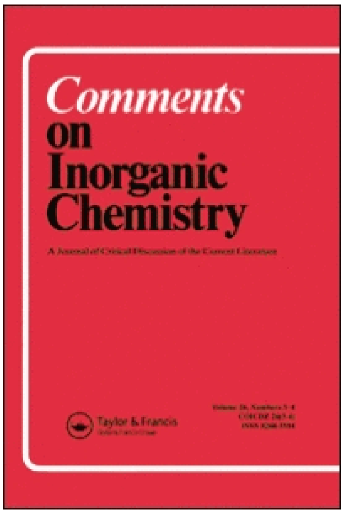
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Polycxometalates: From Magnetic Clusters to Molecular Materials

Eugenio Coronado[a]; Carlos J. Gómez-garcía[a]
[a] Departamento de Química Inorgánica, Universidad de Valencia, Burjasot, Spain

**To cite this Article** Coronado, Eugenio and Gómez-garcía, Carlos J.(1995) 'Polycxometalates: From Magnetic Clusters to Molecular Materials', Comments on Inorganic Chemistry, 17: 5, 255 — 281
**To link to this Article: DOI:** 10.1080/02603599508032707
**URL:** http://dx.doi.org/10.1080/02603599508032707

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Polyoxometalates: From Magnetic Clusters to Molecular Materials

EUGENIO CORONADO and CARLOS J. GÓMEZ-GARCÍA
*Departamento de Química Inorgánica,*
*Universidad de Valencia,*
*Dr. Moliner 50,*
*46100 Burjasot, Spain*

Received January 27, 1995

The potential relevance of polyoxometalate chemistry for providing compounds that can be of interest in molecular magnetism and in the preparation of new classes of molecular materials is discussed. We show that this kind of inorganic complex provides remarkable examples of magnetic clusters for which the number and type of interacting metal atoms can be varied in a controlled manner. They also provide striking examples of high nuclearity mixed valence clusters in which delocalized electrons can interact with the localized moments of the metal centers. Finally, we illustrate the use of polyoxoanions as inorganic components of new molecular materials based on organic donors of the tetrathiafulvalene type. In particular, we discuss the possibility of synthesizing molecular materials coupling localized magnetic moments with delocalized electrons taking advantage of the magnetic character in the polyanion.

**Key Words:** *polybxometalates, magnetic clusters, mixed valence, magnetic exchange, molecular magnetism, molecular conductors*

## INTRODUCTION

Polyoxometalate anions are an enormously rich class of inorganic compounds known for well over a century that in recent years have become

---

*Comments Inorg. Chem.*
1995, Vol. 17, No. 5, pp. 255–281
Reprints available directly from the publisher
Photocopying permitted by license only

of increasing interest due to their topological and electronic versatility, and to their current significance in disciplines as diverse as catalysis, biology, medicine and materials science.[1,2] In spite of the vast number of known polyoxoanions, the number of different structural types is relatively low. Most of them present discrete cluster-like structures of definite sizes and shapes formed by closed and highly symmetrical networks of $MO_x$ polyhedra (usually octahedra and tetrahedra) generally sharing corners and edges. In fact, they can be regarded as molecular fragments of close-packed extended metal oxide lattices,[3] thus providing model systems that can help in the understanding of the processes involved in the catalytic and electronic properties of these solid-state materials.

Several recent reviews[1,2] have described the progress made by polyoxometalates in a variety of directions and areas of active research. In this Comment we present the various aspects and multiple properties of polyoxometalates that can also make these metal–oxygen clusters relevant in two interrelated areas of burgeoning interest: molecular magnetism and molecular materials. The representative examples reported here, taken mainly from our own work, have been completed by references to other studies in order to give a general idea of the role played by polyoxometalates in these areas. We will start by presenting the possibilities offered by polyoxometalate chemistry in the preparation of magnetic clusters of increasing nuclearities, which can contain increasing numbers of exchange coupled moments and in which delocalized electrons can be introduced by reduction. In the second part we present how these inorganic cluster anions can be combined with suitable organic cations in order to produce new classes of molecular materials with active physical properties. We focus on those materials resulting from the assembling of polyoxometalates with $\pi$-electronic donor molecules of tetrathiafulvalene type, which constitute the most widely used molecular components of organic conductors and superconductors. In particular, we discuss the possibility of synthesizing molecular materials coupling localized magnetic moments with delocalized electrons, taking advantage of the magnetic character in the polyanion.

## MAGNETIC CLUSTERS

Compounds containing oligonuclear complexes of exchange-coupled transition metal ions (magnetic clusters) are currently receiving increasing attention in molecular magnetism for several reasons. First, they are in between the molecular systems and the extended solids.[4] Then, the limited number of magnetic centers which are coupled in the clusters often allows us to treat their electronic and magnetic structures with quantum mechanical approaches, avoiding the further approximations required to treat extended solids.[5] On the other hand, when these clusters are large enough, they enter in a range of dimensions (mesoscopic scale) where the transition from the molecular to the bulk state can lead to completely novel magnetic properties, whose investigation is of major interest in solid-state physics.[6] Finally, these clusters may be useful as building blocks for novel molecular-based magnetic materials.[7]

Polyoxometalate anions are particularly interesting in this context because (1) they can act as ligands coordinating groups of paramagnetic ions at specific sites, (2) the heteropoly framework guarantees an effective magnetic isolation of the cluster, at the same time imposing its geometry, (3) their chemistry allows the assembly of stable anion fragments into larger clusters, and (4) they are soluble in both aqueous and nonaqueous solvents. Despite the above characteristics, the magnetic properties of these materials until very recently have been only loosely investigated.[8] With the increasing use of SQUID susceptometers, systematic magnetic studies of these compounds are now beginning to be developed.

An extensive family of compounds that can illustrate the ability of these molecular metal oxides to encapsulate a large variety of magnetic clusters with different kinds of interacting ions and increasing nuclearities is that obtained by reaction of divalent transition metal ions with the trivacant tungstophosphate ligands $[PW_9O_{34}]^{9-}$ and $[P_2W_{15}O_{56}]^{12-}$. These lacunary polyoxoanions result from the removal of a triad of W sites from the well known Keggin and Dawson-Wells anions (Fig. 1). As far as the chemistry is concerned, these compounds illustrate well how to make larger and larger clusters in a controlled manner.[9] For example, by slightly varying the experimental conditions of synthesis (stoichiometry, pH, temperature), reaction of nickel (II) with $[PW_9O_{34}]^{9-}$ anions can lead to magnetic clusters of nuclearities 3, 4 and 9. Thus, when one $[PW_9O_{34}]$ moiety is involved in the reaction, a reconstituted Keggin structure containing the triangular cluster $Ni_3O_{13}$ is obtained[10] (Fig. 2). A second possibility is that two $[PW_9O_{34}]$ moieties encapsulate a rhomb-like

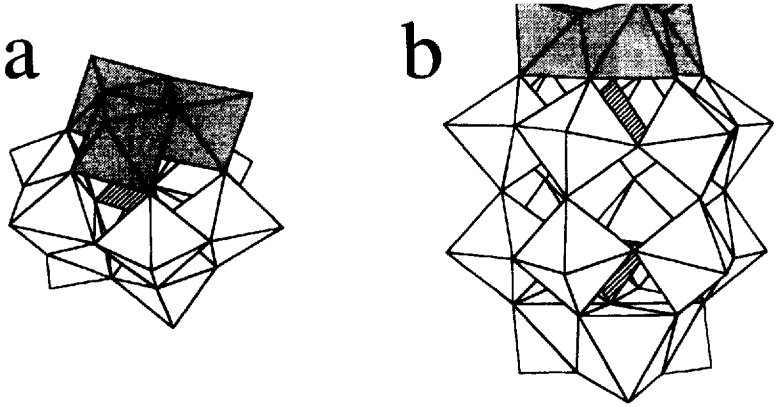


FIGURE 1 Polyhedral representations of (a) the Keggin structure $[XM_{12}O_{40}]^{-n}$ (X = $P^{V}$, $Si^{IV}$, $B^{III}$, $Co^{II}$, $Fe^{III}$, . . .; M = $Mo^{VI}$, $W^{VI}$) and (b) the Dawson-Wells structure $[X_2M_{18}O_{62}]^{-n}$ (X = $P^{V}$, $S^{VI}$; M = $Mo^{VI}$, $W^{VI}$). The shadowed octahedra can be removed to obtain the trivacant ligands $[XM_9O_{34}]^{-9}$ and $[X_2M_{15}O_{56}]^{-12}$, respectively.

