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Multifunctional coordination compounds: design and properties

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Contents

Abstract

Cleverly designed molecular building blocks provide chemists with the tools of a powerful molecular-scale construction set. They enable them to engineer materials that possess a predictable order and useful solid-state properties. Hence, it is in the realm of supramolecular chemistry to follow a strategy for synthesizing materials which combine a selected set of properties, for instance from the areas of magnetism, photophysics and electronics. As a possible approach, host/guest solids which are based on extended anionic, homo- and bi-metallic oxalato-bridged transition-metal compounds with two- and three-dimensional connectivities are investigated. In particular, we report herein in detail about their structural

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properties and their multifunctional characteristics in the area of molecular magnetism and photophysics.

Keywords: Crystal engineering; Supramolecular compounds; Molecular magnetism

1. Introduction

Interest in functional materials based on molecular crystals persists, owing to the potential for manipulating solid-state properties by systematic variation of the molecular structures as well as of the stoichiometries and properties of the molecular components. However, up to now, the crystal engineering of molecular materials has been frustrated by the absence of reliable and general structural paradigms that are needed for systematic design of crystal lattices with predictable structure and desirable functions. Therefore, learning how to create large supramolecular units, and the elucidation of rules mediating their macroscopic organization into multifunctional materials, will offer a fascinating prospect for technology [1–4].

The purpose of the present work is to set an example of a supramolecular system exhibiting molecular self-organization. Thereby, we aim to exploit host/guest solids where each component will contribute its own physical characteristics. In general, the two entities could behave independently resulting in composite properties, or they might interact synergetically, potentially leading to new physical properties, e.g. in the fields of molecular magnetism and photophysics. In particularly, the present work focuses on the transition-metal oxalate system, its fascinating structural versatility and its potential as a multifunctional material mainly in the areas of molecule-based magnetism and photophysics. Starting with a detailed discussion about the structural topology of this supramolecular coordination compounds, we will further present some experimental results in the areas of magnetism and photophysics, altogether this exemplifies a strategy we explored in order to attempt a multifunctional material.

2. Crystal engineering

Our laboratory has reported on the synthesis and structure determination of coordination solids based on transition-metal oxalates, which typically behave as host/guest compounds with different lattice dimensionalities [5–10]. Thereby, the idea of a reasonable strategy looks simple: mix metal ions with a preference for a particular coordination geometry with bridging ligand-systems and under the right conditions and—it is important to control both the kinetics and thermodynamics

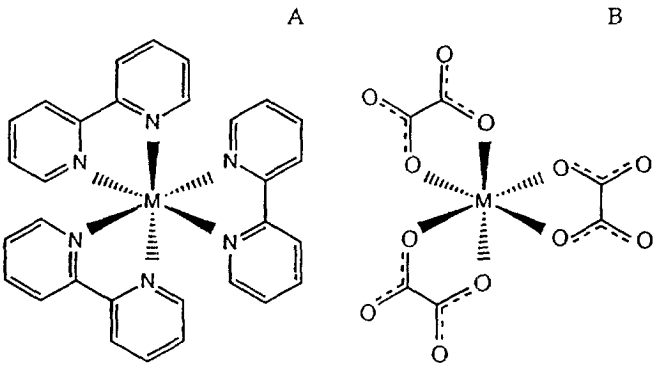

Fig. 1. Schematic representation of the two chiral (the Λ-isomers are shown) preorganized cationic (A) and anionic (B) coordination entities. M = transition-metal ion as spin carrier center.

of the assembly process—a crystalline network will nucleate and grow. Clearly, the strategy relies on the robustness of some coordination subunits and of the supramolecular motif as a whole. Fig. 1 depicts two preorganized transition-metal complexes which act as mutually complementary molecular partners. Due to their specific coordination properties, their similar size and shape, they are predisposed on one hand to act as template molecules and on the other to form extended two- (2D) and three-dimensional (3D) network structures.

