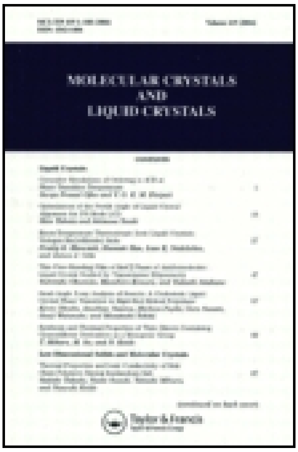

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Materials Coupling Localized Magnetic Moments and Delocalized Electrons

Eugenio Coronado [a] , Jose Ramon Galan-mascaros [a] , Carlos Gimenez-saiz [a] , Carlos J. Gomez-garcia [a] , Smail Triki [a] & Pierre Delhaes [b]

[a] Departamento de Química, Inorgánica Univ. de Valencia;, Dr. Moliner 50, E-46100, Burjasot, (Spain)

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

To cite this article: Eugenio Coronado , Jose Ramon Galan-mascaros , Carlos Gimenez-saiz , Carlos J. Gomez-garcia , Smail Triki & Pierre Delhaes (1995): Molecular Materials Coupling Localized Magnetic Moments and Delocalized Electrons, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 274:1, 89-97

To link to this article: http://dx.doi.org/10.1080/10587259508031869

Mol. Cryst. Liq. Cryst., 1995, Vol. 274, pp. 89–97
Reprints available directly from the publisher
Photocopying permitted by license only

MOLECULAR MATERIALS COUPLING LOCALIZED MAGNETIC MOMENTS AND DELOCALIZED ELECTRONS

EUGENIO CORONADO[a], JOSE RAMON GALAN-MASCAROS[a], CARLOS GIMENEZ-SAIZ[a], CARLOS J. GOMEZ-GARCIA[a], SMAIL TRIKI[a], PIERRE DELHAES[b]

[a] Departamento de Química Inorgánica Univ. de Valencia; Dr. Moliner 50, E-46100 Burjasot (Spain)

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

Abstract. The magnetic properties of the radical salts formed by the organic donor bis-ethylenedithio-tetrathiafulvalene (in short ET) and magnetic polyoxoanions are presented. The used polyoxoanions are $[XM(H_2O)W_{11}O_{39}]^{-n}$ (X = Si, P; M = Mn^{II}, Cr^{III}), with the Keggin structure and $[Co_4(H_2O)_2(PW_9O_{34})_2]^{-10}$, where a ferromagnetic Co^{II}_4 cluster is encapsulated by two trivacant Keggin fragments.

INTRODUCTION

In the last two decades a big effort has been made in the search for new magnetic and conducting molecular materials. However, very little work has been done in the search of molecular solids coupling magnetic and conducting properties[1]. Our approach in this context consists in the combination of molecular metal-oxide clusters (polyoxometalates) containing magnetic centers with organic donors of the tetrathiafulvalene type (Fig. 1) in order to obtain materials in which localized magnetic centers and mobile electrons coexist[2].

Polyoxometalates present several characteristics which make them suitable as inorganic components of new TTF-based radical salts: (i) They present different charges, sizes and shapes which may induce novel structural and electronic properties in the organic counterpart (ii) They are soluble in aqueous and non aqueous solutions, and they maintain their identities in solution as well as in the solid state; (iii) They are electron acceptors which can be reduced by one or more electrons to give rise to mixed-valence clusters; (iv) They can act as ligands incorporating at specific sites of the polyoxoanion structure one or more magnetic transition metal ions.

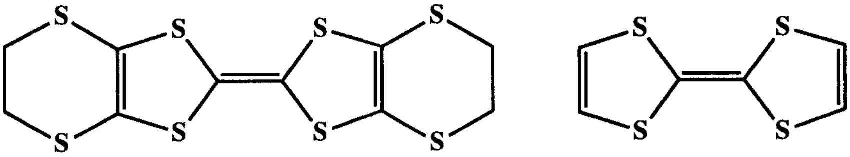

FIGURE 1 Donors of the TTF family: BEDT-TTF (or ET) (left) and TTF (right).

