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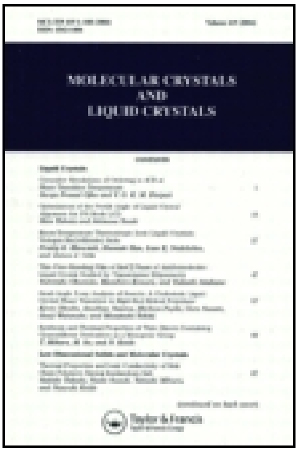

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Conducting Materials Containing Paramagnetic Hexacyanometallate $[Cr(CN)_6]^{3-}$ and Iodine Substituted Organic Donor [DIETS]

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Abstract

Two new compounds containing iodine substituted donor (DIETS = diiodoethylenedithiodithiadiselenafulvalene) and paramagnetic $[Cr(CN)_6]^{3-}$ anion, namely, $(DIETS)_8(Cl)_2[Cr(CN)_6]_{2/3}.2H_2O$ (**1**) and $(DIETS)_3(Et_4N)[Cr(CN)_6].3H_2O$ (**2**) are reported. The structures of both compounds contain two different inorganic layers. In **1**, one layer contains $Cr(CN)_6^{3-}$ anions and water molecules and the second layer contains Cl^- anions. In **2**, the one layer contains $Cr(CN)_6^{3-}$ anions, Et_4N^+ cations and water molecules while the other one does not contain Et_4N^+ cations. The –I...NC– contacts (2.725Å in **1**, 3.05Å in **2**) observed between DIETS and $Cr(CN)_6$ units are extremely short by comparison with the van der Walls separation of 3.65Å. Both compounds are semiconductive, with σ_{300K}= 1 and 0.2 $S.cm^{-1}$ and E_a= 65 and 175meV for **1** and **2** respectively. Despite these short anion...Donor contacts no magnetic interactions were observed between the localized spins and the conducting electrons.

Keywords iodine substituted donors; electrical conductivity; magnetic interactions; crystal structure; hexacyanometallates

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INTRODUCTION

Radical cation salts and charge transfer complexes based on tetrathiafulvalene (TTF) and its derivatives constitute a wide class of organic materials with particular properties ranging from insulating to superconducting [1]. The relative arrangements of the molecules in the solid state was found to be a crucial parameter in determining the property of the target compound [2]. Investigations of organic/inorganic hybrid molecular materials combining conducting electrons and localized spins are still of great interests [3-11]. The aim of the combination of these two properties is to obtain a long-range magnetic coupling between isolated localized spins of the inorganic networks containing transition metals (d-electrons) through the mobile electrons of the organic networks (π-electrons). To satisfy this model which is based on the synergy between electrical conductivity and magnetic interactions, two important conditions are needed, namely good electrical conductivity and interactions between the organic and inorganic networks. However, most of the known materials show a sort of dilemma between the two properties : (i) they are conducting or superconducting and paramagnetic i.e. without any interaction between the localized spins [3]; (ii) they show coexistence of two independent metallic and ferromagnetic lattices [10] or (iii) they are insulating but show magnetic interactions not mediated by the conducting electrons [11]. This is the case of TTF derivative salts containing $[Cr(NCS)_4(phen)]^{-1}$, phen = 1,10-phenanthroline reported recently by P. Day *et al* [11], which were designed with the idea that magnetic interactions can be induced by both S...S contacts and π overlaps between paramagnetic anions and organic radicals. In order to establish magnetic or at least structural interactions between the organic and inorganic sublattices, we decided to explore the assemblies of paramagnetic hexacyanometallates with the unsymmetrical halogen substituted organic donor DIETS (diiodo ethylenedithio dithiadiselenafulvalene) which has two terminal iodine atoms. Actually, the nitrogen-halogen interaction was known in crystal engineering and was used to construct a molecular path [12]. For example, it has been found in the $(DIETS)_4M(CN)_4$ (M= Ni, Pt, Pd) [13] or $(DIETS)_nFeX_4$ (n = 1, 2; X = Cl, Br) systems [14] that this organic donor leads to very short –I...X– [X = CN, Br or Cl] contacts.