In the following, we will present a detailed discussion about the topics of lattice dimensionality and chirality, whereby first we will rely on some distinct topological rules and in a second step we will refer to the appropriate chemical building blocks. Quite surprisingly, there exist simple topological rules [11] which will determine the connectivity and structural dimensionality of many of these molecular assemblies, ranging from infinitely extended one- to three-dimensional motifs (compare Figs. 2–4). In accordance with this structural concept, one easily recognizes that any pattern that repeats regularly in one, two, or three dimensions consists of units that join together when repeated in the same orientation, that is, all units are identical and related only by translation. The repeat unit may be represented by a single point or a group of connected points, and it must have at least two, four, or six free links available for attachment to its neighbours. Consequently, molecular subunits with two free links, represented by 2-connected points, will combine to one-dimensional (1D) molecular chains (Fig. 2). Analogously, as illustrated in Fig. 3, the formation of two-dimensionally (2D) linked assemblies affords subunits possessing

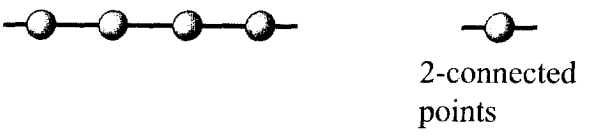

Fig. 2. An atom or a molecular complex forming two bonds comprises a structural unit for a 1D compound.

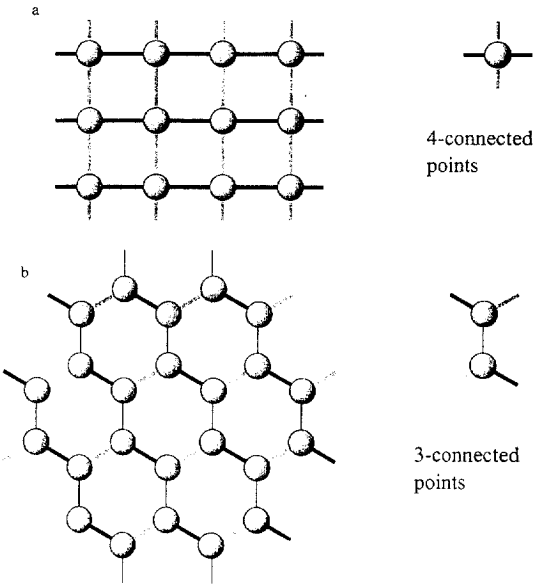

Fig. 3. (a) An atom or a molecular complex forming four bonds comprises a structural unit for a 2D compound; (b) the repeat unit consists of a pair of 3-connected points.

four free links which correspond to two non-parallel lines. Evidently, either 4-connected points or a combination of two 3-connected points will form the appropriate building blocks. In the latter case, the honeycomb lattice type results.

Along this line, extended three-dimensionally (3D) linked assemblies rely on building blocks comprising three non-coplanar lines as free links as represented either by 6-connected points, by a combination of two 4-connected points or by four 3-connected points. Fig. 4 shows that, in each case and very strictly, distinct 3D lattice types are created. Most interestingly, the subunits which will form a 3-connected 3D net must contain four 3-connected points in order to obtain the necessary number of six free links. Similarly oriented subunits must be joined together through the free links, so that decagon circuits are formed. Hence, the structure represents a uniform net in the sense that the shortest path, starting from any point along any link and returning to that point along any other link, is a circuit of ten points.

In the actual case of this report, the molecular subunits are anionic, tris-chelated transition-metal oxalato complexes $[M^{z+}(ox)_3]^{(6-z)-}$, $ox = C_2O_4^{2-}$ (see Fig. 1(B)). Therefore, as a consequence of this $[M(L \wedge L)_3]$ type of connectivity, each coordinated metal ion represents a chiral center with D_3 point-group symmetry, showing either Δ- or Λ-helical chirality. Evidently, this property adds a further aspect to our discussion about molecular topology. Now, if such building blocks of different chirality, while still corresponding to 3-connected points, are alternately linked, the bridged metal ions are confined to lie within a plane, as illustrated in Fig. 5. Consequently, a layered structure motif will result. In contrast, also depicted in Fig.

5, an assembling of building blocks of the same chiral configuration will lead to a 3D framework structure. It remains to apply the topological rules described above in order to define the number of 3-connected subunits which are needed to build closed circuits, hence, extended framework motifs. Fig. 6 illustrates the way that two dimeric subunits may be combined to form the planar honeycomb network. In an analogous manner it can be seen from Fig. 7 that two tetrameric subunits are needed to build closed circuits composed of ten metal centers, which in sum define the chiral 3D decagon framework structures.