Taking advantage of the two former characteristics, several examples have been reported containing diamagnetic polyoxoanions of the type $[X^{+n}M_{12}O_{40}]^{-8+n}$ (X = P, Si; M = W, Mo)[3], $[M_6O_{19}]^{-2}$ (M = Mo, W)[4] and $[Mo_8O_{26}]^{-4}$ anion[5]. The ability of the polyoxoanion to accept electrons from the organic donor (point iii) has also been observed resulting in some cases in materials in which delocalized electrons coexist in both the organic and the inorganic units[6]. Very recently we have started to exploit point iv with the aim to introduce a magnetic character in the polyoxoanion. The most significant result has been the discovery of a family of semiconducting salts[7] formed by alternating layers of the organic donor bis-ethylenedithio-tetrathiafulvalene (in short ET; see Fig. 1) and $[XM_{12}O_{40}]$ Keggin polyoxoanions containing magnetic ions in its tetrahedral cavity (X = Co^{II}, Cu^{II} and Fe^{III}; in black in Fig. 2a).

Unfortunately, the good isolation of the magnetic center imposed by the polyoxoanion has precluded any significant magnetic interaction with the organic spin sublattice. The logical further step in order to bring nearer the two spin sublattices is to put the magnetic centers in the surface of the polyoxoanion (Fig. 2b). We present here the first results along this line. We also show that polyoxoanion chemistry allows to design materials formed by magnetic clusters (in black in Fig. 2c) and organic radicals.

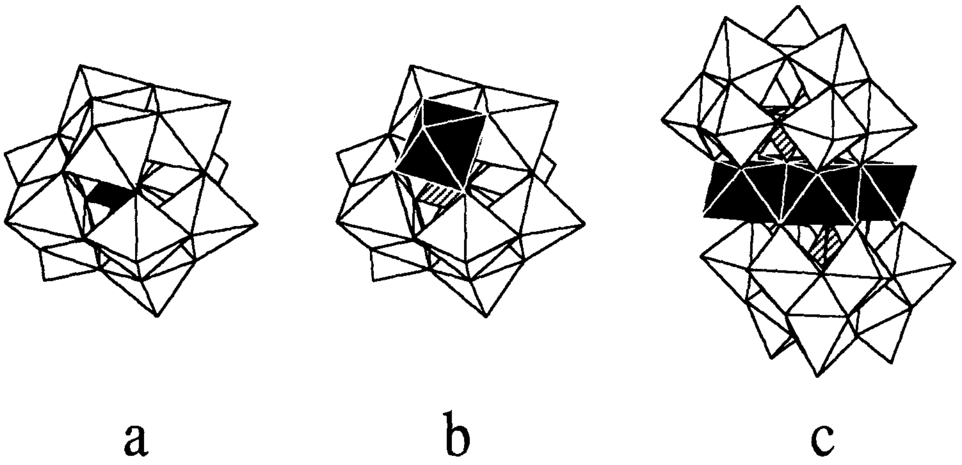

FIGURE 2 Polyoxometalates having one magnetic atom (in black) in the central tetrahedral cavity (**a**) or in the external surface (**b**). The magnetic cluster M_4O_{16} (M = Co^{II}, Cu^{II}, Ni^{II}, Mn^{II}) encapsulated between two trivacant Keggin fragments (**c**).

RESULTS AND DISCUSSION

By removing one or more octahedral metal atoms from the Keggin structure it is possible to obtain vacant polyoxometalates which can form stable complexes with transition metal ions. Thus, the replacement of one of the octahedral sites by a transition metal ion results in the isolation of a substituted Keggin anion of the type $[XM(H_2O)W_{11}O_{39}]^{n-}$ (X = P, Si; M = Mn^{II}, Co^{II}, Ni^{II}, Cr^{III}, Fe^{III}) in which a magnetic ion is pentacoordinated by the polyanion and by a water molecule[8] (Fig. 2b). In a similar way, the reaction of the trivacant anion $[PW_9O_{34}]^{-9}$ with transition metal ions can result in the formation of the polyoxoanion $[M_4(H_2O)_2(PW_9O_{34})_2]^{-10}$ (M= Mn^{II}, Co^{II}, Ni^{II}, Cu^{II},...) which contains a tetranuclear magnetic cluster M_4O_{16} in between the two $[PW_9O_{34}]^{-9}$ moieties (Fig. 2.c).

