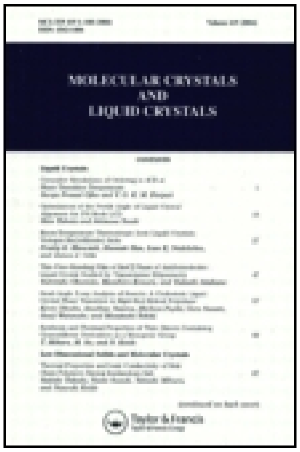


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Materials Containing Conducting and Magnetic Sublattices: Phase Transitions in [k-$(Et_4N)(BEDT\text{-}TTF)_4M(CN)6$, 3 H_2O; M = Fe^{III}, Co^{III}, Cr^{III}]

P. Le Maguer[cgrave]s [a], L. Ouahab [a], P. Briard [a], J. Even [b], M. Bertault [b], L. Toupet [b], J. Rámos [c], C.J. Gómez-García [c] & P. Delhaès [c]

[a] Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA 1495, Université Rennes I, 35042, Rennes, France

[b] Groupe Matière Condensée et Matériaux, URA 804, Université Rennes I, 35042, Rennes, France

[c] Centre de Recherche Paul Pascal, CNRS, Av. A. Schweitzer, 33600, Pessac, France

Version of record first published: 04 Oct 2006

To cite this article: P. Le Maguer[cgrave]s, L. Ouahab, P. Briard, J. Even, M. Bertault, L. Toupet, J. Rámos, C.J. Gómez-García & P. Delhaès (1997): Molecular Materials Containing Conducting and Magnetic Sublattices: Phase Transitions in [k-$(Et_4N)(BEDT\text{-}TTF)_4M(CN)6$, 3 H_2O; M = Fe^{III}, Co^{III}, Cr^{III}], Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 305:1, 479-489

To link to this article: http://dx.doi.org/10.1080/10587259708045081

Mol. Cryst. Liq. Cryst., 1997, Vol. 305, pp. 479–489
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands
under license by Gordon and Breach Science Publishers
Printed in India

MOLECULAR MATERIALS CONTAINING CONDUCTING AND MAGNETIC SUBLATTICES : PHASE TRANSITIONS IN [κ-$(Et_4N)(BEDT\text{-}TTF)_4M(CN)_6$, 3 H_2O ; M = Fe^{III}, Co^{III}, Cr^{III}].

P. Le Maguerès [a], L. Ouahab [a], P. Briard [a], J. Even[b], M. Bertault [b], L. Toupet [b], J. Rámos [c], C.J. Gómez-García [c], P. Delhaès [c].

[a] Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA 1495, Université Rennes I, 35042 Rennes, France.

[b] Groupe Matière Condensée et Matériaux, URA 804, Université Rennes I, 35042 Rennes, France.

[c] Centre de Recherche Paul Pascal, CNRS, Av. A. Schweitzer, 33600 Pessac, France.

Abstract : We report the preparation, structural and physical investigations of BEDT-TTF (ET) salts formulated β-$ET_5M(CN)_6$, 10 H_2O with M = Fe^{III} and Co^{III} and κ-$[Et_4N](ET)_4M(CN)_6$, 3 H_2O with M = Fe^{III}, Co^{III} and Cr^{III}. The κ-phase salts show two phase transitions at 240 K and 150 K, respectively. The first structural transition, at 240 K, is followed by a redistribution of the charges on the ET molecules and the magnetic and electrical properties are explained on the basis of this phenomenon. A facile and convenient route for the preparation of the $(R_4N)_3M(CN)_6$ [R= C_2H_5 and C_4H_9) salts is also presented.

INTRODUCTION

A great challenge in the field of molecular materials is to synthesize new compounds coupling localized magnetic moments and delocalized electrons with the aim to investigate systems in which magnetic and conducting properties could coexist. The main reason of interest in the combination of localized and itinerant electrons is related to the possibility to create new interactions between them, in particular the so-called indirect exchange interaction. So through this kind of interaction and thanks to the infinite delocalization of the conduction electrons, one hope to create a long-range magnetic order in such molecular compound.