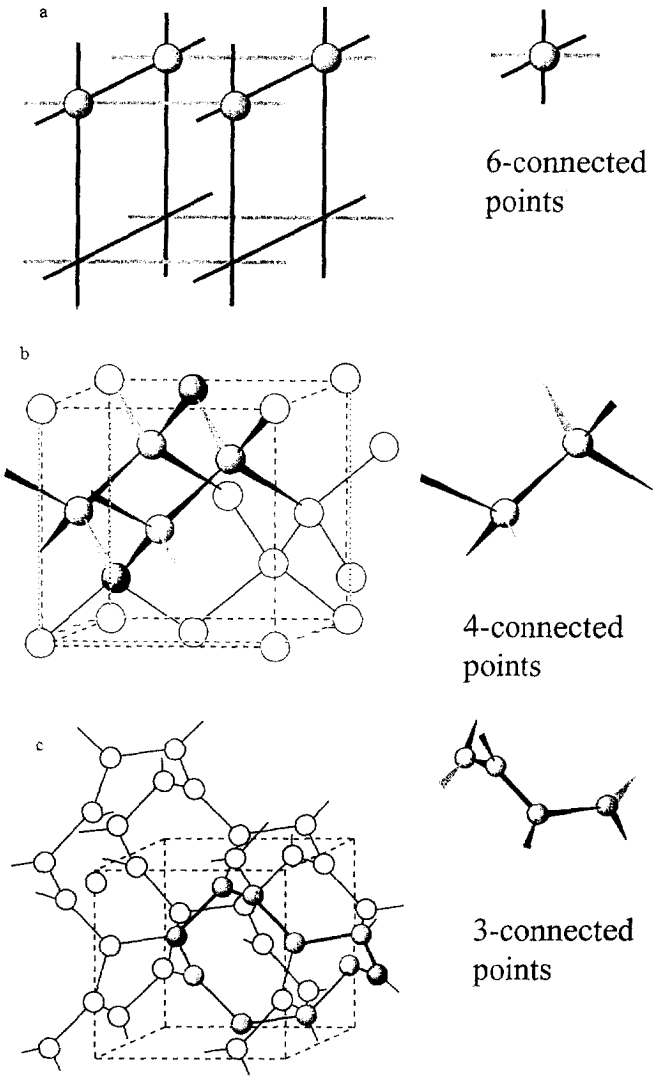

Fig. 4. An atom or a molecular complex forming six bonds comprises a structural unit for a 3D compound; (b) the repeat unit consists of a pair of 4-connected points, leading to a 3D (6,4) network; (c) the repeat unit consists of a tetramer of 3-connected points, leading to a 3D (10,3) network.

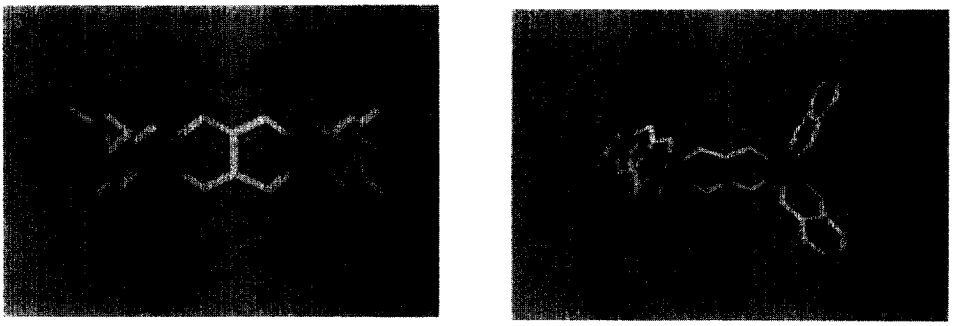

Fig. 5. Chiral $[M^{z+}(ox)_3]^{(6-z)-}$ building blocks assembled with (a) alternating chiral configuration; (b) equal chiral configuration.