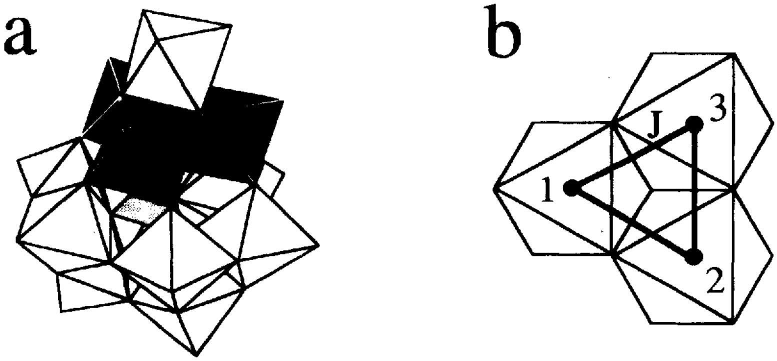


FIGURE 2 (a) Polyhedral representation of the $[PNi_3(H_2O)_3W_{10}O_{39}(H_2O)]^{-7}$ anion. The $Ni^{II}$ atoms are located in the black octahedra. (b) Exchange network of the $Ni_3O_{13}$ cluster.

tetrameric $Ni_4O_{16}$ cluster. This type of cluster is maintained when other divalent metal ions are used (M = Fe, Mn, Co, Cu, Zn)[11-13] and also for the Dawson-Wells derivatives[14,15] (Fig. 3). Finally, when three $[PW_9O_{34}]$ moieties are involved, a nonanuclear cluster is obtained[16] in which three triangular $Ni_3O_{13}$ clusters belonging to three Keggin units are linked through oxygen bridges and two $HPO_4^{-2}$ anions (Fig. 4). This cluster is also known[17,18] for M = $Co^{II}$.

From the magnetic point of view, this family provides nice examples of well isolated ferromagnetic clusters with high spin multiplicity ground states, antiferromagnetic clusters with spin frustration arising from competing exchange interactions, and also clusters with coexistence of both ferro and antiferromagnetic interactions. In Table I we summarize the magnetic parameters for the characterized members of this family. Let us first compare the magnetic properties of the Ni clusters (Fig. 5). For the triangular $Ni_3$ cluster the Ni–Ni pairwise interactions between the spins $S = 1$ are ferromagnetic, as can be seen from the plot of the product $\chi_m T$ (proportional to the square of $\mu_{eff}$) vs. $T$ which exhibits a gradual increase as the temperature is decreased and a plateau below 5 K, in agreement with the $S = 3$ spin ground state of the cluster. This ferromagnetic spin coupling is related to the geometry of the cluster: edge sharing $NiO_6$ octahedra with angles Ni–O–Ni of 90°–100°, which are in the range in which

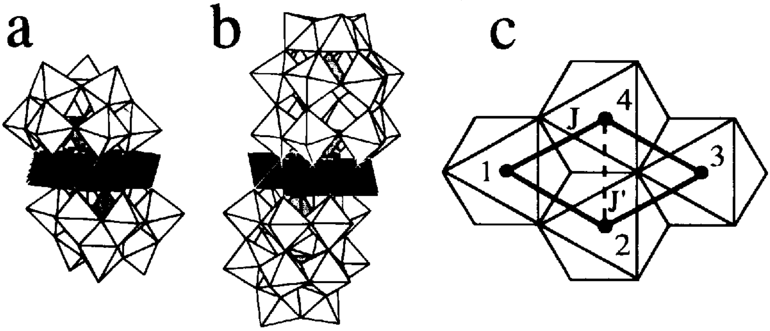


FIGURE 3 Polyhedral representation of (a) the $[M_4(H_2O)_2(PW_9O_{34})_2]^{-10}$ anion (M = $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$), (b) the $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{-16}$ anion (M = $Mn^{II}$, $Co^{II}$, $Ni^{II}$, $Cu^{II}$, $Zn^{II}$). The magnetic metal ions are located in the black octahedra. (c) Exchange network of the $M_4O_{16}$ cluster showing the two different exchange constants $J$ and $J'$.

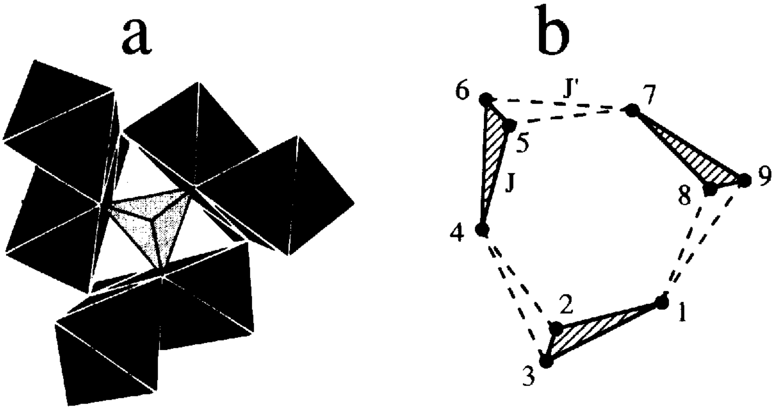


FIGURE 4 (a) Polyhedral representation of the $[M_9O_{36}]$ (M = $Ni^{II}$, $Co^{II}$) cluster. The magnetic ions are located in the black octahedra. (b) Exchange network of the $M_9O_{36}$ cluster showing the intra- and inter-triangle exchange constants $J$ and $J'$.

the Ni–Ni ferromagnetic exchange pathways are dominant (90° ± 14°).[19] What is important in these systems is that these geometrical features are maintained when the nuclearity of the cluster is increased, and so the ferromagnetic interactions. This can be seen in the tetrameric rhomb-like $Ni_4$ cluster which shows ferromagnetic behavior with an $S = 4$ spin ground state (Fig. 5). Notice that other ferromagnetic nickel clusters are known, but in contrast to the preceding example, all these complexes show a cubane-type framework and significant intercluster interactions. Finally, for the nonanuclear $Ni_9$ cluster, which is formed by a triangle of triangular $Ni_3$ clusters, the presence of two types of connections between $NiO_6$ octahedra should lead to two types of pairwise exchange interactions ($J$ and $J'$ in Fig. 4b). Thus, the triangular $Ni_3$ clusters are sharing edges as in the above clusters, while the inter-triangle connections involve corner-sharing octahedra with Ni–O–Ni angles around 120°, which deviate considerably from the orthogonality value. Hence, an unprecedented magnetic cluster with coexistence of both ferro- and antiferromagnetic couplings is to be expected. The magnetic properties confirm this prediction (Fig. 5): The product $\chi_m T$ shows a continuous increase with decreasing temperature, indicating the presence of ferromagnetic exchange interactions within the triangles, but below 25 K it

TABLE I

Properties of magnetic clusters coordinated by polyoxoanion ligands. The exchange parameters are based on a Hamiltonian written as $-2JS_aS_b$, $S_i$ and $S_G$ are the spin values of the interacting ions and of the ground state of the cluster, respectively.

| Cluster | $S_i$ | Exchange Parameters (cm$^{-1}$) | Comments | $S_G$ | Ref. |
|---|---|---|---|---|---|
| $Ni_3O_{13}$ | 1 | $J = 2.9$ | Heisenberg model. Ferromagnetic exchange | 3 | 11 |
| $Cu_4O_{16}$ | 1/2 | $J = -3.5$; $J' = -12.5$ | Heisenberg model. AF exchange. Spin Frustration | 1 | 13 |
| $Mn_4O_{16}$ | 5/2 | $J = -1.7$; $J' = -0.3$ | Heisenberg model. AF exchange | 0 | 14 |
| $Ni_4O_{16}$ | 1 | $J = 5.2$; $J' = 6.9$ | Heisenberg model. Ferromagnetic exchange | 4 | 16, 17 |
| $Co_4O_{16}$ | "3/2" | $J_\parallel = 12$; $J'_\parallel = 19$<br>$J_\parallel/J_\perp = 0.6$ | Anisotropic model. Ferromagnetic exchange | "6" | 13 |
| $Co_9O_{36}$ | "3/2" | $J = 8.4$; $J' = -12$ | Anisotropic Ising model. Ferromagnetic and AF exchange | "9/2" | 19 |
| $Ni_9O_{36}$ | 1 | $J = 3.9$; $J' = -0.97$ | Heisenberg model. Ferromagnetic and AF exchange | 0 | 17 |