However, the incorporation of a localized spin in a molecular conductor has been obtained in only a few cases[1]. Among them, the first one containing paramagnetic metal ions and exhibiting a superconducting state has been recently reported by P. Day et al.[1e]. In this context, our aim is to obtain ET-based radical ion salts associated with inorganic hexacyanometalates. Indeed the π-electronic donor ET is the most widely used molecular precursor in the synthesis of radical cation salts exhibiting conducting and superconducting behaviors[2]. Its anionic partners, the hexacyanometalates, can be diamagnetic (M = Co^{III}) or paramagnetic (M = Fe^{III} and Cr^{III}) and are known to give rise to different kinds of magnetic interactions through the cyano bridges[3].

We have obtained two phases noted respectively β-$ET_5M(CN)_6$, 10 H_2O with M = Fe^{III} and Co^{III} and κ-$[Et_4N](ET)_4M(CN)_6$, 3 H_2O (M = Fe^{III}, Co^{III} and Cr^{III})[1f]. We present here the crystal structures as well as the d.c. conductivity, the magnetic and calorimetric measurements for both phases, focusing however on the κ-phase salts which show two phase transitions at 240 K and 150 K ; in particular, the structural transition at 240 K has been studied by X-ray analysis. A facile and convenient route for the preparation of the $(R_4N)_3M(CN)_6$ [R= C_2H_5 and C_4H_9) salts is also presented.

EXPERIMENTAL SECTION

Preparation of compounds :

β-phase : Isostructural β–phase ET salts were obtained on a platinum wire electrode by anodic oxydation of the organic donor ET (3 x 10^{-3} M) in a U-shape electrocrystallization cell under constant current (I = 1 µa) in the presence of the potassium salts of the anions (2.5 x 10^{-2} M) as supporting electrolyte and of 18-crown 6 (4.7 x 10^{-2} M). A mixture of CH_2Cl_2 and MeOH in a 5 : 1 ratio with 20 drops of water (6 % in volume) in each cell compartment was used. Thick platelike single crystals were obtained for ET salts of $[Fe(CN)_6]^{3-}$ and $[Co(CN)_6]^{3-}$ whereas the $[Cr(CN)_6]^{3-}$ salts give rise to thin plates of bad quality.

κ-phase : Isostructural κ-phase ET salts were obtained with the $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$ and $[Cr(CN)_6]^{3-}$ anions by anodic oxydation of ET (3.6 x 10^{-3} M) under constant (I = 1.3 µa) in the presence of the tetraethylammonium salts of the anions $(Et_4N)_3[M(CN)_6]$, M = Fe^{III}, Co^{III}, Cr^{III} (1.4 x 10^{-2} M) as supporting electrolyte. Block like single crystals were obtained in a mixture of CH_2Cl_2 and CH_3CN in a 4 : 1 ratio.

Synthesis of $(R_4N)_3M(CN)_6$: The synthesis of the $(Et_4N)_3[M(CN)_6]$ salts was conducted according to two ways. In the first one, reported by Masharak[4], a mixture of tetraethylammonium perchlorate and $K_3[M(CN)_6]$ is stirring in methanol under nitrogen during 24 hours. However this procedure involves the formation of the dangerous salt $KClO_4$. So we have investigated an other procedure by synthesizing first the silver salt of hexacyanometalate in aqueous media before the access to the $(Et_4N)^+$ salt. Thus $Ag_3[M(CN)_6]$, M = Fe^{III}, Co^{III}, Cr^{III} was prepared by mixing concentrated aqueous solutions of $K_3[M(CN)_6]$ (20 mmol in 20 ml) and $AgNO_3$ (60 mmol in 25 ml). The precipitate of $Ag_3[M(CN)_6]$ was collected by filtration through a sintered glass filter N°4 and washed with water. A suspension in water of $Ag_3[M(CN)_6]$ (5 mmol in 50 ml) was then treated with an aqueous solution of tetraethylammonium iodide (15 mmol in 20 ml). The residual salt AgI precipitated ($P_s = 8.51.10^{-17}$ mol.l^{-1} at 25 °C in water) and was removed by filtration. The aqueous solution, which contained the soluble $(Et_4N)_3[M(CN)_6]$, was evaporated to dryness and finally the collected powder was recrystallized in acetonitrile.

