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Coordination Chemistry Reviews
178–180 (1998) 1501–1531

COORDINATION
CHEMISTRY
REVIEWS

Coordination complexes in conducting and magnetic molecular materials

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Received 31 October 1997; received in revised form 16 March 1998; accepted 25 March 1998

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Abstract

In this paper we present organic–inorganic molecular materials investigated in our group during the last decade. These materials result from the chemical and electrochemical molecular assemblies of coordination complexes such as tetracyanometallates, hexacyanometallates,

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PII S0010-8545(98)00107-6

metal bis-(dithiolates), metal bis-(dithiolenes), metallocenium complexes and polyoxometalates and organic precursors such as TTF and BEDT-TTF derivatives and paramagnetic nitronyl nitroxide radicals. Taking advantage of the fascinating flexibility of coordination chemistry, the goal of our work is to prepare compounds with particular physical properties such as electrical conductivity, magnetism, spin crossover, and also materials combining two or more of these properties. In the light of the observed results, we present different approaches which we are currently investigating with the aim of increasing interactions between the organic and inorganic components.

Keywords: Electrical conductivity; Ferrocenium; Ferromagnetic interactions; Hexacyanometallates; Inorganic acceptors; Nitronyl nitroxide radicals; Organic donors; Polyoxometalates; Spin crossover

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1. Introduction

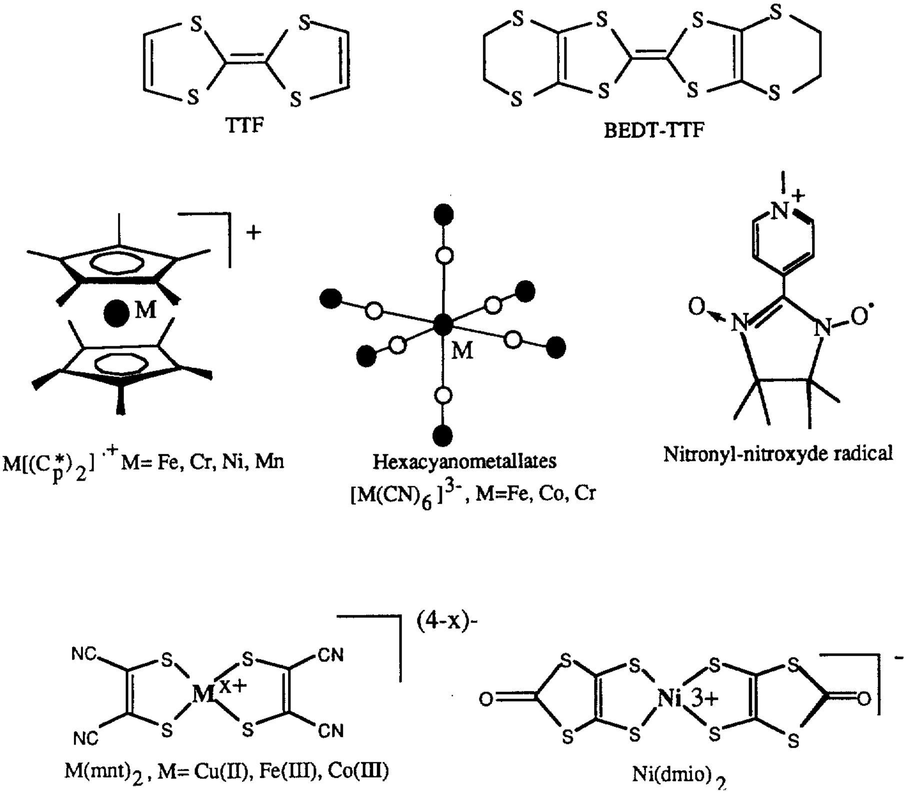
Since the discovery in 1954 by Japanese researchers [1,2] of electrical conductivity ($\sigma_{RT} = 0.1$ S cm^{-1}) in perylene bromine, extensive studies have been devoted to organic and organometallic charge transfer complexes and radical ion salts [3–6] with the aim of obtaining high T_c superconductors or ferromagnets. These low-dimensional compounds have attracted much attention, not only for their potential technological applications but also for fundamental reasons. For example, numerous studies on organic conductors have revealed that they show interesting physical properties such as Pieirls transition, charge density wave, superconductivity, etc. They also display various one-dimensional (1-D) to two-dimensional (2-D) electronic structures [3–6]. Interest in the field is strongly related to its multidisciplinarity and also to the fascinating flexibility of molecular and coordination chemistry [5].

Coordination chemistry was introduced recently in the field of molecular science. Among examples we can mention: the 1-D conducting [$Pt(CN)_4$] chain [7–9]; the superconducting materials based on M(dmit) anions reported by Cassoux and coworkers [10]; the ferromagnets discovered by Miller and coworkers [11–13] based on metallocenium radicals $M(Cp^*)_2$ and those prepared by Kahn's group containing paramagnetic transition metals linked by specific organic ligands such as MnCu(opbOH) [14]; the three-dimensional ferromagnets based on $M(CN)_6^{3-}$ anions discovered in Verdaguer's group [15,16]; and also the superconducting materials containing $M(CF_3)_4$ (M = Cu, Ag, Au) anions reported recently in William's group [17]. The coordination compounds consist of transition metal centers or clusters surrounded by organic ligands. It is theoretically possible to modulate the geometrical and electronic properties by a judicious choice of metal ions and ligands in order to anticipate the physical properties.

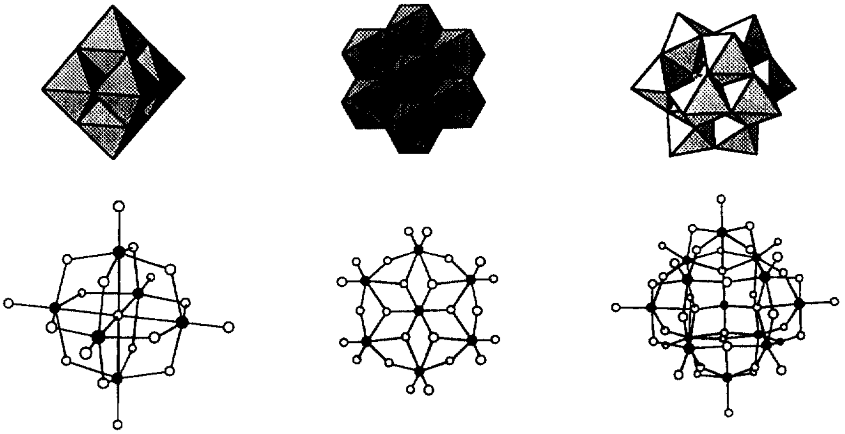
One of the current trends in molecular science is dealing with the investigation of compounds exhibiting, if possible in a synergistic way, multiple physical properties [5,18,19] such as electrical conductivity and magnetic interactions, spin crossover and magnetism, optical and magnetic properties, etc. For example, in organic/inorganic hybrid materials it is possible to couple ferromagnetically isolated and localized spins on transition metals of the inorganic network, thanks to the mobile π electrons of the organic network, according to the so-called indirect exchange mechanism (π–d interactions). This mechanism is equivalent to the so-called RKKY (Ruderman, Kittel, Kasuya, Yoshida) [20,21] model involving s–d or s–f interactions in inorganic compounds. To match such a ferromagnetic coupling in compounds where the interactions occur through space, we need a highly conducting organic network and strong interactions between the organic and inorganic sublattices.

In this paper we will present some organic/inorganic molecular materials that we studied in the last 10 years. These materials are based on coordination complexes and inorganic components such as tetracyanometallates, hexacyanometallates, metal bis-(dithiolates), metal bis-(dithiolenes), metallocenium complexes (Scheme 1) and polyoxometalates (Scheme 2). Concerning the organic part, two kinds of components are chosen (Scheme 1): TTF and BEDT-TTF derivatives which are known for their ability to give highly conducting and superconducting salts [3,4,22–30] and the nitronyl nitroxide radicals which are well known in the field of molecular magnetism [31–39].

Our motivation in the use of such complexes is the following: (i) their geometrical parameters (size and shape) can influence the dimensionality of materials; (ii) the



Scheme 1. Molecular precursors used.



$[M_6O_{19}]^{n-}$ - a -

$[M'(OH)_6M_6O_{18}]^{n-}$ - b -

$[XM_{12}O_{40}]^{n-}$ - c -

Scheme 2. Polyhedral and bond representations of polyoxometalates used in this report: (a) Linquist structure; (b) Anderson–Evans structure; (c) Keggin structure.

large negative charge in the case of polyanions (from −2 to −16) can give rise to strong electrostatic interactions between the two networks; (iii) the presence of transition metals gives flexibility in the sense that we can introduce paramagnetic centers and also modulate the above geometrical and electronic properties (points i and ii), thanks to the coordination chemistry, by changing the ligand on the metal; and finally (iv) these large units are soluble and stable in organic solvent which make possible their molecular assemblies with organic components.

2. The polyoxometalate-containing materials

The polyoxometalates result from the association of MO_6 (M = Mo, W, V, Nb) coordination octahedra by sharing edges or vertices [40–44]. These arrangements (Scheme 2) yield a wide variety of inorganic clusters [45–49] with different size, shape and electronic properties. Depending on the nature of the transition metal we can have inorganic units with different nuclearities and different magnetic moments.

Another important property of these polyoxometalates is their electron acceptor capability. For instance, the Keggin polyanion $[XM_{12}O_{40}]^{n-}$ can accept up to $32e^-$ [50]. This offers the opportunity to prepare organic donor inorganic acceptor (ODIA) materials with a *mixed valence* state on the organic and inorganic units [51–53]. The potentialities of polyoxometalates in material science [19,43,51–56] are exemplified through the properties of the Keggin polyoxometalates which are formulated as $[(XM_{12}O_{40})^{n-}$ or $(XO_4)^{n-}M_{12}O_{36}$, M = Mo, W] and present five isomers (the so-called Baker–Figgis isomers: α, β, γ, δ and ϵ) [57] [see Scheme 2(c)].

These polyanions can be diamagnetic or paramagnetic following reduction processes or by substitution of the central heteroatom or outer metal atoms by paramagnetic ones. Finally, it is possible to substitute terminal oxygen atoms by organic ligands [58–61].

