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Supramolecular Host/Guest Compounds and their Prospects for Multifunctional Materials

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Cleverly designed molecular building blocks provide chemists with the tools of a powerful molecular-scale construction set. They enable them to engineer materials having 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 bimetallic oxalato-bridged transition-metal compounds with two- and three-dimensional connectivities are investigated. In particular, we report herein in detail about their structural properties and their multifunctional characteristics in the area of molecular magnetism and photophysics.

Keywords: *self-organization, extended molecular networks, structural topology, molecule-based magnetism, photophysics, energy-transfer processes*

INTRODUCTION

Interest in functional materials based on molecular crystals persists, owing to the potential for manipulating solid-state properties by system-

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atic 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.^{1,2}

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. 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.

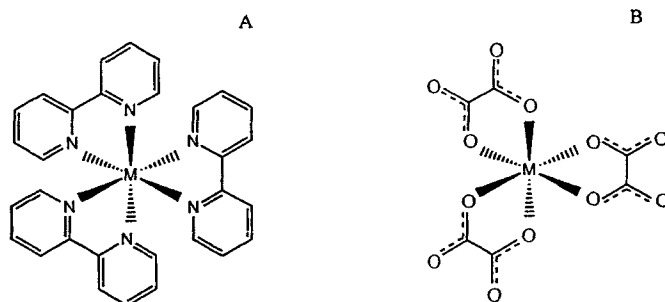
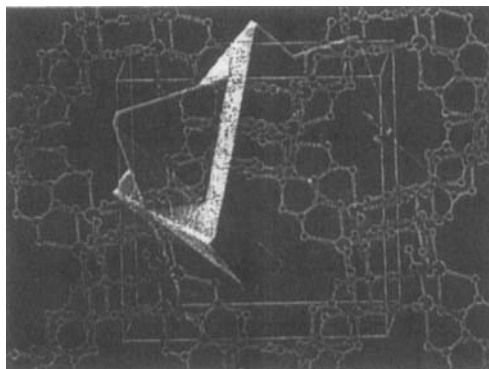


FIGURE 1 Schematic representation of the two chiral (the A-isomers are shown) preorganized cationic (A) and anionic (B) coordination entities. M = transition-metal ion as spin carrier center



PICTURE 1 Single crystal of a chiral 3D molecular network compound with transition-metal ions as spin carriers

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.^{3–8} 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 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. Figure 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

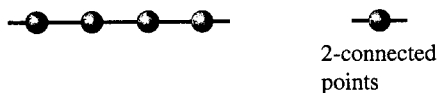


FIGURE 2 An atom or a molecular complex forming two bonds comprises a structural unit for a 1D compound

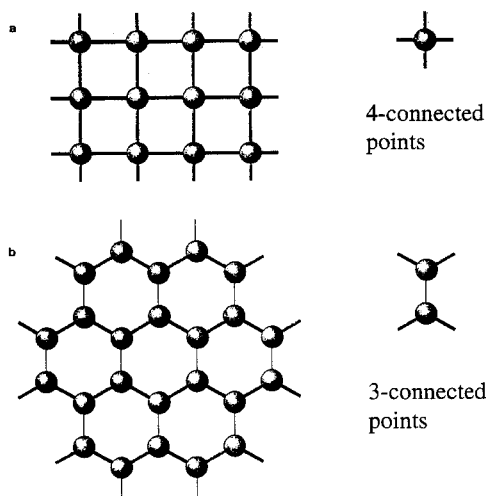


FIGURE 3 (a) An atom or a molecular complex forming four bonds comprises a structural unit for a 2D compound; (b) the repeat unit consists of a pair of 3-connected points

simple topological rules,⁹ which will determine the connectivity and structural dimensionality for 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 for constructing polymeric networks. Consequently, molecular subunits with two free links, repre-

sented 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 four free links which corresponds 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.