The series $ET_8[XM(H_2O)W_{11}O_{39}]$

By electro-oxidation of the organic ET molecule in presence of a solution containing the substituted Keggin anions $[PMn(H_2O)W_{11}O_{39}]^{5-}$ and $[SiCr(H_2O)W_{11}O_{39}]^{5-}$ we have obtained single crystals of the two radical salts $ET_8[PMnW_{11}O_{39}]$ and $ET_8[SiCr(H_2O)W_{11}O_{39}]$ (abbreviated as ET-Mn and ET-Cr). The structural features of the two salts are similar to those previously reported for the Keggin derivatives containing metal ions in its tetrahedral cavity[7]. Thus, in all cases the organic part is formed by two different kinds of stacks: an eclipsed chain with almost totally ionized ET molecules and a dimerized one with partially charged ET molecules that may support electron delocalization and so the semiconducting character of these salts ($\sigma_{RT} \approx 10^{-1}$-$10^{-2}$ S.cm^{-1}). The inorganic packing is also very similar. The only noteworthy difference is observed in ET-Mn for which the Mn atom of one Keggin unit is connected to a W atom of the neighboring one through a common oxygen in order to give a chain that runs along the c axis[9] (Fig. 3); in the ET-Cr salt the Keggin units are isolated as in the other Keggin derivatives, although the magnetic centers are also localized along the c axis.

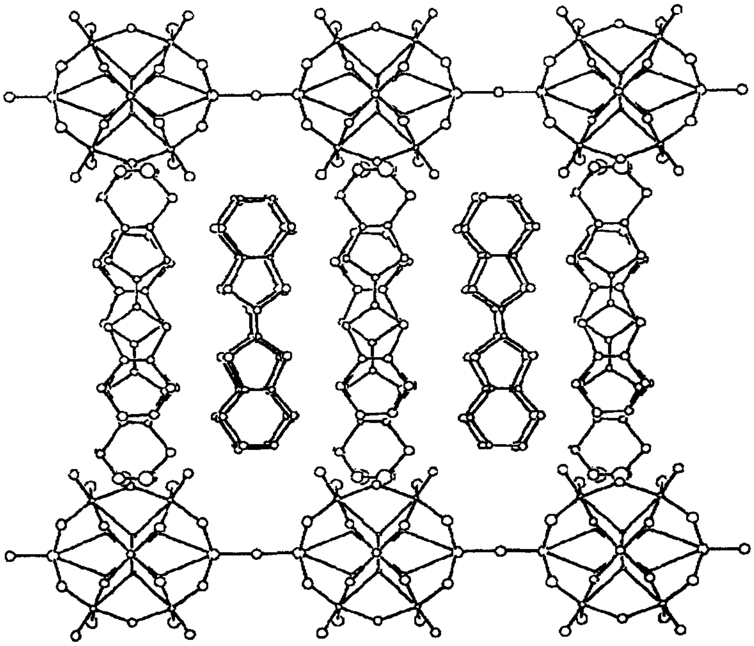

FIGURE 3 Structure of the $ET_8[PMnW_{11}O_{39}]$ radical salt showing the layers of the organic donor and the chains of the inorganic polyoxometalates.