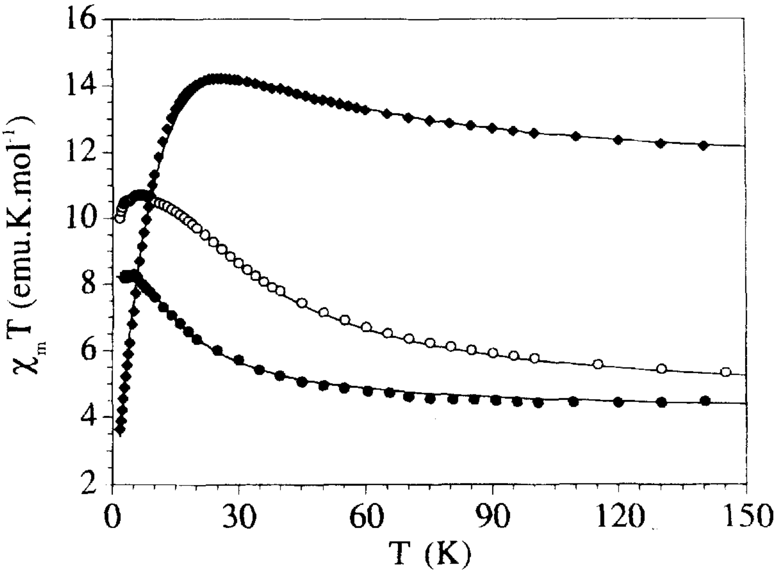


FIGURE 5 Plot of $\chi_m T$ versus $T$ for the three Ni$^{II}$ clusters: $Ni_3O_{13}$ (filled circles), $Ni_4O_{16}$ (open circles) and $Ni_9O_{36}$ (filled squares). Solid lines are the best fit to the isotropic Heisenberg exchange model. The resulting exchange parameters are given in Table I.

exhibits a sharp decrease as a consequence of the antiferromagnetic inter-triangle interactions.

The above examples have shown that thanks to the rigidity imposed by the polyoxometalate ligand, magnetic clusters with unusual geometries and highly symmetrical topologies can be obtained, for which the nuclearity can be increased with ease while maintaining unchanged their relevant structural features, and therefore the sign and magnitude of the exchange parameters. Another interesting aspect in this frame is provided by the possibility of replacing in the cluster the transition metal ions. This aspect is well illustrated by the series containing tetrameric $M_4O_{16}$ clusters (M = Mn, Fe, Co, Ni, Cu) for which we can vary in the same structural support the size and nature of the interacting magnetic moments, as well as sign of the magnetic interactions. Thus, while Mn$^{II}$, Ni$^{II}$ and Cu$^{II}$ ions are well described by isotropic ground spin states ($S$ = 5/2. 1, and 1/

2, respectively), high-spin octahedral Fe$^{II}$ and Co$^{II}$ have orbitally degenerate ground states which should cause the appearance of an exchange anisotropy, preventing the use of the simple Heisenberg spin Hamiltonian in the theoretical treatment of this kind of magnetic clusters. Focusing now on the sign of the exchange interactions, the magnetic properties of Fe$^{II}$ and Co$^{II}$ clusters indicate the presence of ferromagnetic interactions (Fig. 6) that should lead to magnetic ground states. Although in these cases the orbital momentum of the coupled ions prevents a proper description of the states of the cluster in terms of the total spin values, a simple count of the number of parallel spins caused by the ferromagnetic coupling leads to ground states comprising sixteen ("*S*" = 8) or twelve ("*S*" = 6) unpaired electrons for Fe$^{II}$ and Co$^{II}$ clusters, respectively. Notice that these large numbers of unpaired electrons are comparable to those reported in other large iron and manganese clusters (with *S* reaching values from 10 to 14).[20,21]

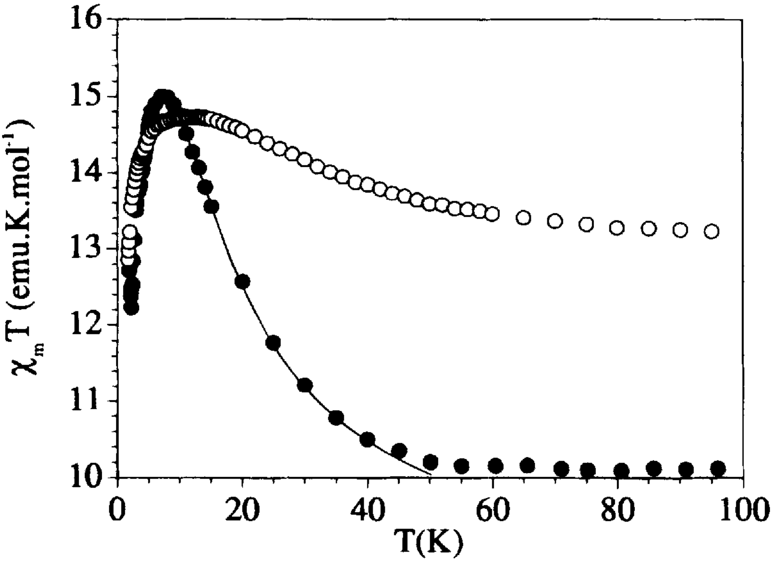


FIGURE 6 Plot of $\chi_m T$ versus $T$ for the $Co_4O_{16}$ (filled circles) and the $Fe_4O_{16}$ (open circles) clusters. The magnetic data for the $Co_4$ cluster were fit to an exchange model that assumes an axial exchange anisotropy of the Ising-type ($J_\parallel > J_\perp$) (solid line in the figure). The resulting exchange parameters are given in Table I.

The ferromagnetic behaviors observed in $Fe^{II}$ and $Co^{II}$ clusters contrast with the antiferromagnetic behaviors exhibited by $Mn^{II}$ and $Cu^{II}$ clusters (Fig. 7). However, it is interesting to notice that while in the Mn case the product $\chi_m T$ vanishes when the temperature approaches absolute zero, in the Cu case it reaches a plateau of 0.86 emu.K/mol at ca. 6 K. This difference indicates that even though both types of pairwise exchange interactions present in these clusters are antiferromagnetic, their spin ground states are different, being magnetic for the $Cu^{II}$ cluster. This is a consequence of spin frustration. Thus, the topology of the cluster is such that the interacting spins are under the influence of two competing interactions, $J$ and $J'$, that tend to orient them in different ways. Under these circumstances the nature of the ground state will depend of the ratio $J'/J$. When the exchange through the diagonal of the rhomb, $J'$, is sufficiently small compared to that through the sides, $J$, the ground state is the antiferromagnetic one (i.e., $S = 0$), as observed in the $Mn^{II}$ cluster for which $J'/J = 0.18$. In turn, when the diagonal exchange interaction dominates, the spin frustration results in the stabilization of an intermediate-spin ground state. This is the situation of the $Cu^{II}$ cluster for

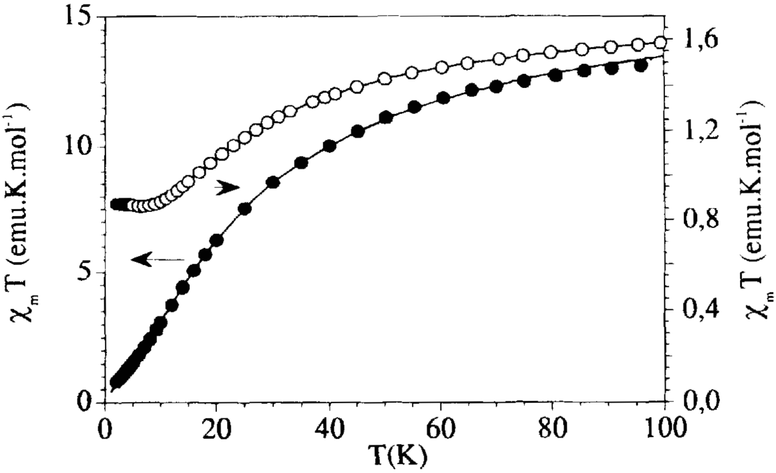


FIGURE 7 Plot of $\chi_m T$ versus $T$ for the $Mn_4O_{16}$ (filled circles) and the $Cu_4O_{16}$ (open circles) clusters. Solid lines represent the best fit to the isotropic exchange model. The resulting exchange parameters are given in Table I.

which the large value of the ratio $J'/J$ (= 3.6) leads to a ground state that contains the spin $S = 1$.

## MIXED-VALENCE CLUSTERS

A way to increase the complexity of a magnetic cluster is to add electrons that can be delocalized over the metal atoms. The result is a magnetic mixed valence cluster in which localized and delocalized electrons can coexist and interact, thus providing the opportunity to investigate the interplay of electron transfer and magnetic interactions at the molecular level. This kind of system has long been of interest in connection with compounds of biological relevance (iron–sulfur proteins, manganese–oxo clusters),[22] but can also be significant in molecular magnetism. In fact, in a mixed valence dimer the theory predicts that electron transfer tends to stabilize the ferromagnetic ground state very strongly, even in the presence of antiferromagnetic exchange interactions through the coupling mechanism of double exchange.[23] However, very little is known about higher nuclearity clusters; only the simple cases of magnetic trimers[24] and tetramers[25] with one delocalized electron have been theoretically treated.

