Polyoxometalate-Based Molecular Materials

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1. Introduction

Molecule-based materials with active physical properties, in particular electrical, magnetic, and optical, are a focus of contemporary materials chemistry research. Certainly, one reason for this interest has been the realization that these materials can exhibit cooperative properties typically associated with the inorganic network solids, as for example metallic conduction or even superconductivity,[1] ferromagnetism,[2] and nonlinear optical properties.[3]

With respect to the electrical properties, many important achievements were obtained in the 1970s with the discovery of the first molecule-based metal in 1972,[4] namely the π-electron donor–acceptor complex [TTF][TCNQ] (TTF = tetrathiafulvalene, TCNQ = tetracyano-*p*-quinodimethane),[5] and the report of the first molecule-based superconductors in 1979 based on the Bechgaard salts [TMTSF]$_2$X (X = PF$_6^-$, AsF$_6^-$; TMTSF = tetramethyltetraselenafulvalene).[6] The recognition of molecule-based ferromagnetic compounds is more recent and has emerged only in the past decade with the discovery of the electron-transfer salt [Fe^{III}(C$_5$Me$_5$)$_2$]$^+$[TCNE]$^-$ (TCNE = tetracyanoethylene) in 1985.[7] Since these pioneering studies, the two areas—molecule-based metals and magnets—have witnessed rapid development, and many new molecules have been designed which, if assembled in the appropriate manner in the solid, will enable researchers to improve the physical properties by increasing superconducting and ferromagnetic critical temperatures.

A current development in the general area of molecule-based materials is to design, from a wise choice of the constituent molecules, new materials that combine properties not normally associated with a single material. Some intriguing applications of this concept would be to couple conductivity or optical phenomena with magnetic properties. In fact, this challenging goal was proposed[8] in the mid-1980s but has only recently begun to be explored. Efforts in this direction nucleated with the design of hybrid materials formed by two molecular networks, such as anion/cation salts or host/guest solids, where each network furnishes distinct physical properties. In these new types of materials, each network contributes distinct physical properties to the solid. Examples include hybrid molecule-based materials, combining inorganic metal complexes that act as structural or magnetic components with an organic π-electron donor or acceptor molecule that furnishes the pathway for electronic conductivity.[9]

Polyoxometalates have been found to be extremely versatile inorganic building blocks for the construction of the aforementioned functionally active solids.[10] The present article highlights recent results and provides a perspective of the use of polyoxometalates in the construction of molecule-based materials. We present herein the different classes of polyoxometalate-based hybrid materials that are of considerable interest due to their electrical or/and magnetic properties. These are (i) organic/inorganic hybrid salts in which the electron donors are organic molecules of the TTF type, (ii) organometallic/inorganic salts in which the electron donor is the decamethylferrocene complex, and (iii) organic/inorganic films in

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Carlos J. Gómez-García was born in 1964 in Valladolid, Spain. He studied Inorganic Chemistry at the University of Valencia where in 1991 he obtained his doctorate under the supervision of E. Coronado. His thesis concerned the study of magnetic polyoxometalates and their use as inorganic component of radical cations salts with organic donors. From 1993 to 1995 he worked as postdoctoral fellow at the Centre de Recherche Paul Pascal (Bordeaux, France) with Dr. P. Delhaes on the physical properties of molecular conductors. Currently he is an Assistant Professor at the University of Valencia. His research deals with the polyoxometalate chemistry and with molecular materials exhibiting magnetic and electrical properties.

which the polyoxometalates are embedded in conducting organic polymers of the polypyrrole type or films that form well-organized multilayers with amphiphilic organic molecules. In addition, we report other classes of charge-transfer salts in which polyoxometalates are combined with "electroactive" molecular cations that give rise to other distinct properties such as nonlinear optical effects among others.

2. Salts Based upon Polyoxometalates and Organic Donors

2.1. Why Polyoxometalates?

Radical cation salts based on planar π-electron donors of the TTF-type (Chart 1) formulated as [Donor]$_m$X$_n$ are formed by cation radicals that result from the oxidation of the donor and a charge-compensating anion X.[11] Typically, this counterion is a simple inorganic monoanion of the type Cl$^-$, Br$^-$, I$_3^-$, PF$_6^-$, AsF$_6^-$, BF$_4^-$, ClO$_4^-$, or NO$_3^-$. The structures of these salts consist of segregated stacks of the planar radical cations interleaved by the inorganic anions. Of paramount importance for the electrical properties of these low-dimensional solids is the structural dimensionality, as it determines the interdonor interactions, and, thus, the electronic dimensionality. The first generation of organic superconductors were based on the donor molecule tetramethyltetraselenafulvalene (TMTSF), which is a molecule similar to the TTF one (see Chart 1). These salts might be expected to be largely one dimensional (1D) in character, with strong electronic instabilities that give rise in principle to metal−insulator transitions at low temperatures. For example, the PF$_6^-$ salt of this donor undergoes a metal−insulator transition at 12 K which is suppressed through the application of hydrostatic pressure to lead to the first observation of superconductivity below T_c = 1.2 K. A major advance occurred

Chart 1. Organic Donors Used in This Work.
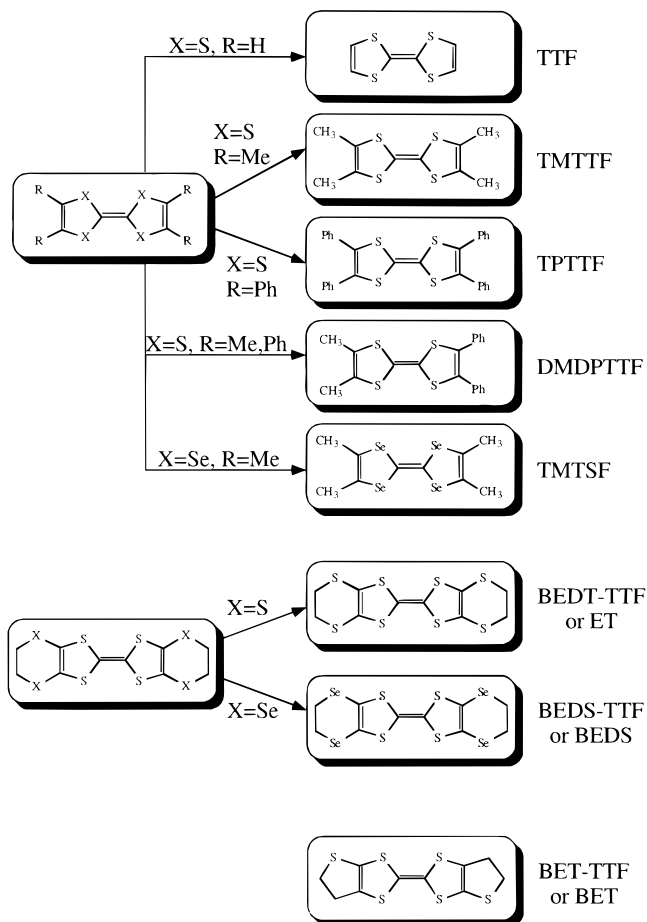
with the discovery of the donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET; see Chart 1) that forms 2D structures with strong interchain S···S interactions. This molecule provided the second generation of organic superconductors by raising T_c by 1 order of magnitude (from 1 to $10-13$ K).[11]

Until recently, the pursuit of higher T_c molecule-based superconductors has focused almost entirely on the design of the organic donor with less efforts being devoted to the identity of the inorganic anion. This situation is rapidly changing, with much attention being devoted to the exploration of the novel lattice architectures and physical properties resulting from the association of organic cation radicals with large molecular anions,[12] or with anions possessing "active" electrons (delocalized frontier orbitals, localized magnetic moments,[13–15] etc.). In this context, polyoxometalates present several characteristics that have made them suitable and attractive as active counterions for new radical cation salts:[16]

(i) They can be made soluble in aqueous and nonaqueous solutions and they maintain their structure in solution as well as in the solid state. These chemical features, and in particular their solubility in polar organic solvents, provide a means to obtain the solid-state associations of these metal-oxide clusters with the organic donors by using the electrocrystallization technique, the method of choice for obtaining single crystals of sufficient quality for structural and physical characterizations.

(ii) These bulky anions have different charges, shapes, and sizes 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 molecules to stack and that of the inorganic clusters to adopt closed-packed lattices. Furthermore, the possibility of varying the anionic charge while maintaining the structure of the polyoxometalate enables the control of the electronic band filling in the resulting salt and, therefore, the physical properties.

(iii) They are electron acceptors which in some cases can be reduced by one or more electrons giving rise to mixed valency clusters. This enables the formation of hybrid materials in which delocalized electrons coexist in both the organic network and the inorganic clusters.

(iv) They can act as ligands that incorporate one or more magnetically active transition metal ions at specific sites of the polyoxoanion structure. The introduction of magnetic character into the polyanion can produce novel materials in which delocalized electrons coexist with localized magnetic moments, thus affording the opportunity for the investigation of molecular systems combining magnetic and conducting properties.

In the following sections we review the range of known radical cation salts with polyoxometalates, with emphasis on the unusual structural and electronic effects induced by the presence of these bulky and electronically active anions on the organic component. We divide the presentation in three parts.

In the first part, we report on the radical cation salts based on TTF and other related donors having tendency to afford 1D packings. In the second and third parts, the radical salts based on ET and other more extended donors leading to 2D packings are discussed. The donor molecules that have been used in these studies are summarized in Chart 1.

2.2. TTF Salts

Previous examples of organic donor–polyoxometalate salts were obtained by combining TTF with polyanions exhibiting the α-Keggin or Lindqvist structures (Figure 1).[17] More recently other polyoxo-
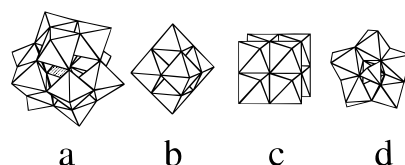

Figure 1. Polyoxometalates used in the synthesis of TTF-based radical salts: (a) Keggin anion; (b) Lindqvist anion; (c) β-octamolybdate anion β-$[Mo_8O_{26}]^{4-}$; and (d) $[S_2Mo_5O_{23}]^{4-}$ anion.

metalates have also been successfully used (see Figure 1). In Chart 2 we summarize the TTF-type radical salts that are produced from this combination.

Chart 2. Organic/Inorganic Hybrid Salts Obtained from Polyoxometalates and TTF-type Organic Donors.
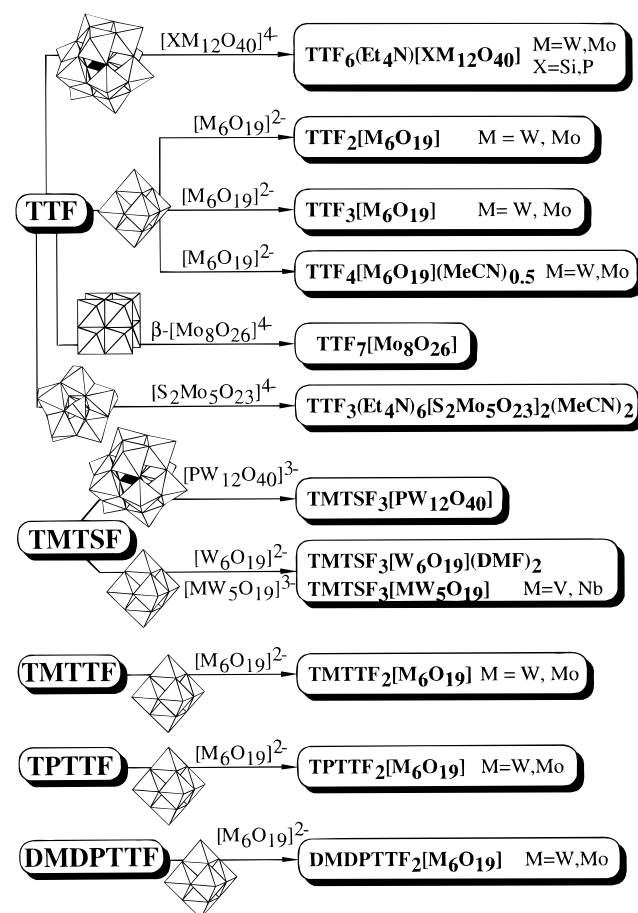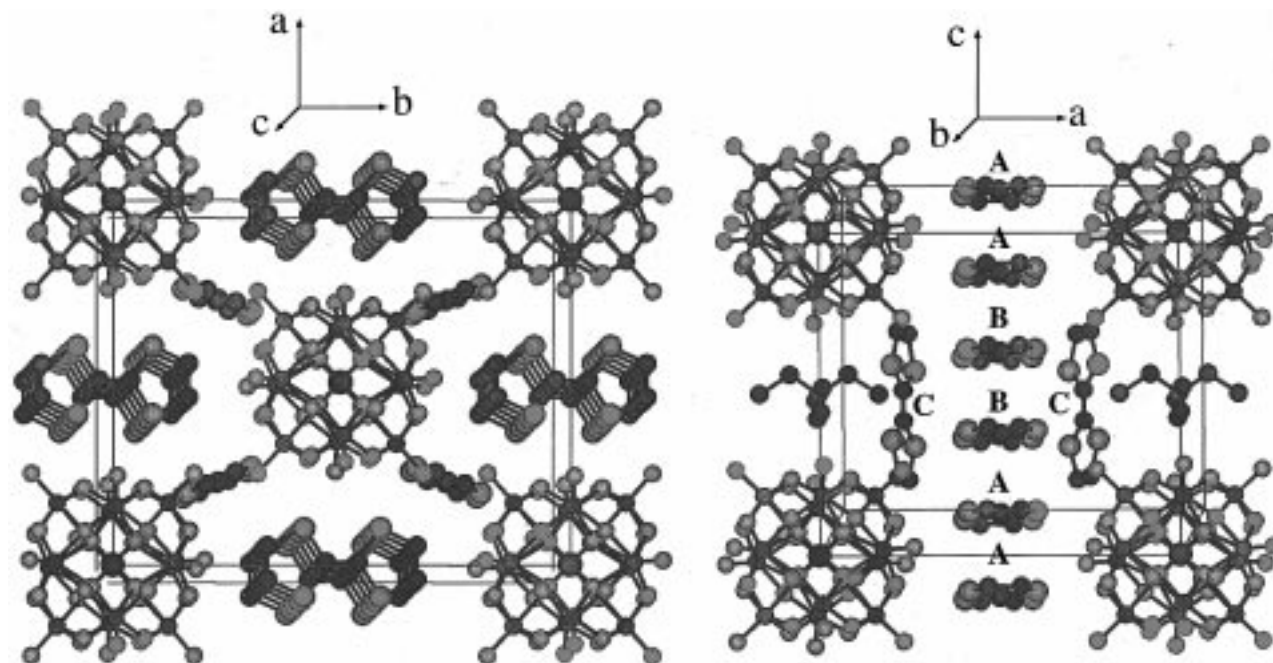
Figure 2. Structure of the series $[TTF]_6[XM_{12}O_{40}](NEt_4)$ (M = W, Mo; X = P, Si). Projections of the structure down to the *ab* (left) and *ac* (right) planes showing the TTF chains and the channels created by the polyoxometalates and by the C-type organic molecules. A, B, and C refer to the three types of TTF molecules.

