JOURNAL OF
Materials
CHEMISTRY

Hybrid molecular materials based on organic molecules and the inorganic magnetic cluster $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ $(M^{2+} = Co, Mn)$†

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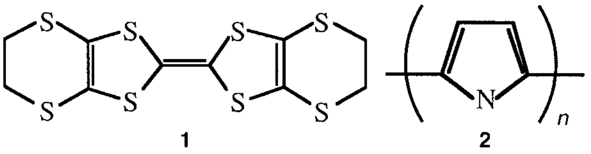
The synthesis and physical characterization of new organic–inorganic hybrids formed by conducting and magnetic networks are reported. The crystalline radical salts are formed by BEDT-TTF type donors as the organic part, and by large metal–oxide clusters of the type $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ $(M^{2+} = Co, Mn)$ as the inorganic part. We also show how these magnetic clusters can be incorporated in conducting organic polymers to give hybrid organic–inorganic films.

The search for new molecule-based materials combining conducting and magnetic properties constitutes a current challenge in materials science, which only very recently has begun to be explored. A convenient chemical approach to obtain such multiproperty materials is the so-called organic–inorganic hybrid approach.[1] It consists of using as building blocks organic molecules or polymers possessing itinerant electrons and inorganic metal complexes possessing localized magnetic moments.

As the organic part one can use π-electron donor molecules of the TTF type which are the basic ingredient for most of the molecular conductors and superconductors.[2] Another interesting possibility is to use conducting polymers of the type polypyrrole or polyaniline. These polymers are relatively simple to obtain by chemical or electrochemical oxidative polymerization of the monomer molecules and they have considerable potential technological applications.[3]

As the inorganic part, a variety of anionic metal complexes of various nuclearities and dimensionalities can be chosen. Starting with the most simple magnetic anions one can find the mononuclear metal halides ($FeCl_4^-$, $CuCl_4^{2-}$, …). These anions are being successfully combined with several organic donors to give radical ion salts with coexistence of localized magnetic moments and itinerant electrons.[4] Another important mononuclear anion is the iron(III) tris(oxalato) complex, $Fe(ox)_3^{3-}$, which combined with the BEDT-TTF donor resulted in the preparation of the first molecular material with coexistence of paramagnetic centers and superconductivity.[5] The most complex class of inorganic complexes we can use are polymeric. Anion magnetic chains or layers are known that on paper can be combined with cation radicals. From the magnetic point of view, polymeric layered complexes such as, for example, the bimetallic oxalato-bridged complexes $[M^{II}M^{III}(ox)_3]^-$ (M^{II} = Mn, Fe, Ni, Co, Cu; M^{III} = Cr, Fe), are the most interesting since they can confer to the hybrid material cooperative magnetic properties such as ferromagnetism.[6] However, these polymeric anions are not easy to handle in terms of the chemistry (extremely insoluble and only stable in the solid state). In fact, only discrete bimetallic oxalato complexes but not polymeric ones have been combined so far with organic donors.[7]

In between these two extreme cases one can find the polyoxometalate complexes. These are big metal–oxide clusters of definite sizes and shapes which can accommodate one or more magnetic centers in their structures. The solubility of such clusters in both aqueous and non-aqueous solvents makes it possible to electrochemically oxidize the organic donor in the presence of these counter-ions so as to obtain crystalline salts of these hybrids.[8] In this context, the most successful results have been obtained from the BEDT-TTF molecule (**1** in Scheme 1) which has allowed the growth of crystals containing polyoxometalates[9] with metal nuclearities comprised between 6 and 18 [Fig. 1(*a*)–(*c*)]. Owing to the difficulty in crystallizing these salts as the complexity of the cluster is increased, obtaining crystalline radical salts containing larger clusters is a chemical challenge.



Scheme 1

With the aim of introducing clusters of higher nuclearities we have tried the reaction of BEDT-TTF with the magnetic polyoxoanions $[M_4(PW_9O_{34})_2]^{10-}$ $(M^{2+} = Co, Mn)$ which have a metal nuclearity of 22 [Fig. 1(*d*)]. We present here the synthesis and physical characterization of these crystalline hybrids. We also report how these magnetic clusters can be incorporated in conducting organic polymers to give hybrid organic–inorganic films.