Polyoxometalates can also play a significant role in the mixed valence area, both from experimental and theoretical points of view. Numerous heteropoly anions can be reversibly reduced to mixed-valence species (heteropoly "blues" and "browns") by addition of various specific numbers of electrons, which are delocalized over a significantly large number of atoms of the heteropoly framework, retaining the gross structures of the oxidized anions.[1] The further introduction into these structures of paramagnetic metal atoms, which contain localized magnetic moments, yields multi-nuclear mixed-valence clusters in which we can have electron interactions between delocalized electrons, between delocalized and localized electrons, and between localized electrons. These possibilities have recently been exploited to prepare and magnetically characterize isomorphous series of heteropoly blue derivatives of Keggin and Dawson-Wells structures (Fig. 1) containing zero, one or two paramagnetic atoms, and one or two "blue" electrons.[26]

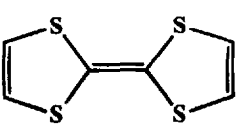
From a theoretical point of view, these heteropoly blues are very suitable as model systems for the study of electron delocalization and magnetic interactions in large clusters. Thus, although the topologies exhibited by these clusters are much more complex than those previously examined in this area, their high symmetries allow us to exploit the group theoretical approach. This facilitates the development of analytical solutions for the energy levels and magnetic properties of the cluster, providing at the same time a clear picture of the role of the different types of electronic processes involved. For example, the problem of delocalization of a pair of electrons has been examined in the two-electron reduced heteropoly blues with Keggin and Dawson-Wells structures.[27] The model has considered (1) the Coulomb interactions between the two delocalized electrons that tend to keep the electrons on fairly widely separated metal atoms; (2) the single and double electron transfer processes that occur through the corners or through the edges of neighboring octahedral metal sites, promoting electron delocalization. This model has shown that electron transfer is at the origin of the complete spin pairing observed in these clusters, making it unnecessary to appeal to a superexchange mechanism in order to explain this very strong antiferromagnetic coupling.

Other striking examples of mixed-valence clusters with magnetic and electron transfer interactions are provided by polyoxovanadates.[28] Several structures are known that comprise a variable number of diamagnetic vanadium (V) and vanadium (IV) ions: the $[H_3KV_{12} \cdot As_3O_{39}(AsO_4)]^{6-}$ anion, which comprises three localized and one delocalized vanadium (IV); the $[V_{12}As_8O_{40}(HCO_2)]^{3-}$ and $[V_{12}As_8O_{40}(HCO_2)]^{5-}$ anions, which comprise four localized and two and four delocalized vanadium(IV), respectively. Simple theoretical models which also take advantage of the symmetry of the clusters have been developed and used to rationalize their magnetic properties,[29] but in some cases puzzling magnetic and EPR behaviors have been observed, which emphasize the complexity of these clusters and the need for deeper theoretical treatments.

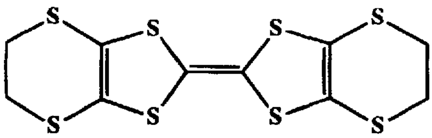
## MOLECULAR MATERIALS: COMBINATION OF POLYOXOMETALATES WITH ORGANIC π-DONORS

In the above we have seen the possibilities offered by polyoxometalate chemistry in the preparation of large clusters comprising exchange-coupled metal ions and/or delocalized electrons, and the relevance of these magnetic clusters in molecular magnetism. But this constitutes only the first part of the story. In the second part we will shift our interest from the molecule to the molecular solid constructed from these building blocks, and, in particular, to the new properties that should be expected when these electroactive molecules interact in the solid.

An attractive situation arises from the combination of these inorganic metal–oxide clusters with organic π-donor molecules (D) of the tetrathiafulvalene type.



**TTF**



**BEDT-TTF or ET**

These organic molecules have been shown to form radical cation salts of the type $D_mX_n$, which show remarkable electrical properties such as metal conductivity and even, superconductivity.[30] In these salts X is typically a small closed-shell inorganic monoanion (X = $Cl^-$, $I_3^-$, $NO_3^-$, $ClO_4^-$, $BF_4^-$, $PF_6^-$, $SCN^-$, etc.). The use of polyoxometalate clusters as inorganic counter-ions in radical-cation salts is quite recent. The features that make polyoxometalates attractive in this context are the following:

(i) These bulky anions show different sizes and shapes which can induce new organic packings and therefore new band structures. In fact, the crystal structures of these organic/inorganic hybrid materials are the result of the tendency of the planar organic cations to stack, and that of the inorganic clusters to adopt close-packed lattices. Furthermore, the possibility of variation of the anionic charge while keeping intact the structure of the polyoxometalate opens up the way to modulate the electronic band filling in the resulting salt and, therefore, the physical properties.

(ii) The ability of the polyanions to act as electron acceptors can give rise to mixed-valence materials in which delocalized electrons coexist in both the organic and the inorganic sublattices.

(iii) The introduction of a magnetic character into the polyanion can produce new classes of molecular materials in which delocalized electrons coexist with localized magnetic moments, thus providing the opportunity for the investigation of systems combining magnetic and conducting behaviors.

Point (i) has been exploited using simple and often commercial polyoxoanions of the type $[X^{n+}M_{12}O_{40}]^{-8+n}$ (X = P, Si; M = Mo, W),[31] $[M_6O_{19}]^{2-}$ (M = Mo, W)[32] and the $[Mo_8O_{26}]^{4-}$ anion.[33] The unusual structural and electronic properties induced by polyoxometalates in TTF radical salts can be illustrated by the compound $TTF_7[Mo_8O_{26}]$. In this semiconducting radical salt, an unusual zigzag mixed-valence chain of TTF molecules with significant interchain interactions through the sulfur atoms is observed (Fig. 8). On the other hand, an inhomogeneous charge distribution for the organic part has been found, with four different types of TTF molecules which are almost completely charged (A type in the figure), almost neutral (B and D types), or have intermediate charge (C type). This is a quite uncommon situation in the organic conducting salts that may be related to the strong electrostatic interactions produced by the high charges of the polyanions. This effect may lead to a charge localization as the temperature is reduced, and accounts for the

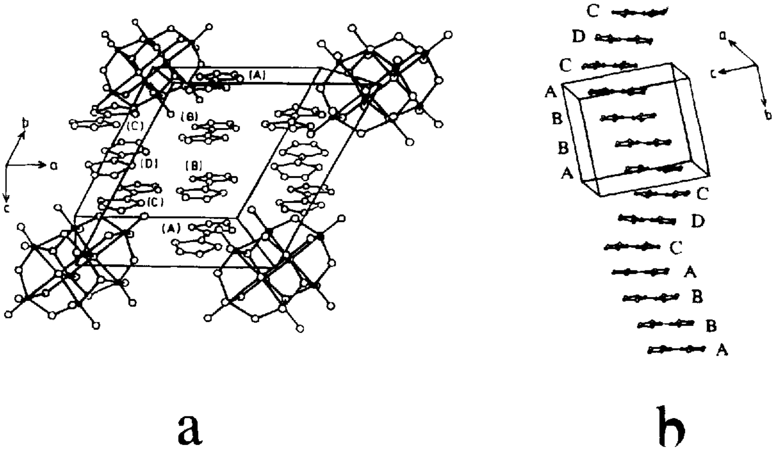


FIGURE 8 Structure of the radical salt $TTF_7[Mo_8O_{26}]$: (a) unit cell; (b) stacking of the TTF molecules.

semiconducting character found in most of the polyoxometalate-containing radical salts.

Hybrid materials with two coexisting mixed-valence states [point (ii)] have been obtained that contain the one-electron reduced Keggin anions $[PM_{12}O_{40}]^{4-}$ (M = Mo, W) and the organic radicals TTF[34] and ET.[35] However, no special properties arise from such a combination due to the lack of electronic interactions between the two sublattices which behave independently.