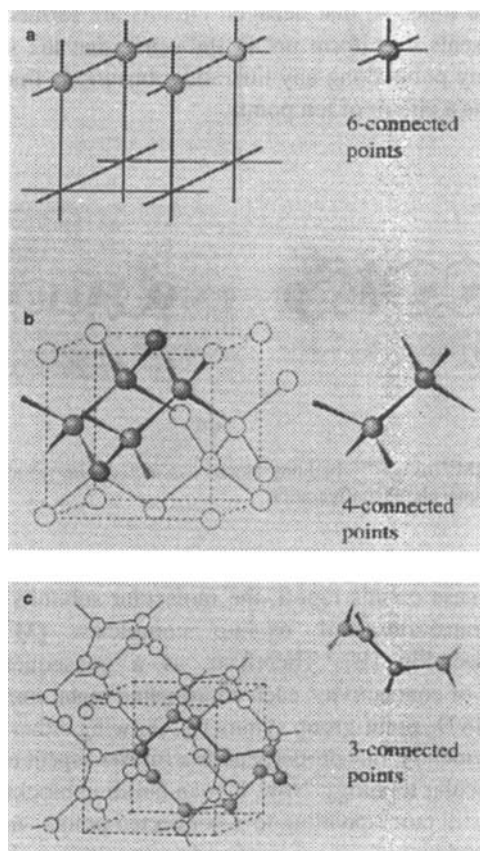


FIGURE 4 (a) An atom or a molecular complex forming six bonds comprises a structural unit for a 3D compound; (b) the repeat unit consists of a pair of 4-connected points, leading to a 3D (6,4) network; (c) the repeat unit consists of a tetramer of 3-connected points, leading to a 3D (10,3) network

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. Figure 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.

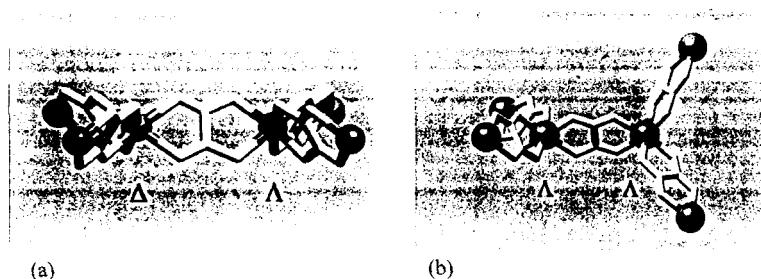
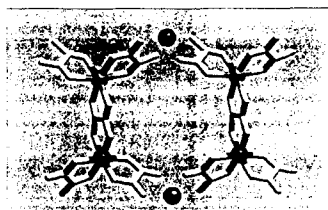
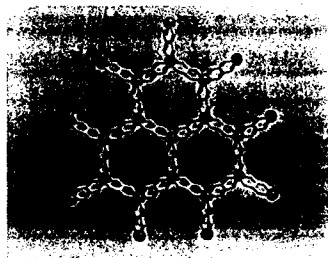


FIGURE 5 Chiral $[M^{z+}(ox)_3]^{(6-z)-}$ building blocks assembled with (a) alternating chiral configuration, (b) equal chiral configuration

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. 1B). Therefore, as a consequence of this $[M(L^A)_3]$ 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, as 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



(a)



(b)

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

the number of 3-connected subunits which are needed to build closed circuits, hence, extended framework motifs. Figure 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.

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 2D or a 3D framework structure relies on the choice of the templating counterion. Evidently, the template cation determines the crystal chemistry. In particular, $[\text{XR}_4]^+$ ($\text{X} = \text{N}, \text{P}$; $\text{R} = \text{phenyl, n-propyl, n-butyl}$,

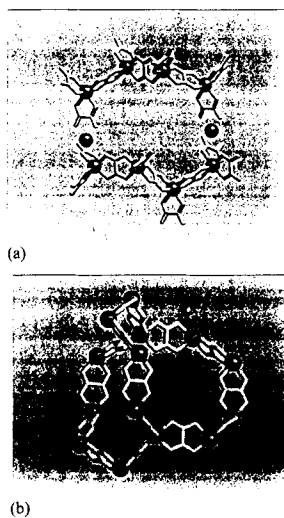


FIGURE 7(a) Two tetrameric units of the same chirality type are necessary to form a closed decagon ring; (b) a fragment of the 3D, chiral framework

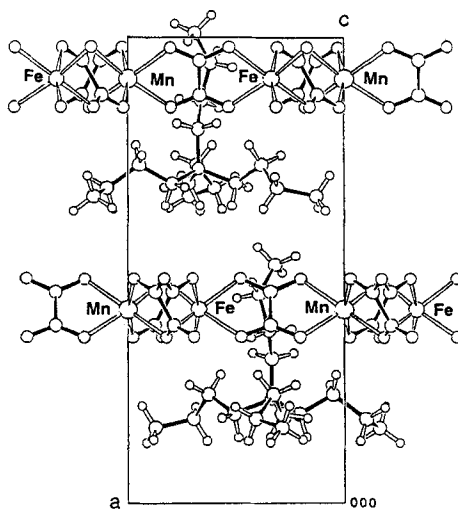


FIGURE 8 [010] projection of $\{[N(n-C_4H_9)_4][Mn^{II}Fe^{III}(C_2O_4)_3]\}_n$

n-pentyl) cations initiate the growth of 2D layer structures containing $[M^{II}M^{III}(ox)_3]_n^{n-}$, $M^{II} = V, Cr, Mn, Fe, Co, Ni, Cu, Zn$; $M^{III} = Al, V, Cr, Fe, Co, Ru, Rh$, 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 the values 9.94 Å, 9.55 Å, 8.91 Å, and 8.20 Å for the n-pentyl, phenyl, n-butyl, and n-propyl derivatives.^{4,8,18}