2.1. *Polyoxometalates and TTF derivatives*

The first report on a TTF charge transfer salt containing a Keggin polyoxometalate as inorganic acceptor component was published by our group in 1988 [51]. In that publication we indicated that the aim of our work is to prepare materials with a *mixed-valence* state on the organic and inorganic parts in order to obtain materials with conducting and magnetic properties. We presented TMTSF and BEDT-TTF materials containing such polyoxoanions at the NATO Advanced Study Institute Meeting (Spetses Island, Greece) in 1989. These compounds, namely $(TMTSF)_3PW_{12}O_{40}$ and $(BEDT\text{-}TTF)_3(PW_{12}O_{40})$, were published in 1991 in the proceedings devoted to that meeting [62]. We published the second report dealing with TTF derivative charge transfer salts with Lindquist polyoxoanions in 1989 [53]. At the same time, Davidson et al. reported the BEDT-TTF salt with a Keggin polyanion [63], namely $(BEDT\text{-}TTF)_8SiW_{12}O_{40}$. In 1990, Bellitto et al. published new TTF salts with Lindquist polyanion [64]. In 1993, Coronado and coworkers reported a TTF salt with $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [65]. In 1994, in collaboration with Delhaès from Bordeaux and Coronado from Valencia (Spain), we investigated BEDT-TTF salts with paramagnetic Keggin polyanions [66,77].

Different radical cation salts resulting from electrochemical assemblies of various polyoxometalates with TTF derivatives prepared in our group are given in Table 1. Beside materials with conducting and magnetic properties, many other compounds were characterized [19,54] with electrical conductivity ranging from metallic behavior [in $(BEDT\text{-}TTF)_5VW_5O_{19}$] [75] to insulator.

The four isomorphous TTF salts [$(TTF)_6(HXM_{12}O_{40})(Et_4N)$, $X=P$, Si and $M=$ Mo, W] have interesting features [51,52]. They constitute the first materials, in the polyoxometalate series, containing conducting electrons and localized spins. Indeed, electron transfer from TTF to polyoxoanion for the two compounds with $X=P$ was observed [51,52,68,76]. In fact, EPR signals corresponding to W^{5+} ($S=1/2$) and Mo^{5+} ($S=1/2$) were observed at 4 K, indicating the polyanions in these materials are paramagnetic.

Following these results, we explored materials with other paramagnetic polyoxometalates containing the BEDT-TTF donor which gives higher conducting organic layers [3,4]. Two different phases [α_1- and α_2-$(BEDT\text{-}TTF)_8(M'W_{12}O_{40})$.(solv)] were characterized, with both paramagnetic and diamagnetic Keggin polyanions [$M'=H_2^{2+}$, B^{3+}, (Fe^{3+}, $S=5/2$), (Co^{2+}, $S=3/2$), (Cu^{2+}, $S=1/2$)] [66,67]. Short contacts (3.10 Å) were observed between terminal O atoms of polyanions and C atoms of the ethylenic groups of the BEDT-TTF molecules, indicating the presence of hydrogen bonding between the organic and inorganic units. All the compounds are semiconducting with room temperature conductivities in the range 10^{-1} to 10^{-3} S. The magnetic measurements showed antiferromagnetic behavior which

Table 1

Space group (S.G.), electrical conductivity σ (S cm^{-1}), activation energy E_a (meV), g-factor, linewidth S (G) for TTF derivative salts with various polyoxometalates

Compound	S.G.	σ (300 K)	E_a	g-Factor	S	Reference
$(TTF)_6(HPW_{12}O_{40})(Et_4N)$	*Cmmm*	2×10^{-2}		NS	NS	[51,52]
$(TTF)_6(HSiW_{12}O_{40})(Et_4N)$	*Cmmm*	5×10^{-4}		NS	NS	[52]
$(TTF)_6(HPMo_{12}O_{40})(Et_4N)$	*Cmmm*	5×10^{-2}		NS	NS	[52,68]
$(TTF)_6(HSiMo_{12}O_{40})(Et_4N)$	*Cmmm*	10^{-4}		NS	NS	[52]
$(BEDT)_3(PW_{12}O_{40})(THF)$	$P\bar{1}$	Ins		NM		[62]
$(TTF)_3W_6O_{19}$	$P\bar{1}$	1.4×10^{-3}	225			[53,69]
$(TTF)_3Mo_6O_{19}$	$P\bar{1}$	5×10^{-4}	230			[53,69]
$(TTF)_4W_6O_{19}(CH_3CN)_{0.5}$	$P2_1/m$	Ins		NM		[70]
$(TTF)_7[\beta\text{-}Mo_8O_{26}]$	$P\bar{1}$	10^{-3}	700			[71,72]
$(TMTSF)_3W_6O_{19}(DMF)_2$	$P2_1/c$	1.3	200	NM		[53,69]
$(TMTSF)_3VW_5O_{19}(DMF)_2$	$P2_1/c$	Ins		NM		[73]
$(BEDT)_2Mo_6O_{19}$	$P2_1/c$	Ins			14	[74]
$(BEDT)_2W_6O_{19}$	$P2_1/c$	Ins			16	[74]
$(BEDT)_5(VW_5O_{19})5H_2O$	$P2_1/c$	13.7			60	[75]
$(BEDT)_5(V_2W_4O_{19})5H_2O$	$P2_1/c$	7×10^{-3}	NM		50	[73]
$\alpha_1\text{-}(BEDT)_8(CoW_{12}O_{40})$	$I2/m$	15×10^{-2}	94	2.0082	95	[66,67]
$\alpha_1\text{-}(BEDT)_8(CuW_{12}O_{40})$	$I2/m$	10^{-3}		2.0100	94	[67]
$\alpha_2\text{-}(BEDT)_8(CoW_{12}O_{40})$	$I2/m$	10^{-3}		2.0072	83	[67]
$\alpha_2\text{-}(BEDT)_8(FeW_{12}O_{40})$	$I2/m$	10^{-3}		2.0114	87	[67]
$\alpha_2\text{-}(BEDT)_8(BW_{12}O_{40})$	$I2/m$	7×10^{-2}	159	2.0118	63	[67]

[a] Numbers in parentheses indicate the temperature dependence of the electrical conductivity. Abbreviations used: SC = semiconducting, M = metallic, Ins = insulator, NS = no signal, NM = not measured.

results from antiferromagnetic interactions in the organic network and revealed no significant magnetic interactions between the organic and inorganic units [66,67] as usually observed in most known radical cation salts containing paramagnetic anions [77–88].

2.2. *Metallocenium-containing materials*

Metallocenium radicals are fundamental building blocks in Miller's ferromagnets [11–13]. Beside their easy accessible reduction potentials which make them suitable molecular precursors for charge transfer complexes, it is possible to modulate their size and their magnetic moments depending on the transition metal [from $S = 1/2$ for Fe(III) to $S = 3/2$ for Cr(III)].

Several ferrocenium-containing compounds were synthesized with both Keggin polyanions and Anderson Evans polyanions. The general formula of those salts with Keggin anions [89] is $(Fe(Cp^*)_2)_4XM_{12}O_{40}.n(solv)$ ($X = P$, Si, Fe, $M = W$, Mo). In many cases two different phases with the same stoichiometry but different crystal structures were obtained in the same batch: (i) in one structural type $[Fe(Cp^*)_2]^+$ cations form linear chains surrounded by columns of polyoxometalates; (ii) in the other type $[Fe(Cp^*)_2]^+$ units occupy the vertices of large cuboctahedra which encapsulate the polyanion [89]. The magnetic properties of these compounds indicate that all salts present very weak antiferromagnetic interactions obeying the Curie–Weiss expression $\chi = C/(T-\theta)$ with small θ values [89].

The Anderson–Evans [47,48] type of polyoxometalate $[M'(OH)_6M_6O_{18}]^{n-}$ [Scheme 2(b)] has two important features: (i) it contains a paramagnetic ion (Cr, Ni, Fe, ...) surrounded by six MoO_6 octahedra [see Scheme 2(b)]; (ii) it is planar and therefore it can give rise to molecular solid state organization reminiscent of $Fe(Cp^*)_2$-TCNE.CH_3CN [11–13], with alternate stacks of $Fe(Cp^*)_2^+$ units and polyanions. The crystal structure of $(Fe(Cp^*)_2)_3Cr(OH)_6Mo_6O_{18}.20H_2O$ represented in Fig. 1, is very unusual. It shows bidimensional layers containing orthogonal alternating stacks of polyanions (POM) and of centrosymmetric trimers of the $Fe(Cp^*)_2^+$ (C) unit. The $Fe(Cp^*)_2^+$ units are perpendicular to each other. The distances between spin carriers are too large and consequently, the magnetic properties indicate weak antiferromagnetic interactions obeying a Curie–Weiss law with small θ value (≈ -0.5 K) [90].

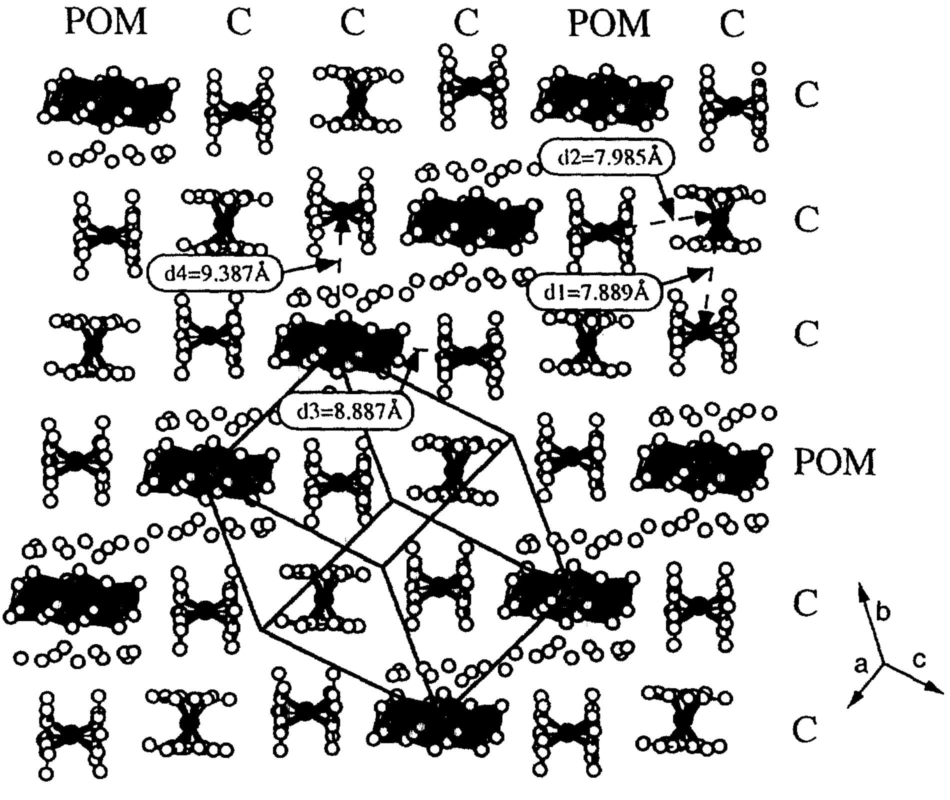


Fig. 1. Crystal structure of $(Fe(Cp^*)_2)_3Cr(OH)_6Mo_6O_{18}.20H_2O$.