The electrocrystallization of DIETS in the presence of $Cr(CN)_6^{3-}$ yields two different phases as plates (major product) and needles (minor product) formulated as $(DIETS)_8(Cl)_2(Cr(CN)_6)_{2/3}$ (**1**) and $(DIETS)_3(Et_4N)(Cr(CN)_6).3H_2O$ (**2**). In this paper we report the preparation, crystal structure, band structure calculations, electrical conductivity for both phases and ESR and magnetic properties of (**1**).

EXPERIMENTAL

Preparation of compounds.

Brown plate and black needle crystals were obtained by galvanostatic oxidation of DIETS [15] (10 mg, 1.5×10^{-2} mmol) on a platinum wire electrode (∅=1mm) under a constant current intensity of ca. 0.7 µA. A solution of $(Et_4N)_3Cr(CN)_6$ (120 mg, 0.2 mmol) in a mixture of CH_2Cl_2 (16 ml) and CH_3CN (4 ml) was used as electrolyte. Stoichiometries were fixed by X-ray crystal structure analysis.

X-ray crystal analysis.

X-ray data were collected at room temperature on a Enraf-Nonius CCD diffractometer using a graphite-monochromatized Mo$K\alpha$ (λ=0.71073Å) radiation. Structures were solved and refined (on F^2) using SHELXS-97 [16, 17]. Crystal data : for (**1**), Monoclinic, $C2$, a= 65.2155(8)Å, b=13.7954(3)Å, c=15.9305(8)Å, β=90.130(3)°, V=14332.2(8) Å^3, $R1$ = 0.0813 for 10963 reflections ($|Fo| > 4\sigma(Fo)$); for (**2**), Monoclinic, $P2_1/a$, a=14.778(3)Å, b=11.203(3)Å, c=38.514(3)Å, β=90.873(3)°, V=6420(5)Å^3, $R1$ = 0.0755 for 4078 reflections ($|Fo| > 4\sigma(Fo)$).

RESULTS AND DISCUSSIONS

Crystal structures

Plate modification : The asymmetric unit contains 8 DIETS molecules noted **A,B,...H**, one $[Cr(CN)_6]^{3-}$ anion with an occupancy factor of 2/3, 4 Cl^- anions and 2 water molecules. From the formula $(DIETS)_8[Cr(CN)_6]_{0.67}Cl_2 2H_2O$, we deduced that the DIETS molecules bear a same mean charge of +0.5. The crystal structure shown in Fig. 1 is unexpected, it contains two types of inorganic layers noted **I** and **II**. Layer **I** contains $Cr(CN)_6^{3-}$ units, while layer **II** contains Cl^- anions which probably comes from dichloromethane used as solvent. The 8 DIETS molecules of the asymmetric unit form two different columns noted **S1** and **S2** within the bc-plane. Column **S1** is formed by

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molecules **A,B,C,D** and column **S2** is formed by molecules **E,F,G,H**. All the organic molecules present head-to-tail overlaps. The organic layers are connected by I...Cl contacts of 3.04 Å and by considerably short –CN...I– contacts (2.722~2.825Å; vdW =3.65 Å) between the organic donors and the $Cr(CN)_6$ units.

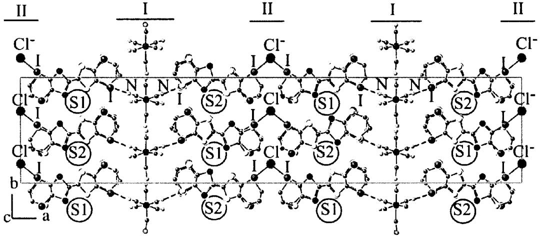

Fig. 1. Crystal structure of (**1**) showing N…I contacts.

Needle modification : The asymmetric unit contains 3 independent DIETS molecules called **A**, **B** and **C**, one Et_4N^+ cation, $3H_2O$ molecules and 2 different $Cr(CN)_6$ units located on 0 0 0 and ½ 0 ½ centers.

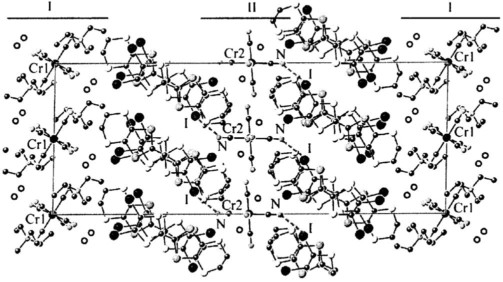

Fig. 2. Crystal structure of (**2**) in *ac* plane showing N…I contacts.