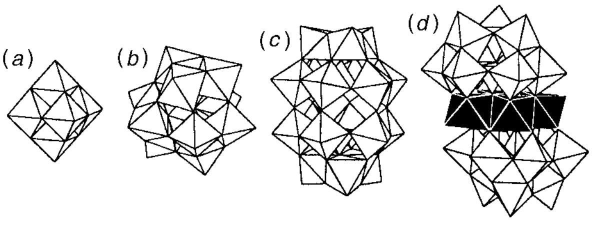


Fig. 1 Polyhedral representation of the: (*a*) Lindquist, $[M_2O_{19}]^2$ (M = Mo, W), (*b*) Keggin $[XM_{12}O_{40}]^{n-}$ (M = Mo, W), (*c*) Dawson–Wells, $[X_2M_{18}O_{62}]^{n-}$ (M = Mo, W) and (*d*) $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ $(M^{2+} = Co, Cu, Mn, Fe, Cr, Ni$ and $Zn)$ polyanions

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† Presented at the 58th Okazaki Conference, Recent Development and Future Prospects of Molecular Based Conductors, Okazaki, Japan, 7–9 March 1997.

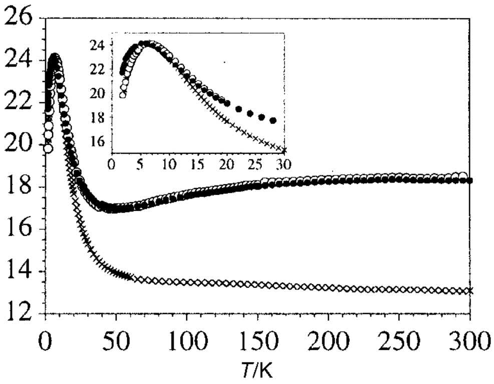

Fig. 2 Plot of $\chi_m T$ *vs.* T for the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ polyanion in its K^+ (×), BEDT-TTF$^+$ (○) and polypyrrole (●) salts

Organic–inorganic crystalline materials based on BEDT-TTF electron donors

The polyoxoanions $[M_4(PW_9O_{34})_2]^{10-}$ are of magnetic interest since they contain the tetranuclear magnetic clusters Co_4 and Mn_4 encapsulated in between two polyoxotungstate moieties $[PW_9O_{34}]$ [see Fig. 1(*d*)]. In the cobalt case the ions are ferromagnetically coupled giving rise to a magnetic ground state comprising 12 unpaired electrons,[10] while in the manganese one this exchange coupling is antiferromagnetic and results in a non-magnetic ground state ($S=0$).[11] Furthermore, the type of exchange coupling is different in both clusters. Thus, while high-spin octahedral Mn^{2+} has a fully isotropic $^6A_1$ ground state, high-spin octahedral Co^{2+} has an orbitally degenerate $^4T_1$ ground state which is split into six anisotropic Kramers doublets by the effect of spin–orbit coupling and distortions of the octahedron. As a consequence the exchange interaction between Co^{2+} ions is highly anisotropic resulting in a complete splitting of the highly degenerate ground state in spin doublets. In fact the ground state of this cluster is an anisotropic Kramers doublet which is well separated in energy from the other excited doublets (the closest energy level is at *ca.* 14 cm^{-1}).[12]

Black crystals of composition $BEDT\text{-}TTF_6H_4[M_4(H_2O)_2(PW_9O_{34})_2]$ ($M^{2+}=Co$, Mn) have been obtained by electrocrystallization. Although they are still not of sufficient quality to be studied by X-ray diffraction, a preliminary study of their unit cells indicates that they are isostructural.‡ In view of the stoichiometry of these salts (6:1), four protons had to be introduced in order to compensate the charges. With this assumption the six organic molecules should be completely charged (+1). Accordingly, the compounds are insulators (the electrical conductivity has been measured on pressed pellets).

The magnetic properties of the BEDT-TTF salts are shown in Fig. 2 and 3 and compared to those of the potassium salts of the two polyanions. In both cases the low temperature magnetic behavior is dominated by the inorganic component.§

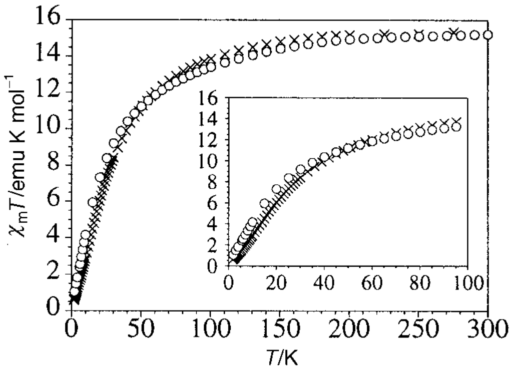

Fig. 3 Plot of $\chi_m T$ *vs.* T for the $[Mn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ polyanion in its K^+ (×), BEDT-TTF$^+$ (○) salts