2.3. *Ferromagnetic interactions in nitronyl nitroxide radical salts* $(p\text{-}rad)_2[M_6O_{19}]$*; M=Mo, W*

Organic radicals derived from nitronyl nitroxide are known to generate organic ferromagnets and constitute one of the most used organic molecular building blocks in molecular magnetism [31–39]. The radical paranitrophenylene nitronyl nitroxide (p-NPNN) reported in 1991 [36,37] is the first organic ferromagnet ($T_c = 0.60$ K) containing only C, H, N and O elements. Another characteristic of these organic radicals is their ability to undergo hydrogen bonding which can be used to design organic ferromagnets with various dimensionalities [91].

Compounds $(p\text{-rad})_2[M_6O_{19}]$ (M = Mo, W) were obtained by the reaction of $(Bu_4N)_2M_6O_{19}$ salts on (p-rad)I in acetonitrile and recrystallized in DMF [92]. In the crystal structure, the radicals form centrosymmetric dimers. The magnetic properties are represented in Fig. 2 in the form of the $\chi_M T$ vs. T plot. The $\chi_M T$ values observed at room temperature correspond to what are expected for two uncorrelated radical spins. It remains constant down to ca. 60 K and then increases as T is lowered and reaches a maximum of 0.85 cm^3 K mol^{-1}. These experimental data can be fitted with the Curie–Weiss law. Such behavior reveals dominant ferromagnetic interactions between the radical spins.

Another interesting feature in these materials concerns the interactions between the organic and inorganic units. In fact, short O...H contacts (2.20 to 2.30 Å) are observed between the H atoms of the organic radical and the O atoms of the polyoxometalates, indicating the existence of hydrogen bonding in these materials. This result is promising and enables us to envisage the use of paramagnetic polyoxometalates in such systems.

3. The polycyano complex-containing materials

Thanks to the CN groups, it is possible to build molecular materials with increased dimensionality and interesting conducting and/or magnetic properties. This is the

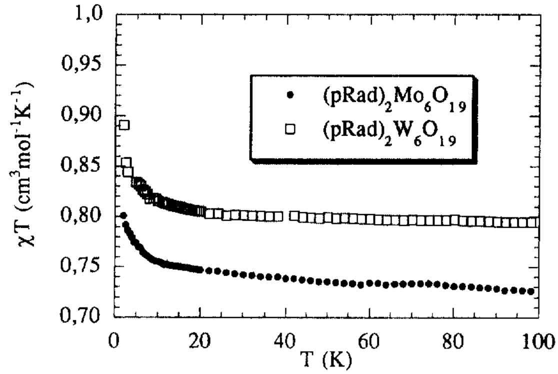


Fig. 2. $\chi_M T$ vs. T curve in the 2–100 K temperature range for $(p\text{-rad})_2[M_6O_{19}]$.

case, for instance, for superconducting BEDT-TTF salts containing polymeric layers of $CuN(CN)_2X$ (X = Cl, Br) and $Cu_2(CN)_3$ units [3,4,93–95]. Another example can be found in the well-known Verdaguer ferromagnets $AB(CN)_6$ (where A and B are transition metals) with high critical temperature (>300 K) [15,16]. We can also relate the work we reported recently concerning nitronyl nitroxide radical salts containing hexacyanometallates, in which we observed ferromagnetic interactions between the organic and inorganic units [96]. The approach used in preparing these materials is based on the overlap between the positive spin density of the nitroxide groups of the organic radicals [97] and the negative spin density of the CN group of the anions [98,99].

3.1. *TTF derivative materials with tetracyanometallates* $[M(CN)_4]^{2-}$*, M = Pt(II), Ni(II), Pd(II)*

Like TTF derivatives, the tetracyanoplatinate complexes give rise to highly conducting 1-D chains [7–9]. One of our goals with these dianions was to mix in the same solid these two mixed-valence conducting networks [100]. Many charge transfer salts (Table 2) with various crystal structures and physical properties based on these two kinds of precursor were reported by several groups including our own [100–111]. Nevertheless, all the known radical ion salts display isolated $M(CN)_4^{2-}$ units, and to our knowledge, tetracyanoplatinate chains have never been stabilized with TTF derivatives up to now. We will focus here only on the BEDT-TTF- and MDT-TTF-containing compounds which display a rich structural polymorphism and related physical properties.

Table 2
Space group (S.G.), electrical conductivity σ ($S\ cm^{-1}$), activation energy E_a (meV), *g*-factor, linewidth *S* (G) for TTF derivative salts with tetracyanometallates

Compound	S.G.	σ (300 K)	E_a	*g*-Factor	*S*	Reference
$(TTF)_5Pt(CN)_4(CH_3CN)_2$	$P\bar{1}$	10^{-5} (SC)	230		1	[100,101]
$(TMTSF)_3Pt(CN)_4$	$P\bar{1}$	0.25 (SC)		NM	NM	[100]
β-$(BEDT)_4Pt(CN)_4$	$P\bar{1}$	12 (M)		2.0127	38	[100,102–104]
β-$(BEDT)_4Ni(CN)_4$	$P\bar{1}$	2 (M)		2.0130	40	[100]
α_1-$(BEDT)_4Pt(CN)_4$	$C2/c$	5 (SC)	425	2.0130	63	[105,106]
α_1-$(BEDT)_4[Ni_{0.55}Pt_{0.45}](CN)_4$	$C2/c$	10^{-1} (SC)	420	2.0112	62	[105]
α_2-$(BEDT)_4[Ni_{0.14}Pt_{0.86}](CN)_4$	$P2_1/n$	10^{-3} (SC)	435	2.0114	36	[105]
δ-$(BEDT)_4Pt(CN)_4$	$P2/c$	10^{-1} (SC)	415	2.0105	28	[103,105,106]
δ-$(BEDT)_4Ni(CN)_4$	$P2/c$	10^{-1} (SC)	415	2.0110	28	[103,105,106]
δ-$(BEDT)_4[Ni_{0.48}Pt_{0.52}](CN)_4$	$P2/c$	10^{-5} (SC)	420	2.0110	28	[105]
κ-$(MDT$-$TTF)_4Pt(CN)_4(H_2O)$	$P\bar{1}$	NM		NM	NM	[107–109]
κ-$(MDT$-$TTF)_4Pt(CN)_4(CH_2Cl_2)$	$P2/n$	5–10 (M)		2.0115	70	[107–109]
κ-$(MDT$-$TTF)_4\ Ni(CN)_4(CH_2Cl_2$	$P2/n$	8 (M)		2.0114	70	[107–109]
b-$(EDT$-$TTF)_4Pt(CN)_4(H_2O)_2$	$C2/m$	0.2 (M)		2.0075	27	[107,109,110]
b-$(EDT$-$TTF)_4Pd(CN)_4(H_2O)_2$	$C2/m$	0.5 (M)		2.0080	25	[107,109,110]

[a] Numbers in parentheses indicate the temperature dependence of the electrical conductivity. Abbreviations used: SC = semiconducting, M = metallic, NM = not measured.

3.1.1. Polymorphism in (BEDT-TTF)$_4$M(CN)$_4$.(solv)

BEDT-TTF is involved in a large number of conducting and superconducting radical ion salts [3,4]. All the salts obtained in the BEDT-TTF/M(CN)$_4^{2-}$ systems have the same 4:1 stoichiometry. Their crystal structures are built of alternating layers of organic and inorganic anions, as commonly observed in such a type of material [3,4]. However, the main difference lies firstly in the packing mode of each organic chain and, secondly in the way these organic chains pack to generate the organic layer. Three kinds of packing modes were observed, namely α, β, and δ modes (see below) [100,102–106]. The κ phase was not observed in the BEDT-TTF series but it can be found in the salts κ-(MDT-TTF)$_4$M(CN)$_4$.(solv)$_x$ [107–109], based on the unsymmetrical donor MDT-TTF. Superconductivity has been detected by Mori et al. [111] in the hydrated salts (BEDT-TTF)$_4$M(CN)$_4$.(H$_2$O), M = Pt(II), Pd(II), while the anhydrous ones exhibit only a semiconducting behavior (Table 2). In order to study the partial anion alloying effect on the structural and physical properties, we also prepared compounds with the general formula α,δ-(BEDT-TTF)$_4$[Ni(CN)$_4$]$_x$[Pt(CN)$_4$]$_{1-x}$.(H$_2$O)$_n$; $x = 0 \rightarrow 1$; $n = 0 \rightarrow 4$ [105].

3.1.1.1. β-(BEDT-TTF)$_4$M(CN)$_4$, M = Pt(II), Ni(II). Firstly, one can note that the β modification was not observed with anion alloying. In the β-organic sublattice the two independent BEDT-TTF molecules form tetramerized slipped stacks (Fig. 3) [100,102–106]. The interstack S...S contacts (> 3.8 Å) are shorter than the intrastack contacts (⩾ 3.8 Å). The two compounds are metallic with room temperature conductivities of 12 and 2 S cm^{-1} for M = Pt and Ni, respectively [Fig. 4(a)]. However, a

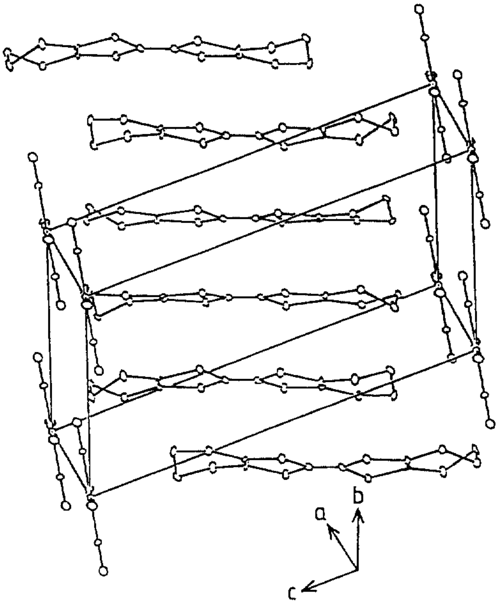


Fig. 3. Crystal structure of β-(BEDT-TTF)$_4$[M(CN)$_4$].