2.2.1. Keggin Anions

The ability of large inorganic clusters such as $[Mo_6Cl_{14}]^{2-}$ or $[Re_6Se_5Cl_9]^-$ to form organic–inorganic salts based on TTF-type donors was first demonstrated by Batail et al.[18] in 1984. This work was subsequently extended to simple polyoxometalate clusters by Ouahab et al.[19] In 1988 these authors reported the preparation and structure of a compound consisting of TTF and the one electron reduced phosphotungstate Keggin anion, $[PW_{12}O_{40}],^{4-}$ in a stoichiometry of 6:1. Later other Keggin anions were used by these authors[20] and by Bellitto et al.[21] to obtain a series of radical cation salts $[TTF]_6[XM_{12}O_{40}]$-(NEt_4) (NEt_4^+ = tetraethylammonium; M = W, Mo; X = P, Si). These salts consist of one-dimensional eclipsed chains of TTF cations lying in the channels created by $[XM_{12}O_{40}]$ units and two isolated neutral TTF molecules (Figure 2). The organic stack is formed by two independent TTF molecules (A and B) arranged according to the sequence ...AABBAA... in such a way that the two A-type molecules are surrounded by four polyoxoanions while the two B-type molecules are surrounded by four neutral TTF molecules (C).

A feature that distinguishes the radical cation salts containing polyoxometalates or other mixed-valence anions from the radical salts with simple inorganic anions is the difficulty in assessing the charge distribution. Thus, due to the ability of the polyoxoanion to accept electrons or to trap protons, the charge on the inorganic component is not always trivial to determine. In this situation the electronic band filling of the organic component may be ambiguous. In the present case this feature has led to propose two different charge distributions for this series. Ouahab *et al.*[20b] proposed the general formula $[TTF]_2^0[TTF_4]^{2+}(NEt_4)^+(H)^+[XM_{12}O_{40}].^{4-}$ In the former

formulation the anions were assumed to be a total charge of 4− in order to be consistent with the magnetic and EPR measurements which indicated that the phosphometalate anions were fully reduced by one electron. To explain the diamagnetic properties of the silicometalate-containing salts, these authors uniformly distributed two positive charges over the four TTF molecules in the chain, giving rise to a half-filled band for the chain. This necessitates the presence of a proton per formula unit to compensate for charges. In turn, Bellitto et al.[22] proposed the formula $[TTF_2]^0[TTF_4]^{3+}(NEt_4)^+[PMo_{12}O_{40}].^{4-}$ The main difference is that now the proton is not required since the charge over the tetrameric TTF unit is (3+) distributed according to the scheme: ...(D^+D^+)-$(D^{0.5+}D^{0.5+})(D^+D^+)$.... Such inhomogeneous charge distribution was postulated on the basis of the resonance Raman and low-temperature infrared spectra since some normal modes of the TTF molecule are sensitive to its degree of ionicity. The different points of view of the two groups notwithstanding, both agree with the presence of a mixed-valence state in the organic chain and also in the phosphometalate Keggin anions. Therefore, this series provides good examples of organic donor–polyoxometalate acceptor compounds where *mixed-valence states coexist in the two molecular components*.

In addition to the formulation of the compounds it is important to understand the electrical properties of these compounds. According to the charge distributions proposed in the mixed-valence chains, all the bands are not filled and, therefore, an electron delocalization leading to a metallic behavior would be expected. However, the compounds behave as semiconductors with very low conductivities at room temperature (between 10^{-4} and 5×10^{-2} S cm^{-1}). This electron localization has been attributed to the
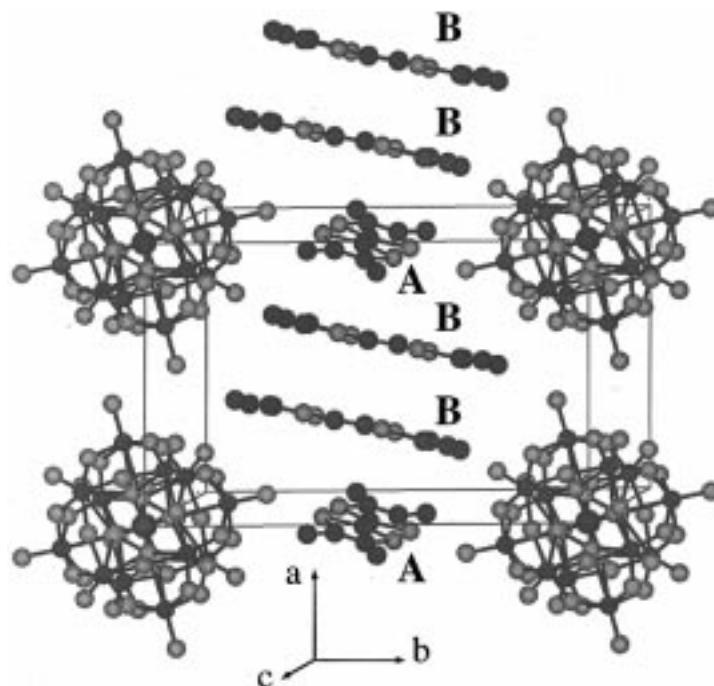
Figure 3. View of the molecular packing of [TMTSF]$_3$[PMo$_{12}$O$_{40}$] projected in the *ab* plane showing the criss-cross-type arrangement of the two types of TMTSF molecules (A and B in the figure).

combined effect of a weak tetramerization of the chains due to its 1D character (Peierls-like distortion) and of the interactions with localized charges and spins on the large polyoxoanions. In fact, A- and B-type TTF molecules that form the organic chains have different electrostatic interactions with the anions. This tends to localize the charges of the organic chain. As will be apparent from the examples provided in this article, strong electrostatic interactions produced by the *high charges* of the polyanions are a general feature in the polyoxometalate-containing radical salts that will make it difficult to achieve high electrical conductivities and metallic behaviors for these materials.

Apart from the above series, a salt of the TMTSF donor with the phosphododecatungstate anion has been reported which can be formulated as [TMTSF]$_3$-[PMo$_{12}$O$_{40}$].[23] The organic packing consists of chains of fully oxidized TMTSF molecular cations parallel to the *a* axis of the monoclinic cell. These chains display a criss-cross-type arrangement formed by alternating dimers and monomers (Figure 3). No physical properties have been reported for this compound, although in view of the lack of mixed valency in the organic component, the compound is most likely an insulator.

2.2.2. Lindqvist Anions

The combination of the Lindqvist anions [M$_6$O$_{19}$]$^{2-}$ (M = W, Mo) with TTF and related donors has given rise to several crystalline phases with stoichiometries of 2:1, 3:1, and 4:1 for the donor:anion. The first reported phase is the 3:1 series, which was studied independently by the groups of Ouahab[24] and Bellitto[25] who used TTF and TMTSF donors. Three different compounds belonging to this phase are known, namely [TTF]$_3$[W$_6$O$_{19}$], [TTF]$_3$[Mo$_6$O$_{19}$], and [TMTSF]$_3$[W$_6$O$_{19}$](DMF)$_2$ (DMF = *N,N*-dimethyl-

formamide). The X-ray structures of the two tungsten derivatives were reported by Ouahab et al.,[24a] while the structure of the molybdenum derivative, which is isostructural to that of the tungsten one, was reported by Bellitto et al.[25a] All of the compounds contain two independent organic molecules, A and B, that stack to form a chain of trimers ...BAB···BAB... with strong intratrimer S···S contacts that fill the channels formed by the hexametalate dianions (Figure 4). In the TTF salts the organic molecules exhibit a criss-cross arrangement inside the trimers, similar to that reported in [TMTSF]$_3$[PMo$_{12}$O$_{40}$], leading to strong overlaps between the 3p sulfur orbitals, with the intertrimer S···S overlaps being quite negligible (the S–S distances are longer than the van der Waals distances). In contrast, the molecules in the TMTSF salt overlap in a zigzag fashion, leading to very strong intertrimer Se···Se contacts (shorter than those observed in the Bechgaard salts) and to weak intertrimer contacts (the Se···Se distances are in the range of the van der Waals distances).

In view of the 3:1 stoichiometry of these salts, the organic part should be in a mixed-valence state. In fact, extended Hückel molecular calculations performed on the BAB trimers[24b] have predicted that two positive charges are distributed over the three organic molecules in such a way that a charge of +0.5 can be assigned to the two outside B molecules, while the central A molecule bears a charge of +1. Such charge distribution is in agreement with the differences observed in the interatomic TTF distances between A- and B-type molecules.[25b] The most convincing experimental evidence for mixed valency in these salts, however, comes from the optical properties (IR–vis) in the near-IR region which reveal the "so-called" A band (at ∼6000 cm^{-1} and ∼4000 cm^{-1} in the TTF and TMTSF salts, respectively), which is typical of a mixed-valence system.

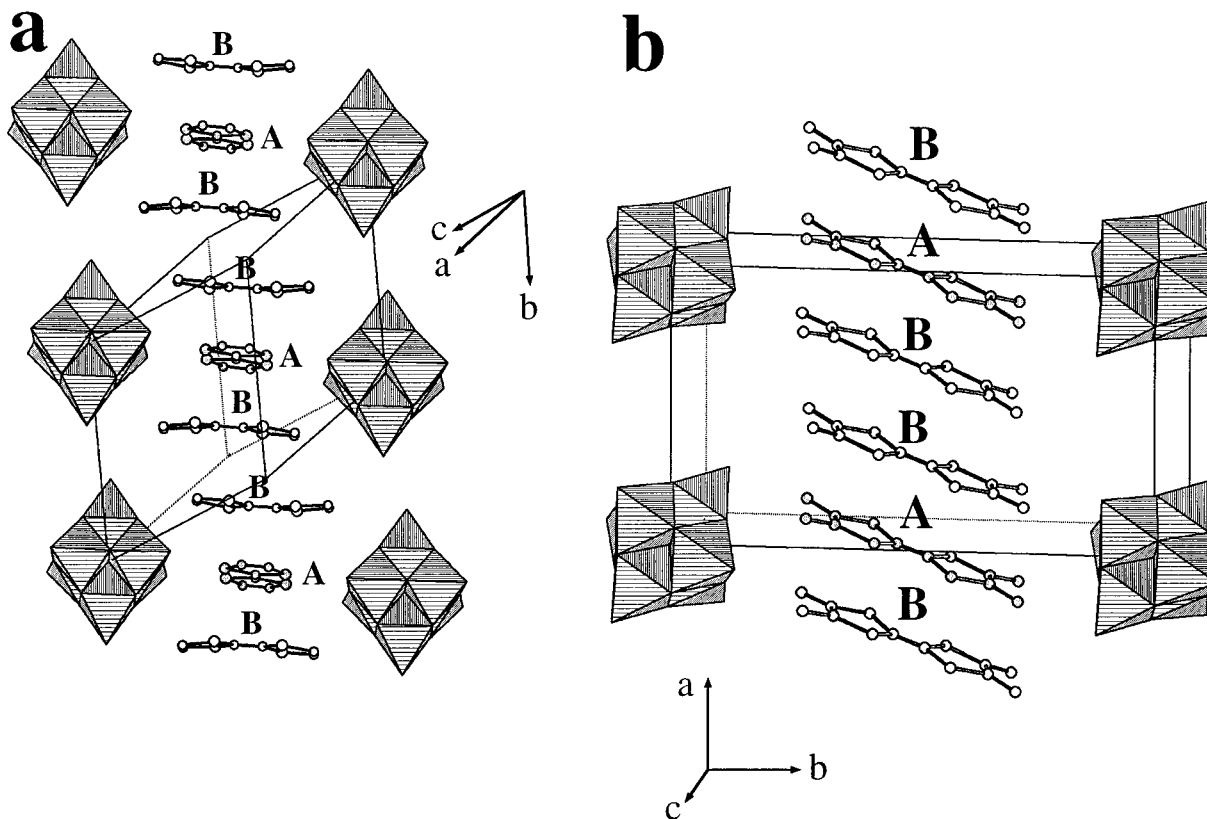**Figure 4.** Structures of the 3:1 radical salts of TTF and TMTSF with Lindqvist anions: (a) $[TTF]_3[M_6O_{19}]$ (M = W, Mo) and (b) $[TMTSF]_3[W_6O_{19}](DMF)_2$.

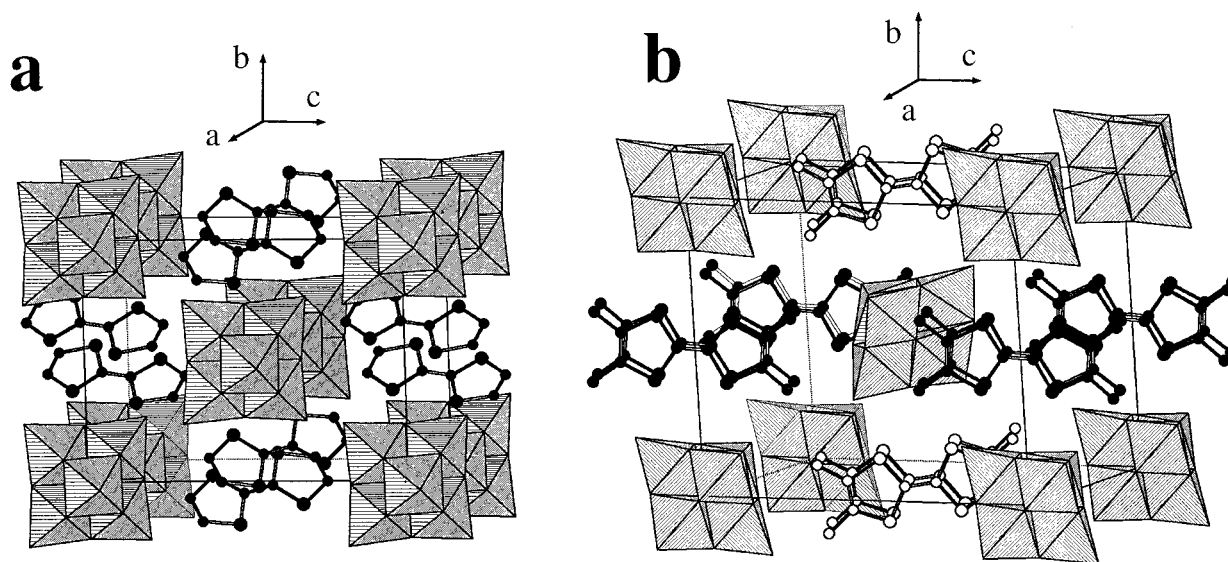**Figure 5.** Structures of the 2:1 radical salts of TTF and TMTTF with Lindqvist anions: (a) $[TTF]_2[M_6O_{19}]$ (M = W, Mo) and (b) $[TMTTF]_2[M_6O_{19}]$ (M = W, Mo).

All of these compounds are semiconductors with conductivities at room temperature of $\sim 10^{-3}$ S cm^{-1} and an activation energy of 0.2 eV (measured for the TMTSF salt), as expected from the localization effect induced by the presence of two different organic molecules and by the trimerized chain arrangements. Band calculations confirm the semiconducting behavior and predict a bandgap of $\sim$0.45 eV in the TTF derivatives and $\sim$0.14 eV in the TMTSF salt in accordance with the electrical properties.[24b] The possibility of varying the electronic band filling in the resulting salt by changing the charge of the polyoxo-

metalate anion has been illustrated in the TMTSF system. By changing the dianion $[W_6O_{19}]^{2-}$ by the trianion $[M^VW_5O_{19}]^{3-}$ (M^V=V, Nb), the organic portion reverts from a mixed-valence state to a completely ionized state. As expected, the electrical properties change from semiconducting to insulating.[26]

The remaining crystalline phases were obtained by slightly varying the experimental conditions (polyoxometalate salt, solvent, intensity of the current, etc.). Thus, if the electrocrystallization is carried out by using the *n*-tetrabutylammonium salt of the
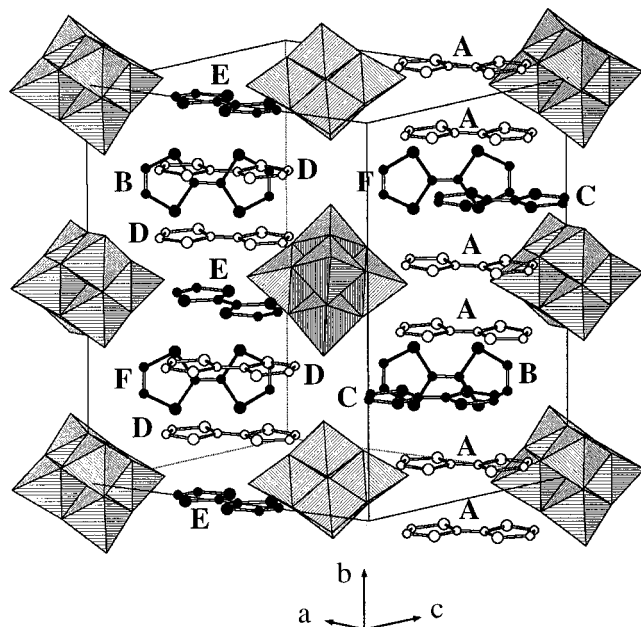
Figure 6. Structure of the 4:1 radical salt of TTF with the Lindqvist anion $[W_6O_{19}]$:$^{2-}$ $[TTF]_4[W_6O_{19}]\cdot0.5(MeCN)$. The six different types of TTF molecules are indicated (A–F).