No influence coming from the organic component on the magnetic coupling within or among the clusters is detected down to 2 K. Thus, in the Co derivative the product $\chi_m T$ shows a sharp increase below 50 K upon cooling and a maximum at *ca.* 6 K. Such a behavior is analogous to that observed in the K^+ salt (see Fig. 2) and unambiguously demonstrates that the ferromagnetic cluster is maintained when we change K^+ to BEDT-TTF$^+$. Furthermore, it is indicative of a lack of interactions between the two components as a consequence of the good insulation of the Co_4 cluster provided by the polyoxotungstate framework. Low temperature EPR spectra support such a conclusion (Fig. 4). We observe that at 4.2 K the two samples show the same spectrum: a very broad and anisotropic signal mainly coming from the ground Kramers doublet of the cluster, centered around 1620 G ($g=4.1$), which extends from 1000 to 4000 G. This signal has to be attributed to the Co_4 cluster. No signal coming from the organic radical is observed at this temperature. This should indicate that the unpaired electrons located at the BEDT-TTF$^+$ cations are strongly coupled in the solid so that they are magnetically silent at low temperature.

The similarity between the BEDT-TTF$^+$ and K^+ derivatives is also evident in the Mn case (Fig. 3). Thus, the two magnetic curves are coincident in the whole temperature range, within the experimental error. This result proves that the antiferromagnetically coupled Mn_4 cluster is maintained intact in the radical salt. The close coincidence between the two magnetic

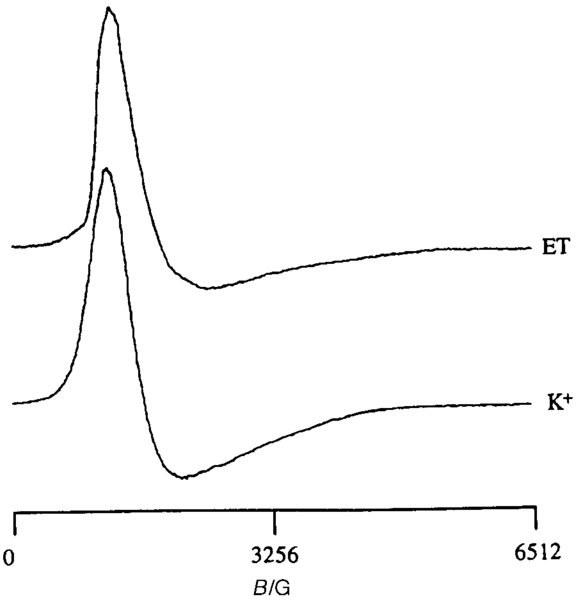

Fig. 4 EPR spectra of the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ polyanion in its K^+ and BEDT-TTF salts

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‡ Unit cell of the cobalt(II) derivative (from indexation of 17 reflections): $a=11.85(2)$, $b=13.23(1)$, $c=27.741(5)$ Å, $\alpha=83.15(5)$, $\beta=87.17(4)$, $\gamma=73.85(9)$°; unit cell of the manganese(II) derivative (from indexation of 16 reflections): $a=11.79(1)$, $b=13.23(1)$, $c=27.48(1)$ Å, $\alpha=88.95(6)$, $\beta=89.96(4)$, $\gamma=73.79(8)$°.

§ At high temperatures the magnetic moments of both the BEDT-TTF salt and the polypyrrole film are higher than that observed in the potassium salt (see Fig. 2). The origin of such differences may come from the large anisotropy of the magnetic cluster. Slightly different octahedral distortions within the clusters can give rise to significant variations in the local Landé tensors and therefore in the magnetic properties. In fact, if one compares the magnetic properties of the Co_4 cluster encapsulated by the $[PW_9O_{34}]$ ligands or by the $[P_2W_{15}O_{56}]$ ones, we observe that in the former case $\chi_m T$ varies from 14 emu K mol^{-1} at high T to 24 emu K mol^{-1} at 6 K, while in the latter this variation is only from 10 to 15 emu K mol^{-1}. However, the position of the characteristic maximum in $\chi_m T$ stays constant in both cases.

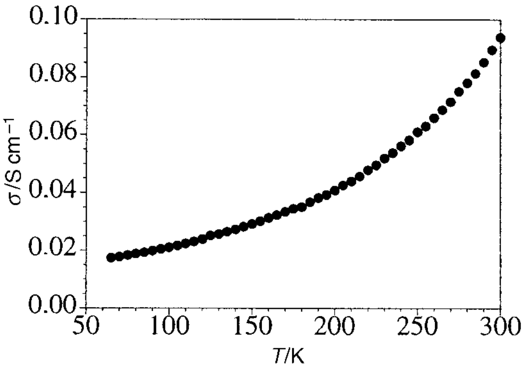

Fig. 5 Plot of the conductivity *vs.* T of a $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$–polypyrrole film

curves also shows that the presence of BEDT-TTF$^+$ radicals does not affect the magnetic coupling within or between the Mn_4 clusters. As for the EPR spectra, these are dominated by a broad signal centered at $g=2$ arising from the Mn_4 cluster. A sharp signal of very weak intensity is superimposed onto the cluster signal. This may be associated with paramagnetic radical impurities. The above crystalline materials demonstrate the ability of this type of large magnetic clusters to form crystalline organic–inorganic radical salts with the BEDT-TTF donor, despite its big size and charge.