Very recently we have started to explore the possibility of forming conducting radical salts containing magnetic polyoxoanions [point (iii)]. Before presenting the most relevant examples obtained in this context, it should be of interest to point out the general reasons that justify the intense effort currently devoted to the molecular solids which exhibit coexistence of localized and delocalized electrons. The first reason is related to the possibility of obtaining a long-range magnetic order by taking advantage of the ability of the conduction electrons to couple the localized magnetic moments via an indirect exchange mechanism of the type RKKY (Ruderman, Kittel, Kasuya, Yosida).[36] This kind of exchange interaction is of long-range, in contrast to the superexchange one, and presents an oscillatory behavior which can give rise alternatively to ferro- or antiferromagnetic couplings, depending on the distance between moments. This interaction has been proposed for explaining ferromagnetism in metals and alloys of 3d transition elements such as iron, cobalt and nickel, and also in rare earth metals; it involves, respectively, interactions between 3d or 4f electrons with the conduction electrons (which are mainly of s character). In molecular materials the idea of the indirect interaction mechanism—which now should involve the interaction between localized d-electrons and delocalized conduction p-electron bands—to obtain a conducting magnet is quite recent. The very few examples of radical salts so far reported are formed by inorganic anions of the type $[MCl_4]^{2-}$ ($M^{II}$ = Cu, Co, Mn) and organic donors TTF and ET.[37] Up until now, however, only very weak intermetallic magnetic couplings have been detected. This is probably due to the small electron interactions between the two sublattices, since the intermolecular cation–anion contacts are at van der Waals distances.[38] The second reason for interest is related to the question of the simultaneous coexistence of ferromagnetism and superconductivity in a material. This question has been the subject of long debate in solid state physics, and has been investigated from both theoretical and experimental points of view in extended inorganic lattices,[39] but never in molecular systems. The weak interactions between localized and delocalized electron sublattices found in these materials, which in the previous case were a drawback, can now become suitable to allow this coexistence.

The first examples of TTF-based radical salts containing magnetic polyoxometalates were obtained by electrocrystallization of a mixture of TTF and the anions $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Cr^{III}(OH)_6Mo_6O_{18}]^{3-}$ in an organic solvent.[40] In these cases, however, the electrocrystallization technique did not allow us to grow single crystals, and only powder amorphous materials of composition $Co_4$:TTF 1:12 and Cr:TTF 1:3 were deposited at the platinum wire anode. Much better results have recently been obtained by combining the ET molecule with Keggin anions containing paramagnetic centers, and with the ferromagnetic cluster anion $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$.

In the first step we have used Keggin anions $[XW_{12}O_{40}]^{-8+n}$ which contain diamagnetic ($X^{+n} = 2(H^+)$, $Zn^{II}$, $B^{III}$, $Si^{IV}$) or paramagnetic ($X^{+n} = Co^{II}$, $Cu^{II}$, $Fe^{III}$) centers in the tetrahedral site. In this way we have prepared an extensive family of cation–radical salts with the general formula $ET_8[XW_{12}O_{40}](solv)_n(solv = H_2O, CH_3CN)$.[41] The structures of these materials consist of alternating layers of the organic ET donors with an α packing mode, and the Keggin polyoxoanions which form close-packed pseudohexagonal layers[42] (Fig. 9). The organic layers are formed by two different types of stacks: in one stack the ET molecules are packed in an eclipsed way, while in the other stack a zigzag chain of ET dimers is observed. The shortest interchain S . . . S distances, ranging from 3.46 to 3.52 Å, are significantly shorter than the intrachain ones from 3.86 to 4.04 Å, emphasizing the bidimensional character of the packing. Another important feature of this structure is the presence of short contacts between the organic and the inorganic layers which take place between the S atoms of the eclipsed chains and some terminal O atoms of the polyoxoanions, and via hydrogen bonds between the ethylene groups of the ET molecules and several O atoms of the anions.

From the electronic point of view, an inhomogeneous charge distribution in the organic sublattice has been found in which the eclipsed chain is formed by almost completely ionized ET molecules, while

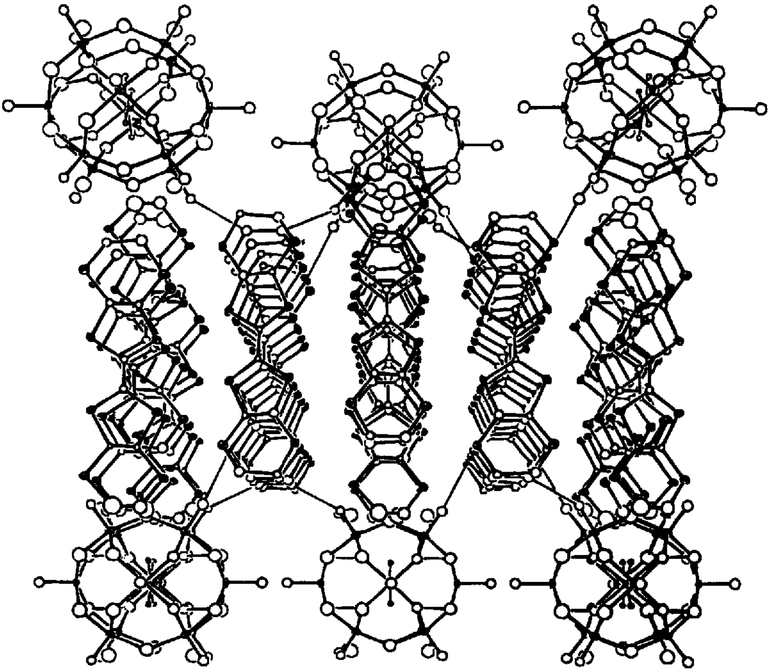


FIGURE 9 Structure of the radical salts $ET_8[XW_{12}O_{40}]$ ($X = Co^{II}, Cu^{II}, Fe^{III}, 2(H^+)$, $Si^{IV}$ and $B^{III}$) showing the layers of Keggin polyoxoanions and the two types of stacks in the organic layers.

the dimeric chain contains partially charged molecules.[43] This situation, which is quite new in these 2-D systems, accounts for the electrical and magnetic properties of these salts. Thus, a semiconducting behavior (with room *T* conductivities ranging from 0.03 to 0.15 $S.cm^{-1}$ and activation energies ranging from 100 to 150 meV, see inset of Fig. 10) has been found for all the salts, independent of the charge in the organic sublattice, while band calculations predict semiconducting behavior when this charge is +4 (as in the $Si^{IV}$ derivative), but a semi-metallic character when the charge is +5 (as in the $B^{III}$ derivative). This disagreement is certainly related to the existence of different ET molecules in the solid as a consequence of the inhomogeneous charge distribution, which leads to different site energies and thus to charge localization. As far as the magnetic

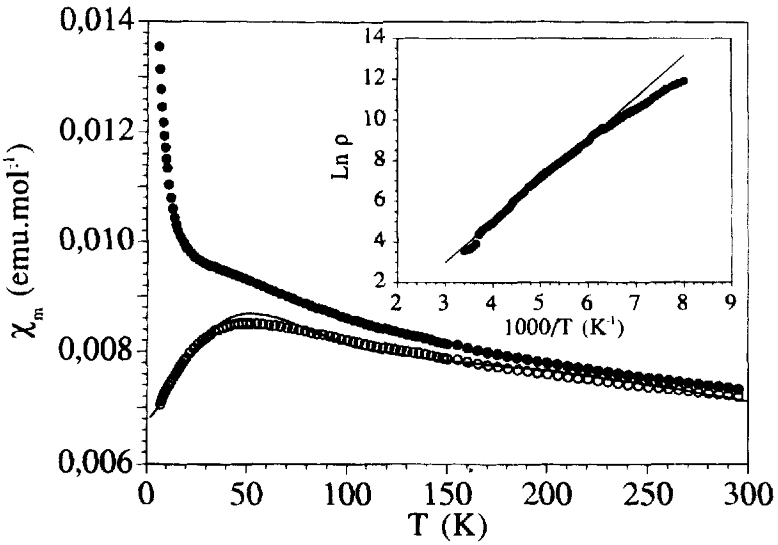


FIGURE 10 Plot of the magnetic susceptibility versus $T$ for the $ET_8[BW_{12}O_{40}]$ radical salt (filled circles). Open circles correspond to the corrected magnetic susceptibility after subtracting a paramagnetic Curie-type contribution. Solid line represents the best fit to a model that assumes an antiferrimagnetic Heisenberg chain behavior (with $J \sim -30\ cm^{-1}$) for the eclipsed chain, and an activated magnetic contribution (with $J \sim -150\ cm^{-1}$) coming from the dimeric chain. Inset: Semilogaritmic plot of the d.c. electrical conductivity, ρ (Ω.cm), versus 1000/$T$.

properties are concerned, this effect also explains why the salts containing diamagnetic anions behave as 1-D Heisenberg antiferromagnets[35a] (Fig. 10). In fact, the electron distribution in the organic sublattice may lead to the coexistence of localized electrons in the eclipsed chain (one unpaired electron per ET), which interact and account for the chain antiferromagnetism, with delocalized electrons moving in the mixed-valence dimeric chain, which account for the semiconducting character.

For those salts containing magnetic polyanions, the good insulation of the magnetic center, which is situated in the central tetrahedral cavity of the Keggin structure, precludes any magnetic interaction with the organic spin sublattice. Therefore, the magnetic properties are simply the sum of those corresponding to the two spin sublattices.