X-ray diffraction : X-ray data collections were performed on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromatized MoKα radiation by θ–2θ scan. The structures were solved by direct methods and successive Fourier difference synthesis and were refined by full matrix least squares method with anisotropic thermal parameters for all non-hydrogen atoms (H-atoms included in computed positions and not refined). The low temperature unit cell parameters were obtained by cooling the samples in a nitrogen stream with a FR558SH cryostat mounted on the diffractometer.

Physical measurements : D.c. conductivity experiments were carried out using the four-probe method on single crystals. Magnetic measurements were performed on polycrystalline samples with a magnetometer equipped with a SQUID sensor (Quantum Design MPMS). ESR measurements at variable temperature were recorded on single crystals at X-band with a Bruker ESP 300E spectrometer equipped with a helium cryostat. Calorimetric experiments were performed on polycrystalline powder samples weighting from 20 to 30 mg encapsulated in 50 μl pans using a differential scanning calorimeter (Perkin-Elmer DSC7) cooled with liquid nitrogen.

CRYSTAL STRUCTURES

β-phase : The crystal structure[5] was solved for β-$ET_5Fe(CN)_6$, 10 H_2O. It consists of alternating layers of ET and $[Fe(CN)_6]^{3-}$ anions (Fig. 1). The inorganic sublattice is constituted by the centrosymetric $[Fe(CN)_6]^{3-}$ anions, situated at the origin of the cell, and 10 water molecules. The organic sublattice is built of two and one half crystallographically independent ET molecules noted A, B and C (Fig 1). These ET molecules form pentamerized stacks parallel to the [2,1,0] direction with the sequence ...BACAB... These stacks are packed in a β-type fashion[2] and form conducting sheets parallel to (001) plane. Strong S..S contacts are observed between ET molecules from neighbouring stacks (they range from 3.325(4) Å and 3.617(4) Å and are shorter than the sum of Van Der Waals radii ≈ 3.65 Å). The intrastack S..S contacts are considerably weaker (≥ 3.666(5) Å). Due to these stong side-by-side interactions, the ET molecules form "ribbons" in the [3,-1,0] direction with the same sequence ...BACAB... as that in the direction of the chains. From the comparison of the intramolecular C=C and C-S bond lengths with those of other ET molecules under different oxydation states, we can assume that the distribution of the charge on the ET molecules is irregular.

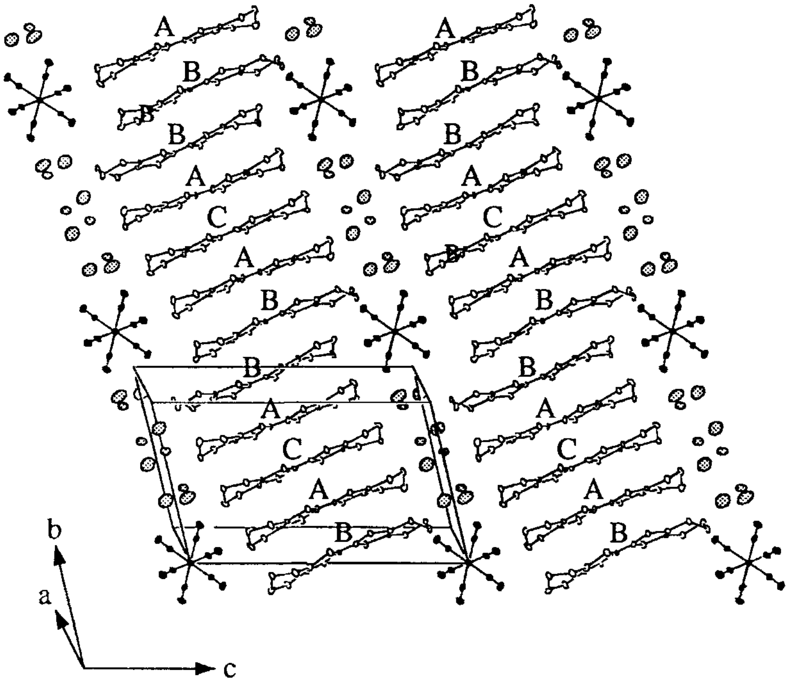


FIGURE 1 : Crystal structure for β-$ET_5Fe(CN)_6$, 10 H_2O. Only the anions along the [2,1,0] direction have been represented. Circles in grey are water molecules.