The main feature of the structure (Fig. 2) is the presence of two different inorganic layers (I and II). Layer I contains one $Cr(CN)_6^{3-}$ (Cr1) anion, water molecules and Et_4N^+ cation, while layer II contains only $Cr(CN)_6^{3-}$ (Cr2) anion and water molecules. In both layers I and II, the $Cr(CN)_6^{3-}$ units are connected through a network of hydrogen bonding involving the water molecules and the nitrogen atoms of the CN groups with N...O distances ranging from 2.74(3)Å to 2.94(4)Å. In layer I, the $[Cr(CN)_6]^{3-}$ anion is completely isolated and does not have any contact with the organic molecules, while very short –N...I-contacts of 3.05Å (N…I vdW = 3.65Å) exist in layer II. The DIETS molecules are stacked along the *b* axis with the...(ABC)(ABC)... sequence The positive charges on each organic donor were assumed equal to +2/3. In the stack the **A/B** and **A/C** molecules present a head-to-tail overlap while the **B/C** molecules present a head-to-head overlap. The columns are arranged side by side in the *a* direction to form a β-type like [1] of packing in the *ab* plane. Some interchain contacts, in the vdW range, between heteroatoms are observed.

Physical properties.

Electrical conductivity :

The dc electrical conductivity measurements over the range 20–300K were performed on single crystals by the standard four-probe method. The conductivity shows a semiconductive behavior with $\sigma_{RT} \sim 1$ and 0.2 $S.cm^{-1}$ and $E_A = 170$ and 65K for needle and plate modifications respectively. The +0.5 oxidation state assumed for each donor in **1** is preferable for the metallic conduction. The possible reason for the semiconducting behavior is a slight deviation in the stoichiometry, which may leads to a deviation from this formal oxidation state.

Static magnetic susceptibility :

We report only magnetic properties of plate modification which is obtained as major product (**1**).

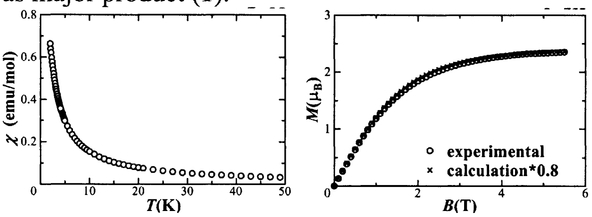

Fig. 3. Temperature dependence of the magnetic susceptibility at B =1T (Right) and magnetization curve measured at 2K (left) for (**1**)

Magnetic measurements were performed using a non-oriented sample (~2mg). The susceptibility (Fig. 3) obeys the Curie-Weiss law (C = 1.571emu $K^{-1}mol^{-1}$, $\Theta = -0.2K$), and there is no magnetic ordering down to 1.7K. The small Weiss temperature and the absence of the magnetic phase transition show that the exchange interaction between the magnetic anion is small. This paramagnetic behavior is also supported by the magnetization curve measured at 2K (Fig. 3), which is well fitted on the Brillouin curve for S=3/2. The absence of the magnetic interaction may come from the long distance between the

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anions. The short -CN...I- contacts do not participate in the exchange interaction, since the spin concentration on the CN ligands is small, and the iodine atom little contribute to the HOMO of the donor molecule.

Electron Spin Resonance

Plate modification : The angular dependences of the line width and *g*-value are measured at room temperature, rotating the sample along the *a*-axis. Since the line-shape cannot be fitted with a single Lorentzian curve, the half-width and *g*-value (Fig. 4) are estimated from the integrated absorption curves.

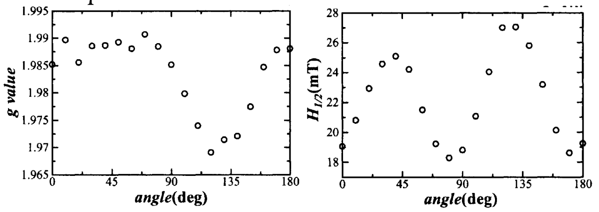

Fig. 4. Angular dependence of the *g*-value (left) and line-width (right) of (**1**) measured at room temperature. The magnetic field is applied along the *b*-axis when the angle is 0 degree.