Organic–inorganic films based on polypyrrole

In view of the stability of the above clusters in both aqueous and non-aqueous solutions we have examined the possibility of obtaining conducting polymers incorporating this kind of magnetic polyoxometalates. Preliminary results with the Co_4 cluster show that by aqueous electrochemical polymerization of pyrrole (**2** in Scheme 1) in the presence of this polyoxometalate, organic–inorganic films containing *ca.* 80 pyrrole units per cobalt cluster can be obtained.¶ The magnetic properties are very close to those observed in the K^+ salt (Fig. 2) indicating that the structure of the ferromagnetic cluster is maintained in the film. The electrical properties show a semiconducting behavior with an electrical conductivity at room temperature of *ca.* 0.1 S cm^{-1} (Fig. 5). The material constitutes a clear example of the ability of large polyoxometalate clusters to be incorporated in polymer films. It represents the first hybrid film formed by a high spin cluster embedded in a polypyrrole polymer in which the large magnetic moments localized on the polyoxometalate coexist with a delocalized electron framework. The strategy presented here is general and can be extended to other kinds of magnetic polyoxometalates (such as the Mn_4 derivative, for example) and to other conducting films.

Concluding remarks

In the attempt to obtain hybrid organic–inorganic materials with coexisting itinerant electrons and localized spins in the same material, this contribution has illustrated the use of the polyoxometalate clusters $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ ($M^{2+}=$ Co, Mn) as the magnetic component of new hybrids in which the organic component can be either the electron donor BEDT-TTF or polypyrrole. In the former case crystalline charge transfer salts containing these magnetic clusters have been obtained. The resulting molecular materials are unprecedented in several aspects: (i) this type of inorganic anions are the biggest ever used in the synthesis of radical cation salts, and (ii) the salts constitute the first known examples of hybrid materials containing a magnetic cluster and an organic donor.

In the second case we have shown that these magnetic clusters can be incorporated in polypyrrole films to give magnetic films having semiconducting properties. More hybrid films of this kind can now be prepared in which new functional properties can be introduced by playing for example with the electrochromic character of the polyoxometalate component. Another aspect that is being developed in this context in order to improve the properties of the film is that of creating well organized hybrid films by using the Langmuir–Blodgett technique.[13]

Experimental

Single crystals of the radical salts BEDT-TTF$_6$H$_4$[M$_4$-(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$] ($M^{2+}=$Co, Mn) were obtained on a platinum wire electrode by anodic oxidation of the organic donor ET (2×10^{-3} M in a 1 : 2 mixture of CH_3CN–$CHCl_2CH_2Cl$) in a U-shaped electrocrystallization cell under low constant current ($I=1.2$ μA) in the presence of a solution of the polyanion in toluene. After two weeks very small hexagonal plate-like single crystals were observed in the anode. They were collected, washed with CH_3CN and air dried. Found: C, 10.37; H, 0.96; N, 0.16; S, 22.01. BEDT-TTF$_6$H$_4$[Co$_4$(H$_2$O)$_2$-(PW$_9$O$_{34}$)$_2$]·(CH$_3$CN)·5(H$_2$O) requires C, 10.36; H, 0.90; N, 0.19; S, 21.40%. Found: C, 9.91; H, 1.05; N, 0.0; S, 20.85. BEDT-TTF$_6$H$_4$[Mn$_4$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$]·9H$_2$O requires C, 10.02; H, 1.04; N, 0.0; S, 21.41%. The IR spectra of both salts are very similar and show all the characteristic bands of the polyanion and BEDT-TTF molecules.

The films of polypyrrole with the cobalt-containing polyanion were prepared by electrochemical oxidation in a N_2 atmosphere of an aqueous solution of pyrrole (0.5 M) in the presence of the polyanion (3.6×10^{-3} M). The intensity of the current was fixed at 5 mA and after several minutes the polypyrrole–polyanion films were collected from the anode.

We thank the Spanish DGICYT for founding this work (Grant PB94–0998). M. C. L. and J. R. G. M. thank the Generalitat Valenciana for a predoctoral Grant.

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¶ The given ratio pyrrole : polyanion has been determined by chemical analysis as well as by the magnetic measurements. The possibility of obtaining other ratios by varying the experimental conditions (starting materials, intensity of the electrical current, times of reaction, *etc.*) is being currently investigated.

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Paper 7/06864F; *Received* 23*rd September*, 1997