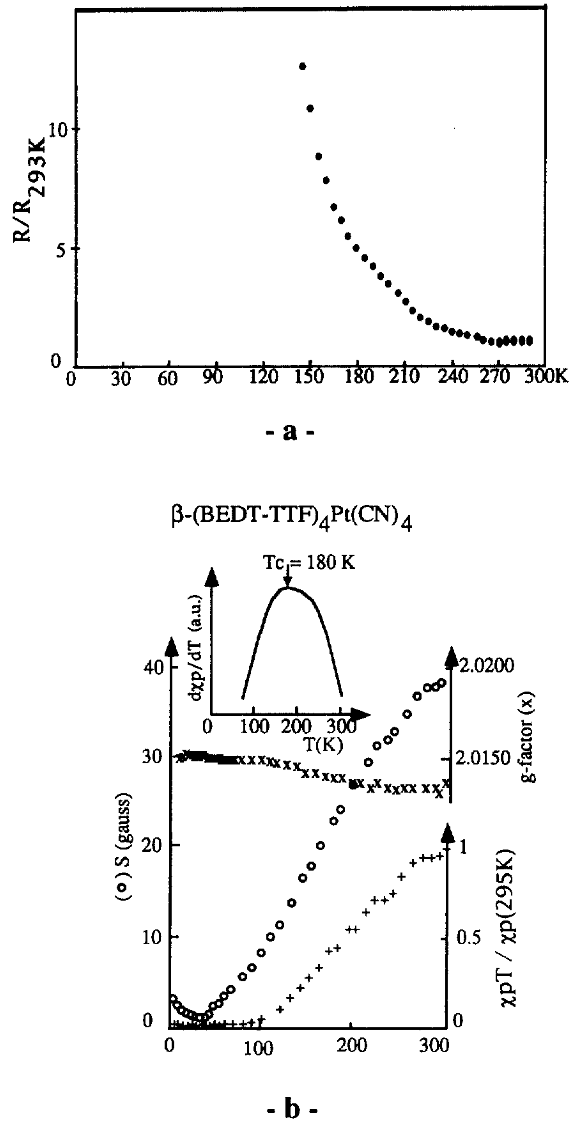


Fig. 4. β-$(BEDT\text{-}TTF)_4[M(CN)_4]$: (a) temperature dependence of the resistivity; (b) temperature dependence of *g*-factor, ESR linewidth and spin susceptibility.

progressive electronic localization is observed at 250 K and 230 K for the two salts, giving rise to metal insulator transitions. The EPR investigations given in Fig. 4(b) show a decrease of the linewidth as well as the spin susceptibility over a wide range of temperature. Similar behavior was observed in other β phases such as $(BEDT\text{-}TTF)_2AsF_6$ and $(BEDT\text{-}TTF)_2SbF_6$ for which a metal to insulator transition was also observed at low temperature [112]. In the case of low dimensional materials, a maximum in the variation of dχ/dt vs. temperature (where χ is the static magnetic susceptibility) [113] can indicate some transitions. In fact, as shown in Fig. 4(b), the maximum observed at $T_c = 180$ K can be attributed to a structural transition. From the low temperature X-ray crystal structure investigations, we observed that the crystal structures at 293 K and 100 K are not significantly different. The only difference concerns the terminal ethylenic groups of the BEDT-TTF molecules which become ordered at low temperature [114,115].

3.1.1.2. α-(BEDT-TTF)$_4$[Ni(CN)$_4$]$_x$[Pt(CN)$_4$]$_{1-x}$(H$_2$O)$_n$; $x = 0 \rightarrow 1$; $n = 0 \rightarrow 4$. In the α-organic sublattice the unit cell contains two layers. The normals to the molecular planes, located on two adjacent stacks, are inclined with opposite direction with dihedral angles between the molecules of roughly 50°. Two structural modifications were obtained, namely α_1 and &[alpha];$_2$.

In the α_1-(BEDT-TTF)$_4$[Ni(CN)$_4$]$_x$[Pt(CN)$_4$]$_{1-x}$ ($x = 0$, 0.48, 1) [105,106] three independent molecules (A, B, C) generate two molecular stacks (Fig. 5). The first chain is exclusively made of A molecules [AAAA...]. The A molecules dimerize and are displaced from each other in the main molecular axis direction. Such a displacement is not observed in the second chain which adopts a [BCBC...] packing scheme. Many interstack contacts are observed and characterized by short S–S distances lower than the van der Waals sum of radii. An identical organic structural scheme is encountered in the BEDT-TTF salts based on polyoxometalate anions [66,67]. Despite the significant difference in charge, size and symmetry between Keggin polyoxometalate and tetracyanometallate anions, the ET molecules do build a quasi-identical 2-D framework.

The electrical and EPR properties of the α_1 salts are very similar. From the plot of the variation of the resistivity vs. T [Fig. 6(a)], two semiconducting regimes are observed between 280 K and 245 K ($E_a = 425$ meV) and below 245 K ($E_a = 915$ meV). Concerning the EPR properties [Fig. 6(b)], the α_1 phase presents a rather surprising linewidth and spin susceptibility temperature dependence.

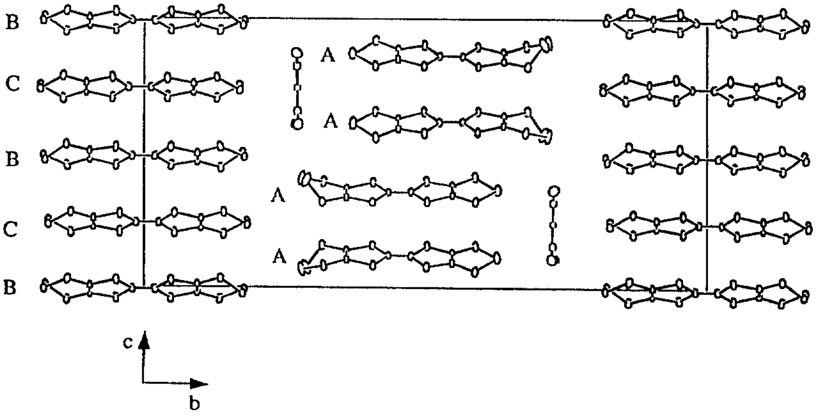
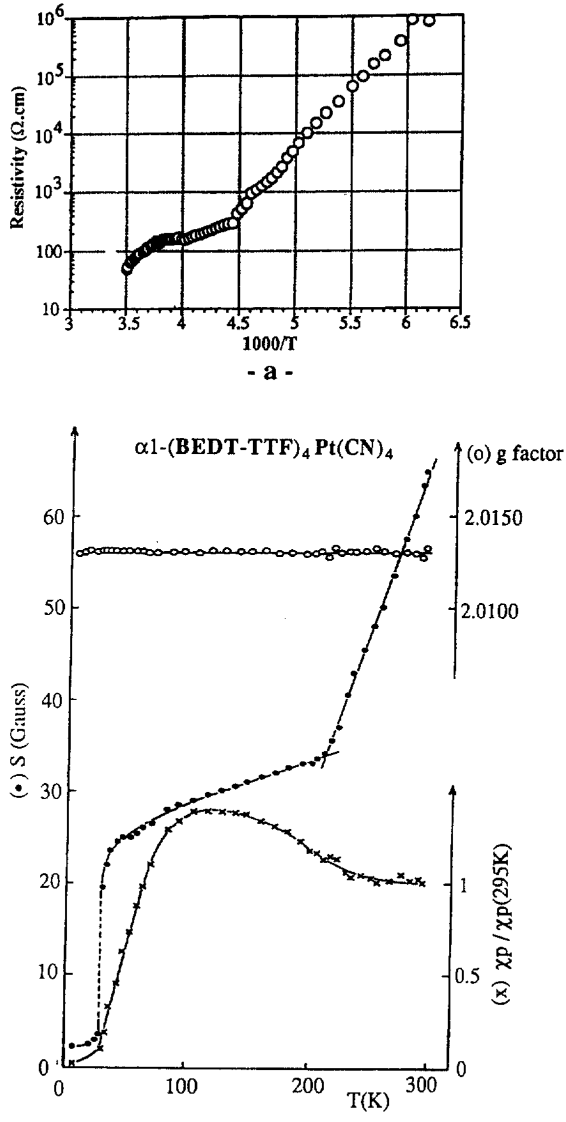


Fig. 5. Crystal structure of α_1-(BEDT-TTF)$_4$[Ni(CN)$_4$]$_x$[Pt(CN)$_4$]$_{1-x}$.



- a -

- b -

Fig. 6. α_I-(BEDT-TTF$)_4$[Ni(CN$)_4]_x$[Pt(CN$)_4]_{1-x}$: (a) temperature dependence of the resistivity; (b) temperature dependence of *g*-factor, ESR linewidth and spin susceptibility.

Apparently, two regime changes occur: the first one around 200 K which is detected only by the modification of the spin dynamic, i.e. a linewidth narrowing; and the second one at 30 K which appears as a structural phase transition. Indeed, in this temperature range, the spin susceptibility decreases sharply. This is characteristic of the opening of an energy gap at the Fermi level, i.e. a low dimensional structural instability giving rise to a diamagnetic and insulating ground state.

The α_2 modification formulated as $(BEDT\text{-}TTF)_4[Ni(CN)_4]_{0.14}[Pt(CN)_4]_{0.86}\cdot(H_2O)_4$ was obtained only with the anion alloying [105]. Unlike α_1, the α_2 structural type is generated by only two independent molecules both located on a general position and giving rise to one independent dimerized chain: [ABAB...] (Fig. 7). In this case, the dimer components show a slight shift along the minor molecular axis, and dimers are displaced in the main molecular axis direction as observed in [AAAA...] chain of the α_1 phase.