Lindqvist polyanion instead of the tetraethylammonium derivative, the 2:1 phase $[TTF]_2[M_6O_{19}]$ (M = W, Mo) is mainly isolated.[25] Other 2:1 phases have been reported for the substituted TTF donors TMTTF (tetramethyl-TTF),[27] TPhTTF (tetraphenyl-TTF),[28] and the DMDPhTTF (dimethyldiphenyl-TTF).[29] The 4:1 phase crystallizes as an acetonitrile solvate salt[30] and can be formulated as $[TTF]_4[W_6O_{19}]\cdot0.5(MeCN)$. Structures of the 2:1 phases do not show chains as in the 3:1 stoichiometry but rather isolated dimers of radical cations interspersed with the polyanions

(Figure 5). Accordingly these phases are diamagnetic insulators. Interestingly the fact that the dimers are fairly well isolated renders these compounds suitable as model systems for studying the coupling of electrons with molecular motions in radical salts of TTF.[31] The 4:1 salt is an insulator formed by organic chains of dimers separated by isolated molecules (Figure 6). What is unusual in this salt, compared with the cation radical salts containing simple inorganic anions, is the presence of up to *six independent TTF molecules.*

2.2.3. Other Anions: the Polyoxomolybdates β-$[Mo_8O_{26}]^{4-}$ and $[S_2Mo_5O_{23}]^{4-}$

To explore the influence of the shape of the inorganic polyoxoanion on the packing of the organic network, we have used the anions β-$[Mo_8O_{26}]^{4-}$ and $[S_2Mo_5O_{23}]^{4-}$ (Figure 1c,d). The former one possesses an elongated shape, while the latter one has a planar disk shape. The unusual structural and electronic properties induced by polyoxometalates in the TTF radical salts are exemplified by the compound $[TTF]_7$-$[Mo_8O_{26}]$.[32] Thus, from the structural point of view this compound exhibits an *irregular chain packing* formed by *four independent TTF molecules* which are distributed according to the sequence ...−C−A−B−B−A−C−D-... (Figure 7). A remarkable structural result is the presence of *strong interchain interactions* through the sulfur atoms of TTF molecules, giving rise to an increase of the organic dimensionality. This is quite unusual for a TTF radical salt, which, at best tends to form 1D packings with negligible interchain interactions. From the electronic point of view, the four positive charges required to compensate the polyanion charge are distributed over the seven TTF molecules in an *inhomogeneous* way. We find that the TTF molecules closer to the polyoxoanions are

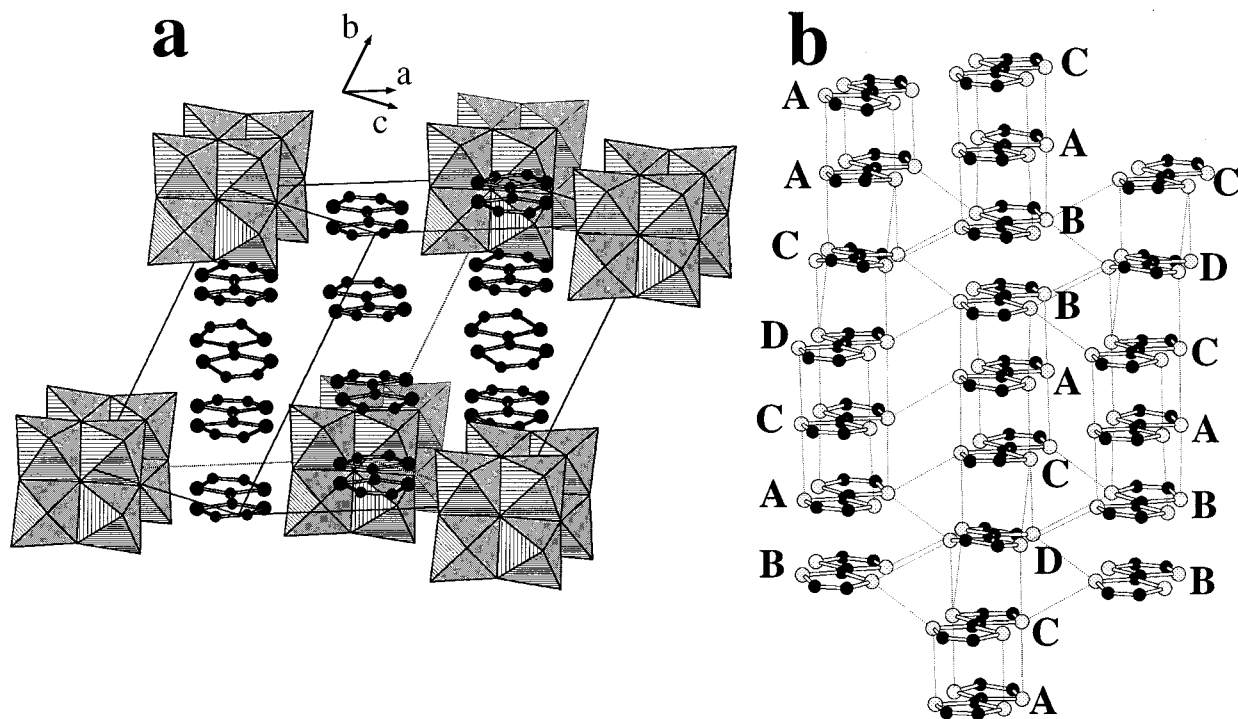**Figure 7.** Structure of the radical salt $[TTF]_7[Mo_8O_{26}]$: (a) unit cell and (b) molecular packing of the organic part showing the strong interchain connections and the four different types of TTF molecules (A–D).
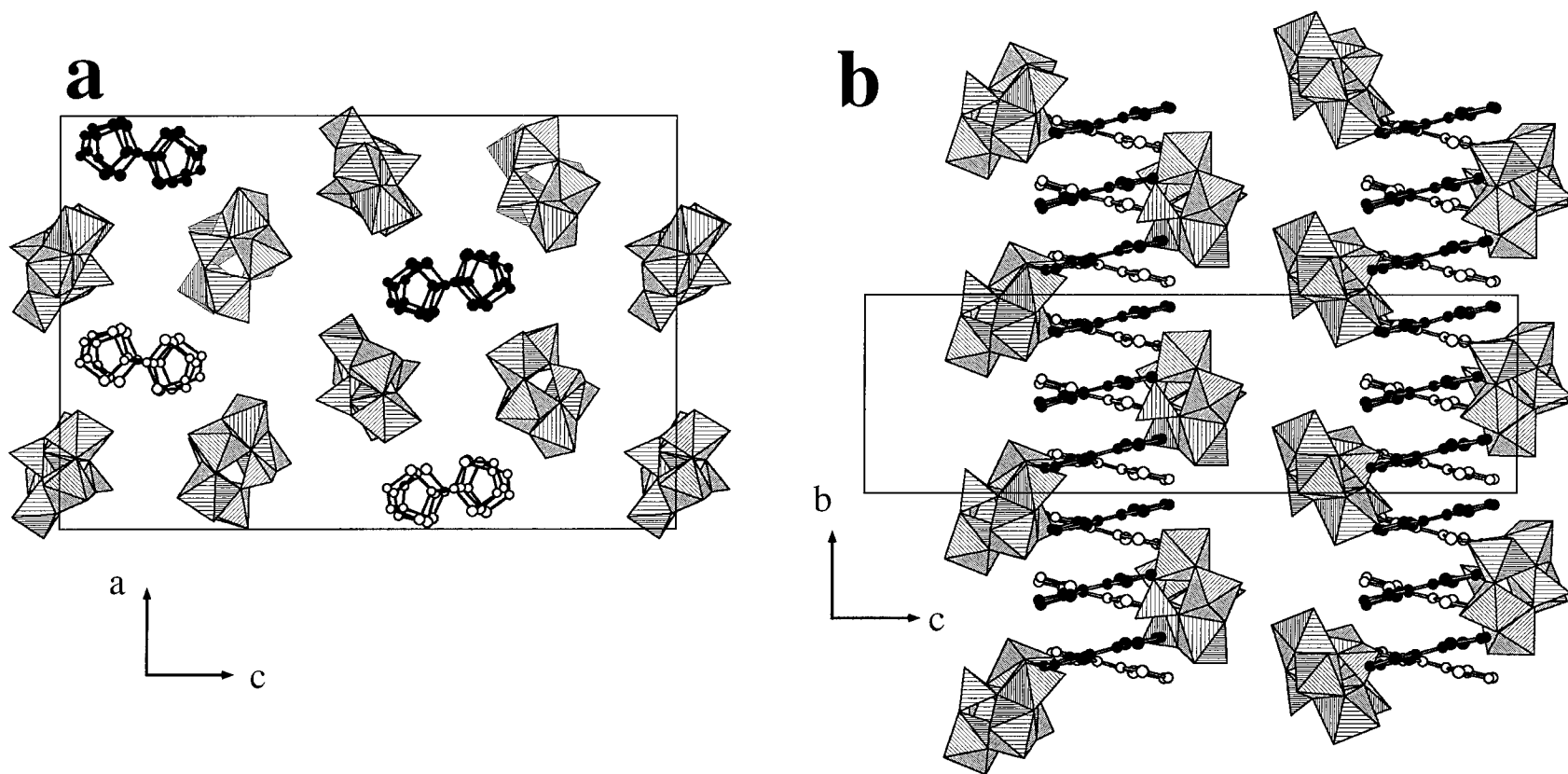
Figure 8. Structure of the radical salt [TTF]$_3$[S$_2$Mo$_5$O$_{23}$]$_2$((NMe$_4$)$_6$·2MeCN showing the channels created by the polyanions (a) and the TTF chains (b).

almost completely charged (A type in the figure), while the others are almost neutral (B and D types) or possess intermediate charge (C type). This effect tends to reduce the electron delocalization in this mixed-valence system and accounts for the semiconducting character of the compound ($\sigma \approx 10^{-3}$ S cm^{-1} at room temperature (activation energy $E_a \approx 0.7$ eV)).

The use of the $[S_2Mo_5O_{23}]^{4-}$ anion has allowed for the synthesis of a new radical salt formulated as $[TTF]_3[S_2Mo_5O_{23}]_2(NMe_4)_6 \cdot 2MeCN$ (NMe_4^+ = tetramethylammonium).[33] The most significant structural feature of this compound is that the polyanions and NMe_4^+ cations comprise layers which form channels in which the TTF molecules reside (Figure 8). As a result, the TTF chains are well isolated, in contrast to the previous example. These chains contain *three independent TTF molecules* arranged in trimers ...ABC... which are in a mixed-valence state (two positive charges distributed over three TTF molecules). The central molecule (B type), which is expected to exhibit the largest degree of ionization, is in fact closest to the polyanions.

2.3. BEDT-TTF Salts

The ET donor has been the most widely used molecule in the synthesis of molecular superconductors.[11] The crystal structures of the cation radical salts usually consist of alternating layers of the organic donor and anions. Depending on the packing adopted by the ETs in these layers, up to five different phases, namely α, β, θ, δ, and κ, are commonly encountered with simple anions. These are depicted schematically in Figure 9. Although the use of this organic donor in the preparation of polyoxometalate-based materials is quite recent, many examples have already been reported with polyoxometalates having increasing metal nuclearities (from 6 to 22; see Figure 10) and magnetic moments. The most significant results are summarized in Chart 3.

2.3.1. Lindqvist Anions

The Lindqvist polyoxometalates (Figure 10a) form various types of ET radical salts with stoichiometries such as 2:1, 5:1, and 6:1, although only the 2:1 and 5:1 phases have been structurally characterized. The 2:1 phase is obtained from the unsubstituted dianions $[M_6O_{19}]^{2-}$ (M = W, Mo).[34] Its structure is built by alternating organic and inorganic layers. The organic layer is formed by an orthogonal arrangement

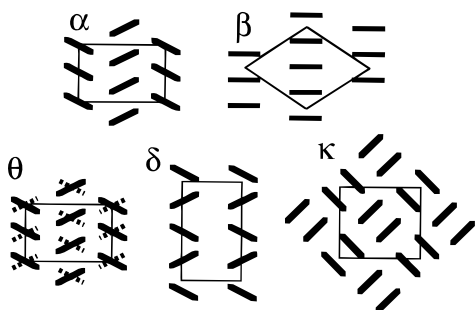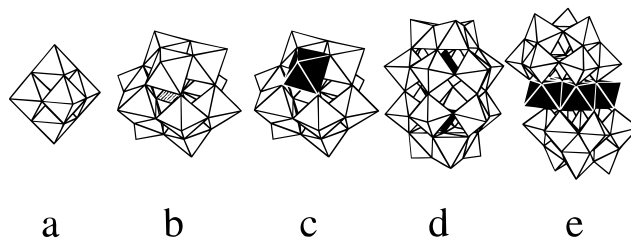**Figure 10.** Different polyoxometalates used in the synthesis of ET-based radical salts: (a) Lindqvist anions, $[M_6O_{19}]^{2-}$ (M = W, Mo), $[VW_5O_{19}]^{3-}$, $[V_2W_4O_{19}]^{4-}$; (b) nonsubstituted Keggin anions, $[PW_{12}O_{40}]^{4-}$ and $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (X = 2(H$^+$), Zn^{II}, B^{III}, Si^{IV}, Cu^{II}, Co^{II}, Fe^{III}); (c) monosubstituted Keggin anions, $[X^{n+}Z^{m+}(H_2O)M_{11}O_{39}]^{(12-n-m)-}$ (X = P^V, Si^{IV}; M = Mo^{VI}, W^{VI}; Z = Fe^{III}, Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}); (d) Dawson–Wells anion: $[P_2W_{18}O_{62}]^{6-}$; (e) the polyoxometalate $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ containing the tetrameric magnetic cluster M_4O_{16} (M = Co^{2+}, Mn^{2+} in black).