Although the topological rules give an understanding of the different structural possibilities, the synthetic chemists still need to find the optimal reaction and crystallization conditions for each specific material. In the actual case of these tris-chelated transition-metal oxalato complexes, the discrimination between the formation and crystallization either of a 2 or a 3D framework structure relies on the choice of the templating counterion. Evidently, the template cation determines the crystal chemistry. In particular, $[XR_4]^+$ (X = N, P; R = phenyl, n-propyl, n-butyl, n-pentyl) cations initiate the growth of 2D layer structures containing $[M(II)M(III)(ox)_3]_n^{n-}$, M(II) = V, Cr, Mn, Fe, Co, Ni, Cu, Zn; M(III) = V, Cr, Fe, network stoichiometries. The structures consist of anionic, 2D, honeycomb networks which are interleaved by the templating cations. Although these 2D compounds are not chiral, they express a structural polarity due to the specific arrangement of the templating cations (see Fig. 8). These organic cations, which are located between the anionic layers, determine the interlayer separations. From single-crystal X-ray studies, these distances have been determined to be 9.94, 9.55, 8.91, and 8.20 Å for the n-pentyl, phenyl, n-butyl, and n-propyl derivatives, respectively [6,10,20].

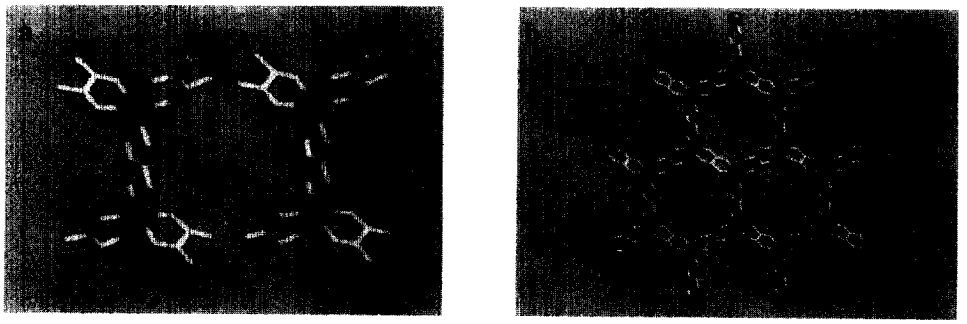

Fig. 6. (a) Two dimeric units of the alternating chirality type are necessary to form a closed hexagon ring; (b) the resulting planar network motif.

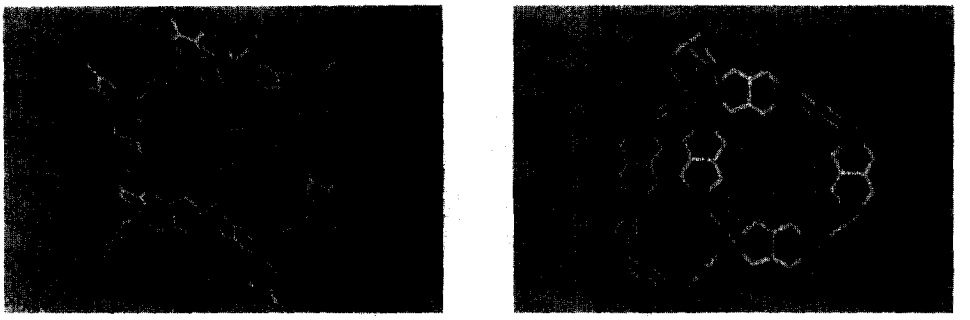

Fig. 7. Two tetrameric units of the same chirality type are necessary to form a closed decagon ring; (b) a fragment of the 3D chiral framework.

Remarkably, the cationic, tris-chelated transition-metal diimine complexes, $[M(bpy)_3]^{2+/3+}$ (see Fig. 1(A)), act as templates for the formation and crystallization of the 3D decagon framework structures. As outlined above, the topological principle implies to the 3D case that only subunits of the same chiral configuration are assembled. Consequently, the uniform anionic 3D network-type with stoichiometries like $[M(II)_2(ox)_3]_n^{2n-}$, $[M(I)M(III)(ox)_3]_n^{2n-}$ or $[M(II)M(III)(ox)_3]_n^{n-}$ is chiral, as it is composed of $2n$ centers exhibiting the same kind of chirality.