κ-phase : The crystal structures were solved for nearly all the compounds : κ-$(Et_4N)ET_4$ $M(CN)_6$, 3 H_2O (M = Co^{III}, Fe^{III}, Cr^{III}) at room temperature and κ-$(Et_4N)ET_4M(CN)_6$, 3 H_2O (M = Fe^{III}, Cr^{III}) at low temperature (Table 1).

TABLE 1 : Crystal and refinement data for κ-$(Et_4N)ET_4M(CN)_6$, 3 H_2O, M = Fe^{III}, Co^{III} and Cr^{III} at 300 K and 115 K.

	Fe^{III}		Co^{III}		Cr^{III}	
T (K)	300 K	115 K	300 K	115 K	300 K	115 K
Sp. Gr.	$P\bar{1}$		$P\bar{1}$		$P\bar{1}$	
a (Å)	8.949(2)	17.628(8)	8.945(2)	17.56(2)	8.967(1)	17.687(9)
b (Å)	14.254(7)	14.14(1)	14.234(3)	14.180(5)	14.251(5)	14.13(1)
c (Å)	21.482(4)	21.417(9)	21.482(6)	21.397(9)	21.578(3)	21.451(9)
α (°)	88.18(3)	89.01(7)	88.11(3)	89.42(7)	89.15(2)	88.84(5)
β (°)	111.53(2)	110.29(3)	111.73(2)	109.94(5)	110.81(1)	110.25(4)
γ (°)	127.89(4)	128.41(7)	127(68)	128.87(5)	127.87(2)	128.33(7)
V ($Å^3$)	1941(2)	3779(7)	1940(1)		1962(1)	3805(6)
Z	1	2	1	2	1	2
d_{calc} ($g.cm^{-3}$)	1.656	1.700	1.659		1.635	1.685
No rflcns	4164	4128	3311		4095	2537
$I \geq n\sigma(I)$	(n = 6)	(n = 4)	(n = 6)		(n = 6)	(n = 3)
R(F)	0.052	0.044	0.058		0.068,	0.062
$R_{\omega}(F)$	0.079	0.0671	0.081		0.107	0.080

The room temperature crystal structure shows layers of anions and organic molecules alternating in the *c* direction. The centrosymetric hexacyanometalates are situated at the origin of the cell. The trianions are connected along the a and b axis via several oxygen bridges from water molecules creating cavities in which disordered cations $(Et_4N)^+$ are located. The organic sublattice is built of two crystallographically independent molecules, noted A and B, which are arranged in two different kinds of dimer with a ring-to-double bond overlap in each dimer, giving rise to the first κ-phase ET salts involving a trianion. The intermolecular S-S distances are very similar in both dimers. They range from 3.340(3) Å and 3.661(3) Å in the three salts and are shorter than the intradimer ones.

The low temperature unit cell parameters have been determined on single crystals for κ-$(Et_4N)(ET)_4M(CN)_6$, 3 H_2O (M = Fe^{III}, Co^{III} and Cr^{III}) and studied in the range 300-115 K (Fig 2). In all cases, we observed a reversible doubling of the *a* parameter at about 240 K which remains unchanged down to 115 K.