Chart 3. Organic/Inorganic Hybrid Salts Obtained from Polyoxometalates and BEDT-TTF-type Organic Donors.
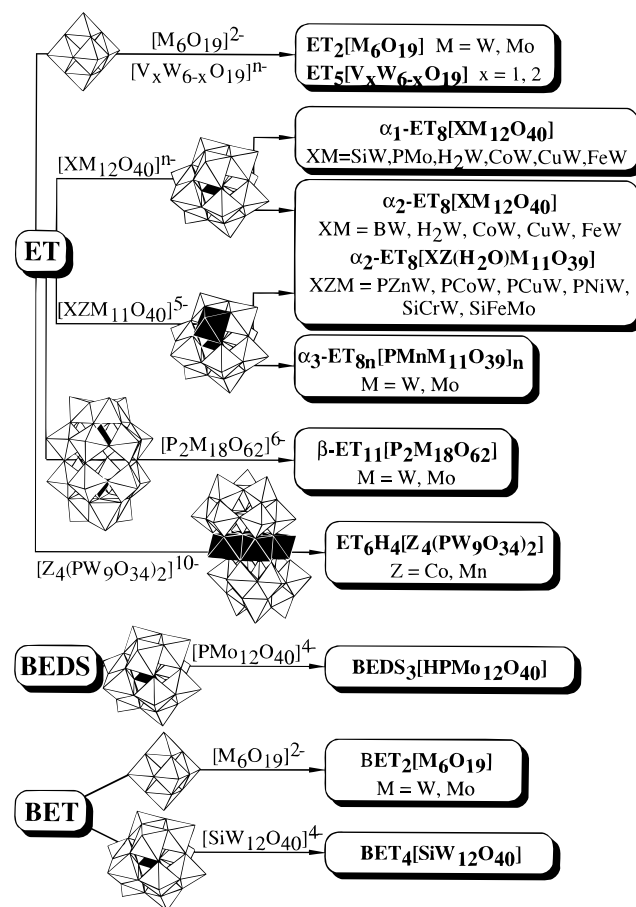
of organic dimers $(ET^{\cdot+})_2$ with short intradimer and interdimer contacts (Figure 11). Such arrangement is reminiscent of that observed in the superconducting κ-phases. However, the ETs are fully ionized (charge of +1) and the salts are electrical insulators. More interesting from the physical point of view is the 5:1 phase[35] obtained from the mixed-metal Lindqvist anions $[VW_5O_{19}]^{3-}$ and $[V_2W_4O_{19}]^{4-}$. The two resulting compounds are isostructural and can be formulated as $[ET]_5[VW_5O_{19}] \cdot 5H_2O$ and $[ET]_5[V_2W_4O_{19}] \cdot 5H_2O$. The inorganic layers are formed by

Figure 9. Most common organic packings adopted by the ET radical salts.
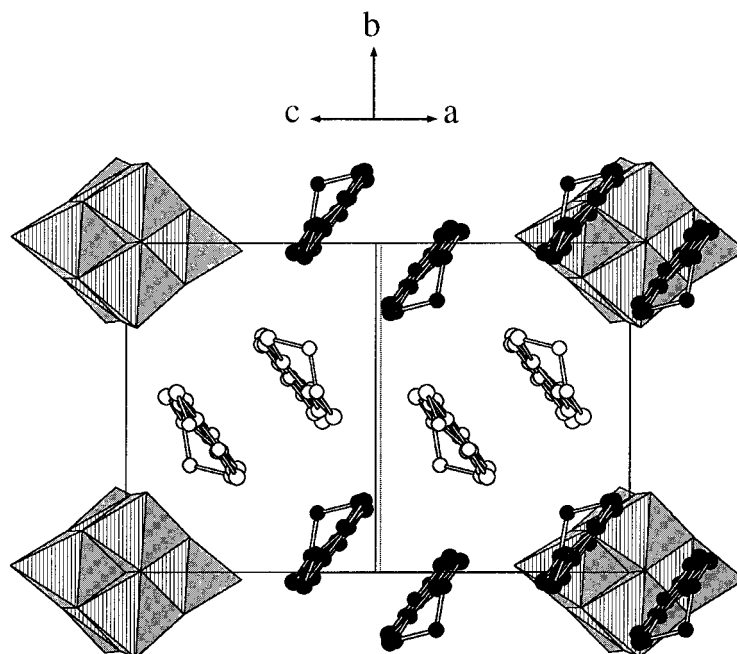
Figure 11. Structure of the 2:1 radical salts of ET with Lindqvist anions: $[ET]_2[M_6O_{19}]$ (M = W, Mo).

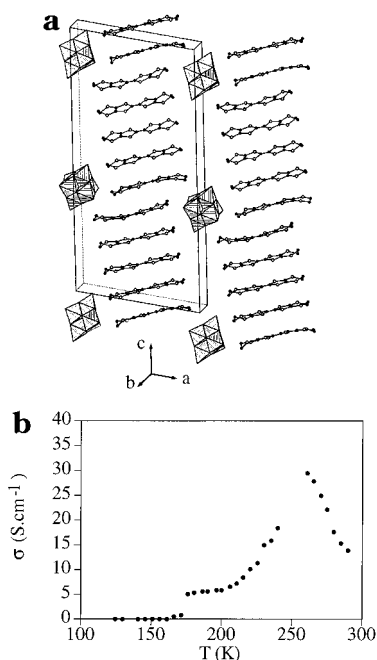**Figure 12.** The 5:1 radical salts of ET with Lindqvist anions: (a) structure of the $[ET]_5[VW_5O_{19}] \cdot 5H_2O$ and $[ET]_5$-$[V_2W_4O_{19}] \cdot 5H_2O$ salts and (b) single-crystal electrical conductivity of $[ET]_5[VW_5O_{19}] \cdot 5H_2O$.

the Lindqvist anions and the water molecules and the organic layers are generated by five independent ET molecules (A–E) that form chains along the c axis with short interchain chalcogen⋯chalcogen contacts (Figure 12a). These compounds exhibit a metallic behavior (Figure 12b) with conductivities that increase upon cooling from 14 S cm^{-1} at room temperature to reach a maximum value of ∼ 30 S cm^{-1} at 250 K. Below this temperature a metal–insulator transition occurs which has been attributed to cracks on the single crystals resulting from a loss of water molecules. This result demonstrates that due to the increase in the electronic dimensionality when pass-

ing from TTF to ET salts, higher conductivities and a *metallic-like behavior* can be obtained in radical salts containing polyoxometalates, despite the localization effect caused by the presence of different organic molecules in the crystal.

2.3.2. Keggin Anions

The ability of the Keggin structure to accommodate magnetic centers has prompted their use in molecule-based materials with coexistence of localized and delocalized electrons. Before presenting the most relevant results obtained in this context, it is of interest to point out the general reasons that justify the intense effort currently being devoted to this type of solids.

The first reason is related with the possibility of obtaining a *molecule-based conducting ferromagnet* 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, and presents an oscillatory behavior which can give rise alternatively to ferro- or antiferromagnetic couplings, depending on the distance between moments. This interaction was proposed in order to explain the ferromagnetism in some metals and alloys of the d and f blocks. In these cases the exchange mechanism involves a very strong intraatomic coupling between the conduction electrons (which are mainly of s character) and the localized d or f unpaired electrons. This direct coupling induces a large spin polarization of the conduction electrons, which spreads over relatively long distances, leading to an effective indirect coupling between the localized magnetic moments. In the field of molecule-based materials, an indirect-type interaction can also be imagined wherein the localized d electrons and the conduction π electrons are exchange coupled[37] (Figure 13). However, this in-
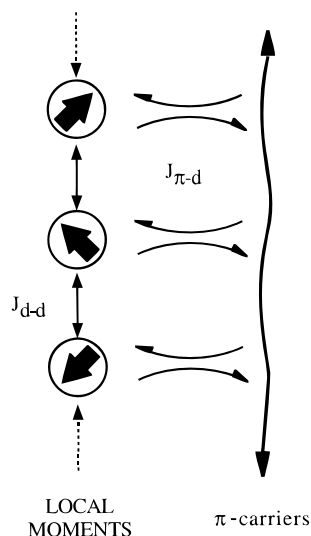
Figure 13. Mechanism for an indirect coupling between the local spins via the conduction electrons in a hybrid material formed by π-electron organic donors and inorganic magnetic complexes. J_{d-d} represents the indirect coupling between the magnetic moments located at the d-transition metal ions; $J_{\pi-d}$ represents the direct coupling between the localized spins and the itinerant electrons.

teraction is expected to be significantly different from that occurring in the inorganic classical metals both in terms of the nature and strength of the phenomenon. Thus, most often the interaction between localized and conduction electrons involves a d−π intermolecular exchange coupling which must be several orders of magnitude smaller than the intra-atomic d−s or f−s exchange coupling occurring in inorganic metals. As a consequence, the resulting indirect interactions between the localized d electrons are expected to be extremely weak in the molecular systems.[38] On the other hand, the electron correlation effects are much more important in the molecular metals than in the inorganic ones, and therefore, the RKKY free electron model may be a too crude approach to account for the indirect exchange interactions occurring in these hybrid materials. This indirect mechanism has been recently proposed in order to account for the weak intermetallic couplings found in conducting molecular materials formed by organic donors and magnetic anions of the type $[MX_4]^{n-}$ (M = Fe^{III}, Cu^{II}, Co^{II}, Mn^{II}; X = Cl^-, Br^-).[39] In some cases these kinds of compounds have been observed to exhibit unusual electrical or magnetic phase transitions.[15,40]

The second reason for the interest in molecule-based materials that contain both localized and delocalized electrons is related to the possibility of creating compounds with coexistence of cooperative magnetic and electrical properties such as *ferromagnetism and superconductivity*. These two properties might normally be considered to be mutually exclusive. The weak interactions between localized and delocalized electron sublattices found in the molecule-based materials, which in the previous case were a drawback, can now become beneficial for enabling this simultaneous coexistence. Although materials of this kind have not been discovered thus far, a striking example of the combination of superconduc-

tivity in an ET lattice with paramagnetism arising from the magnetic moments localized on the anion complexes $[M^{III}(ox)_3]^{3-}$ (M^{III} = Fe, Cr; ox = oxalato dianion), has been recently reported in the $[ET]_4$-$(H_2O)[M(ox)_3]\cdot C_6H_5CN$ radical salts.[14]

2.3.2.1. BEDT-TTF Salts with Nonsubstituted α-Keggin Anions. The ability of the Keggin anions to be combined with ET molecules was first demonstrated in 1989 by Batail et al.[41] By electrochemical oxidation of ET in the presence of α-$[SiW_{12}O_{40}]^{4-}$ these authors obtained a radical cation salt formulated as $[ET]_8[SiW_{12}O_{40}]$. With the aim of studying the effect of the anion charge on the electrical properties, and of introducing a magnetic character in the polyoxoanion, we have used other nonsubstituted α-Keggin anions of the type $[X^{n+}W_{12}O_{40}]^{(8-n)-}$ (abbreviated as $[XW_{12}]$, Figure 10b). As a result, an extensive series of radical salts has been prepared having the general formula $[ET]_8[XW_{12}O_{40}](solv)_n$ (solv = H_2O, MeCN) where the central tetrahedral XO_4 site may contain a diamagnetic heteroatom ($2(H^+)$, Zn^{II}, B^{III}, and Si^{IV}) or a paramagnetic one (Cu^{II}, Co^{II}, Fe^{III}, etc.).[42] This series constitutes the first examples of hybrid materials based on polyoxometalates in which *localized magnetic moments and itinerant electrons coexist in the two molecular networks.*

The compounds crystallize in two closely related structure types namely α_1 and α_2 consisting of alternating layers the inorganic Keggin anions forming close-packed pseudohexagonal layers in the *ac* plane, and ET radicals with an α-packing mode (Figure 14). In the organic layers there are three (α_1 phase) or two (α_2 phase) crystallographically independent ET molecules which form two types of stacks: a dimerized chain and an eclipsed one. The shortest interchains S···S distances, ranging from 3.46 to 3.52 Å, are significantly shorter than the intrachains ones (from 3.86 to 4.04 Å), emphasizing the two-dimensional nature of the packing. Another important feature of this structure is the presence of short contacts between the organic and the inorganic layers which involve the S atoms of the eclipsed chains and some terminal O atoms of the polyoxoanions (3.15 Å) as well as hydrogen bonds between the ethylene groups of the ET molecules and several O atoms of the anions (3.13 Å).

From the electronic point of view, an inhomogeneous charge distribution in the organic layer was found by Raman spectroscopy, in which the eclipsed chain is formed by almost completely ionized $(ET)^{\bullet+}$ ions, while the dimerized chain contains partially charged ETs. This charge distribution accounts for the electrical and magnetic properties of these salts. All of these salts exhibit semiconducting behavior ($\sigma_{RT} \approx 10^{-1}-10^{-2}$ S cm^{-1} and $E_a \approx 100-150$ meV), independent of the charge in the organic sublattice (see inset in Figure 15). Notice that band calculations predict a semiconducting behavior when the charge is +4 or +6 (as in the Si^{IV}, Co^{II}, Cu^{II}, and $2(H^+)$ derivatives), and a metallic character when the charge is +5 (as in the Fe^{III} and B^{III} derivatives). This disagreement is related to the existence of different ETs in the solid, which leads to different site energies
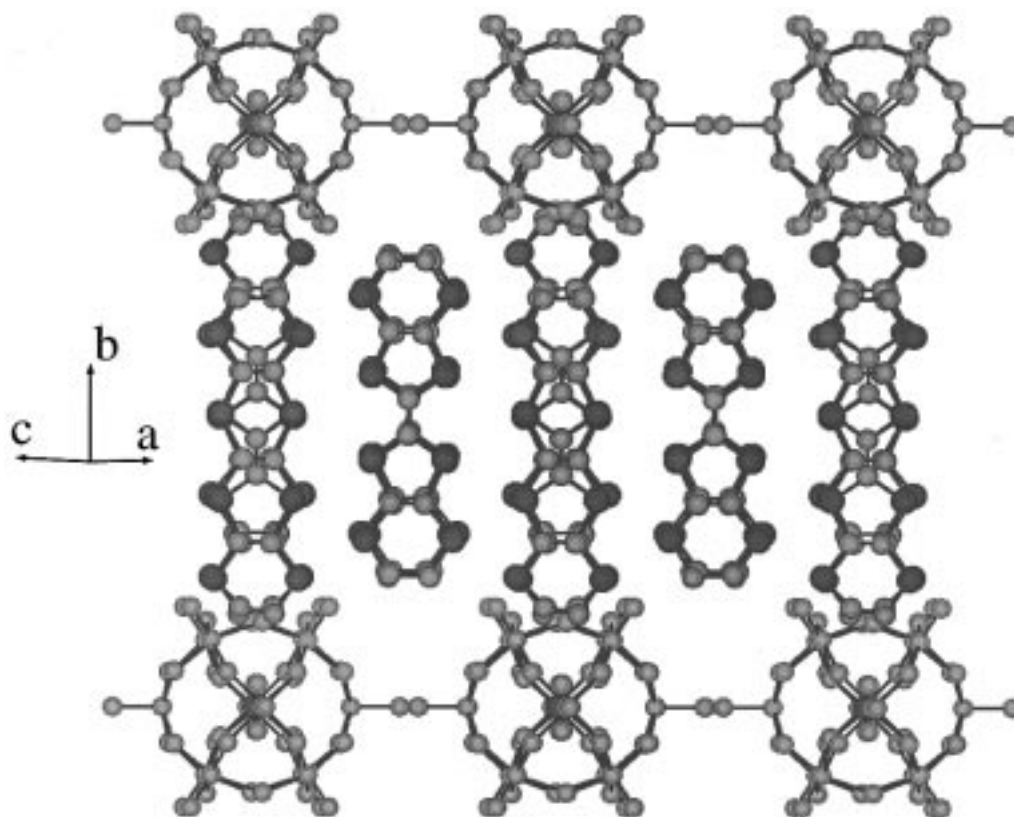
Figure 14. Structure of the radical salts $[ET]_8[XW_{12}O_{40}]$ ($X = Co^{II}$, Cu^{II}, Fe^{III}, $2(H^+)$, Si^{IV}, and B^{III}) showing the layers of Keggin polyoxoanions and the two types of stacks, eclipsed, and dimerized, in the organic layers.
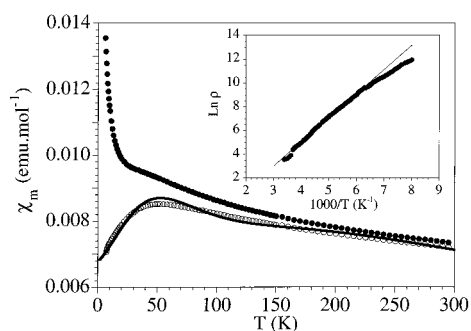

Figure 15. Plot of the magnetic susceptibility (χ_m) vs T for the $[ET]_8[BW_{12}O_{40}]$ radical salt (filled circles). Open circles correspond to the corrected magnetic susceptibility (after subtracting a paramagnetic Curie-type contribution. Solid line represents the best fit to a model that assumes an antiferromagnetic Heisenberg chain behavior (with $J \approx -30$ cm^{-1}; the exchange Hamiltonian is written as $-2JS_iS_j$) 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 electrical resistivity (Ω. cm) vs reciprocal temperature.

and charge localization. As far as the magnetic properties are concerned (Figure 15), this effect also explains why the salts with diamagnetic anions behave as 1D Heisenberg antiferromagnets.[43] In fact, the electron distribution in the organic sublattice may lead to the coexistence of localized electrons in eclipsed chains with delocalized electrons in the mixed-valence dimeric chain; the former chains contain one unpaired electron per ET which interact and account for the chain antiferromagnetism, and the mixed-valence chains account for the presence of an activated magnetic contribution at high temperatures

and for a Curie tail contribution ($\chi = $ constant/T) at low temperatures.