The magnetic properties of these two salts have been investigated in the temperature range 1.7-300 K at a magnetic field of 0.1 T, using a SQUID susceptometer. The results are displayed in Figures 4 and 5 together with those of the Bu_4N^+ salts of the corresponding polyoxoanions. In the two compounds the χ_mT product shows a gradual decrease as the temperature is decreased, approaching to the value of the corresponding isolated ion at low temperatures. Such a decrease of the magnetic moment has to be attributed to antiferromagnetic interactions in the organic part. In fact, in the ET salts containing diamagnetic Keggin anions (X = Si, B, H_2^{2+}) an antiferromagnetic chain-like behavior with an exchange constant J ≈ - 60 cm^{-1} has been found.

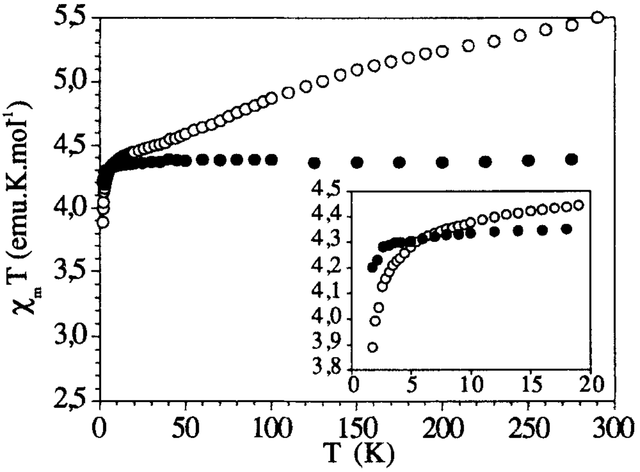

FIGURE 4 Magnetic behavior of the ET-Mn salt (open circles) and of the Bu_4N^+ salt of the anion $[PMn(H_2O)W_{11}O_{39}]^{-5}$ (filled circles). The low temperature region is shown in the inset.

On the other hand, a close inspection of the low temperature behavior allows to observe clear differences between ET and Bu_4N^+ salts. Thus, the magnetic behavior of the ET-Mn salt exhibits a steady decrease of $\chi_m T$ (from 4.3 emu.K.mol^{-1} at T = 6 K to 3.9 emu.K.mol^{-1} at 1.7 K), crossing below 6 K the curve of the isolated Mn^{II} ion which shows a constant value of $\chi_m T$ (4.3 emu.K.mol^{-1}, S = 5/2) down to 3 K (Inset of Fig. 4). These differences are more pronounced in the Cr^{III} derivatives. Thus, the behavior of ET-Cr shows a minimum in $\chi_m T$ of ca. 2.06 emu.K.mol^{-1} at T ≈ 5 K and a sharp divergence at lower temperatures (Inset of Fig. 6), while the curve for isolated Cr^{III} stays nearly constant down to 5 K ($\chi_m T$ = 1.85 emu.K.mol^{-1}, S = 3/2), decreasing below this T due to single-ion zero-field splitting effects. The above results are indicative of weak antiferromagnetic or ferromagnetic interactions between the metal ions in these two radical salts. Owing to the large intermetallic separations (the shortest M-M distance is of ca. 12 Å), these interactions can not be explained in terms of a dipolar coupling, nor by assuming a superexchange mechanism (in the Mn case, the shortest pathway involves a linear bridge -O-P-O-W-O-). A third possibility could be then to consider the presence of a coupling with the organic part.

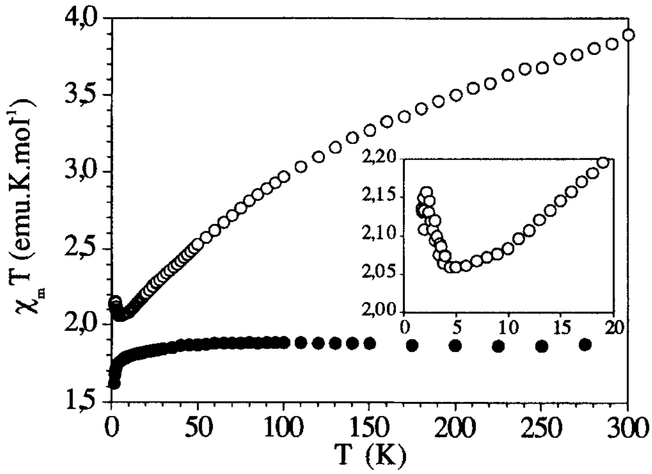

FIGURE 5 Magnetic behavior of the ET-Cr salt (open circles) and of the Bu_4N^+ salt of the anion $[SiCr(H_2O)W_{11}O_{39}]^{-5}$ (filled circles). The low temperature region is shown in the inset.