The *g*-value and the line width (Fig.4) vary from 1.97 to 1.99 and 18 to 28 mT, respectively, showing the complex angular dependence (i.e. non-sinusoidal). This complex behavior presumably comes from the distortion of the $Cr(CN)_6$ complex from the regular octahedron. According to the X-ray structure analysis, very short intermolecular N…I contacts exist between the anion and donor. These contacts severely distort the coordination geometry of the $Cr(CN)_6$ complex from the regular octahedron. If the $Cr(CN)_6$ complex were in the O_h symmetry, the electronic state of the complex would be spherical, and no anisotropy of the ESR *g*-value would be observed just as in the case of $K_3Cr(CN)_6$. Due to Se atoms with large spin-orbit interaction, the line width of the absorption from donor is too wide to be observed. The possibility for the effect of the exchange interaction between donor and anion spins cannot be fully ruled out, since the coalescence of the two ESR absorptions occurs even if the magnitude of the exchange interaction is so weak that the static susceptibility shows the Curie-like behavior.

Electronic band structure calculations :

Overlap integrals and band structures (Fig. 5) of the title compounds

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have been obtained with the semi-empirical Extended Hückel Method (EHT), using the program from reference [18]. Semi-empirical parameters for Slater-type *s* and *p* orbitals [19] were used.

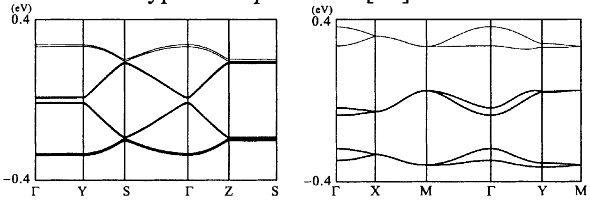

Fig. 5. Dispersion energy bands for (**1**) Γ (0, 0, 0); Y (0, 1/2*b**, 0); S (0, 1/2*b**, 1/2*c**); Z (0, 0, 1/2*c**) (left) and (**2**) M (1/2*a**, 1/2*b**, 0) (right). Thick and thin lines represent fully occupied and unoccupied bands.

Plate modification : The intracolumn integral overlaps range from -15.2×10^{-3} to -12.7×10^{-3} while all the inter-column overlaps range from -0.48×10^{-3} to -0.08×10^{-3} indicating that the system should have an almost 1D electronic structure. From the tight binding approximation, 4 pairs of almost degenerated 1D-bands are calculated. From the formal charge of +0.5 of the donor molecules, lower 6 bands (3 pairs) are fully occupied and upper two bands are unoccupied. Estimated energy gap between 4th and 5th band is 5~6 meV.

Needle modification : As found from the X-ray results (see above), in the donor column along the *b* direction, two donor molecules (A, B) are strongly dimerized with overlap integral $S= -26.4\times10^{-3}$. The other interactions between the dimer and C molecule are almost 3 time smaller ($S \sim -9\times10^{-3}$). Three pairs of quasi-degenerated bands are calculated and from the formal charge of the donor molecules (+2/3), lower 4 bands are fully occupied and upper 2 bands are unoccupied. The calculated energy gap between the 4th and 5th bands is *ca.*200 meV which agrees with the activation energy estimated from the electrical conductivity measurements.

CONCLUSION

Two new compounds containing conducting and paramagnetic networks were prepared and characterized. The compounds are semi-conducting with a 1D structure. For both compounds, we did not observe direct intermolecular contacts between paramagnetic anions (shortest N...N : 5.2Å), whereas short I...N contacts (2.722~2.825Å in

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1 and 3.05 Å in **2**) were observed between donors and anions. However, despite these very short contacts no magnetic exchange interactions between donor π-electrons and anion d-electrons were observed. Actually the unusually strong contacts lead to the deformation of the $Cr(CN)_6^{3-}$ anion. Hence the magnetic and orbital characters of the Cr and CN group in the anion might be quite different from a usual manner as shown in the ESR measurements. Investigations of other similar salts with the paramagnetic $Fe(CN)_6^{3-}$ and diamagnetic $Co(CN)_6^{3-}$ anions would contribute to understand the physical properties.

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