For those salts containing magnetic polyanions, the isolation of the magnetic center (situated in the central tetrahedral cavity of the Keggin structure) precludes any significant magnetic interaction with the organic spin sublattice. Accordingly, the magnetic properties are simply the sum of those corresponding to the two spin sublattices. Furthermore, the electron paramagnetic resonance (EPR) spectra show both the sharp signal of the radical cation and the signals associated with the paramagnetic metal ions.

Finally, the salt containing the one electron reduced polyoxometalate $[PMo_{12}O_{40}]^{4-}$ crystallizes in the α_1 structure as in the $[SiW_{12}O_{40}]^{4-}$ derivative, although some structural disorder has been found.[44] From the electronic point of view, this compound may be of special interest as it contains delocalized electrons in the mixed-valence inorganic sublattice. However, the magnetic properties of this compound, in particular the EPR spectroscopy, indicate that these "blue" electrons are not interacting with those of the organic sublattice.

2.3.2.2. BEDT-TTF Salts with Monosubstituted α-Keggin Anions. In the previous series, the two spin sublattices are magnetically independent. One way to increase the magnetic interaction between these two molecular components is to bring the magnetic moments localized on the Keggin polyanions, closer to the π electrons placed on the organic molecules. With this aim in mind, we have used monosubstituted Keggin anions of the type
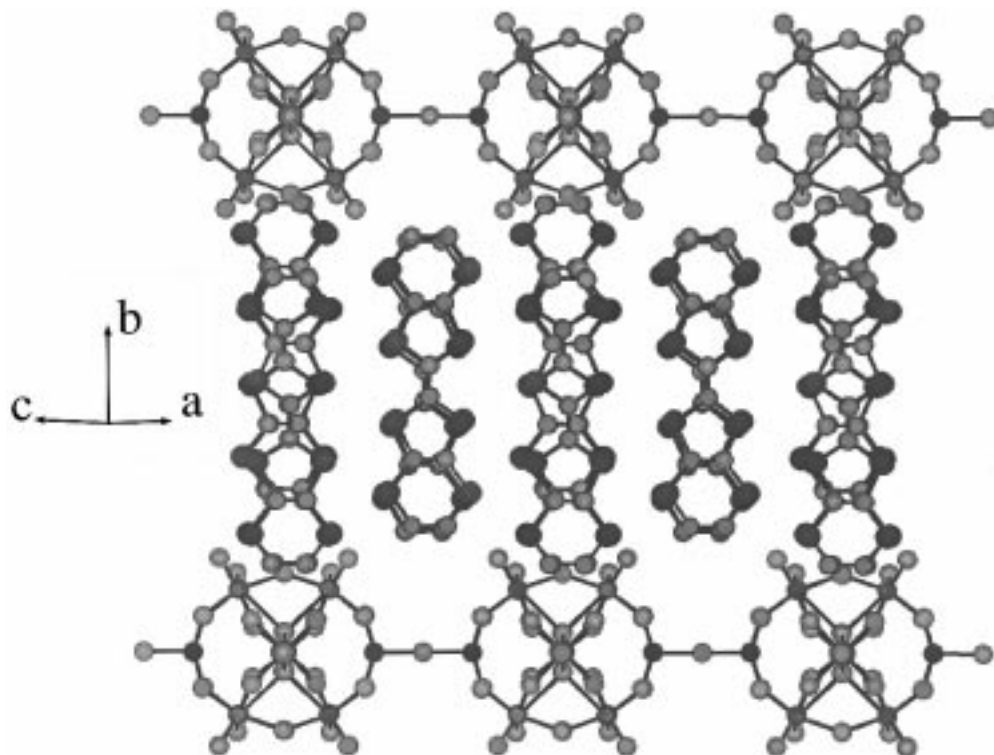
Figure 16. Structure of the $\{[ET]_8[PMnW_{11}O_{39}]\}_n$ radical salt showing the chains formed by the Keggin units.

$[X^{n+}Z^{m+}(H_2O)M_{11}O_{39}]^{(12-n-m)-}$ (X = P^V, Si^{IV}; M = Mo^{VI}, W^{VI}; Z = Fe^{III}, Cr^{III}, Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}), (abbreviated as [XZM$_{11}$], Figure 10c). These anions can be considered as being derived from the nonsubstituted Keggin anions $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ by simple replacement of one of the external constituent atoms and its terminal oxygen atom by a 3d transition metal atom, Z, and a water molecule, respectively.

As expected, the new series of semiconducting ET radical salts maintains the general stoichiometry (8:1) and the structural characteristics of the previous family.[45] In fact, most of them crystallize in the α_2 structure (Z = Fe^{III}, Cr^{III}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}; see Chart 3). Interestingly, an unexpected arrangement of the Keggin anions has been observed in the Mn derivatives $[ET]_8[PMn^{II}M_{11}]$ (M = W, Mo). Here a related structure referred to as α_3 has been found wherein the ETs are packed as in the other two phases, but the Keggin units are linked through a bridging oxygen atom which gives rise to an *unprecedented chain of Keggin anions* that runs along the *c* axis of the monoclinic cell (Figure 16). From a chemical point of view the formation of this chain involves a displacement of the molecule of water coordinated to Mn in one Keggin unit by a terminal O atom on W in another unit. As a result the charge of the Keggin anion in the chain is the same as in the free cluster.

In the preceding section, we have emphasized the ability of polyoxometalates to stabilize novel packing in the organic donor molecules, in particular in the case of TTF salts. The present example shows that also the organic part is able to induce novel packings in the polyoxometalate clusters. In fact, while the organic stacking remains nearly unchanged for the three crystalline α phases, the packing in the inor-

ganic layers shows significant differences in the intercluster distances (Figure 17). Thus, in the α_1 phase the shortest distances in the two directions of the layer, namely *d*1 and *d*2, are very close (*d*1 ≈ *d*2 ≈ 6.0 Å), while in the α_2 and α_3 phases, *d*2 remains almost constant (*d*2 ≈ 6.1−6.2 Å) but *d*1 decreases significantly to 3.7 Å in α_2 and to zero in α_3. These changes indicate a reduction in the dimensionality of the anionic network from the two-dimensional α_1 phase to the one-dimensional α_3 phase, with the α_2 phase adopting an intermediate dimensionality. It is interesting to note that a simple structural relationship relates the three phases, namely that the α_1 phase can be converted to the other two phases by displacing in opposite directions the dimerized stacks I$_{+1}$ and I$_{-1}$ by one or two intrastack ET−ET distances (Δ ≈ 4 Å), the eclipsed stacks (type I) remaining fixed (Figure 18a). Since these displacements are in fact along the stacking axis, this process changes the relative position of the chains, but the interchain ET distances and the packing within the chains remain practically invariant. As the polyoxometalates lie in the holes left by the two dimerized stacks of consecutive layers (Figure 18b), they must accompany the organic motion. Therefore, a shortening of the distances between terminal oxygen atoms of neighboring Keggin units (O_t and $O_{t'}$ in the Figure 17) along the *c* direction occurs. This accounts for the significant changes observed in the dimensionality of these inorganic layers.

Besides the formation of chains of Keggin anions, another remarkable structural feature of this series is the localization of the external metal heteroatom Z over two of the 12 possible octahedral sites of the monosubstituted Keggin anion. This ordering is quite difficult to detect by X-ray diffraction studies
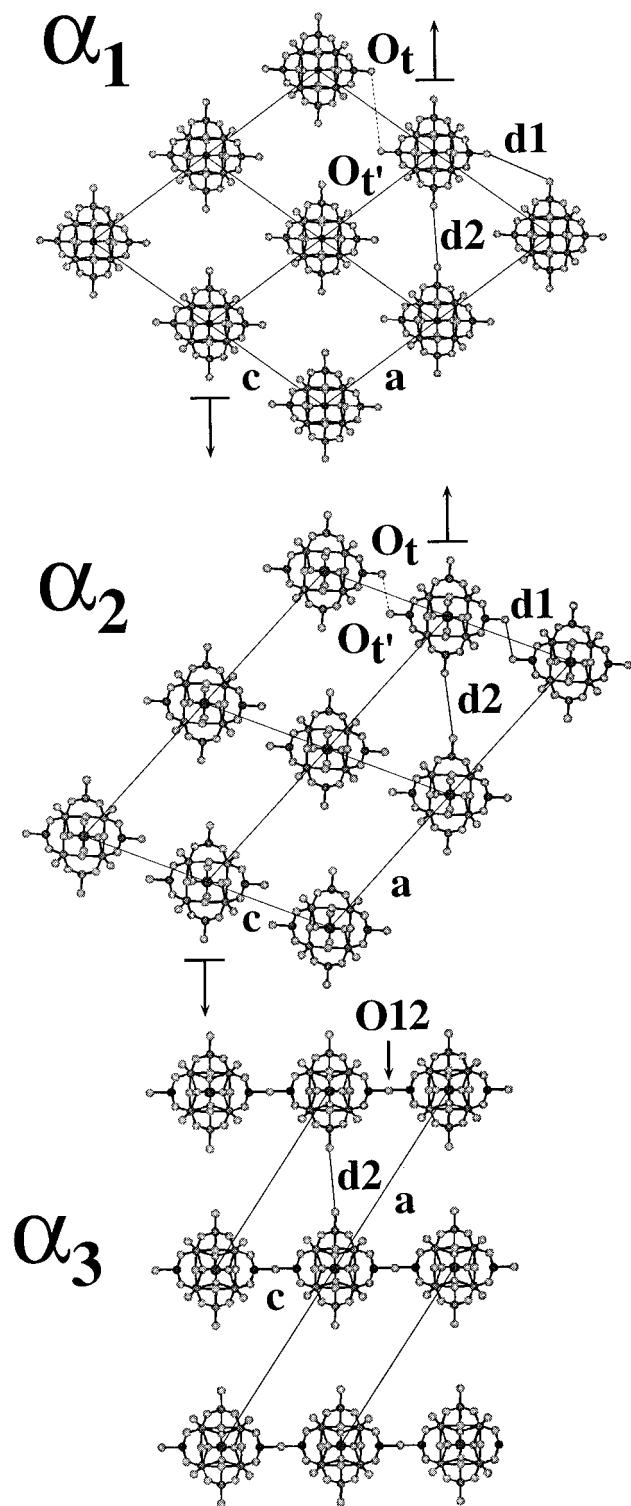
Figure 17. View of the inorganic layers in the three crystallographic phases (α_1, α_2, and α_3) showing the shortening in the inter-anion distances when passing from α_1 ($d1 = 6.0$ Å, $d2 = 6.0$ Å) to α_2 ($d1 = 3.7$ Å, $d2 = 6.2$ Å) to α_3 ($d1 = 0$ Å, $d2 = 6.1$ Å).

since, in most of the Keggin salts, e.g., with $[NBu_4]^+$ or alkaline cations, these anions impose a high cubic symmetry for the crystal packing. The metal atom Z, then, appears to be fully disordered over the 12 metal sites[46] even when the anion is not located on a special position.[47] The lower symmetry of the monoclinic crystals imposed by the packing of these bulk organic cations has allowed the Z metal to be located
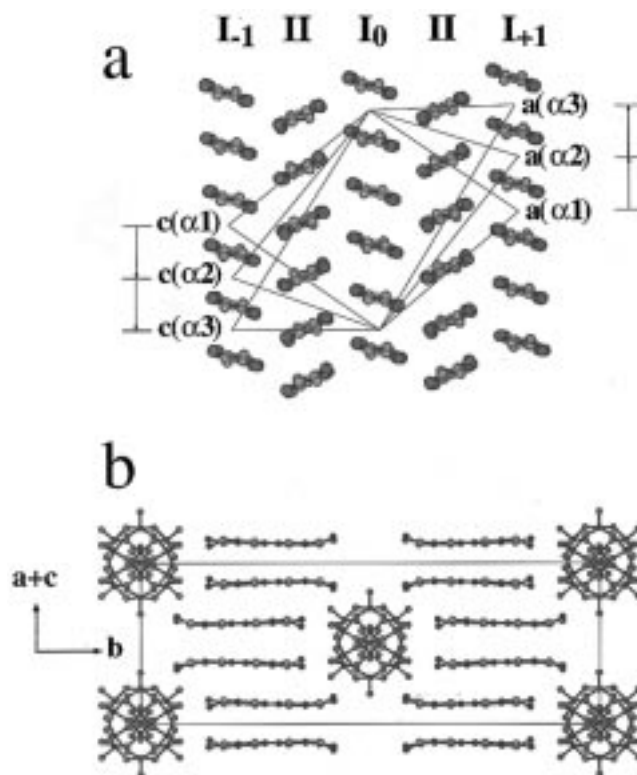

Figure 18. (a) Projection in the *ac* plane of the organic layer showing the structural relationship between the three α-phases. I and II refer to the dimeric or eclipsed chains respectively. (b) Side view of the dimeric chain showing the location of the polyanions.

along the *c* axis and distortions in the polyanion to be determined. What is surprising in this respect is that this metal ion ordering is found not only when the Keggin units are forming a chain but also when they are isolated (as in the α_2 phase). This supramolecular ordering of the Keggin anions is probably related to the anisotropy of the inorganic layer which favors an orientation of the $[XZ(H_2O)W_{11}O_{39}]^{5-}$ anions in such a way that the sites occupied by the Z ions are those having the shortest oxygen–oxygen distance, $d1 \approx 3.7$ Å. This distance is too long to involve intercluster hydrogen bond interactions. However, from the electrostatic point of view this orientation is favored since then the oxygen–oxygen repulsions between neighboring Keggin units are minimized. Instead of having a repulsion between two terminal oxo groups, the interaction takes place between a negatively charged oxo group and the water molecule coordinated to Z.