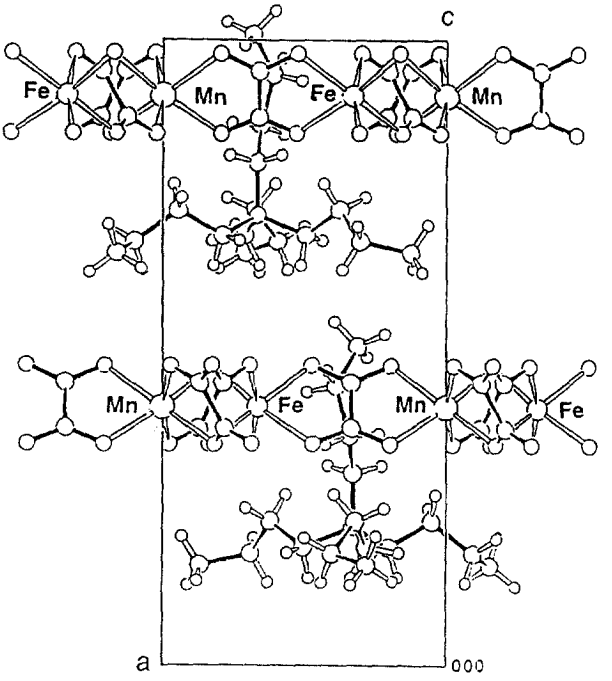

Fig. 8. [010] projection of $\{[N(n\text{-}C_4H_9)_4][Mn(II)Fe(III)(C_2O_4)_3]\}_n$.

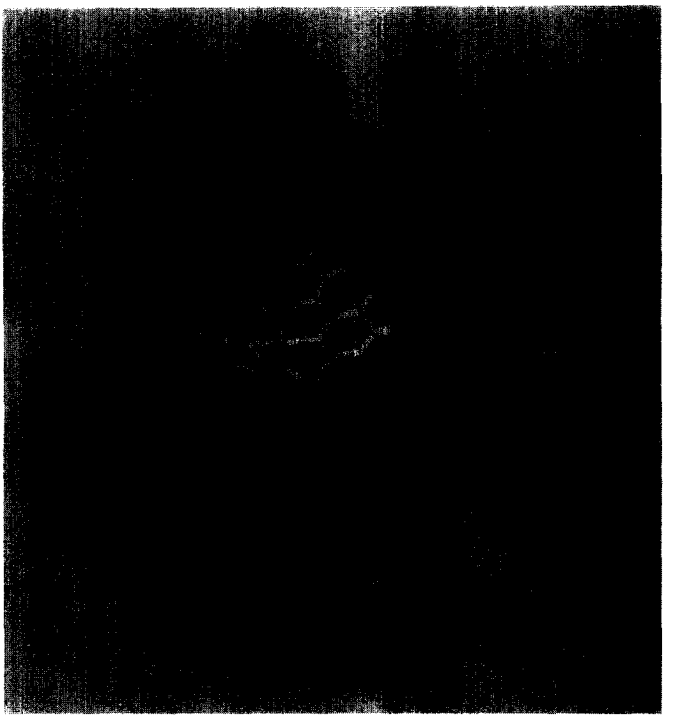

Fig. 9. The 3D host/guest compound. Only one guest molecule is shown within the chiral framework.

Naturally, this chiral topology is in line with the symmetry elements which are present in the crystalline state of the 3D frameworks, which in sum constitute either one of the enantiomorphic cubic space groups $P4_332$ or $P4_132$ for the former and the cubic space group $P2_13$ for the latter bimetallic stoichiometries. Thereby, the $2n$ metal ions occupy special sites with a three-fold symmetry axis. Fig. 9 depicts a view of the 3D host/guest assembly.

Overall, with a straightforward synthetic method which is mainly based on the function of appropriate molecular templates and specific molecular building blocks, extended 2 and 3D supramolecular materials are accessible. Thereby, some general topological rules elegantly describe the resulting distinctive architectures.

3. Molecular magnetism

The magnetic properties of molecule-based materials have become an important focus of scientific interest in recent years [12–14], whereby the search for molecule-based ferromagnets that order at or above room temperature is a major driving force moving this field [15]. Moreover, the synthesis of materials combining two or more functional properties, e.g. from the area of magnetism and photophysics or magnetism and superconductivity, represents a current challenge for the preparative chemists.

When did the research activities in the area of molecule-based magnetism start? The first genuine molecular compound displaying a ferromagnetic transition was described by Wickman et al. [16] as early as 1967. This compound, a chlorobis(diethyldithiocarbamato)iron(III) complex, exhibiting an intermediate spin $S = 3/2$, orders ferromagnetically at 2.46 K. Since then, over the years, a scientific community has been established throughout the world focusing on the aspects of molecular magnetism, and an increasing number of international conferences have uncovered a lot of new chemistry and brought synthetic chemists into close contact with physics and material science.