The salt $ET_6H_4[Co_4(H_2O)_2(PW_9O_{34})_2]$

In the above case we used as inorganic component of the radical salt Keggin anions with a single magnetic ion on the surface of the unit. With the aim of increasing the magnetic nuclearity of the inorganic component we have tried the reaction of ET with the polyoxoanion $[Co_4(H_2O)_2(PW_9O_{34})_2]^{-10}$. This anion is of interest since it contains a ferromagnetic Co_4 cluster; so, it provides the opportunity of constructing a material formed by a high spin cluster and an organic radical. Black crystals of composition $ET_6H_4[Co_4(H_2O)_2(PW_9O_{34})_2]CH_3CN.5H_2O$ have been obtained by electro-oxidation. The magnetic properties of this salt are reported in Fig. 6 and compared with those of the potassium salt. We notice that the ferromagnetic character of the Co^{II} cluster is maintained in the radical salt. Thus, both salts exhibit a sharp increase of the χ_mT product for $T < 30$ K as the temperature is decreased, followed by a round maximum at 6 K. If we assume that this maximum arises from the presence of antiferromagnetic inter-cluster interactions, the fact of observing the maximum in the same position in both salts suggests that these interactions are also maintained. Furthermore, the low temperature EPR spectra of the radical salt show two signals associated to the organic radical and to the Co cluster. The above results indicates that the two magnetic sublattices are independent in this salt. If there is any magnetic coupling between the two sublattices, this should be smaller than the inter-cluster interaction.

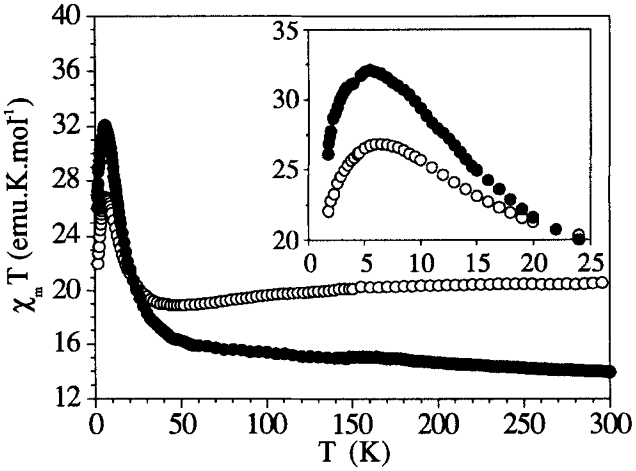

FIGURE 6 Magnetic behavior of the ET$_6$H$_4$[Co$_4$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$] salt (open circles) and of the K$^+$ salt of the anion [Co$_4$(H$_2$O)$_2$(PW$_9$O$_{34}$)$_2$]$^{-10}$ (filled circles). The low temperature region is shown in the inset.

CONCLUSIONS

One of the main goals of this investigation is to obtain organic/inorganic molecular materials in which localized magnetic moments from the inorganic part are coupled via the conduction electrons of the organic one. This indirect exchange term presents an oscillatory behavior which can give rise alternatively to an AF or Ferromagnetic coupling. The practical synthesis of such materials opens new possibilities as the obtaining of conducting molecular ferromagnets or the stabilization of a superconducting state in a magnetically ordered molecular lattice. We have shown that polyoxometalate anions containing one or more magnetic centers can be used successfully as magnetic components of conducting salts based on the bis-ethylenedithio-tetrathiafulvalene organic donor. Small magnetic interactions between the metal centers have been detected when the metals are situated on the surface of the polyanion, although no cooperative magnetic interactions have been observed. More molecular materials of this kind are to be explored with larger conductivities and closer contacts between the two components.