As far as the magnetic interactions within and between the two constituent networks are concerned, we notice that in all these organic/inorganic molecule-based hybrids the common electronic feature is the *coexistence of localized and itinerant electrons*. However, depending on the compound, different kinds of electronic arrangements are possible. The most simple case occurs when a nonmagnetic anion is used as inorganic component (i.e., the $[PZnW_{11}]^{5-}$ derivative), since then only the organic part is electronically active. As for the ET salts with nonsubstituted Keggin anions, such a system behaves as an antiferromagnetic uniform chain with localized electrons
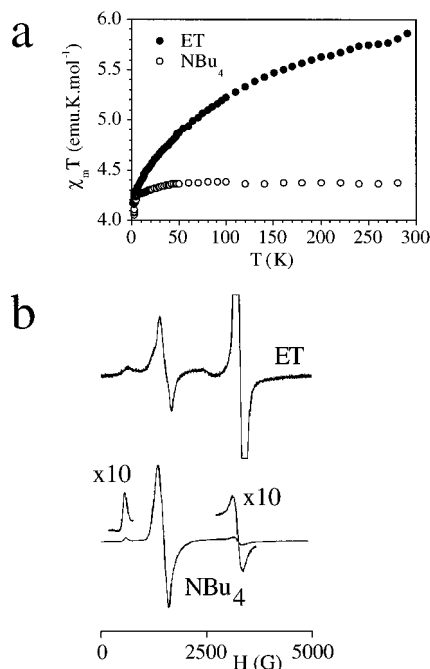
Figure 19. Magnetic properties of the $[ET]_8[SiFe^{III}(H_2O)$-$Mo_{11}O_{39}]$ compared to the tetrabutylammonium (NBu_4) salt of the $[SiFe^{III}(H_2O)Mo_{11}O_{39}]^{5-}$ anion: (a) plot of the $\chi_m T$ product (proportional to the square of the magnetic moment) vs T and (b) comparison between the EPR spectra performed at 4 K. In the spectrum of the ET salt we observe the coexistence of the signal associated to the radical (sharp signal centered at 3360 G ($g = 2$)), with the low-field signals coming from the Fe^{III} ion (centered at 750 G ($g = 8.9$) and 1640 G ($g = 4.1$)).

on π orbitals and a mixed-valence dimerized chain where the itinerant electrons reside.

When paramagnetic ions are introduced into the polyanions, localized electrons in d orbitals are added to the hybrid system. No magnetic effects arising from the d$-\pi$ interaction between these localized d electrons and the itinerant π electrons are detected down to 2 K, even if the two sublattices are closer than in the salts of the nonsubstituted Keggin anions.[48] In fact, upon cooling, the magnetic behavior of the members of α_2 phase shows a decrease of the magnetic moment which must be attributed, as before, to antiferromagnetic interactions in the organic sublattice. At low temperature the behavior is that of the isolated paramagnetic metal ions Z (Figure 19a). On the other hand, in all cases, EPR measurements performed at 4 K reveal the characteristic signals of the two sublattices, viz., a narrow signal at $g \approx 2$ with line widths of 25−40 G arising from the ET radicals, plus broad signals that closely match those observed in the $[NBu_4]^+$ salts of the corresponding paramagnetic Keggin anions (Figure 19b). The only case in which an apparent weak antiferromagnetic coupling between the Z metal ions has been detected is the $[PMnW_{11}]^{5-}$ derivative (Figure 20a). Below 15 K the magnetic moment of this compound is slightly below that of the $(NBu_4)_4$-$(H)[PMn(H_2O)W_{11}O_{39}]$ salt (Figure 20b). In this case the presence of chains may provide a superexchange pathway to couple the Mn^{II} ions. However, the long Mn−Mn distances within the chains (11.2 Å) as well as the complexity of the superexchange pathway, that
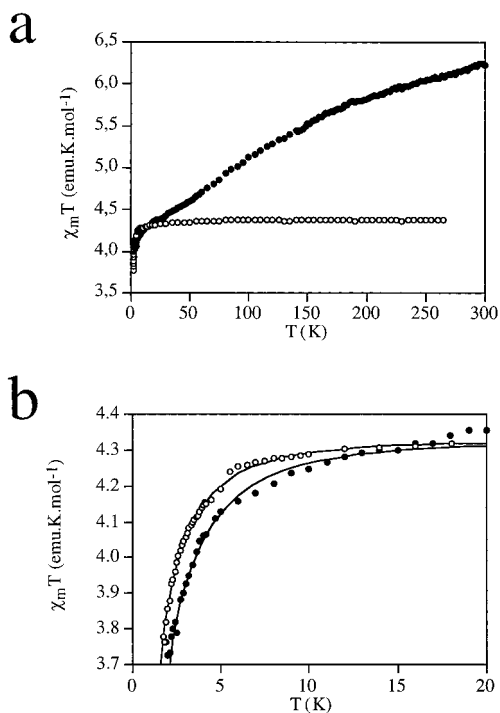

Figure 20. (a) Magnetic properties of the $\{[ET]_8$-$[PMnW_{11}O_{39}]\}_n$ radical salt compared to the NBu_4 salt of the $[PMn^{II}(H_2O)W_{11}O_{39}]^{5-}$ anion and (b) magnetic behavior at low temperatures showing the differences between the two salts. Solid lines are the fits to a spin $S = {}^5/_2$ with zero-field splitting parameters of $D = 1.25$ cm^{-1} (NBu_4 salt) and 1.60 cm^{-1} (ET salt).

involves a bridge as long as −O−P−O−W−O, prevents this mechanism from being effective. It is more reasonable to relate the observed differences in the magnetic curves to the elongation of the octahedral Mn site when the chain is formed, as such distortion may lead to an increase in the zero-field splitting parameter of the manganese-spin $S = {}^5/_2$ from $D = 1.25$ cm^{-1} in the $[NBu_4]^+$ salt[49] to 1.60 cm^{-1} in the ET salt (solid lines in the figure).

2.3.2.3. The Salt $[BEDS]_3(H)[PMo_{12}O_{40}]$.[50] In the 8:1 ET salts with Keggin anions the electrons on the organic part are strongly localized as a consequence of the large negative charges on the polyoxoanion. Therefore, low electrical conductivity and semiconducting behavior has been observed in all cases. In an attempt to increase the conductivity, the Keggin anion $[PMo_{12}O_{40}]^{3-}$ was combined with BEDS-TTF (in short BEDS or BEST), a seleno-substituted molecule related to ET (see Chart 1), in which the greater extended π orbitals of the selenium are expected to enhance the donor−donor overlap and therefore the electron delocalization. This small modification of ET (change of S by Se in the periphery) leads to a novel crystalline phase with stoichiometry 3:1 showing different packing and charge distribution on the organic molecules. Thus, this salt is formed by the mixed-valence Keggin anion reduced by one electron $[PMo_{12}O_{40}]^{4-}$ as demonstrated by EPR and magnetic susceptibility data, and by fully charged (BEDS)$^{\bullet+}$ cations. Note that a proton per formula unit is required in order to compensate for charges. On the other hand, it can also be noticed that although in the electrochemical cell the electrolyte is $[PMo_{12}O_{40}]^{3-}$,
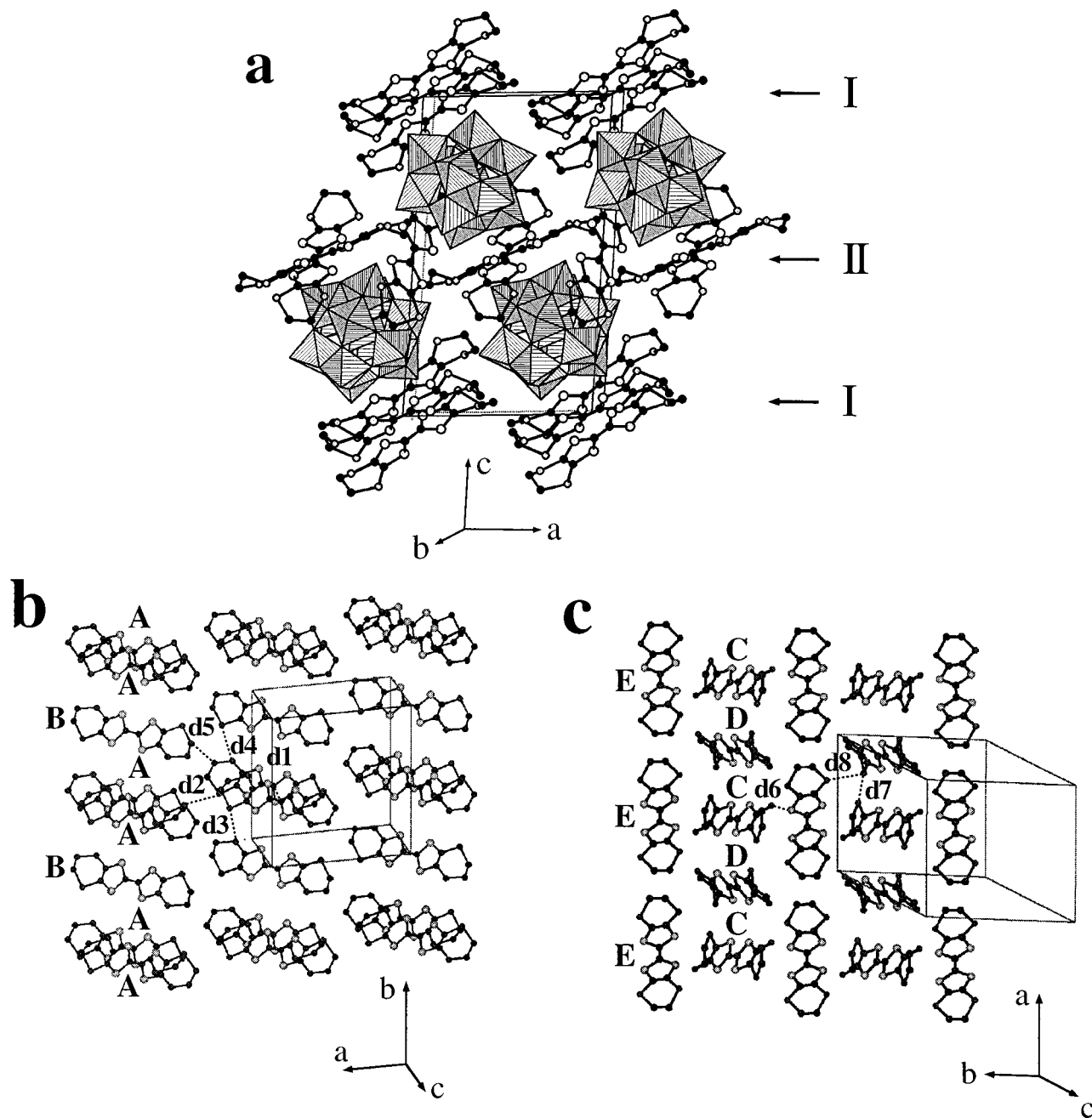
Figure 21. The radical salt $[BEDS]_3(H)[PMo_{12}O_{40}]$: (a) structure showing the layers of $[PMo_{12}O_{40}]^{4-}$ anions alternating with two different layers of BEDS radical cations. Packing of the two types of organic layers I (b) and II (c).

in the final salt the phosphomolybdate cluster is the 4-charged anion. This result is general for all the cation radical salts containing this anion (vide supra) and emphasizes the easy electron acceptor character of this anion.[51]

The structure of this new insulating salt consists of layers of the anions alternating with layers of the cation radicals (Figure 21a). The most attractive aspect in this structure is the unprecedented packing of the organic molecules which form layers with side intermolecular contacts (Figure 21b and 21c) instead of forming the typical π stacking in order to maximize the intermolecular contacts. Numerous short intermolecular distances involving the Se atoms are observed both within and between the layers, giving rise to a 3D electronic character for the organic network in which all the unpaired spins of the

(BEDS)$^{\bullet+}$ radicals are strongly antiferromagnetically coupled (in fact they are magnetically silent even at room temperature). Two different layers (I and II) which are parallel to the ab plane alternate along the c direction. Layer I is formed by parallel dimers of A molecules alternating in the b direction with isolated B molecules (Figure 21b). Layer II is formed by C, D, and E molecules arranged in a criss-cross fashion (Figure 21c).

It should be noted that another radical salt of stoichiometry 3:1 formed by ET and the phosphomolybdate Keggin anion has been found to exist.[52] This insulating salt exhibits a different structure from the previous one being formed by trimers of fully ionized ETs, but the full details have not yet been reported.

2.3.3. Dawson–Wells Anions: The Salt $[ET]_{11}[P_2W_{18}O_{62}]\cdot 3H_2O^{53}$

The organic donor-polyoxometalate hybrids described thus far in this work are based on polyoxometalates with metal nuclearities ranging from 6 (Lindqvist structure) to 12 (Keggin structure). $[P_2W_{18}O_{62}]^{6-}$ has been used with the aim of exploring the chemistry of ET radical salts with polyoxometalates possessing higher nuclearities and different shapes. This diamagnetic anion exhibits the well-known Dawson–Wells structure in which 18 WO_6 octahedra share edges and corners leaving two tetrahedral sites inside which are occupied by P^V atoms. The external appearance of this anion shows two belts of six octahedra capped by two groups of three octahedra sharing edges (Figure 10d). Electrochemical oxidation of ET in the presence of this polyanion leads to the new radical salt $[ET]_{11}$-$[P_2W_{18}O_{62}]\cdot 3H_2O$.

The structure of this compound consists of layers of anions and ETs alternating in the *ac* plane of the monoclinic cell (Figure 22a). The Dawson–Wells anions form close-packed layers with the 3-fold axis of the anion parallel to the *c* direction. The organic layers are formed by parallel chains of ET molecules with the shortest interchain S⋯S distances (3.32 Å) being shorter than the intrachain ones (3.67 Å), as in other 2D ET salts. The organic molecules of neighboring chains are also parallel, leading to a β phase. A remarkable feature in this structure is the presence of six crystallographically independent ET ions (noted as A–F in Figure 22b) situated in such a way that each chain is formed by the repetition of groups of 11 ETs following the sequence ...ABCDE-FEDCBA... stacked in an *exotic zigzag* manner. These unusual structural features illustrate, once again, the ability of polyoxometalates to create novel packings in the organic component. Another important structural feature is the presence of two strong intermolecular contacts between the organic molecules and the inorganic clusters. The first occurs between one sulfur atom of the E-type molecules and a terminal oxygen atom belonging to the belt of the anion (2.80 Å). The second type of interaction is a hydrogen bond between terminal oxygen atoms of both the belt and the cap of the anion and the carbon atoms of the ethylene groups of the ET molecules (3.1 Å). The strength of the C−H⋯O interactions, which is stronger that those found in other reported ET salts, is most likely related to the high charge and close packing imposed by the polyanion.

