1,10-phenanthroline, M = Cr (**I**) and Fe (**II**)) are described. The structures consist of alternating stacks of dimerised TTF^+ cations and $[M(phen)(CN)_4]^-$ anions and they are linked together by many short S···S contacts and hydrogen bonds. Within the organic stack, two dimerised TTF^+ cations are arranged in a slipped face-to-face mode with short intra-dimer and long inter-dimer S···S distances. Strong antiferromagnetic exchange was found in the TTF^+ dimers. Conductivity measurements show that compound **I** is a semiconductor.

Keywords: Charge transfer salts; Tetrathiafulvalene; Cyanometallates; Crystal structures; Short contacts; Electrocrystallization

1. Introduction

Charge transfer salts based on tetrathiafulvalene (TTF) and its derivatives constitute a wide class of organic materials famous for their transport properties ranging from insulating through semiconducting to metallic and superconducting depending on the different packing of the organic donors and the overlap between the pπ-orbitals of the neighboring donors [1]. However, to make charge transfer salts that show long-range magnetic order rather than coherent electron transport, one strategy is to design a lattice in which magnetic exchange coupling occurs between the localized d-electrons of the anion and the pπ-electrons of the organic cations. Importantly, the magnetic interactions could be induced by both π–π interactions and/or S···S contacts between the organic radicals and the paramagnetic anions. Some charge transfer salts showing long-range π–d ferrimagnetic order have already been prepared using this concept [2] but it is found that only salts containing both S···S contacts and π–π cation–anion stacking show bulk magnetism [3–8]. Although extended Hückel molecular orbital calculations on $[TTF][Cr(phen)(NCS)_4]$ and $[BEDT\text{-}TTF][Cr(isoq)_2(NCS)_4]$ (BEDT-TTF = ethylenedithio(tetrathiafulvalene), phen = 1,10-phenanthroline and isoq = isoquinoline) suggest that S···S contacts contribute more than the π–π stacking [9], that π–π cation–anion stacking which contributes to forming the alternating cation–anion stacking is necessary for observing bulk magnetic order in this class of compounds which has been demonstrated by some negative examples. Despite S···S cation–anion contacts being present, the structures do not have the alternating arrangement of cations and anions and they are simple paramagnets down to 2.0 K [10–14]. Among this group, the anion–cation arrangements in the structures of $[TTF]_3[Cr(phen)(NCSe)_4]$ and $[BEDT\text{-}TTF]_3[Cr(phen)(NCSe)_4] \cdot CH_2Cl_2$ [11] are completely different from that in $[TTF][Cr(phen)(NCS)_4]$. To try and see what will happen if no cation–anion S···S contacts are possible and at the same time to keep the shape of the anion similar to that of $[M(phen)(NCS)_4]^-$

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[*] Corresponding author. Tel.: +44 2076702901; fax: +44 2076702958.
E-mail address: profpday@msn.com (P. Day).

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and $[M(phen)(NCSe)_4]^-$, we chose the $[M(phen)(CN)_4]^-$ anions (M = Cr or Fe) which are related to $[M(phen)(NCS)_4]^-$ and $[M(phen)(NCSe)_4]^-$ by replacing the isothiocyanates and isoselencyanates with cyanides. Herein, we report the preparation, crystal structures and magnetic properties of [TTF][$Cr(phen)(CN)_4$] (**I**) and [TTF][$Fe(phen)(CN)_4$] (**II**).

2. Experimental

2.1. Syntheses

All the chemicals were of analytical grade and purchased from Aldrich. $(TTF)_3(BF_4)_2$ [15], $(Ph_4P)[Cr(phen)(CN)_4]\cdot H_2O\cdot CH_3OH$ [16] and $(Ph_4P)[Fe(phen)(CN)_4]\cdot 2H_2O$ [17] were prepared by the published methods.

*[TTF][Cr(phen)(CN)$_4$] (**I**)*. A solution of $(TTF)_3(BF_4)_2$ (12 mg) in hot acetonitrile (20 ml) was filtered and to it was added an acetonitrile solution (10 ml) of $(Ph_4P)[Cr(phen)(CN)_4]\cdot H_2O\cdot CH_3OH$ (21 mg). Storage at room temperature overnight afforded black needle-like crystals of the desired salt **I**. Yield: 50% based on [Cr]. *Anal.* Calc. for $C_{22}H_{12}N_6S_4Cr$: C, 48.89; H, 2.22; N, 15.56. Found: C, 48.99; H, 2.26; N, 15.66%.