The α_2 phase exhibits a lower absolute room temperature conductivity ($\sigma_{RT} \approx 10^{-3}$ S cm^{-1}). However, similar behavior to α_1 is noticed upon lowering the temperature [Fig. 8(a)]. Concerning the EPR properties [Fig. 8(b)], the experimental results are completely different in spite of strong structural analogies with the α_1 phase. The spin susceptibility T-dependence obeys a classical Curie–Weiss law with a Weiss temperature $\theta = -25$ K, characteristic of rather weak antiferromagnetic interactions. This result is in agreement with the presence of strongly localized spins on a strongly dimerized stack, which behaves as a regular magnetic chain with a weak intrachain exchange coupling constant, as is well known for some TCNQ salts [116]. This is supported firstly by the weak d.c. conductivity observed for this compound, and secondly the low temperature behavior below 30 K of both the linewidth and the line position is reminiscent of antiferromagnetic fluctuations [105].

3.1.1.3. δ-$(ET)_4[Ni(CN)_4]_x[Pt(CN)_4]_{1-x}\cdot(H_2O)_n$; $x = 0 \rightarrow 1$; $n = 0 \rightarrow 4$. The δ-organic sublattice observed in the salts $(BEDT\text{-}TTF)_4[Ni(CN)_4]_x[Pt(CN)_4]_{1-x}\cdot(H_2O)_y$

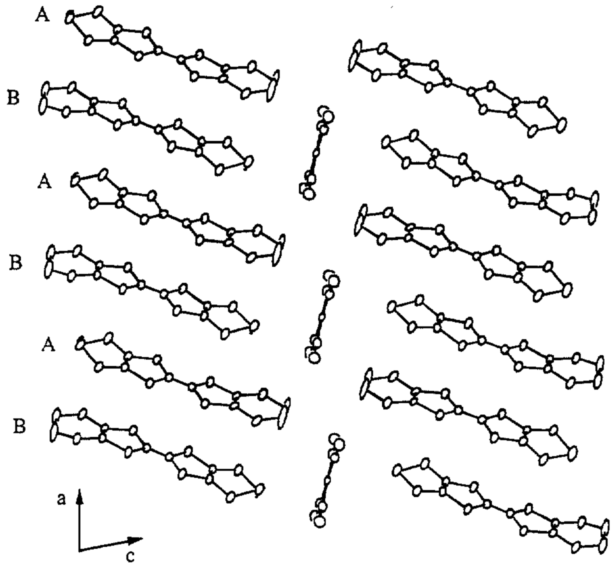


Fig. 7. Crystal structure of α_2-$(BEDT\text{-}TTF)_4[Ni(CN)_4]_{0.14}[Pt(CN)_4]_{0.86}\cdot(H_2O)_4$.

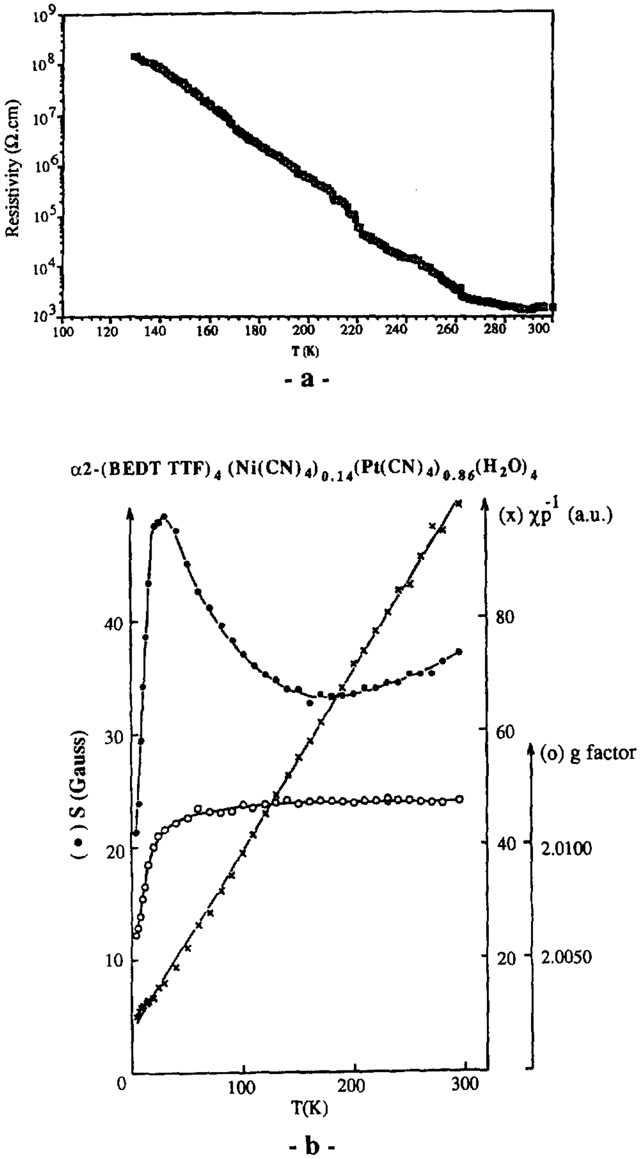


Fig. 8. α_2-(BEDT-TTF)$_4$[Ni(CN)$_4$]$_{0.14}$[Pt(CN)$_4$]$_{0.86}$·(H$_2$O)$_4$: (a) temperature dependence of the resistivity; (b) temperature dependence of *g*-factor, ESR linewidth and spin susceptibility.

[102,103,105] shows particular molecular stacks parallel to the *c*-direction. In the compounds, twisted ET dimers are rotated with respect to each other about the stacking axis by ca. 30° (Fig. 9). The ET chains are strongly dimerized and present weak interdimer contacts.

The EPR properties of compound δ-(ET)$_4$Ni(CN)$_4$, representative of the δ phases,

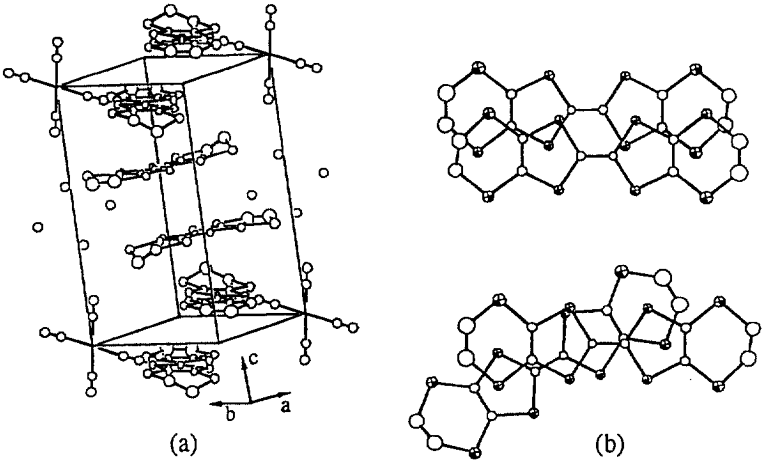


Fig. 9. Crystal structure of δ-$(ET)_4[Ni(CN)_4]_x[Pt(CN)_4]_{1-x}\cdot(H_2O)_n$.

are given in Fig. 10(a). A rather sharp phase transition is observed through the linewidth and the spin susceptibility temperature dependence, in agreement with the d.c. conductivity experiments which reveal a metal–insulator transition in the same temperature range [Fig. 10(b)].

The four different types of organic sublattices observed in the case of the BEDT-TTF/$M(CN)_4^{2-}$ systems as well as their different observed ground states are summarized in Fig. 11. Concerning these systems, one can notice: (i) the electrochemical crystal growth in aqueous mixtures yields the δ type as the major product, but not the superconducting hydrated phase reported by Mori et al. [111]; (ii) the alloying on the anionic sublattice allowed the stabilization of a molecular structural modification (α_2) which does not seem to be achievable with the pure anionic precursors; (iii) the β modification was not obtained with this alloying [105]; (iv) finally, two kinds of packing are observed for the α phase, namely the α_1 and α_2 modifications (see Fig. 11). These two α modifications show low temperature semiconducting regimes which contrast with the corresponding data in other α phases, and in particular in α-$(ET)_2[MHg(SCN)_4]$. The latter remains metallic down to very low temperature, at which a superconducting ground state ($M=NH_4$) [117] or an antiferromagnetic ground state (M = alkaline atom) [118,119] can be observed.

3.1.1.4. κ-$(MDT\text{-}TTF)_4[M(CN)_4].(solv)_2$, M = Pt(II), Ni(II), solv = CH_2Cl_2 and H_2O. Two κ modifications formulated κ-$(MDT\text{-}TTF)_4[M(CN)_4].(CH_2Cl_2)_2$ and κ-$(MDT\text{-}TTF)_4[M(CN)_4].(H_2O)_2$ were obtained in the same batch and characterized [107–109]. The two salts which contain different solvent molecules crystallize in the monoclinic and triclinic space groups *P*2/*n* and *P*$\bar{1}$, respectively. Their general crystal structure (Fig. 12) consists of alternating layers of organic and inorganic units. The solvent molecules are located in the inorganic layer. In the organic layer the MDT-TTF molecules are arranged in perpendicular dimers typical of the

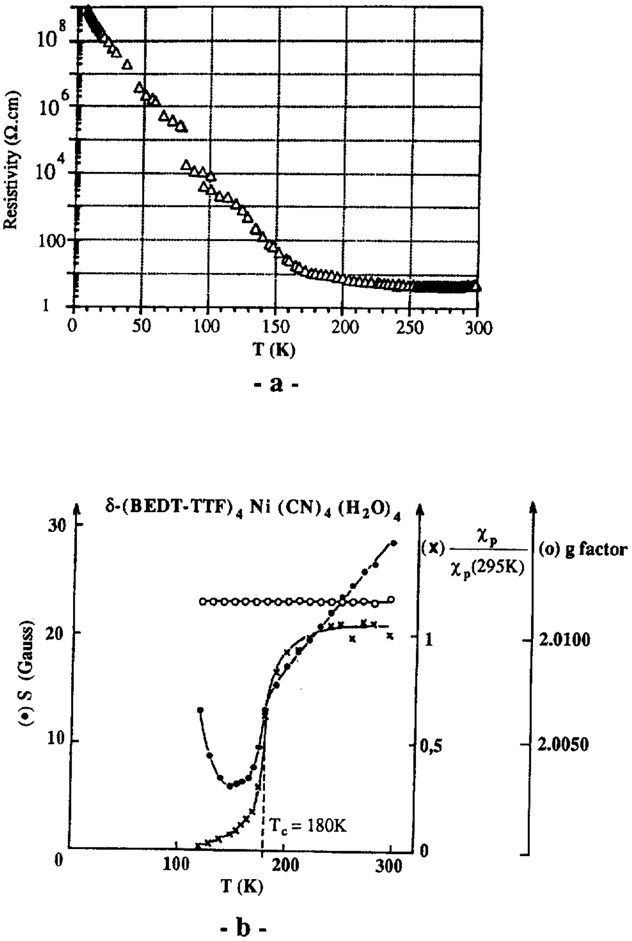


Fig. 10. δ-$(ET)_4[Ni(CN)_4]_x[Pt(CN)_4]_{1-x}.(H_2O)_n$: (a) temperature dependence of the resistivity; (b) temperature dependence of *g*-factor, ESR linewidth and spin susceptibility.

so-called κ structure. This arrangement might be quite favorable for the observation of superconductivity [3,4,120]. Only compounds containing CH_2Cl_2 solvent molecules which yield big crystals have been characterized [107–109].