The electrical properties of this salt are quite interesting. It exhibits a *metallic-like* behavior characterized by an increase from ∼5 S cm^{-1} at room temperature to 5.5 S cm^{-1} at 230 K. Below this temperature the salt becomes a semiconductor with a very low activation energy value (Figure 22c). This result illustrates how a change in the packing of the organic molecules (from α in the Keggin phases to β in the Dawson–Wells derivative) can give rise to hybrid molecular materials with higher conductivities, despite the large size of the Dawson–Wells anion. The magnetic properties of this compound indicates that it is diamagnetic. The syntheses of
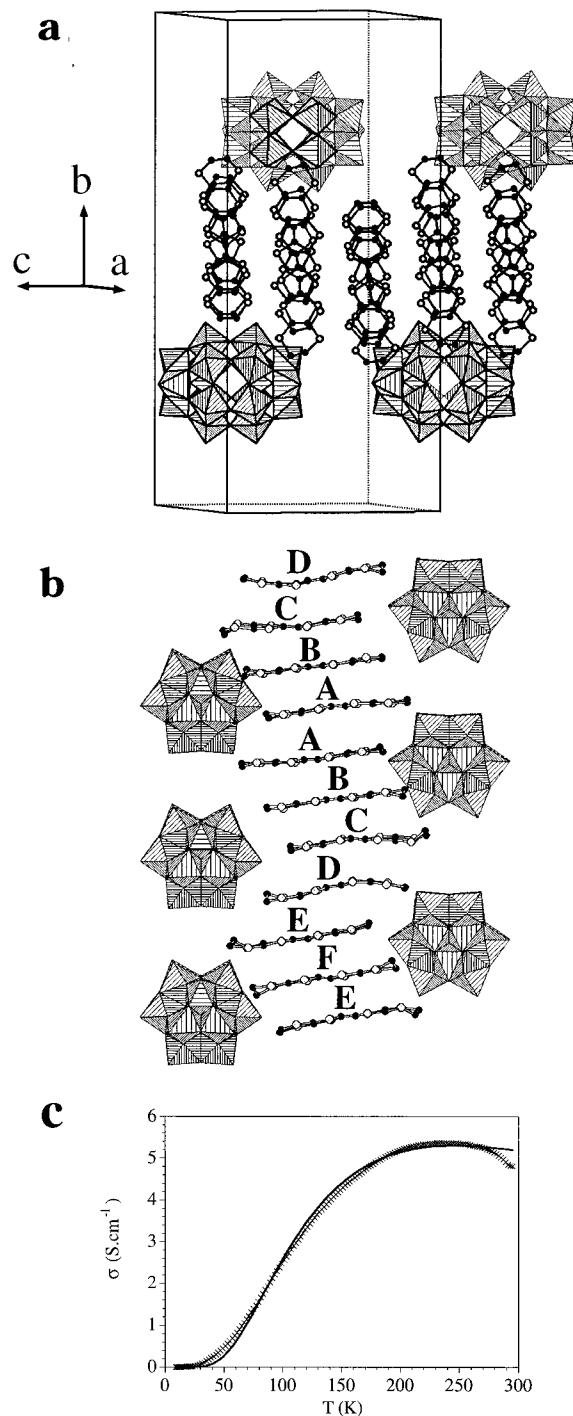
Figure 22. The radical salt $[ET]_{11}[P_2W_{18}O_{62}]\cdot 3H_2O$: (a) structure showing the alternating organic and inorganic layers, (b) view of the organic stacking showing the 6 different ETs (A−F), and (c) Thermal variation of the dc electrical conductivity in the *ac* plane. The solid line is the fit to a semiconductor model with a very small activation energy (E_a = 27 meV) in which the effect of the electron mobility on the conductivity has been taken into account.

similar metallic salts having magnetic centers in the peripheral sites of the Dawson–Wells anion are currently under investigation. In view of the large electrical conductivity and the strong intermolecular anion–cation contacts, the resulting magnetic salts are expected to be good prospects for observing indirect exchange coupling between the magnetic metal centers via the conducting electrons.

a

b

Figure 23. Magnetic properties of the ET salts containing the magnetic polyoxoanions $[M_4(PW_9O_{34})_2]^{10-}$ (M = Co^{2+}(a), Mn^{2+}(b)).

2.3.4. Higher Nuclearity Clusters: The Magnetic Anions $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (M = Co^{2+}, Mn^{2+})

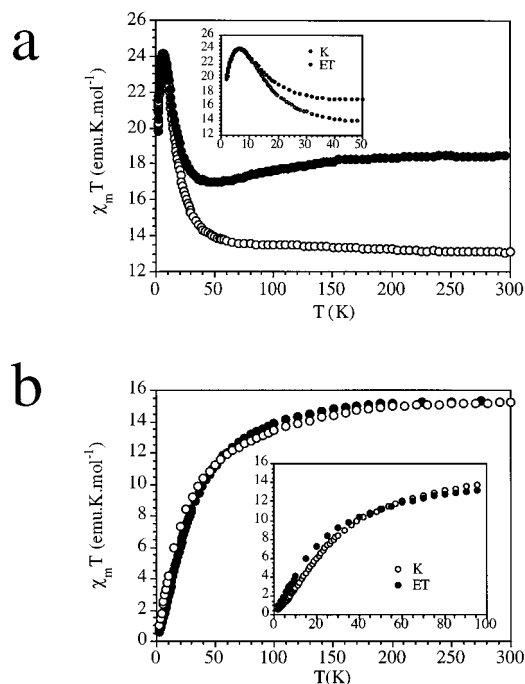Polyoxometalates of higher nuclearities have also been associated with organic donors. Thus, the magnetic polyoxoanions $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ (M^{2+} = Co, Mn) of nuclearity 22, produce black powders with TTF[54] and crystalline solids with ET.[55] These polyoxoanions are of magnetic interest since they contain the Co_4 and Mn_4 magnetic clusters encapsulated between two polyoxotungstate moieties $[PW_9O_{34}]$ (see Figure 10e). In the cobalt case, the ions are ferromagnetically coupled giving rise to a magnetic ground state having 12 unpaired electrons,[56] while in the manganese instance the coupling is antiferromagnetic and the ground state is nonmagnetic (S = 0).[57] These classes of magnetic systems are currently being investigated since polyoxometalate chemistry provides ideal examples of magnetic clusters of increasing nuclearities in which the exchange interaction phenomenon, as well as the interplay between electronic transfer and exchange can be investigated at the molecular level.[10b,58]

The electrochemical oxidation of ET in the presence of these magnetic anions affords isostructural crystalline materials with the composition $[ET]_6(H)_4[M_4-(H_2O)_2(PW_9O_{34})_2]$ which contain four protons that compensate for the charge. The six ETs are completely charged (+1),[59] and the compounds are insulators. In the magnetic properties of these salts no influence from the organic component within or among the clusters has been detected down to 2 K. In the Co derivative the χT product shows a sharp increase below 50 K upon cooling and a maximum at ~9 K (Figure 23a). Such a behavior is analogous to that observed in the K^+ salt and demonstrates that the ferromagnetic cluster is maintained when we exchange K^+ with ET^+. This is also indicative of a

lack of interactions between the two components. This conclusion is supported by the EPR spectra performed at 4K that show the same spectrum for both salts which is a very broad, anisotropic signal from 1000 to 4000 G centered at ~1620 G (g = 4.1) characteristic of the Co_4 cluster. No signal from the organic radical is observed which indicates a complete pairing of the spins of the $(ET)^{•+}$ cations in the solid at low temperature. The similarity between ET^+ and K^+ salts is also evident in the Mn case (Figure 23b). Thus, within experimental error, the two magnetic curves are coincident over the whole temperature range in agreement with a lack of interactions between the two components.

The two aforementioned compounds demonstrate the ability of the high nuclearity polyoxometalates $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ to form crystalline organic/inorganic radical salts with the ET donor. These constitute the first known examples of *hybrid materials containing a magnetic cluster and an organic π-electron donor*.

2.4. BET-TTF Salts

BET-TTF (BET) is an organic donor similar to the ET in that it has peripheral sulfur atoms that are capable of enhancing the structural and electronic dimensionalities of the solid (Chart 1). This donor has demonstrated an ability to form conducting radical salts with simple monoanions[60] as, for example, with $(XF_6)^-$ (X = P, As, Sb) or $(SCN)^-$, and also with magnetic anions[39c] of the type $(FeCl_4)^-$. In most cases BET salts afford poor quality crystals and furthermore lead to the formation of more than one compound from the same experiment.

By using the Lindqvist polyoxometalates (W and Mo derivatives) which are the anions that most well crystallize with organic donors, we recently obtained 2:1 salts of these anions.[61] The structure consists of face to face $(BET^{•+})_2$ dimers with short contacts between the central C and S atoms, surrounded by polyanions such as to form a *unusual 3D packing* of cations and anions reminiscent of NaCl (Figure 24a). In this structure, short intermolecular contacts between the cation pairs are present along the a and b directions of the triclinic cell (Figure 24b). Despite the high dimensionality of these salts, they are insulators with low conductivity (σ_{RT} = 3.2 × 10^{-6} S cm^{-1}) and high activation energies (E_a = 240 meV in the range 240–300 K), in agreement with the charge +1 on the BET radicals.

A radical salt has also been obtained with the silicododecatungstate $[SiW_{12}O_{40}]^{4-}$ which can be formulated as $[BET]_4[SiW_{12}O_{40}]\cdot CH_3CN\cdot 2H_2O$. In this case, the poor quality of the crystal prevented the determination of a complete structural characterization, nevertheless some structural features have been extracted from the X-ray study. The polyanions form a 2D hexagonal packing in the ac plane, while the BET^+ radical cations are again associated by pairs that are situated in the anion plane, or disordered within the hexagonal channels created by the anions. The four BETs are completely ionized (charge +1) and, not surprisingly, the salt is also an insulator.
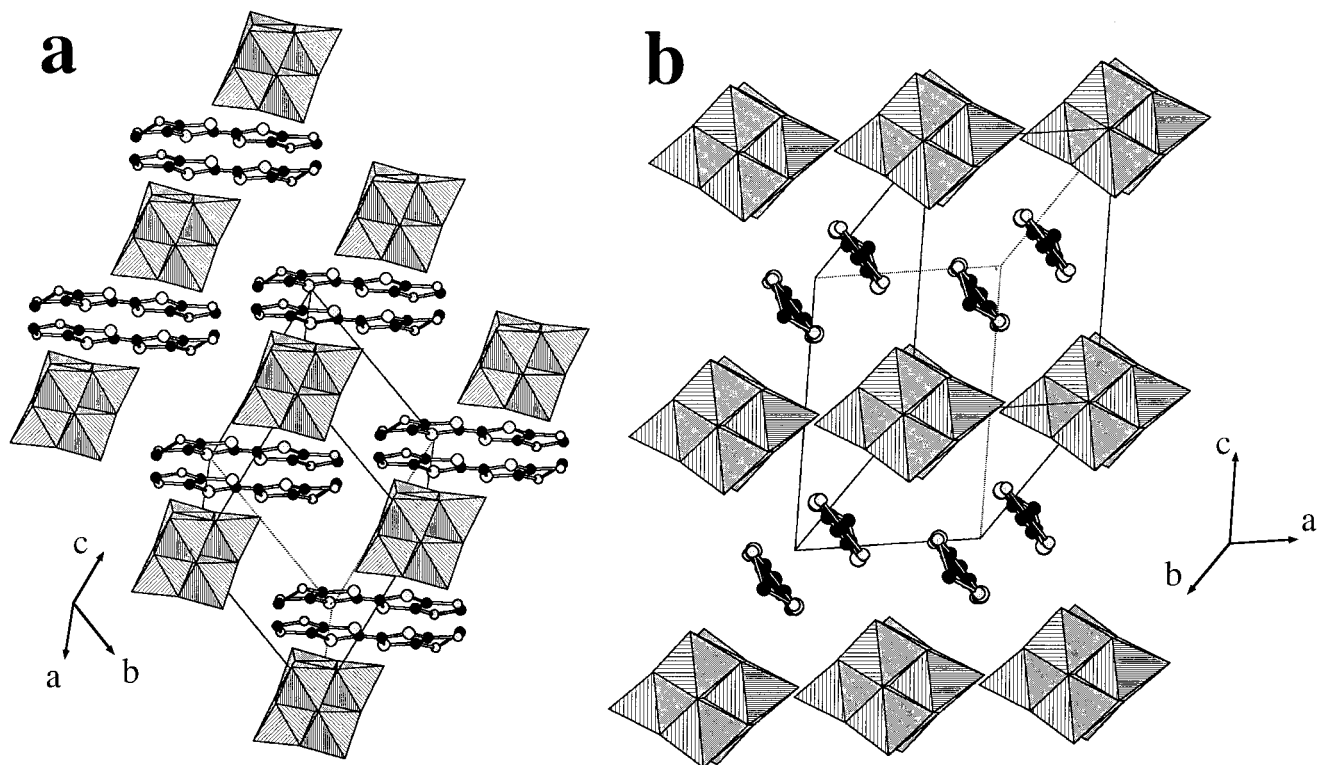
Figure 24. Structure of the 2:1 radical salts of BET with Lindqvist anions, [BET]$_2$[M$_6$O$_{19}$] (M = W, Mo): (a) View in the (101) plane showing the 3D organic/inorganic packing, and (b) View in the (012) plane showing the contacts between (BET$^{\bullet+}$)$_2$ dimers in the a direction.

3. Salts Based on the Organometallic Donor Decamethylferrocene

Besides the planar organic donors of the TTF type, other electroactive donor molecules can be combined with polyoxometalate acceptors to prepare donor–acceptor hybrid materials. One of these donors is the decamethylferrocene, Fe^{II}(C$_5$Me$_5$)$_2$ (in short FeCp*$_2$). This organometallic complex has attracted much interest in the field of molecular magnetism since it was used in the synthesis of the first molecule-based ferromagnet: the electron-transfer salt [Fe^{III}Cp*$_2^+$][TCNE$^-$] which forms 1D mixed stacks of donors and acceptors.[7]

In polyoxometalate chemistry, the spin = $^1/_2$ deca-methylferrocenium cation has been recently combined with Keggin anions[62] to afford the salts [FeCp*$_2$]$_4$[Keggin](solv)$_n$ with Keggin = [SiMo$^{VI}_{12}$-O$_{40}$]$^{4-}$, [SiW$^{VI}_{12}$O$_{40}$]$^{4-}$, [PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$, and [HFe-W$^{VI}_{12}$O$_{40}$]$^{4-}$, and solv = H$_2$O, DMF, or MeCN. The three former salts are isostructural and contain a 1D decamethylferrocenium network. The organometallic cations form linear chains which create hexagonal channels that incorporate columns of polyanions (Figure 25a). In turn, the iron(III)dodecatungstate derivative exhibits a 3D structure in which the organometallic cations form a large cuboctahedron that contains the Keggin anion (Figure 25b) in its cavity. Despite the magnetic character of the two latter polyanions (the reduced phosphomolybdate contains a delocalized spin $S = ^1/_2$, and the iron(III)-dodecatungstate contains a localized spin $S = ^5/_2$ on the iron), no evidence for magnetic interactions between the two parts has been detected down to 2
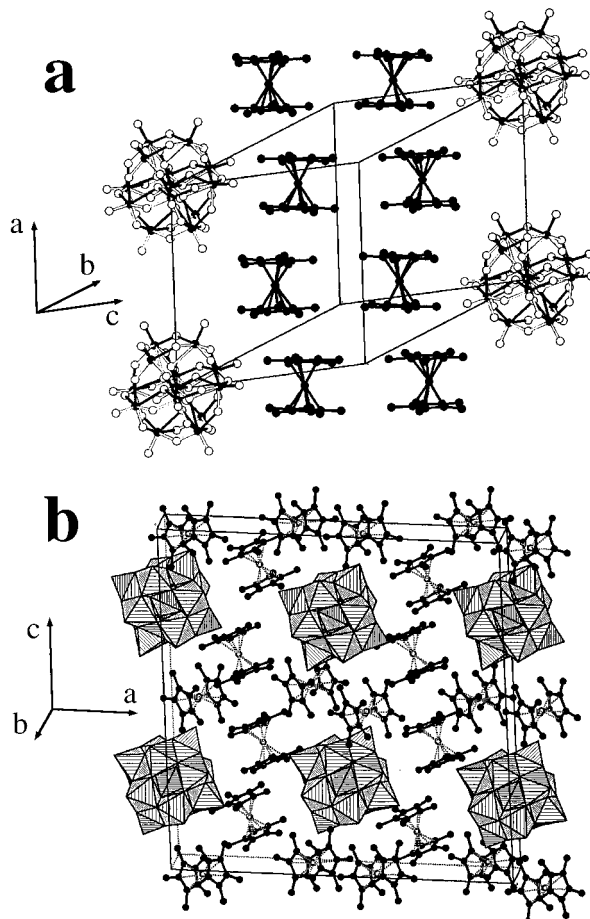