A way to increase the interaction between the two sublattices is to bring nearer their magnetic moments by putting the paramagnetic centers on the surface of the polyanion. Polyoxometalate chemistry allows us to do that. Thus, the replacement of one of the octahedral W atoms from the Keggin structure by a 3d transition metal atom results in the isolation of a substituted Keggin anion of the type $[XW_{11}M(H_2O)O_{39}]^{n-}$ (X = P, Si; M = $Mn^{II}$, $Co^{II}$, $Ni^{II}$, $Cr^{III}$, $Fe^{III}$) in which a paramagnetic atom is pentacoordinated by the polyanion and by a water molecule (Fig. 11). Then, in the second step we have used these monosubstituted polyanions to extend the above family of radical salts.[44] The new series so obtained maintains the structural characteristics of the above family. The only noteworthy difference has been observed in the $Mn^{II}$ derivative 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 of Keggin anions that runs along the c axis (Fig. 12). From the structural point of view, this chain-like structure is unprecedented in polyoxometalate chemistry.[45] Furthermore, in this salt X-ray analysis has allowed us to locate the Mn positions in the Keggin anion and to discern the distortions in the polyanion. This is a quite unusual situation since in the reported crystalline salts containing the $XMW_{11}$ Keggin anion, the M positions are fully disordered as a consequence of the cubic crystal lattice imposed by the polyanion, and therefore the lowered symmetry of the Keggin anion is masked by disorder. The lower

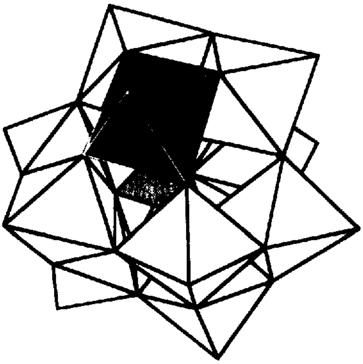


**FIGURE 11** Polyhedral representation of the Keggin structure. The black octahedron represents the magnetic center.

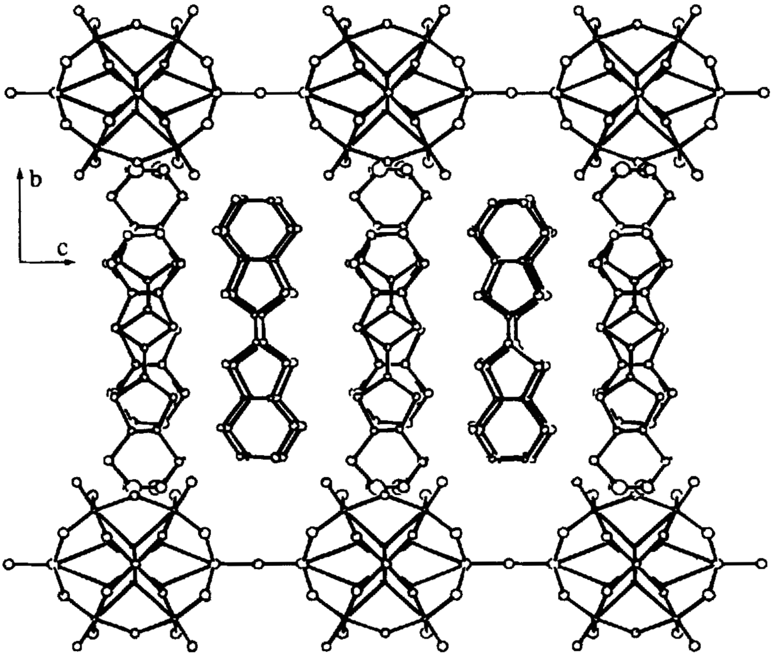


FIGURE 12 Structure of the $\{ET_8[PMnW_{11}O_{39}]\}_n$ radical salt showing the chains formed by the Keggin units.

symmetry of this and the other related radical salts (monoclinic) demonstrates how the use of these bulk organic cations can be useful in this respect. In fact, for the other members of the series (M = $Co^{II}$, $Ni^{II}$, $Cr^{III}$ and $Fe^{III}$) it has been found that even if the Keggin units are isolated, the M positions can be located, also being localized along the c axis.

The magnetic properties of these salts are indicative of the presence of weak magnetic interactions between the metal ions. Thus, for the Mn derivative, the $\chi_m T$ product shows a gradual decrease as the temperature is decreased, approaching the value of the isolated $Mn^{II}$ ion at low temperatures (Fig. 13). Such a decrease of the magnetic moment must be attributed, as before, to the antiferromagnetic interactions in the organic sublattice. However, a close inspection of data in the low temperature region (inset of the figure) allows us to

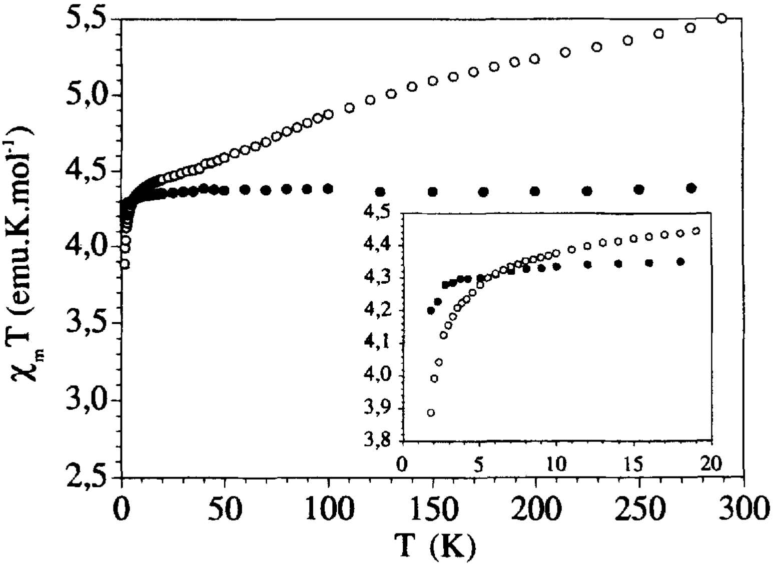


FIGURE 13 Plot of $\chi_m T$ versus $T$ for the $\{ET_8[PMnW_{11}O_{39}]\}_n$ radical salt (filled circles). The behavior for the tetra-buthyl-ammonium salt is given as open circles. Inset shows the low temperature region.

observe that the magnetic moment of the Mn-containing radical salt crosses the curve of the isolated Mn$^{II}$ ion below 6 K. This very weak interaction between the manganese (II) ions may involve some kind of interaction with the organic part since it can not be explained in terms of a dipolar coupling (the intermetallic separations are larger than 12 Å), nor by assuming a superexchange mechanism (the shortest pathway should involve a linear bridge–O–P–O–W–O–).

With the aim of increasing the magnetic nuclearity in the inorganic component, we have tried, in the third step, the reaction of ET with the polyoxoanion $[Co_4(PW_9O_{34})_2]^{10-}$. This anion is of interest since it contains the ferromagnetic $Co_4$ cluster; thus it provides the opportunity to construct the first material formed by a high spin cluster and an organic radical.[44a] Black crystals of composition $ET_6H_4[Co_4(PW_9O_{34})_2]$ have been obtained and the magnetic properties studied; but, unfortunately, the two magnetic sublattices behave independently, as can be seen from the comparison of the magnetic

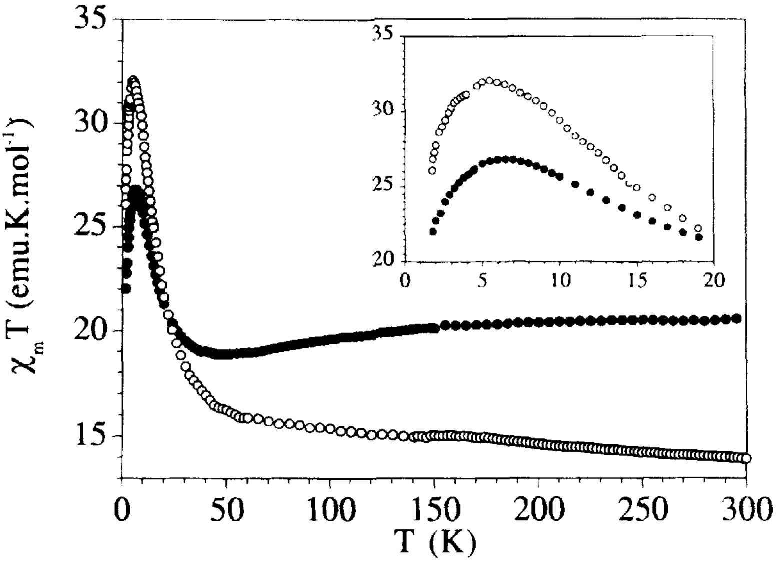


FIGURE 14 Plots of $\chi_m T$ versus $T$ for the potassium (open circles) and ET (filled circles) salts of the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{-10}$ anion. Inset represents the low temperature region.

data of this radical salt with that of the potassium salt (Fig. 14). We notice that the ferromagnetic character of the Co cluster is maintained in the radical salt, but does not seem to be sensitive to the presence of the organic spin sublattice. This result can be the consequence of the good insulation of the $Co_4$ cluster provided by the polyoxotungstate framework.