Notice that there are several features of potential practical impact that distinguish magnetic materials based on molecules from their analogs consisting of continuous ionic or metallic lattices. Examples would include the search for materials combining two or more functional properties, e.g. magnetism and transparency for magneto–optical applications or the design of mesoscopic molecules possessing large magnetic moments. Synthetic methods will also be quite different, and consequently, magnetic thin films might be deposited with methods such as solvent evaporation.

A brief comment on the characteristics of the elements that constitute a magnetic molecular solid will give us a feeling for the extension, complexity and wide diversity of magnetic phenomena that can be found in these materials. Generally, a magnetic molecular solid can be formed by free radicals, transition-metal ions, rare earth ions and diamagnetic ligands. Any combination of these components is possible, although only the free radicals can form a magnetic molecular solid by themselves. In the following, we will concentrate only on coordination compounds, where the importance of transition-metal ions as spin carrier centers stems from at least three main reasons. (i) Transition-metal to ligand interactions are extremely variable, thus, the building up of novel higher-dimensional architectures can profit very much from the coordination algorithm of the metal ions as well as from the availability of various bridging ligand systems; (ii) transition-metals are prone to quick and reversible redox changes, hence, supramolecular functions like energy- and charge-transfer processes can anticipate from it; (iii) the collective features of components bearing free spins may result in supramolecular assemblies exhibiting molecule-based magnetic behavior, whereby the critical role of the dimensionality of the compounds is simultaneously taken into account. Accordingly, molecular precursors implying transition-metal ions entail the synthesis of ferro and antiferromagnetic systems with a tuneable critical temperature.

In addition, any synthetic strategy aimed at designing molecular magnets has to answer the questions of (i) how to control the interaction between the nearest neighbouring magnetic spins and (ii) how to control parallel alignment of the magnetic spin vectors over the 3D lattice. Naturally, if the compounds assume a 2D layer structure, the magnetic properties depend on the nature of both the intra- and inter-layer magnetic interactions.

With respect to the first question, it is well known that the oxalate-bridge is a good mediator in both antiferromagnetic and ferromagnetic interactions between similar and dissimilar metal ions, therefore it has been widely used to construct

polynuclear compounds in the search for new molecular-based magnets [13]. Naturally, in search for an answer to the second question, effort has to be given to the investigation of the magnetic ordering behavior of the above-described 2 and 3D systems.

Along this line, a successful molecular design of two-dimensionally extended metal-complex magnets which are based on trioxalatochromium(III) building blocks (compare Fig. 1(B)), has been reported in 1992 [17]. Within a series of layered, oxalate-bridged bimetallic compounds, ferromagnetic ordering behavior has been shown to occur at temperatures < 14 K. Since then, a variety of analogous two-dimensional (2D) bimetallic assemblies, also with mixed-valency stoichiometries, have been prepared and characterized [18–22]. Overall, many of these layered compounds exhibit ferro-, ferri- or antiferromagnetic long-range ordering behavior and in some cases they show evidence of at least short-range interactions.

In general, different experimental techniques are needed in order to reveal the actual magnetic dimensionality of these compounds and specifically, the combined use of calorimetric and frequency dependent magnetic measurements can help to gain a deeper insight into the magnetic behavior of these systems. For example, Fig. 10 shows the heat capacity (C_p) of the extended 2D compound [P(Ph)][MnCr(ox)] from 3 to 30 K. A clear lambda peak appears at $T_c = 5.8$ K indicating the establishment of long-range magnetic ordering. This result is in agreement with a sharp peak observed in the in-phase component (χ') of the ac susceptibility ($T_m = 5.6$ K), which is accompanied by a strong out-of-phase component. At 1.8 K the magnetization, M, saturates at low applied fields at nearly the expected value for a parallel alignment of the spins.