Figure 25. Keggin salts with the decamethylferrocenium cation [Fe^{III}Cp*$_2$]$^{\bullet+}$: (a) structure of the 1D phase (Keggin = [SiMo$^{VI}_{12}$O$_{40}$]$^{4-}$, [SiW$^{VI}_{12}$O$_{40}$]$^{4-}$, [PMo^{V}Mo$^{VI}_{11}$O$_{40}$]$^{4-}$) and (b) structure of the 3D phase (Keggin = [HFeW$^{VI}_{12}$O$_{40}$]$^{4-}$.)
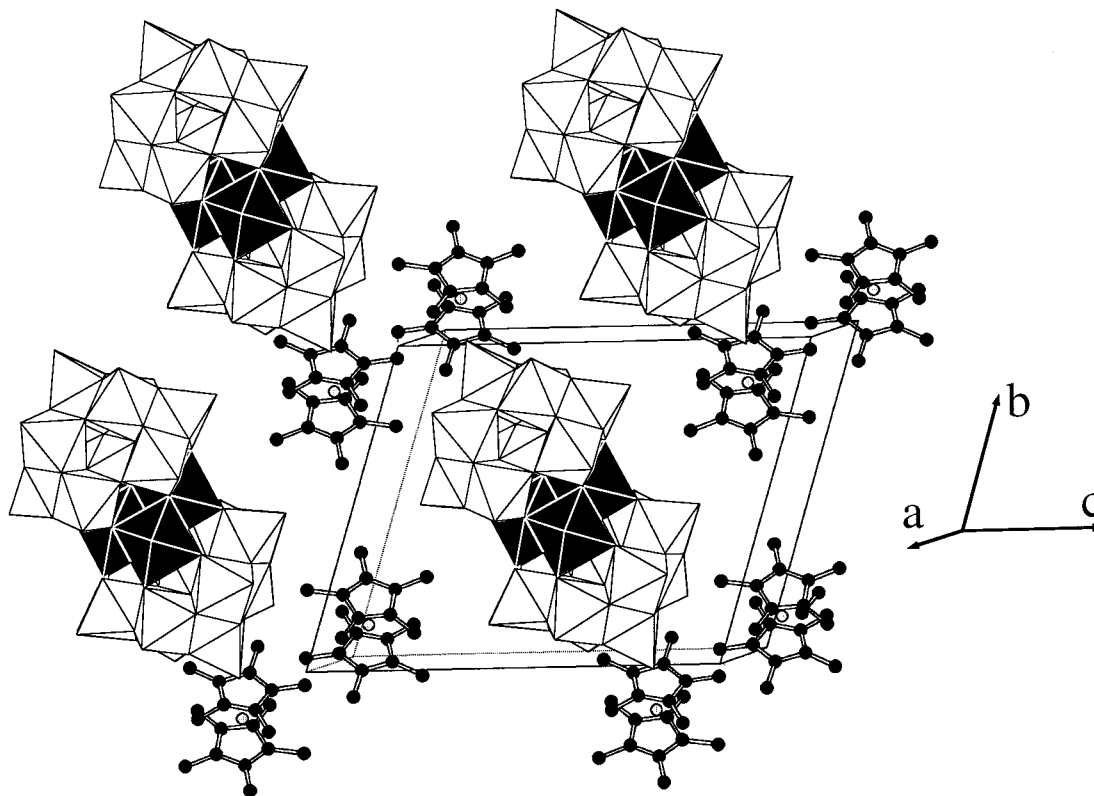
Figure 26. Structure of the salt $K_8[Fe^{III}Cp^*_2]_2[Co^{II}_4(H_2O)_2(PW_9O_{34})_2]$.

K. This is not unexpected in view of the weak anion—cation contacts and large distances. This family illustrates the structural role of the polyoxometalates in the stabilization of 1D or 3D packings for the organometallic cation. The synthesis of ternary phases incorporating the organic acceptor TCNE has been proposed to be a promising research for new molecular ferromagnets with increasing critical temperatures, although to date the attempts to obtain such materials have been unsuccessful.[62]

The polyanions are either diamagnetic or contain one paramagnetic center in the above family of compounds. To increase the magnetic character of the polyanion, the ferromagnetic cluster $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ has been used.[63] A salt containing one polyoxometalate anion, two decamethylferrocenium cations and eight K^+ cations in the unit cell has been obtained. In this structure the two decamethylferrocenium moieties are related by an inversion center located in the centrosymmetric tetrametallic unit Co_4O_{16} of the polyanion. In contrast to the K^+ salt, an interesting structural feature is that now all the polyanions have the same orientation (Figure 26). Such a feature will enable future detailed studies of the magnetic anisotropy of the Co_4O_{16} cluster. The magnetic properties of this hybrid salt indicate that, down to 2 K, the two magnetic sublattices behave independently. In fact, the maximum in χT at 9 K, characteristic of the ferromagnetic cobalt cluster, is maintained when potassium cations are exchanged with the organometallic magnetic cations. The magnetic cations, therefore, appear to have no significant effect as far as the intercluster interactions are concerned.

4. Organic/Inorganic Films

Polyoxometalates embedded in conducting polymers such as polypyrrole, polyaniline, and polythiophene have been recently prepared and used as conducting electrodes in electrocatalysis and other related applications.[64] Furthermore, they have also been incorporated into conducting organic polymers to yield *hybrid functional materials* that can work as insertion electrodes[65] and could lead to the harvesting of their electrochemical, photoelectrochemical[66] and magnetic activities in the form of collective physical properties.[65c] In this respect, hybrid materials based on polypyrrole and polyaniline, of formula $(C_4H_3N)_9(PMo_{12}O_{40})$[65b–d] and $(C_6H_5N)_9(PMo_{12}O_{40})$[65c–e] have been prepared both as bulk materials[65c,d] and as electrochemically grown thin films[65b,c,e] and have been reported as cation-insertion electrodes with phosphomolybdate *as the only doping anion* in the hybrid.[65c]

This precedent opens the possibility of obtaining conducting organic polymers incorporating magnetic polyoxoanions. Preliminary results with the $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ anion show that by electrochemical polymerization of pyrrole in the presence of this anion, organic/inorganic films containing ~80 pyrrole units per cobalt cluster are obtained.[55] The magnetic properties are very close to those observed in the K^+ salt, indicating that the structure of the ferromagnetic cluster is maintained in the film. The electrical properties reveal semiconducting behavior with a conductivity at room temperature of ~0.1 S cm^{-1} which smoothly decreases upon cooling to a value of ~0.02 S cm^{-1} at 50 K. This organic/inorganic material constitutes a clear example of the ability of
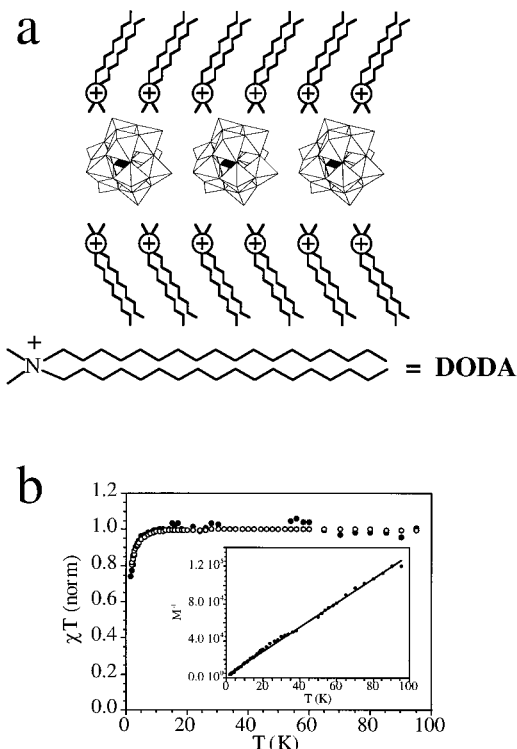
Figure 27. Langmuir–Blodgett films of Keggin anions and DODA: (a) idealized structure of the LB films and (b) magnetic properties of the LB film of the anion $[Co^{II}W_{12}O_{40}]^{6-}$ and DODA (fill circles) compared to the properties of the potassium salt of the anion (open circles).

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. Such a strategy is general and can be extended to other kinds of magnetic polyoxometalates and conducting films.
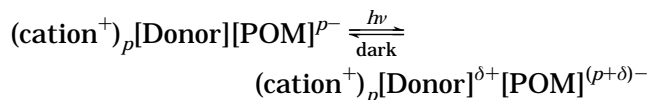
A second strategy is to create polyoxometalate-containing Langmuir–Blodgett films.[67] This approach allows for the formation of *well-organized layers of polyoxoanions*. By using the adsorption properties of Keggin heteropolyanions along a positively charged monolayer of a lipid such as the dimethyldioctadecylammonium cation (DODA in Figure 27), new organic/inorganic superlattices have been constructed. Independent of charge and heteroatom included in the Keggin structure, these polyanions can be organized in monolayers which are contained in well-defined LB films (Figure 27a). Thus, by using the anion $[Co^{II}W_{12}O_{40}]$,[6-] LB films with DODA have been obtained. The magnetic susceptibility of these films measured after deposition of ~300 layers onto a diamagnetic Mylar sheet exhibits Curie law behavior down to about 10 K (inset of Figure 27b), as expected for an isolated Co^{II} in a tetrahedral environment. Below this temperature, the magnetic moment decreases because of the zero-field splitting of the $S = {}^3/_2$ Co^{II} ion similar to the behavior observed for the potassium salt of this anion (Figure 27b). These experiments demonstrate that the magnetic site of the polyanion embedded in the LB film is not sensitive to the surrounding charge of the DODA molecules. Furthermore, they allow one

to calculate a ratio of DODA molecules to the paramagnetic polyanions in the film of 5 ± 1 which is close to the charge of the polyanion (−6). These preliminary results clearly indicate that the method can be extended to many kinds of polyanions and other charged clusters, leading to new lamellar organized materials. The appropiate choice of polyoxometalate and lipid molecules should allow for LB films with particular magnetic, optical, electrochromic, or electrochemical properties to be constructed.

5. Other Molecular Hybrids

In the aforementioned article, we have focused our attention on the combinations of polyoxometalate anions with organic and organometallic molecular cations, giving rise to molecule-based materials having electrical and/or magnetic properties. This kind of organic/inorganic association has also been investigated very recently as a means of obtaining novel polyoxometalate-based molecular materials that exhibit optical properties. In this context, the two goals are the synthesis of truly reversible photochromic materials and the synthesis of materials with nonlinear optical properties.
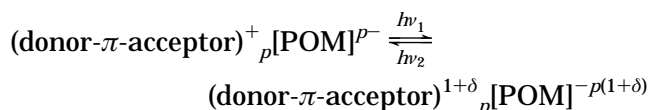
In the former class of materials a *reversible* photoinduced electron-transfer process that does not involve major structural changes or further chemical evolution (e.g., oxidation or protonation) must occur between an organic donor molecule and the polyoxometalate acceptor, POM, as illustrated by the following equation:

$$(\text{cation}^+)_p[\text{Donor}][\text{POM}]^{p-} \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}}$$
$$(\text{cation}^+)_p[\text{Donor}]^{\delta+}[\text{POM}]^{(p+\delta)-}$$

Although many photochromic polyoxometalate salts have been reported in the literature[68] they always lead to irreversible redox processes. The synthetic strategy adopted by Attanasio et al. is aimed at obtaining reversible photochromic materials and consists of combining polyoxometalate anions with electron-rich aromatic organic molecules as the quinolin-8-ol[69] and the N,N,N',N'-tetramethyl-p-phenylenediamine,[70] or the tetraphenylporphyrinato Zn^{II} complex (ZnTPP).[71] The polyoxoanions that have been used are the Keggin anions $[XM_{12}O_{40}]$ (X= P, Si; M= Mo, W) as well as the β-$[Mo_8O_{26}]^{4-}$ anion. However, the quite weak organic/inorganic interactions allowed in the solid state by these charge-transfer salts have prevented the occurrence of an effective electron transfer between the two components and no photochromism has been detected. To allow a strong electronic communication between the two units, the synthesis of related compounds in which the donor molecule is covalently linked to the polyoxoanions is being pursued by this group at the present time.

The second class of materials combines a polyoxometalate with a dipolar organic molecule containing an electron donor and an electron acceptor. In these organic molecules an intramolecular electron transfer can occur that results in large second-order hyperpolarizability coefficients β. Crystals composed of

these kind of molecules may exhibit nonlinear optical properties (second harmonic generation, SHG) if they adopt a noncentrosymmetric space group. In this vein, the use of noncentrosymmetric anions such as those of the Keggin structure may induce noncentrosymmetric crystal structures to form. Furthermore an intermolecular electron transfer between the organic and the inorganic units may enhance this nonlinear optical response:

$$(\text{donor-}\pi\text{-acceptor})^+{}_p[\text{POM}]^{p-} \underset{h\nu_2}{\overset{h\nu_1}{\rightleftharpoons}}$$
$$(\text{donor-}\pi\text{-acceptor})^{1+\delta}{}_p[\text{POM}]^{-p(1+\delta)}$$

With these ideas in mind, You et al. investigated charge-transfer salts resulting from the combination of Lindqvist and α-Keggin-type anions with hemicyanine dyes which are known to have the largest SHG efficiency to date (1000 times of urea), and hexamethylphosphoramide which has a large dipole moment. The results indicate the presence of a definite (albeit weak) second-order optical response in the charge-transfer salt resulting from the reaction of the silicododecatungstate acid with the hexamethylphosphoramide base[72] which crystallizes in the noncentrosymmetric space group $P2_1$, while the combination of $[\text{Mo}_6\text{O}_{19}]^{2-}$ anion with hemicyanine dyes has revealed an absence of SHG due to centrosymmetry of the crystals.[73] The highest second-order nonlinear optical response has been observed in the noncentrosymmetric charge-transfer complex $[4\text{-DMSP}]_4(\text{NH}_2\text{Me}_2)_2[\text{HSiFeMo}_{11}\text{O}_{40}]\cdot3\text{H}_2\text{O}$ (4-DMSP = 4[p-(dimethylamino)styryl]pyridine). This compound exhibits SHG of 1064 nm radiation with an efficiency 1.2 times that of KH_2PO_4 under the same conditions.[74]

6. Concluding Remarks

In this review, we have presented the main achievements in the field of the molecule-based materials that involve polyoxometalates as the anionic component. This recent application of polyoxometalates has witnessed rapid progress. In particular, the *hybrid approach* in which polyoxometalate anions are combined with an electroactive molecular cation, has proven to be the most successful approach for preparing new types of molecule-based materials combining two or more functional properties. The design and synthesis of such molecular hybrids, which are at the forefront of the materials chemistry research, is still in its infancy. One of the main achievements in the context of the polyoxometalates has been the combination of these molecular metal oxides with TTF-type organic donor molecules. By altering the shapes, sizes, and charges on the polyanion, novel series of organic/inorganic radical cation salts which can undergo electron delocalization and even a metallic-like behavior have been obtained. Furthermore, the ability to accommodate one or several magnetic centers at specific positions of the polyanion framework enables a magnetic character to be added to the radical salt. This results in molecular hybrids with coexistence of localized and itinerant electrons which

is the critical first step toward the preparation of materials combining useful magnetic and electrical properties. Thus far, however, the weak nature of the intermolecular organic/inorganic contacts as well as the semiconducting behavior of most of the reported materials has prevented the occurrence of an effective indirect interaction between the magnetic centers via the conducting electrons.

It is obvious from the aforementioned results that polyoxometalates offer a large range of opportunities for the design of novel molecule-based materials with functional properties from the exploitation of the unique electronic and structural characteristics of these molecular metal oxides. Most of the work has focused on the structural and magnetic properties of these systems in combination with the conducting properties of organic donors. Nevertheless, only a reduced number of polyoxometalates has been used so far and more magnetic radical salts will be surely obtained soon from other polyoxometalates. Of particular interest will be thiopolyoxometalates with sulfur atoms on the surface, since they may enable stronger interactions with the sulfur-containing organic donors. On the other hand, as was noted earlier, polyoxometalates can also exhibit interesting optical properties such as electrochromism or luminescence. The preparation of hybrid materials in which these properties are combined with a second property coming from the molecular cation, e.g., magnetism, conductivity or nonlinear optics is expected to be the focus of future developments in this field. The third development in view of the potential applications of the materials that one can envisage is the preparation of organic/inorganic hybrids films. Several promising results have already been obtained in this respect as for example the creation of well-organized films of polyoxometalate layers by using the Langmuir–Blodgett technique.

7. Acknowledgments

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