ACKNOWLEDGEMENTS

This work is supported by the Spanish Ministerio de Educación y Ciencia (CICYT) and the Generalitat de Cataluña (CIRIT) (Grant QFN91-4220), the European Union (Network on New Molecular Conductors and post-doctoral grant to CJG-G), and the Caja de Ahorros del Mediterráneo. ST thanks the CICYT for a post-doctoral grant.

REFERENCES

1. (a) M. Y. Ogawa, B. M. Hoffman, S. Lee, M. Yudkowsky and W. P. Halperin, Phys. Rev. Lett., 57, 1177 (1986); (b) P. Day, M. Kurmoo, T. Mallah, I. R. Marsden, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseau, J. Gaultier, G. Bravic and L. Ducasse, J. Am. Chem. Soc., 114, 10722 (1992); (c) H. Oshio, E. Ino, I. Mogi and T. Ito, Inorg. Chem., 32, 5697 (1993).
2. (a) C. J. Gómez-García, J. J. Borrás-Almenar, E. Coronado, P. Delhaes, C. Garrigou-Lagrange and L. C. W. Baker, Synth. Metals, 55-57, 2023 (1993); (b) E. Coronado and C. J. Gómez-García, in Polyoxometalates: From Platonic Solids to Anti-retroviral Activity, edited by M. T. Pope and A. Müller (Kluwer Acad. Pub., The Netherlands, 1994).
3. (a) L. Ouahab, M. Bencharif and D. Grandjean, C. R. Acad. Sci. Paris, Série II, 307, 749 (1988); (b) C. Bellito, M. Bonamico and G. Staulo, Mol. Cryst. Liq. Cryst., 232, 155 (1993); (c) A. Davidson, K. Boubekeur, A. Pénicaud, P. Auban, C. Lenoir, P. Batail and G. Hervé, J. Chem. Soc. Chem. Commun., 1373 (1989).
4. (a) S. Triki, L. Ouahab, J. Padiou, and D. Grandjean, J. Chem. Soc. Chem. Commun., 1068 (1989); (b) S. Triki, L. Ouahab, D. Grandjean and J. M. Fabre, Acta Cryst., C47, 645 (1991); (c) S. Triki, L. Ouahab, J. F. Halet, O. Peña, J. Padiou, D. Grandjean, C. Garrigou-Lagrange and P. Delhaes, J. Chem. Soc. Dalton Trans., 1217 (1992).
5. C. J. Gómez-García, E. Coronado, S. Triki, L. Ouahab and P. Delhaes, Adv. Mater., 4, 283 (1993).
6. (a) A. Mhanni, L. Ouahab, O. Peña, D. Grandjean, C. Garrigou-Lagrange and P. Delhaès, Synth. Metals, 41-43, 1703 (1991); (b) L. Ouahab, M. Bencharif, A. Mhanni, D. Pelloquin, J. F. Halet, O. Peña, J. Padiou, D. Grandjean, C. Garrigou-Lagrange, J. Amiell and P. Delhaès, Chem. Mater., 4, 666 (1992); (c) L. Ouahab in Polyoxometalates: From Platonic Solids to Anti-retroviral Activity, edited by M. T. Pope and A. Müller (Kluwer Acad. Pub., The Netherlands, 1994), and references therein;
7. C. J. Gómez-García, L. Ouahab, C. Gimenez-Saiz, S. Triki, E. Coronado and P. Delhaes, Angew. Chem., Int. Ed. Engl., 33, 223 (1994).
8. (a) M.T. Pope Heteropoly and Isopoly Oxometalates (Springer-Verlag: Berlin, 1983); (b) M. T. Pope and A. Müller Angew. Chem., Int. Ed. Engl., 30, 34 (1991).
9. J. R. Galán-Mascarós, C. Gimenez-Saiz, S. Triki, C. J. Gómez-García, E. Coronado and L. Ouahab, Angew. Chem. (submitted).