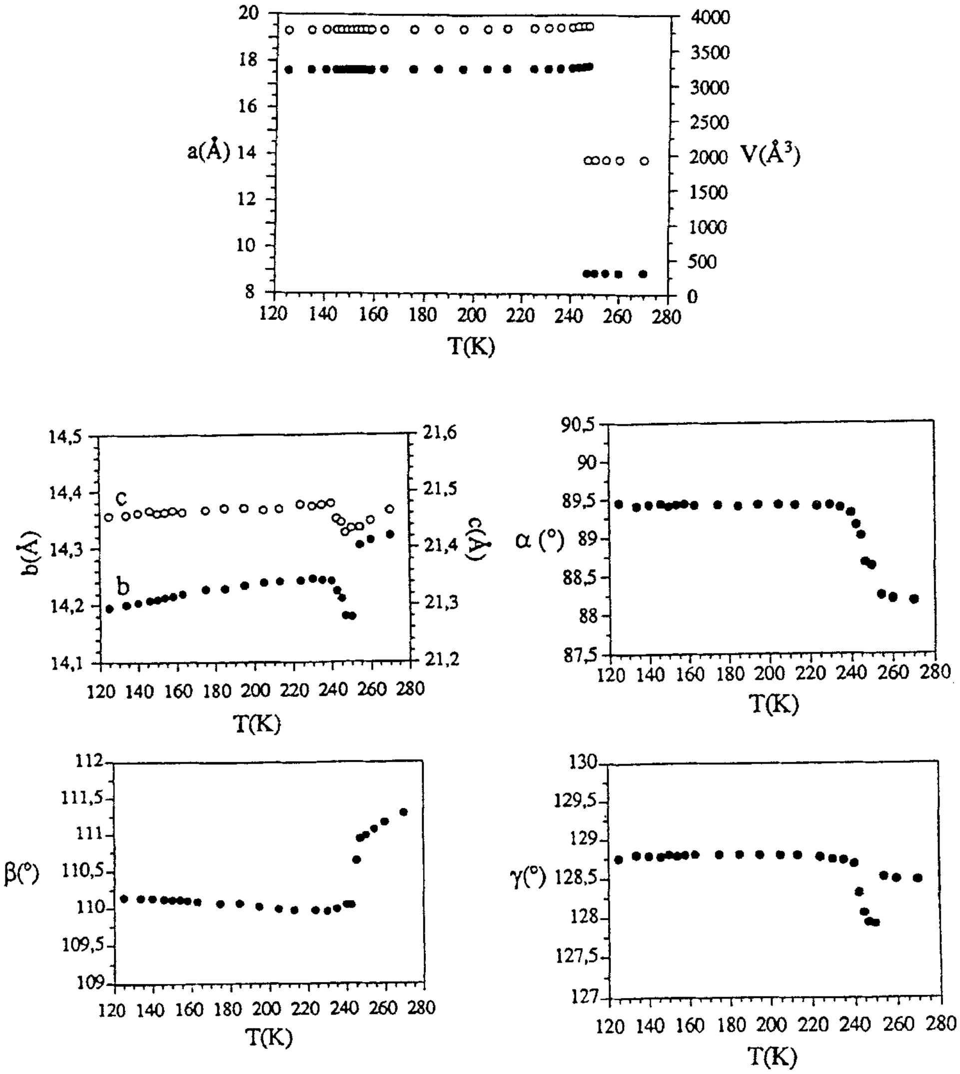


FIGURE 2 : Evolution of the cell parameters between 300 K and 115 K for κ-$(Et_4N)ET_4Fe(CN)_6$, 3 H_2O.

The crystal structure at 115 K was solved for the Fe^{III} and Cr^{III} salts (Fig. 3). In both cases, the origin of the cell is displaced along the a direction so that the anions are now situated close to (1/4, 0, 0). Moreover, the $(Et_4N)^+$ cations show a great orientational disorder which is not solved even at low temperature. The organic sublattice is built of four crystallographically independent ET molecules, libelled A, B, C and D, forming four kinds of dimers. The interdimer S-S distances range from 3.176(5) Å and 3.635(5) Å and the shortest intradimer S-S distance is 3.503(6) Å. From the intramolecular bond lengths determined by X-ray data, we can estimate that at room temperature both different ET molecules bear a charge of +0.5 whereas at 115 K one of the four different molecule is completely ionized, one other is neutral and the two last keep a charge of +0.5. Thus, the structural transition occuring at about 240 K is accompanied by a redistribution of the charges on the ET molecules, as already described in a few cases in other ET radical ion salts[6], and is characterized by the coexistence of the organic molecules in three different oxidation states at low temperature. We assume that this charge redistribution is a dismutation in which two dimers $[ET^{+0.5}]_2$ built with mixed valence ET radicals at room temperature change in one neutral dimer $[ET^0]_2$ and one other containing two completely ionized molecules $[ET^{+1}]_2$ at low temperature (scheme 1).