*[TTF][Fe(phen)(CN)$_4$] (**II**)*. It was prepared using the similar method to [TTF][$Cr(phen)(CN)_4$] except using $(Ph_4P)[Fe(phen)(CN)_4]\cdot 2H_2O$ (24 mg) as the starting material. Yield: 35% based on [Fe]. *Anal.* Calc. for $C_{22}H_{12}N_6S_4Fe$: C, 48.53; H, 2.21; N, 15.44. Found: C, 48.04; H, 2.20; N, 15.08%.

2.2. Physical measurements

Variable temperature DC magnetization experiments were made with a Quantum Design MPSM1 SQUID magnetometer using randomly orientated polycrystalline material (21.5 mg of compound **I** and 10.7 mg of compound **II**) in a gelatin capsule. Magnetization was recorded from 2.0 to 300 K with an applied field of 100 G. The data were corrected for the core diamagnetism estimated from the sums of Pascal constants as -280×10^{-6} (**I**) and -279×10^{-6} (**II**) emu mol^{-1} for **I** and **II**, respectively. Two-probe DC transport measurements were made with an Oxford Instruments Maglab 2000 equipped with an EP probe. Gold wire electrodes (0.0025 mm diameter) were attached to the crystals of compound **II** and to the pellets of compound **I** using Au paste. The X-ray diffraction measurements were performed with a Nonius KappaCCD area detector at 120 K using ϕ scans and ω scans to fill the asymmetric unit sphere for compounds **I** and **II**. All structures were solved by direct methods using the program SHELXS-97 and refined on F^2 by full-matrix least-squares procedures using SHELXL-97.

2.3. Crystal structures

Single crystals of salts **I** and **II** were found to be suitable for single-crystal X-ray diffraction. The crystal and refinement data are given in Table 1. Selected bond lengths and bond angles of each compound are listed in Table 2 and short contacts in Table 3. Standard ORTEP drawings of salts **I** and **II** are shown in Figs. 1 and 2 with the atom numbering scheme and 50% thermal ellipsoids. Since the two compounds are isostructural, herein we only describe the chromium salt in detail.

The asymmetric unit of [TTF][$Cr(phen)(CN)_4$] (**I**) contains one crystallographically independent cation TTF^+ and one anion $[Cr(phen)(CN)_4]^-$ (Fig. 1). The bond lengths and bond angles within the $[Cr(phen)(CN)_4]^-$ unit are in good agreement with those reported previously containing such units [16]. The Cr atom has a distorted octahedral coordination formed by two nitrogen atoms from a phenanthroline ligand and four carbon atoms from cyanides. The Cr–C (cyano) bond lengths range from 2.060(2) to 2.096(2) Å. The Cr–C–N bond angles (176.31(19)–178.35(18)°) depart slightly from the strict linearity. The TTF^+ cation has C=C bond lengths of 1.334(3)–1.395(3) Å and C–S bond lengths of 1.716(2)–1.730(2) Å, which are consistent with those reported in other TTF^+ charge transfer salts [3,4]. Using the empirical correlation between C–S and C=C bond lengths and the donor charges for BEDT-TTF salts [18], **I** has a TTF charge of 1.0 ± 0.1, which is in agreement with the stoichiometry.

The structure of **I** consists of alternating stacks of dimerised TTF^+ cations and $[Cr(phen)(CN)_4]^-$ anions, linked together by many kinds of short contacts and hydrogen bonds. A crystal packing diagram for compound **I**,

Table 1
Crystal and refinement data for compounds **I** and **II**

	I	II
Formula	$C_{22}H_{12}CrN_6S_4$	$C_{22}H_{12}FeN_6S_4$
Formula weight	540.62	544.47
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9113(2)	7.7951(2)
b (Å)	9.4788(2)	9.5008(2)
c (Å)	15.9195(4)	15.8903(4)
α (°)	75.156(2)	75.237(2)
β (°)	89.6280(10)	88.971(2)
γ (°)	76.1180(10)	75.221(2)
Z	2	2
V (Å^3)	1118.33(5)	1098.94(5)
D_{calc} (g cm^{-3})	1.605	1.645
T (K)	120(2)	120(2)
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.910	1.091
$F(000)$	548	552
hkl Range	$-10\leqslant h\leqslant 10$; $-11\leqslant k\leqslant 12$; $-20\leqslant l\leqslant 20$	$-10\leqslant h\leqslant 10$; $-12\leqslant k\leqslant 12$; $-20\leqslant l\leqslant 20$
Collected	26640	21705
Unique	5100	5013
Parameters	298	298
Goodness-of-fit	1.037	1.050
R_1 [$I>2\sigma(I)$]	0.0333	0.0356
wR_2 [$I>2\sigma(I)$]	0.0781	0.0877
$D_{max/min}$ (e A^{-3}) map	0.402/−0.464	2.133/−0.478