## CONCLUSIONS

In this Comment we hope to have shown the potential importance of polyoxometalate chemistry for providing compounds that can be of interest in molecular magnetism and in the preparation of new classes of molecular materials.

In the former aspect, we have shown that these metal–oxygen molecular assemblies provide us with many interesting examples of magnetic clusters for which the number and type of interacting metal atoms can be varied in a controlled manner, with the consequent variation in the type and topology of the exchange interactions. Besides, the rigidity imposed by the polyoxometalate ligands has been shown to be very useful in maintaining the structural features of the magnetic clusters, with M–O–M angles favoring the ferromagnetic exchange pathways when the octahedral sites share edges, yielding clusters comprising large numbers of unpaired electrons in the ground state. In the near future, these factors should favor the development of appropriate strategies (hydrothermal methods, for instance) to obtain metalate complexes of increasing complexity, comprising larger and larger numbers of exchange-coupled metal ions. Another feature of interest arises from the remarkable electron storage capacity shown by heteropoly anions, which allows us to obtain mixed-valence magnetic systems in which localized and delocalized electrons can coexist and interact. In this context, polyoxometalates are ideal model systems on which the interplay of electron transfer and magnetic interactions can be investigated at the molecular level. Therefore, they can contribute not only to the development of a general theory of double exchange in multinuclear and multielectronic mixed-valence systems, but also to the understanding of the electrical and magnetic properties of bulk materials in which these two electron processes are operative (extended metal oxides, for example). Until now, very few examples of this kind have been investigated. Quite a lot of interesting situations can be imagined, however, which justify the preparation of new polyoxometalate compounds. Just to mention an example, consider the case of a heteropoly complex containing delocalized "blue" electrons and two localized magnetic centers which are widely separated. This compound should be of interest because it may present a coupling of the two magnetic centers via the blue electrons, which is the molecular analog of the RKKY interaction in extended systems.

With respect to the use of polyoxometalates in molecular materials, the state of the art is at the very beginning. Some promising results have already been obtained, however, when these soluble metal oxide anions are combined with organic donors of the TTF-type. Thus, by playing with the charge, size and shape of the polyanions, new conducting inorganic/organic radical salts have been obtained, showing unusual organic packings and/or a mixed-valence state in both molecular sublattices. In a further step, polyoxometalates containing magnetic centers or magnetic clusters have been combined with organic donors with the aim of preparing molecular materials with unusual associations of properties (electrical and magnetic in this case), or superconducting salts containing localized magnetic impurities. Such an approach has resulted in the preparation of new molecular materials in which localized and delocalized electrons coexist in the solid. However, in the reported materials the good insulation of the magnetic unit provided by the polyoxometalate framework, together with the large intermolecular organic–inorganic separations, have prevented the occurrence of an effective interaction between the two sublattices. On the other hand, low electrical conductivities and semiconducting behaviors have been observed in most cases. Much remains to be done, especially in the search for materials having stronger organic–inorganic interactions and/or higher conductivities. Several chemical strategies can be imagined to improve these interactions, such as the use of ET derivatives with O or Se substituting the S atoms. In the former case, the O atom may be involved in hydrogen bridges with the water molecule coordinated to the magnetic metal atom, leading to an increase in the organic–inorganic interaction. In the second case, the more extended $\pi$ orbitals of Se atoms should favor larger organic–organic contacts and therefore an increase in the electrical conductivity. Finally, it should be stressed that not only the combination of magnetic polyoxometalates with organic donors are suitable. Other interesting combinations of properties can be imagined. For instance, some polyoxometalates that exhibit luminescence[47] can be combined with the organic donors in order to create new materials combining electrical and luminescent properties.

## Acknowledgments

This work has been supported by the European Union (Networks CHRX-CT92-0080 and CHRX-CT93-0271, and a Post-Doctoral Fellow Grant to C.J.G.), the Ministerio de Educación y Ciencia (CICYT and DGICYT), and the Generalitat de Catalunya (Grants QFN93-4510 and PB91-0652). We are indebted to all our colleagues and co-workers, whose names appear in the references, for important contributions to the work reported herein.

## References

1. (a) M. T. Pope, *Heteropoly and Isopoly Oxometalates* (Springer-Verlag, Berlin, 1983); (b) M. T. Pope and A. Müuller, Angew, Chem. Int. Ed. Eng. **30**, 34 (1991).
2. *Polyoxometalates: from Platonic Solids to Anti-retroviral Activity*, eds. M. T. Pope and A. Müler (Kluwer Acad. Pub., The Netherlands, 1994).
3. L. C. W. Baker, *Advances in the Chemistry of Coordination Compounds* (MacMillan, New York, 1961), p. 604.
4. D. Gatteschi, Adv. Mater. **6**, 635 (1994).
5. C. D. Delfs, D. Gatteschi and L. Pardi, Comments Inorg. Chem. **15**, 27 (1993).
6. G. Schmid, Chem. Rev. **92**, 1709 (1992); (b) R. D. McMichael, R. D. Shull, L. J. Swartzendruber and L. H. Bennett, J. Magn. Magn. Mater. **111**, 29 (1992); (c) P. C. E. Stamp, E. M. Chudnovsky and B. Barbara, Int. J. Mod. Phys. **6**, 1355 (1992).
7. D. N. Hendrickson *et al.*, *Magnetic Molecular Materials*, eds. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio (Kluwer, Dordrecht, 1991).
8. The former works showing the presence of magnetic exchange interactions in polyoxometalates were reported some years ago by Baker's group. in a series of isomorphous complexes containing various pairs of paramagnetic ions: L. C. W. Baker, V. Simmons, S. H. Wasfi, G. Candela and A. H. Kahn, J. Am. Chem. Soc. **94**, 5499 (1972); *ibid.* J. Chem. Phys. **56**, 4917 (1972).
9. (a) See E. Coronado and C. J. Gómez-García in Ref. 2, p. 233; (b) J. J. Borrás-Almenar, E. Coronado, J. R. Galán and C. J. Gómez-García, J. Magn. Magn. Mater. **140–144**, 809 (1995).
10. C. J. Gómez-García. E. Coronado and L. Ouahab, Angew, Chem. Int. Ed. Engl. **31**, 240 (1992).
11. (a) T. J. R. Weakley, H. T. Evans, J. S. Showell, G. F. Tourné and C. M. Tourné. J. Chem. Soc. Chem. Comm. 139 (1973); (b) H. T. Evans, G. F. Tourné, C. M. Tourné and T. J. R. Weakley, J. Chem. Soc. Dalton Trans. 2699 (1986); (c) M. W. Finke, R. G. Droege and P. J. Domaille, Inorg. Chem. **26**, 3886 (1987).
12. (a) C. J. Gómez-García, E. Coronado and J. J. Borrás-Almenar, Inorg. Chem. **31**, 1667 (1992); (b) N. Casañ-Pastor, J. Bas, E. Coronado, G. Pourroy and L. C. W. Baker J. Am. Chem. Soc. **114**, 10380 (1992); (c) C. J. Gómez-García, E. Coronado, J. J. Borrás-Almenar, M. Aebersold, H. U. Gudel and H. Mutka, Physica B **180–181**, 238 (1992).
13. C. J. Gómez-García, E. Coronado, P. Gómez-Romero and N. Casañ-Pastor, Inorg. Chem. **32**, 3378 (1993).
14. (a) T. J. R. Weakley and R. G. Finke, Inorg. Chem. **29**, 1235 (1990); (b) R. G. Finke an T. J. R. Weakley, J. Chem. Crystallogr. **24**, 123 (1994).
15. C. J. Gómez-García, J. J. Borrás-Almenar, E. Coronado and L. Ouahab, Inorg. Chem. **33**, 4016 (1994).
16. E. Coronado, J. R. Galán, C. J. Gómez-García and B. S. Tsukerblat, manuscript in preparation.
17. T. J. R. Weakley, J. Chem. Soc. Chem. Commun. 1406 (1984).
18. J. R. Galán, C. J. Gómez-García, J. J. Borrás-Almenar and E. Coronado, Adv. Mater. **6**, 221 (1994).
19. A. P. Ginsberg, Inorg. Chim. Acta Rev. **5**, 45 (1971).
20. P. D. W. Boyd, Q. Li, J. B. Vincent, K. Folting, H. R. Chang, W. E. Streib, J. C. Huffman, G. Christou and D. N. Hendrickson, J. Am. Chem. Soc. **110**, 8537 (1988).
21. D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, Science **265**, 1054 (1994).