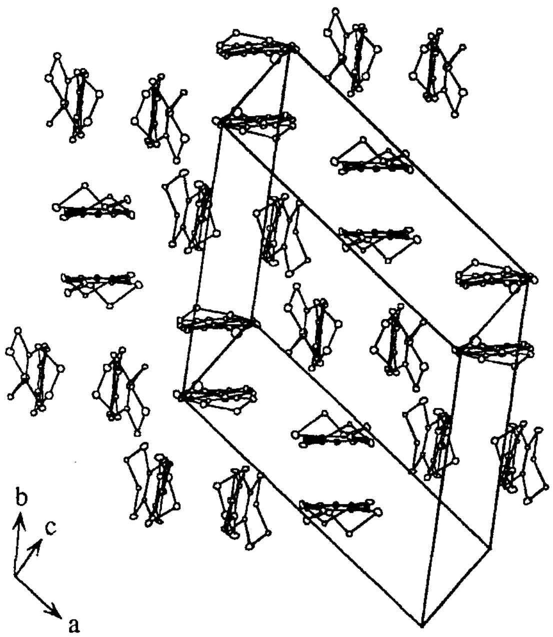
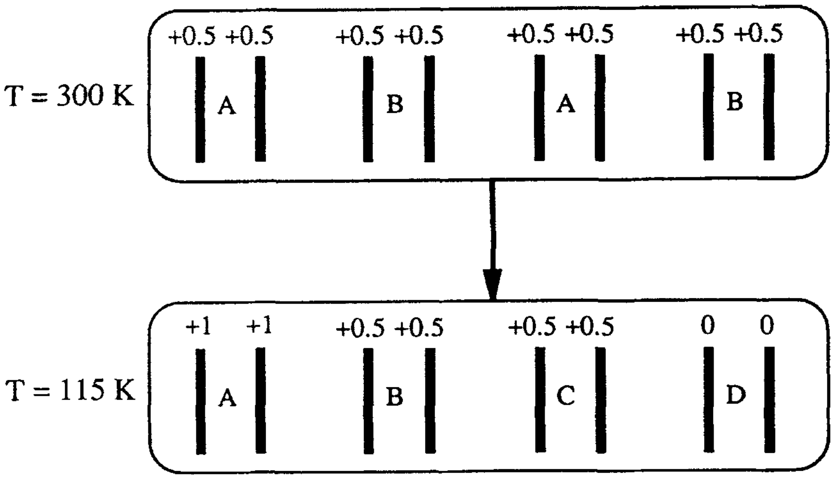


FIGURE 3 : Organic sublattice for κ-$(Et_4N)ET_4M(CN)_6$, 3 H_2O (M = Fe^{III} and Cr^{III}) at 115 K.



SCHEME 1 : Redistribution of the charges on the crystallographically independent dimers for κ–$(Et_4N)ET_4M(CN)_6$ (M = Fe^{III} and Cr^{III}) between 300 K and 115 K.

PHYSICAL MEASUREMENTS

ß-phase : The Fe^{III} and Co^{III} salts are semi-conductors with room temperature conductivites of 0.02 $S.cm^{-1}$ and 0.5 $S.cm^{-1}$ respectively. The values of the normalized spin susceptibility calculated from the E.S.R. spectra as well as those of the molar paramagnetic susceptibility remain unchanged in the temperature range 4.2 - 300 K for both salts. This behavior independent of the temperature, also called Paüli-type paramagnetism, is characteristic of conduction electrons and show the absence of significative magnetic interactions between the organic and inorganic sublattices. this is confirmed by the magnetic moment of the Fe^{III} salt which corresponds to the sum of the contributions of the paramagnetic $[Fe(CN)_6]^{3-}$ anion with that of the organic sublattice.

κ-phase : The electrical measurements of single crystals of the Co^{III}, Fe^{III} and Cr^{III} salts reveal a semiconducting behavior for the three salts ($\sigma_{300K} \approx 10$ $S.cm^{-1}$, ≈ 0.2 $S.cm^{-1}$ and ≈ 0.15 $S.cm^{-1}$ respectively for M = Co^{III}, Fe^{III} and Cr^{III}). The thermal dependence of the normalized resistance of the Co^{III} salt show a slop change in the semiconducting behavior at 240 K and 150 K. For the two other salts, the measurements have been carried out up to about 220 K only but they indicate a significant increase of the normalized resistance from 250 K.

The ESR spectra were carried out on single crystals for Co^{III} and Fe^{III} salts. The values of the normalized spin susceptibility and the linewidth calculated from the ESR spectra reveal for the Co^{III} and Fe^{III} salts two transitions at about 240 K and 150 K.