The plot of the temperature dependence of the resistivity for compound κ-$(MDT\text{-}TTF)_4[M(CN)_4].(CH_2Cl_2)_2$ displayed in Fig. 13(a) shows metallic behavior ($\sigma_{RT} = 5$–10 S cm^{-1}) down to 170 K, where a broad change in the metal–semiconductor regime is observed. This is attributed to the presence of an inhomogeneous charge distribution on the two crystallographically independent MDT-TTF molecules observed in the structure, which seems to be favorable to charge localization. The temperature dependence of the *g*-factor and linewidth *S* is shown in Fig. 13(b). The room temperature linewidth which is large, as for other κ phase salts [3,4], decreases monotonically with temperature.

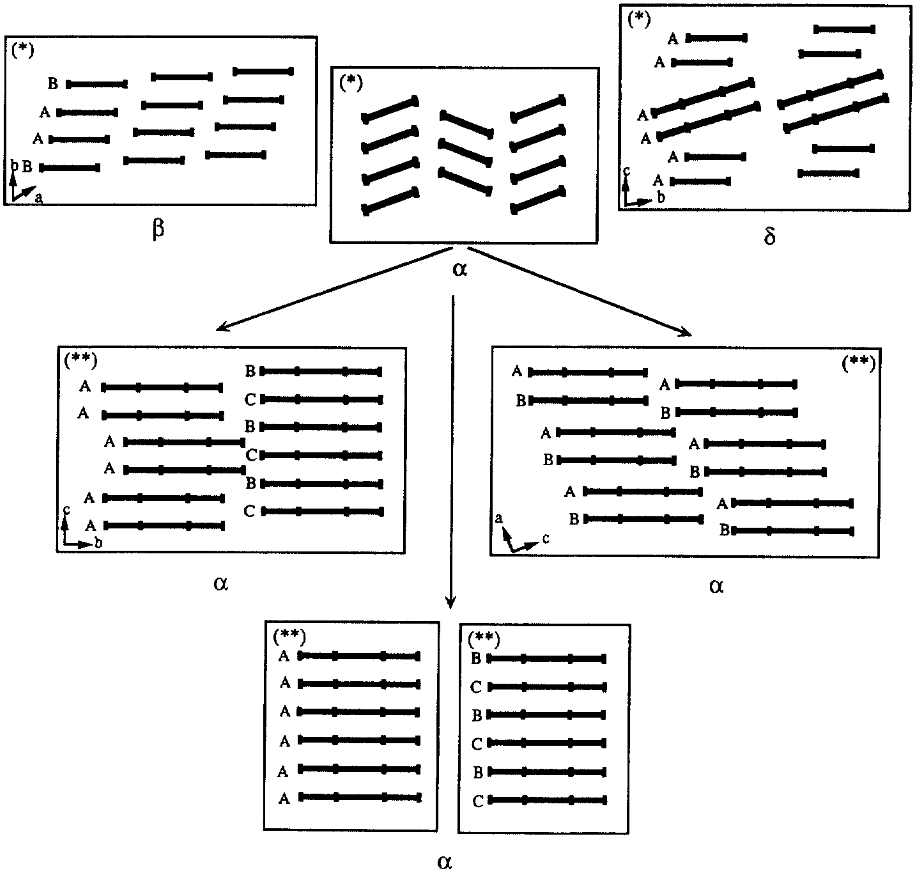


Fig. 11. Schematic diagrams of the different structural types α_1, α_2, β and δ encountered in the ET/M(CN)$_4$ systems compared with α-(ET)$_2$MHg(SCN)$_4$: (α0) [117]. Views along the main (*) and minor (**) molecular axes of the ET unit are represented.

3.2. *TTF derivative materials with hexacyanometallates* $[M(CN)_6]^{3-}$, $M = Co^{3+}$, Fe^{3+}, Cr^{3+}]

The electrochemical assemblies of hexacyanometallates with TTF and BEDT-TTF derivatives [87,121–123] yield several modifications as already observed for BEDT-TTF salts [3,4]. The crystal data and electrical conductivities of some of these modifications are given in Table 3. In this contribution we wish to stress the κ modifications which present interesting phase transitions.

The three isostructural compounds formulated as κ-(ET)$_4$(Et$_4$N)M(CN)$_6$.3H$_2$O, M = [Co(III), $S = 0$], [Fe(III), $S = 1/2$] and [Cr(III), $S = 3/2$] [87,122,123] showed interesting features. Their crystal structure presents alternate organic and inorganic layers. The organic layer is built up from two independent BEDT-TTF molecules A and B. These molecules generate orthogonal

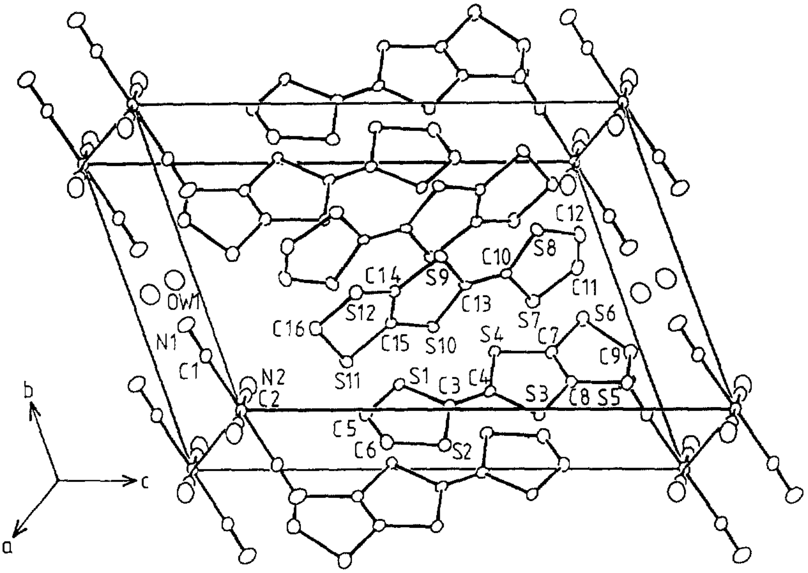


Fig. 12. Crystal structure of κ-(MDT-TTF)$_4$[M(CN)$_4$].(CH$_2$Cl$_2$)$_2$.

centrosymmetric dimers characteristic of the well known κ type of packing in this kind of material [3,4]. The electrical conductivity measurements reveal semiconducting behavior with, however, rather high room temperature conductivity (σ_{RT} = 10.0, 0.1 and 0.2 S cm^{-1} for Co-, Fe- and Cr-containing salts, respectively). The room temperature EPR linewidths are in the range of what is commonly observed for other κ-BEDT-TTF salts (ΔH_{max} = 87, 104 and 185 G, respectively for Co-, Fe- and Cr-containing salts). The high value of the linewidth observed in the case of Cr is due to the overlap of the signal of BEDT-TTF and the signal of the Cr atom.

From the magnetic properties performed by both EPR spin susceptibility and SQUID measurements, we observed two magnetic anomalies at 240 K and 150 K, whether the salts contain diamagnetic or paramagnetic hexacyanometallate polyanions. This indicates that these magnetic anomalies arise from the organic part. From differential scanning calorimetry (DSC) measurements we observed endothermic peaks at 240 K and 150 K corresponding to first order transitions, which means that we are in the presence of structural transitions. The low temperature crystal structure was solved below the transition at 240 K. The structure of the organic part is built up from four BEDT-TTF molecules (A, B, C and D) instead of two molecules at room temperature (see above). These molecules generate orthogonal and centrosymmetric dimers. The positive charges of the BEDT-TTF molecules were estimated from their geometrical parameters. We found that at room temperature the BEDT-TTF molecules bear the same mean charge of +0.5, while an inhomogeneous charge distribution was observed at low temperature: the A molecule is neutral, the B and C molecules bear the same mean charge of +0.5, and the D molecule bears a mean

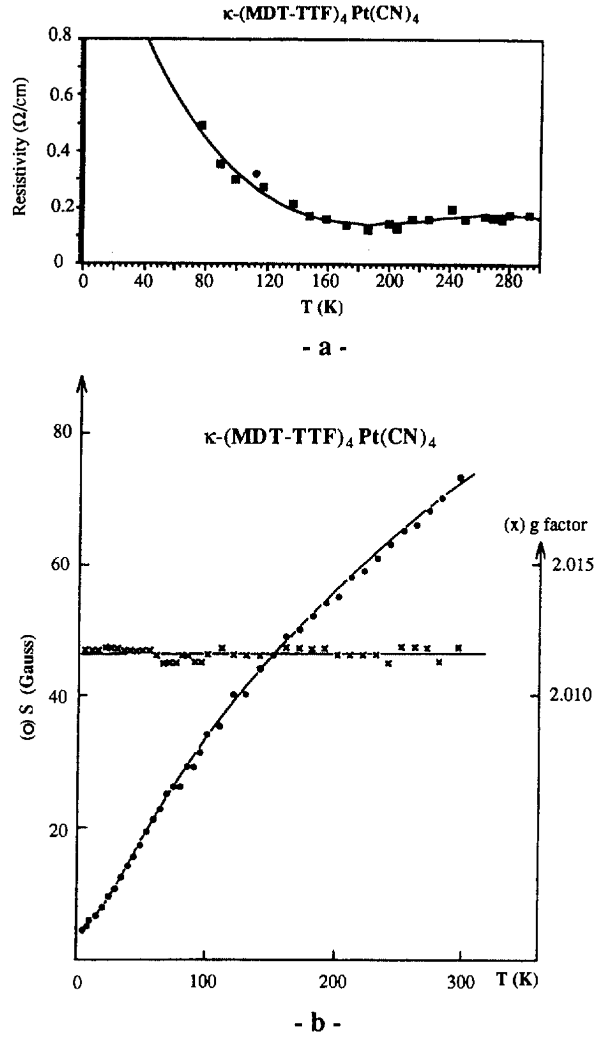


Fig. 13. κ-(MDT-TTF)$_4$[M(CN)$_4$].(CH$_2$Cl$_2$)$_2$: (a) temperature dependence of the resistivity; (b) temperature dependence of *g*-factor, ESR linewidth and spin susceptibility.