In contrast to the large body of experimental results which has been published from magnetic susceptibility and magnetization measurements with molecule-based magnetic materials, very limited experience has been gained so far from elastic

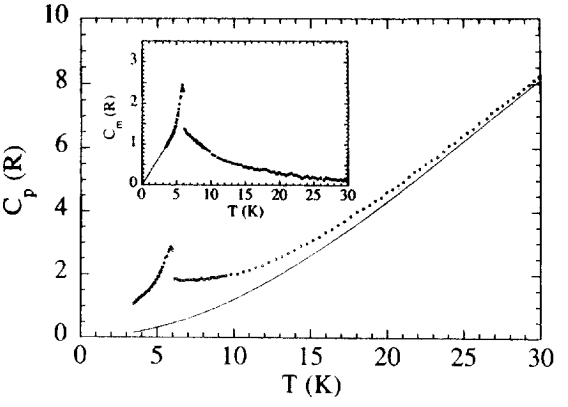

Fig. 10. Heat capacity of $[P(Ph)_4][MnCr(ox)_3]$ and estimated lattice contribution (continuos line). The insert shows the magnetic contribution to the heat capacity and the spin-waves extrapolation (continuos line).

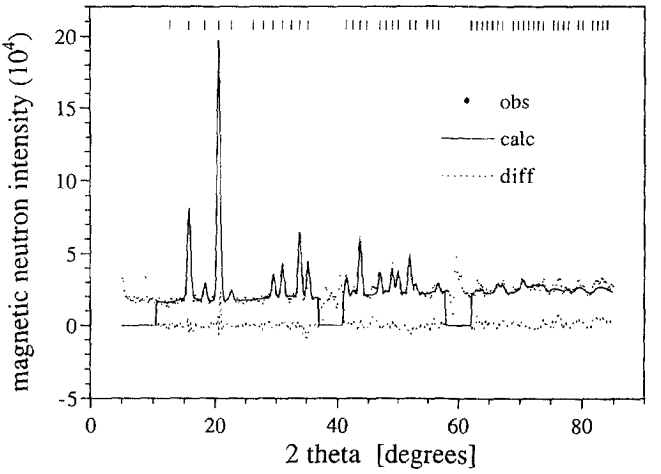

Fig. 11. Observed (difference $I(1.8\ K) - I(30\ K)$), calculated and difference magnetic neutron diffraction patterns of a polycrystalline sample of $[Fe(II)(d_8\text{-bpy})_3]_n^{2+}$ $[Mn(II)_2(ox)_3]_n^{2n-}$.

neutron-scattering experiments aimed at elucidating the spin structure in the magnetically ordered phase. Therefore, in the following, a brief account of the current state of the ongoing investigations by means of the neutron-scattering technique will be given. Thereby, complementary to the above mentioned 2D systems, a 3D molecular network compound will be chosen for a brief discussion.

Thus, we briefly report on neutron diffraction experiments performed on a 3D polycrystalline sample with stoichiometry $[Fe(II)(d_8\text{-bpy})_3]_n^{2+}$ $[Mn(II)_2(ox)_3]_n^{2n-}$, with the goal to determine the magnetic structure of this helical supramolecule in the antiferromagnetically ordered phase, thus below $T_N = 13$ K [23]. The existence of this magnetically ordered phase has formerly been suggested from magnetic dc-susceptibility measurements which revealed a rounded maximum at about 20 K in the χ_M versus T curve (thus $T_N < 20$ K) as well as a Weiss constant Θ of -33 K in the $1/\chi_M$ versus T plot [7]. Accordingly, a magnetic ac-susceptibility experiment revealed an ordering temperature around 15 K. This long-range magnetic ordering basically originates from the exchange interaction between neighbouring Mn^{2-} ions, mediated by the bridging oxalate ligands.

As anticipated from these bulk measurements, an increase of the intensities due to long-range antiferromagnetic ordering of the Mn^{2+} ions could be detected with the neutron diffraction measurements performed in the temperature range of 30–1.8 K. Fig. 11 illustrates the observed (difference $I(1.8\ K) - I(30\ K)$), calculated and difference magnetic neutron diffraction patterns. Thereby, it should be noted that the increase in intensities corresponds to a propagation vector $\mathbf{K} = 0$, i.e. a magnetic unit cell being equal to the chemical cell. The temperature dependence of the dominant magnetic intensity (210) at $2\Theta = 21.1°$ indicates an ordering temperature $T_N = 13(0.5)$ K, in good agreement with the magnetic susceptibility experiments.