The thermal dependance of the molar paramagnetic susceptibility has been studied on the Fe^{III} compound and show the occurence of two transitions at about 240 K and 150 K (Fig. 4). However, the intensity of the transition at 150 K depends on the cooling rate of the sample, the transition at 240 K remaining unchanged. Thus, when the sample is cooled to 5 K and then warmed slowly from 5 K to 300 K, the transition at 150 K is as intense as the one at 240 K if the cooling has been slow. But it is very less intense - and even absent - if the sample has been quenched at 5 K. This behavior induces the appearance of a large hysteresis for the transition at 150 K. The magnetic moment of the Fe^{III} salt corresponds to the sum of the contributions of the paramagnetic $[Fe(CN)_6]^{3-}$ anion with that of the organic sublattice. This result demonstrates the absence of significative magnetic interactions between the organic and inorganic counterparts.

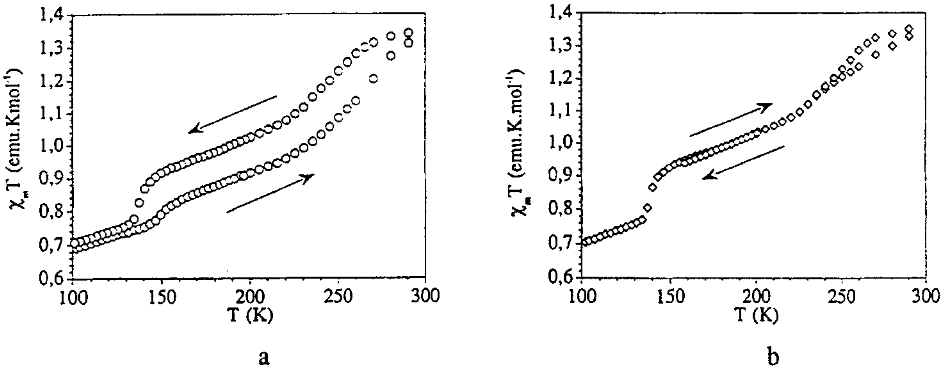


FIGURE 4 : Temperature dependence of the product (χ_m.T) for compound κ-$(Et_4N)ET_4Fe(CN)_6$, 3 H_2O when the sample has been previously quenched at 5 K (a) and when it has been smoothly cooled from 300 K to 5 K (b).

Several consecutive decreases and increases of temperature have also been carried out for the Co^{III} salt with a slow cooling rate. This time, we have only observed the transition at 150 K whereas the ESR measurements have shown two transitions at 150 K and 240 K[1f].

Finally, Different Scanning Calorimetry measurements were performed between 125 K and 300 K for the Fe^{III} and Co^{III} salts. For both salts, the transition are characterized by endothermic peaks. The peaks are mainly observed at about 150 K and are attributed to a first-order transition and the calculated enthalpies are 1.5 $J.g^{-1}$ and 0.4 $J.g^{-1}$ respectively for the Co^{III} and the Fe^{III} salts.

In the κ-phase salts, the decrease in the static and ESR susceptibilies occuring in both transitions corresponds approximately to the loss of the half of the magnetic contribution from the organic sublattice at room temperature. The first transition at about 240 K could be related to the dismutation of two ET dimers $[ET^{+0.5}]_2$ in one neutral dimer $[ET^0]_2$ and one other completely ionized $[ET^{+1}]_2$ (see scheme 1). The neutral dimer do not have any magnetic moment and we can assume the existence of a singlet ground state in the completely ionized ET molecules. So the magnetic contribution comes from the two other crystallographically independent ET radicals which are partially oxidized ($\rho \approx 0.5$). The second transition has not been evidenced by X-ray study ; however, the DSC measurements show a very clear endothermic peak characteristic of a first-order transition suggesting that this transition might also be accompanied by a structural modification.