charge of +1. The magnetic anomalies have been interpreted on the basis of this charge distribution. Fig. 14 gives a schematic representation of the room temperature and low temperature crystal structures for the organic layers. It also presents a schematic drawing of the magnetic behavior assuming that the decrease in static and EPR susceptibility occuring in both transitions corresponds approximately to the loss of half the magnetic contribution. We assume that the magnetic susceptibility measured at room temperature results from the contribution of four spins 1/2 coming from the partially oxidized dimers. The first transition at 240 K leads to the dismutation of two BEDT-TTF dimers $[ET^{+0.5}]_2$ into one neutral dimer $[ET^0]_2$ and one

Table 3
Space group (S.G.), electrical conductivity σ (S cm^{-1}), activation energy E_a (meV), g-factor, linewidth S (G) for TTF derivative salts with hexacyanometallates

Compound	S.G.	σ (300 K)	E_a	g-Factor	S	Reference
$(TTF)_{11}Fe(CN)_6.5(H_2O)$	$P\bar{1}$	10^{-3} (SC)	NM	NM		[121]
β-$(ET)_4Co(CN)_6.10(H_2O)$	$P\bar{1}$	5×10^{-1} (SC)	15.5	2.0120	56	[87,122,123]
β-$(ET)_4Cr(CN)_6.10(H_2O)$	$P\bar{1}$	10^{-1} (SC)	42.5	2.0122	52	[87,122,123]
β-$(ET)_4Fe(CN)_6.10(H_2O)$	$P\bar{1}$	2×10^{-2} (SC)	52.6	2.0080	64	[87,122,123]
κ-$(ET)_4Co(CN)_6.3(H_2O)$	$P\bar{1}$	10 (SC)	125	2.0103	87	[87,122,123]
κ-$(ET)_4Cr(CN)_6.3(H_2O)$	$P\bar{1}$	0.2 (SC)	140	2.0030	185	[87,122,123]
κ-$(ET)_4Fe(CN)_6.3(H_2O)$	$P\bar{1}$	0.15 (SC)	160	2.0096	104	[87,122,123]
κ-$(ET)_4Fe(CN)_6.2(H_2O)$	$P2$		150	2.0110	105	[124]
$K_{0.33}(ET)_4\,[Fe(CN)_6]_{0.66}.2H_2O$	$P\bar{1}$					[124]

[a] Numbers in parentheses indicate the temperature dependence of the electrical conductivity. Abbreviations used: SC = semiconducting, Ins = insulator, NM = not measured.

fully oxidized one $[ET^{+1}]_2$. The neutral and diamagnetic dimer do not contribute to the magnetic susceptibility as well as the fully ionized dimer, for which a singlet ground state is considered. Then, below the first transition at 240 K the magnetic susceptibility comes from the two partially ionized dimers (B and C) [87,122,123].

4. Metal bis-(dithiolene) and bis-(dithiolate) complexes

Several authors [125–128] state that it is possible to obtain molecule-based ferromagnets by stabilization of the triplet state either in charge transfer complexes with alternate stacks of donors and acceptors or in radical ion salts with separate stacks of donors and acceptors. The metallocenium salts of metal bis-(dithiolenes) and metal bis-(dithiolates) are among the best examples of electron donor–acceptor (D^+A^-) charge transfer magnetic molecular materials [129–139]. In this context, several materials based on such kinds of coordination complexes were obtained and studied in our group. Three examples are presented below.

The first example deals with ferromagnetic interactions in $Fe(Cp^*)_2Ni(III)(dmio)_2.CH_3CN$ [138]. The crystal structure of this salt is reminiscent of $Fe(Cp^*)_2$-$Ni(III)(dbs)_2.CH_3CN$, bds $= (Se_2C_6H_4)^{2-}$ = 1,2-benzenediselenolate [133], and consists of anion (A^-)–cation (D^+) mixed layers with the sequence $\ldots A^-D^+D^+A^-D^+D^+A^-\ldots$. The magnetic properties of this salt are shown in Fig. 15 as $\chi_M T$ vs. T. The $\chi_M T$ product is almost constant down to 80 K and then increases rapidly as T is lowered down to 2.90 K and reaches a maximum at that temperature. When T is lowered below 2.9 K, $\chi_M T$ decreases but χ_M continues to increase and exhibits no maximum down to 1.7 K. This behavior is typical of dominant ferromagnetic interactions on which very weak antiferromagnetic interactions are superimposed.

The second example concerns the series α-$[Fe(Cp^*)_2]_2[M(mnt)_2]_2$, M = [Fe(III), $S = 1/2$] and [Co(III), $S = 0$] [135]. The crystal structure (Fig. 16) of these salts

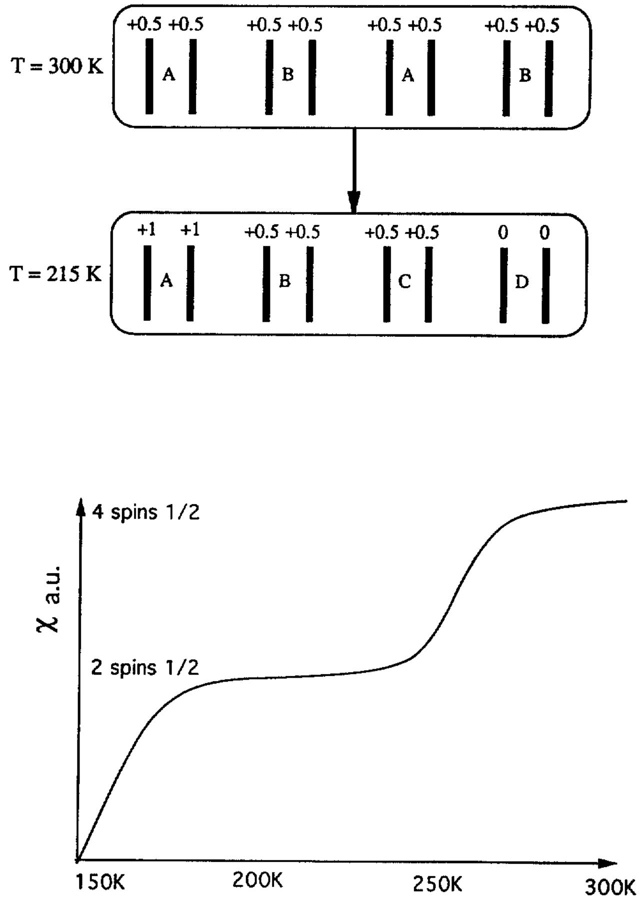


Fig. 14. Schematic representation of the room and low temperature crystal structures of the organic layer and schematic representation of the magnetic susceptibility.

shows a particular and quite unusual arrangement. The $(M(mnt)_2)^{2-}$ units pack parallel to their main axis to build narrow columns surrounding the $Fe(Cp^*)_2^+$ stacks. The $[Fe(Cp^*)_2]^+$ units are arranged in a perpendicular manner along the $(a+c)$-direction. With such an arrangement, the singly occupied orbitals of one Fe(III) center are orthogonal to that centered on the adjacent Fe(III) center. Therefore, their overlap integral is equal to zero, preventing any antiferromagnetic interactions from occuring. On the other hand, the orthogonality of these magnetic orbitals could favor ferromagnetic interactions. This does not happen in this case because the distances between nearest neighboring Fe(III) centers (8.382 Å) are too long.

The third example is the coordination compound $Fe(mnt)_2$-rad [rad = 2-(para-N-methylpyridinium) 4,4,5,5-tetramethylimidazoline-1-oxyl] which exhibits three particular features of molecular magnetism, namely intermediate spin state, spin cross-

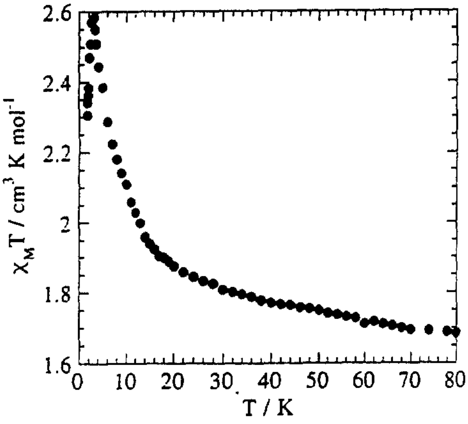


Fig. 15. Magnetic properties of $Fe(Cp^*)_2$-Ni(III)$(dmio)_2$ from ref. [138].