Furthermore, it remains to discuss the determined magnetic moment configuration of this three-dimensionally linked Mn^{2+} network. With respect to space group $P4_132$, the Mn^{2+} ions occupy sites 8c; x,x,x with $x = 0.64907$. The best agreement between observed and calculated magnetic neutron intensities was achieved with a collinear, antiferromagnetic arrangement of Mn^{2+} moments according to the three-dimensional irreducible representation τ_4, which is derived from the enantiomorphic pair of the chiral, cubic crystallographic space groups $P4_332/P4_132$ [24]. Thereby, the ordered magnetic moment at 1.8 K amounts to $\mu_{Mn} = 4.6(1)\ \mu_B$, where μ_B is the electron Bohr magneton. The saturation magnetization, M_S, is related to the equation $M_S = g \times \mu_B \times N \times S$, where S is the spin quantum number, N the Avogadro number and g the electron g-factor. Thus, a $g \times S$ value corresponding to the number of unpaired electrons of 4.6 is obtained, which is compatible with the expected five unpaired electrons ($g = 2$) from the Mn^{2+} ions. Naturally, in the present experiment, no information about a preferred direction of the magnetic moments with respect to the crystallographic axes can be gained from the polycrystalline sample with cubic symmetry.

Fig. 12 depicts the pattern of the magnetic structure within the 3D manganese(II) network. Despite the three-dimensional helical character of the framework structure incorporating the magnetic ions, a two-sublattice antiferromagnetic spin arrangement has proved to occur, hence no helimagnetic structure has shown up. After all, the behavior is in accordance with the typical isotropic character of the Heisenberg ion Mn^{2+}.

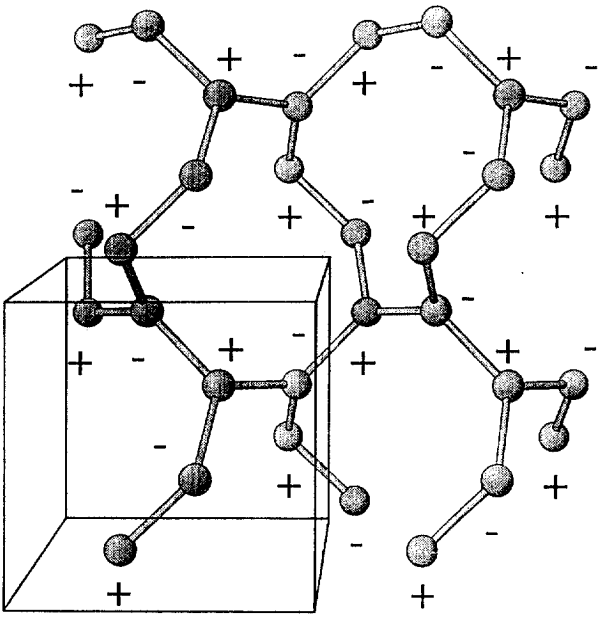

Fig. 12. Scheme of the antiferromagnetic collinear configuration of the magnetic moments originating from the Mn^{2+} ions, which constitute the chiral 3D network compound.

This example of the extended 3D Mn^{2+} coordination solid illustrates the potential of the elastic neutron-scattering technique to elucidate the spin structures within the magnetically ordered phases occurring in such polymeric molecular materials.

4. Photophysics

Here, we will only mention that a large variety of excitation energy-transfer processes exist within the 3D supramolecular host/guest compounds. Depending upon the relative energies of the excited states of the chromophores, energy-transfer is observed either from the guest system with the tris-bipyridine cations as donors to the host system where the oxalate-backbone acts as acceptor sites or vice versa. In addition, energy-transfer between identical chromophores occurs within the host as well as within the guest system. For a further discussion the reader is referred to the literature [8,25,26].

5. Summary

Nowadays, the synthetic chemists have turned their attention to an ambitious architectural goal, namely the assembly of relatively simple molecules into complex, polymeric structures. The big challenge of building new, ever more intricate molecules is to learn how to control the ordering of the component molecules so that the supramolecular assembly has the desired structure, stability and properties. Accordingly, the results presented in this paper show a straightforward concept for the synthesis of 2 and 3D network structures. Thereby, the oxalate ion, although a fairly ubiquitous ligand, plays a key role in the formation of a whole class of transition-metal based supramolecular host/guest systems. Ongoing studies focus on the elucidation of the magnetic structures for different magnetically ordered phases and on the investigation of the fascinating photophysical behavior. Overall, we are looking for synergistic properties within this class of multifunctional materials.

Acknowledgements

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