DISCUSSION AND CONCLUSION

The combination of inorganic hexacyanometalate anions with the organic donor ET has led to new hybrid molecular materials in which localized magnetic moments and itinerant electrons coexist. We have obtained two phases, noted β-$ET_5M(CN)_6$, 10 H_2O with M = Fe^{III} and Co^{III} and κ-$(Et_4N)ET_4M(CN)_6$, 3 H_2O with M = Co^{III}, Fe^{III} and Cr^{III}. All these compounds are semiconductors and do not reveal any significant magnetic exchange between the organic and inorganic sublattices. This situation is attributed to the inhomogeneous repartition of the charges on the ET molecules in the κ-phase as revealed by the crystallographic data. Indeed the irregular repartition of the charges, which may be due to the strong electrostatic interactions produced by the high charges of the hexacyanometalate anions, induces a progressive charge localization when the temperature is lowered and accounts for the decrease in the d.c. conductivity values. In consequence, we assume that the weak delocalization of the conduction electrons prevents any significative interactions between the itinerant π-electrons and the localized magnetic moments of the paramagnetic hexacyanometalate anions.

Indeed these κ-phase salts can be considered as lamellar compounds made with alternate organic and inorganic layers. In such quasi 2-D systems specific electronic instabilities, inducing either a superconducting state or a magnetic ground state, have been already discovered. But we have shown here that structural distortions giving rise to new surstructures are competiting with these instabilities. These structural phenomena are reminiscent of the polytypes observed in inorganic lamellar compounds and open the way to new molecular systems with combined periodicities.

Acknowledgment We thank Dr. T. Mallah, LCMT- URA 419, Université Pierre et Marie Curie, Paris VI, for a generous gift of $K_3Cr(CN)_6$.

REFERENCES

1. See for examples : (a) R.T. Henriques, L. Alcácer, J.P. Pouget, D.Jérome, J. Phys. C. Solid State Physics, 17, 5197, (1984). (b) A. Aumuller, P. Erk, G. Klebe, S. Hunig, J.U. Schutz, H.P. Werener, Angew. Chem. Int. Ed. Engl., 25, 740 (1986). (c) C.J. Gómez-García, C.Giménez-Saiz, S. Triki, E. Coronado, P. Le Maguerès, L. Ouahab, L. Ducasse, C. Sourisseau, P. Delhaès, Inorg. Chem., 34, 4139 (1995). (d) *C.J.* Gómez-García, L. Ouahab, C. Giménez-Saiz, S. Triki, E. Coronado, P. Delhaès, Angew. Chem. Int. Ed. Engl., 33, 223 (1994). (e) A.W. Graham, M. Kurmoo, P. Day, J. Chem. Soc., Chem. Commun., 2061 (1995). (f) P. Le Maguerès, L. Ouahab, N. Conan, C.J. Gómez-García, P. Delhaès, J. Even, M. Bertault , Solid. State Comm., 97, 27 (1996).
2. (a) J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini, M. H. Whangbo ; Organic Superconductors, Synthesis, Structure, Properties and Theory (Ed.: R. N. Grimes), Prentice Hall, Englewood Cliffs, New Jersey, USA (1992). (b) P. Delhaès, In NATO ASI Lower Dimensional Systems and Molecular Electronics ; Metzger, R. M. , DAY, P. ; Papavassiliou, G. C. Eds ; Plenum Press : New York, p43 (1991).
3. (a) T. Mallah, S. Thiébault, M. Verdaguer, P. Veillet, Science, 262, 1554 (1993). (b) C. Michaut, L. Ouahab, P. Bergerat, O. Kahn, A. Bousseksou, J. Am. Chem. Soc., 118, 3610 (1996).
4. P. K. Mascharak, Inorg. Chem., 25-3, 245, (1986).
5. Crystal data for β-$ET_5Fe(CN)_6$, 10 H_2O : triclinic, $P\bar{1}$, a = 9.391(2), b = 12.730(3), c = 19.148(3) Å, α = 104.11(2), β = 92.60(2), γ = 98.64(2) °, V = 2187(1) $Å^3$, Z = 1, d_{calc} = 1.758 $g.cm^{-3}$, R = 0.032 and R_ω = 0.045 using 3810 reflections with $I \geq 3\sigma(I)$.
6. (a) M.L. Doublet, E. Canadell, R.P. Shibaeva, J. Phys. I France, 4, 1479 (1994). (b) J. Moldenhauer, C. Horn, H.I. Pokhodonia, D. Schweitzer, I. Heinen, H.J. Keller, Synth. Metals, 60, 31 (1993). (b) J. Moldenhauer, C. Horn, H.I. Pokhodonia, D. Schweitzer, I. Heinen, H.J. Keller, Synth. Metals, 60, 31 (1993).