22. G. Blondin and J. J. Girerd, Chem. Rev. **90**, 1359 (1989) and references therein.
23. (a) C. Zener, Phys. Rev. **82**, 403 (1951); (b) P. W. Anderson and H. Hasagawa, Phys. Rev. **100**, 675 (1955).
24. (a) G. Pourroy, E. Coronado, M. Drillon and R. Georges, Chem. Phys. **104**, 73; (1986) (b) M. I. Belinskii, Mol. Phys. **60**, 793 (1987); (c) C. J. Gómez-García, E. Coronado and G. Pourroy, J. Appl. Phys. **67**, 5992 (1990); (d) C. J. Gómez-García, E. Coronado, R. Georges and G. Pourroy, Physica B **182**, 18 (1992); (e) J. J. Borrás-Almenar, E. Coronado and B. S. Tsukerblat, Chem. Phys. **177**, 1 (1993); (f) S. A. Borshch, E. L. Bominaar, G. Blondin and J. J. Girerd, J. Am. Chem. Soc. **115**, 5155 (1993).
25. (a) J. J. Borrás-Almenar, E. Coronado, R. Georges and *C. J. Gómez-Garcia, Chem. Phys.* **166**, 139 (1992); (b) A. V. Palii, S. M. Ostrovsky B. S. Tsukerblat, New J. Chem. **16** 943 (1992); (c) M. I. Belinskii, Chem. Phys. **173**, 27 (1993); *ibid.* **176**, 15 (1993); (d) J. J. Borrás-Almenar, E. Coronado, R. Georges and C. J. Gómez-Garcia, Chem. Phys. **177**, 15 (1993).
26. (a) N. Casañ-Pastor and L. C. W. Baker, *J. Am. Chem. Soc.* **114**, 10384 (1992); (b) N. Casañ-Pastor and L. C. W. Baker, in Ref. 2, p. 203.
27. (a) J. J. Borrás-Almenar, J. M. Clemente, E. Coronado, R. Georges and B. S. Tsukerblat, J. Mag. Mag. Mater. **140–144**, 197 (1995); (b) J. J. Borrás-Almenar, J. M. Clemente, E. Coronado and B. S. Tsukerblat, Chem. Phys., in press.
28. See D. Gatteschi, L. Pardi, A. L. Barra and A. Müller, in Ref. 2, p. 219.
29. (a) A. L. Barra, D. Gatteschi, B. S. Tsukerblat, J. Doring, A. Müller and L. C. Brunei, Inorg. Chem. **31**, 5132 (1992); (b) D. Gatteschi and B. S. Tsukerblat, Mol. Phys. **79**, 121 (1993); (c) D. Gatteschi, B. S. Tsukerblat, A. L. Barra, L. C. Brunel, A. Müler and J. Doring, Inorg. Chem. **32**, 2114 (1993).
30. J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M. H. Whangbo, *Organic Superconductors, Synthesis, Structure, Properties and Theory,* ed. R. N. Grimes (Prentice Hall, Englewood Cliffs, New Jersey, 1992).
31. L. Ouahab, in Ref. 2, p. 245.
32. (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) D. Attanasio, C. Bellitto, M. Bonamico, V. Fares and P. Imperatori, Gazzeta Chim. Ital. **121**, 155 (1991); (d) S. Triki, L. Ouahab, J. F. Halet, O. Peña. J. Padiou, D. Grandjean, C. Garrigou-Lagrange and P. Delhaès, J. Chem. Soc. Dalton Trans. 1217 (1992).
33. (a) C. J. Gómez-García, E. Coronado, S. Triki, L. Ouahab and P. Delhaes, Synth. Met. **55–57**, 1787 (1993); (b) C. J. Gómez-Garcia, E. Coronado, S. Triki, L. Ouahab and P. Delhaès, Adv. Mater. **4**, 283 (1993).
34. (a) L. Ouahab, M. Bencharif and D. Grandjean, C. R. Acad. Sci. Paris, Série II **307**, 749 (1988); (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).
35. (a) C. Bellitto, M. Bonamico and G. Staulo, Mol. Cryst. Liq. Cryst. **232**, 155 (1993); (b) M. Kurmoo, P. Day and C. Bellitto, Synth. Met., in press.
36. (a) N. F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, New York Philadelphia, 1990); (b) For a detailed description of the RKKY interaction see also J. R. Elliott, *Magnetism,* eds. Rado and Suhl (Academic Press, New York, 1965), Vol IIA, p. 385.
37. (a) M. Lequan, R. M. Lequan, C. Hauw, J. Gaultier, G. Maceno and *P. Delhàes, Synth.* Metals **19**, 409 (1987); (b) T. Mallah, C. Hollis, S. Bott, P. Day M. Kurmoo, Synth. Metals **27**, A381 (1988); (c) T. Mori, P. Wang, K. Imaeda, T.

Enoki, H. Inokuchi. F., Sakai and G. Saito, Synth. Metals **27**, A451 (1988); (d) P. Day, M. Kurmoo, T. Mallah, I. R. Marsden, R. H. Friend, F. L. Pratt, W. Hayes, D. Chasseu, J. Gaultier, G. Bravie and L. Ducasse, J. Am. Chem. Soc. **114**, 10722 (1992); (e) M. Kurmoo, P. Day, M. Allan and R. H. Friend, Mol. Cryst. Liq. Cryst. **234**, 199 (1993).

38. Indirect magnetic interactions in molecular systems have been found to be weak even when the contacts between the magnetic ion and the conducting system are stronger [for example, Cu(phthalocyanine) I, which contains $Cu^{II}$ ions embedded in a conducting column: M. Y. Ogawa, J. Martisen, S. M. Palmer, J. L. Stanton, J. Tamaka, R. L. Greene, B. M. Hoffman and J. A. Ibers, J. Am. Chem. Soc. **109**, 1115 (1987)], or involve genuine bonds [in $[Mn^{II}$ (tpa) (TCNQ) $(CH_3OH)]$ $(TCNQ)_2$. $CH_3CN$, one of the TCNQ ions directly coordinates to the $Mn^{II}$ ion: H. Oshio, E. Ino, I. Mogi and T. Itors, Inorg. Chem. **32**, 5697 (1993)].
39. See for example: (a) M. A. Jensen and H. Suhl, in Ref. 36b, p. 183. (b) T. Matsubara and A. Kotani, *Superconductivity in Magnetic and Exotic Materials*, Springer Series in Solid State Science (Springer-Verlag, Berlin, 1984), Vol. 52, pp 1–211.
40. C. J. Gómez-García, J. J. Borrás-Almenar, E. Coronado, P. Delhaes, C. Garrigou-Lagrange and L. C. W. Baker, Synth. Met. **55–57**, 2027 (1993).
41. (a) C. J. Gómez-García, L. Ouahab, C. Gimenez-Saiz, S. Triki, E. Coronado and P. Delhaès, Angew, Chem. Int. Ed. Engl. **33**, 223 (1994); (b) C. J. Gómez-García, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Ouahab, L. Ducasse and P. Delhaès, Synth. Met., **70**, 783 (1995).
42. A. Davidson, K. Boubekeur, A. Pénicaud, P. Auban, C. Lenoir, P. Batail and G. Herve, J. Chem. Soc., Chem. Commun. 1373 (1989).
43. C. J. Gómez-García, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Le Magueres, L. Ouahab, L. Ducasse, C. Sourisseau and P. Delhàes, Inorg. Chem., in press.
44. (a) E. Coronado, J. R. Galán-Mascaros, C. Gimenez-Saiz, C. J. Gómez-García, S. Triki and P. Delhaes, Mol. Cryst. Liq. Cryst., in press; (b) J. R. Galán-Mascarós, C. Gimenez-Saiz, S. Triki, C. J. Gómez-García, E. Coronado and L. Ouahab, Angew. Chem., in press.
45. A similar polymeric structure for the $Et_3NH^+$ salts of the anions $PCoW_{11}$ and $AsCoW_{11}$ has been suggested by T. J. R. Weakley and H. T. Evans. However, in their case the precision in the structure determinations has been limited by gross disorder of the $Et_3NH^+$ and $H_2O$ (private communication).
46. H. T. Evans, Jr., Perspectives Structural Chem. **4**, 1 (1971).
47. See T. Yamáse, in Ref. 2, p. 337.