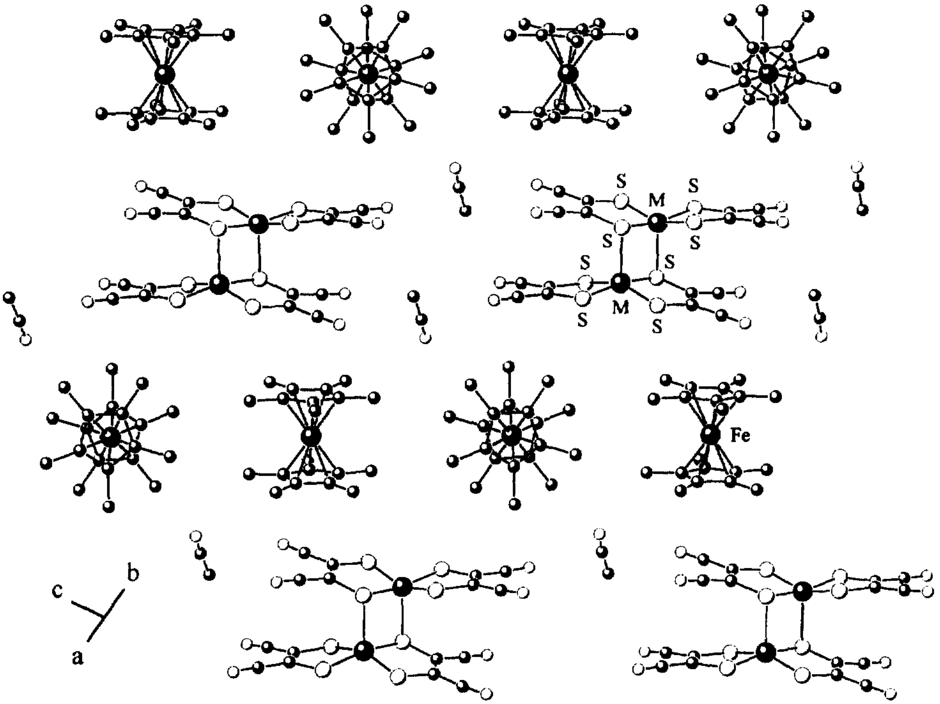


Fig. 16. Crystal structure of α-$[Fe(Cp^*)_2]_2[M(mnt)_2]_2$, M = Fe(III) and Co(III).

over, and antiferromagnetic interactions [140]. In this compound the Fe(III) ion adopts a square pyramidal coordination. The oxygen atom of the nitroxide group of the rad$^+$ moiety is linked to the iron atom of $[Fe(mnt)_2]^-$ in the apical position. All the intermolecular contacts are large, and therefore the molecules can be considered as magnetically isolated in the crystal lattice. The magnetic properties are given in Fig. 17. The value of $\chi_M T$ at room temperature corresponds to what is expected for two non-interacting spins, one ($S=3/2$) from the iron ion and the second one

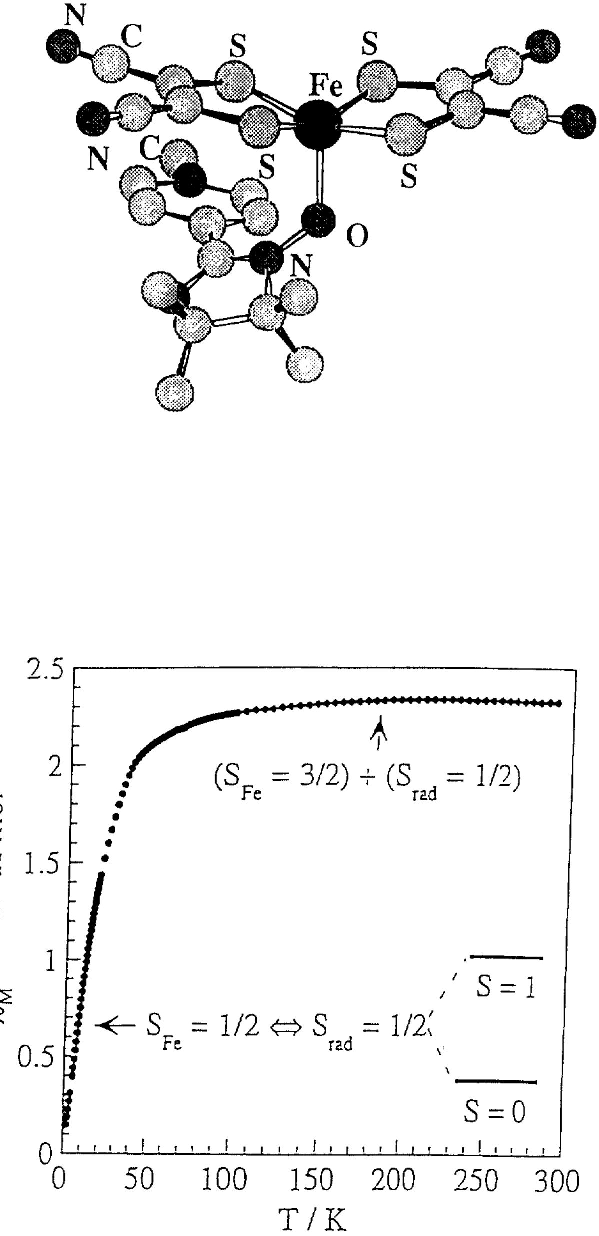


Fig. 17. Molecular structure and temperature dependence of the $\chi_M T$ product for Fe(mnt)$_2$-rad.

($S=1/2$) from the rad$^+$. Below 100 K, the value of this product decreases rapidly as the temperature is lowered. Additionally, the temperature dependence of the molar susceptibility indicates that the low temperature ground state of this compound is a spin singlet. This non-magnetic state can only arise from an antiferromagnetic interaction between the spin of the rad$^+$ unit ($S=1/2$) and the spin of the iron atom which should be $S=1/2$. In other words, the $Fe(mnt)_2]^-$ moiety exhibits a spin crossover between $S_{Fe}=3/2$ at high temperature and $S_{Fe}=1/2$ at low temperature [19,140].

5. Concluding remarks

The fascinating flexibility of coordination chemistry enables unexpected molecular compatibility and assemblies of molecular precursors that are different in size, shape, electronic charge and intrinsic properties. This yields "organic/inorganic hybrid materials" with rich solid state organizations and physical properties. The hybrid character of the resulting compounds is reflected on the one hand through the ability of the organic sublattices to accommodate the size and shape of the inorganic component, and on the other hand in the association of multiproperties such as electrical conductivity and magnetism or spin crossover and magnetic interactions in the same compound.

As suggested by some theoretical predictions, the orthogonality of orbitals, stabilization of the triplet state in charge transfer salts, the control of band filling, indirect exchange and superexchange, must be realized to observe particular physical properties. Thanks to its flexibility, coordination chemistry might contribute to the achievement of these objectives.

With the few examples presented here, we demonstrated the potentialities of coordination complexes such as polyoxometalates, polycyanometallates, metal bis-(dithiolates), metal bis-(dithiolenes) and metalloceniums, as precursors for molecular materials. The chemical and electrochemical molecular assemblies of these complexes with organic donors derived from TTF or organic radicals of the nitronyl nitroxide type led to a large variety of materials with various crystal structures and properties.

In the case of the α-$(BEDT\text{-}TTF)_8[M'M_{12}O_{40}]$.(solv) series (Section 2.1), as well as in the case of the $(prad)_2(M_6O_{19})$ series (Section 2.3), hydrogen bonding between the organic and inorganic sublattices was observed. These kinds of interactions were found to play an important role in the conducting [93,119] and magnetic properties [91].

The preparation of material exhibiting multiphysical properties is one of the current challenges in molecular materials science. The aim of synthesizing such compounds containing conducting and paramagnetic sublattices is to obtain conducting or superconducting molecular ferromagnets. Following the so-called indirect exchange mechanism, it is expected to couple ferromagnetically localized spins on d orbitals of the paramagnetic transition ions of the inorganic part with the conducting electrons of the organic part. The point that we want to discuss here concerns the absence of significant magnetic interactions in such materials. To our knowledge, despite the amount of work [77–88] devoted to this chemistry, all attempts have failed up to now. This is due to the weak conductivity of the materials and/or to the weak interactions between the organic and inorganic sublattices. The most significant results have been obtained by Day and coworkers who characterized the first superconducting material with a paramagnetic anion [86]. If it is possible to obtain highly conducting or superconducting salts with paramagnetic anions, it is difficult to control the molecular packing and to increase the interactions between conducting and paramagnetic networks. Much effort is now being devoted to the search for through-space interactions. Strategies based on the synthesis of new TTF derivatives containing chalcogen atoms or specific functions that can undergo hydrogen bonding are being developed [141–143].

Concerning the materials presented here, weak electrical conductivities are observed in most cases preventing any magnetic interactions. This weak conductivity is the result of strong charge localization in the organic part. As pointed out above, we observed different crystallographically independent molecules for all the salts, which favors a non-homogeneous charge distribution upon temperature lowering. This is a direct consequence of the high negative charge of the polyanion. In fact, while these high negative charges are expected to increase the electrostatic interactions between the organic and inorganic networks, their negative effect is to induce systematically a non-homogeneous charge distribution on the organic charge carriers. In order to prevent such a localization, several strategies can be envisaged, such as: (i) the decrease of the global positive charge of the inorganic part by substitution of the Et_4N^+ cation observed in compounds $[(TTF)_6[HPW_{12}O_{40})(Et_4N)]$ and κ-$(BEDT\text{-}TTF)_4(Et_4N)M(CN)_6.3H_2O$ by polycations (Ba^{2+}, Ca^{2+}, ...); (ii) the diminution of the negative charge of the polyanions by substitution of the “negative” ligands (O^{2-} or CN^- in the polyoxometalates or hexacyanometallates, respectively) by neutral ligands (NH_3 or H_2O).

The other strategy developed in our group consists of the preparation of new organic/inorganic molecular precursors in which the organic donor derived from TTF and the inorganic acceptor of the polyoxometalate type are covalently linked. In the case of a conjugated chemical link, electron delocalization between the two units may induce a better interaction between the organic and inorganic networks. If the chemical bridge is non-conjugated, electron hopping between the two moieties can be expected for photoconducting materials for instance.

Acknowledgements

I am grateful to all my coworkers (graduates, doctorates, postgraduate fellows and associate researchers) and collaborators whose names appear in the reference section. Work supported by the CNRS, Université de Rennes 1, Région Bretagne et Pays de la Loire and the European Union (Network CHRXCT93-0271).

Abbreviations

BEDT-TTF or ET	($C_{10}H_8S_8$) bis-(ethylenedithiotetrathiafulvalene)
Cp	(C_5H_5) cyclopentadienyl
Cp*	($C_5(CH_3)_5$) pentamethylcyclopentadienyl
DMF	N,N-dimethylformamide
dmio	(S_4C_3O) 2-oxo-1,3-dithiol-4,5-dithiolate
dmit	($C_4H_6S_2$) dimercaptoisotrithione
EPR	electron paramagnetic resonance
M	transition metal
MDT-TTF	($C_7H_4S_6$) methylenedithiotetrathiafulvalene
mnt	($C_4N_2S_2$) maleonitrile dithiolate
m-rad	meta N-methyl pyridinium nitronyl nitroxide radical
p-rad	para N-methyl pyridinium nitronyl nitroxide radical
pba	propylene bis oxamato
RT	room temperature
TCNQ	($C_{12}H_4N_4$) tetracyano-p-quinodimethane
TMTSF	($C_{10}H_{12}Se_4$) tetramethyl tetraselenafulvalene
TTF	($C_6H_4S_4$) tetrathiafulvalene

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