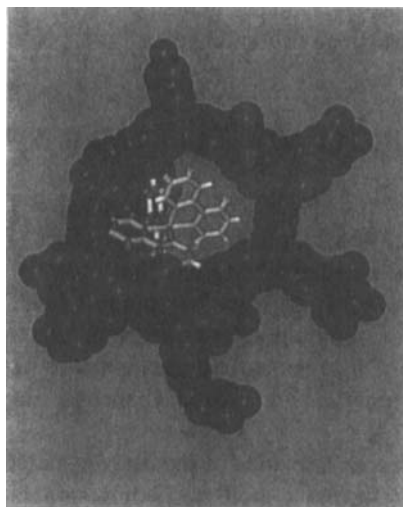


FIGURE 9 3D host/guest compound. Only one guest molecule is shown within the chiral framework

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

$[M^{II}_2(ox)_3]^{2n-}$, $[M^I M^{III}(ox)_3]^{2n-}$ or $[M^{II} M^{III}(ox)_3]^{n-}$ is chiral, as it is composed of $2n$ centers exhibiting the same kind of chirality. 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 homometallic 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. Figure 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 2D and 3D supramolecular materials are accessible. Thereby, some general topological rules describe elegantly the resulting distinctive architectures.

MULTIFUNCTIONALITY: MOLECULAR MAGNETISM

The magnetic properties of molecule-based materials have become an important focus of scientific interest in the last years,^{10–12} whereby the search for molecule-based ferromagnets that order at or above room temperature is a major driving force moving this field.¹³ 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.*¹⁴ 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 turned up 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 analogues 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 of 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.¹¹ Naturally, in search of an answer to the second question, effort has to been given to the investigation of the magnetic ordering behavior of the above-described 2D 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. 1B) was reported in 1992.¹⁵ 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.^{16–19} Overall, many of these layered compounds exhibit ferro-, ferri- or antiferromagnetic long-range ordering behavior, and in some cases they show evidence for at least short-range interactions.

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 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 $[\text{Fe}^{\text{II}}(\text{d}_8\text{-bpy})_3]^{2+}_n[\text{Mn}^{\text{II}}_2(\text{ox})_3]^{2n-}_n$, with the goal to determine the magnetic structure of this helical supramolecule in the antiferromagnetically ordered phase, thus below $T_N = 13$ K.²⁰ 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.⁵ Accordingly, a magnetic ac-susceptibility experiment revealed an ordering temperature around 15 K. This long-range magnetic ordering originates basically from the exchange interaction between neighbouring Mn^{2+} ions, mediated by the bridging oxalate ligands.

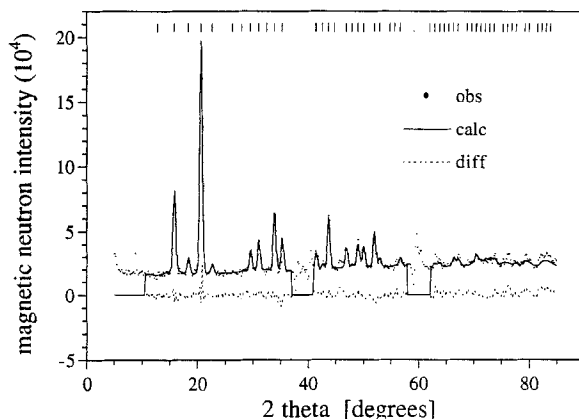


FIGURE 10 Observed [difference $I(1.8\text{ K}) - I(30\text{ K})$], calculated and difference magnetic neutron diffraction patterns of a polycrystalline sample of $[\text{Fe}^{\text{II}}(\text{d}_8\text{-bpy})_3]^{2+}_n[\text{Mn}^{\text{II}}_2(\text{ox})_3]^{2-}_n$

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 from 30 K to 1.8 K. Figure 10 illustrates the observed [difference $I(1.8\text{ K}) - I(30\text{ K})$], calculated and difference magnetic neutron diffraction patterns. Thereby, it has to be noted that the increase of the 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 $2\Theta = 21.1^\circ$ indicates an ordering temperature $T_N = 13(0.5)\text{ K}$, 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 $P4_332/P4_132$.²¹ Thereby, the ordered magnetic moment at 1.8 K amounts to

$\mu_{\text{Mn}} = 4.6(1) \mu_{\text{B}}$, where μ_{B} is the electron Bohr magneton. The saturation magnetization, M_{S} , is related to the equation $M_{\text{S}} = g \cdot \mu_{\text{B}} \cdot N \cdot S$, where S is the spin quantum number, N the Avogadro number and g the electron g -factor. Thus, a $g \cdot S$ value corresponding to the number of unpaired electrons of 4.6 is obtained, which is compatible with the expected 5 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.

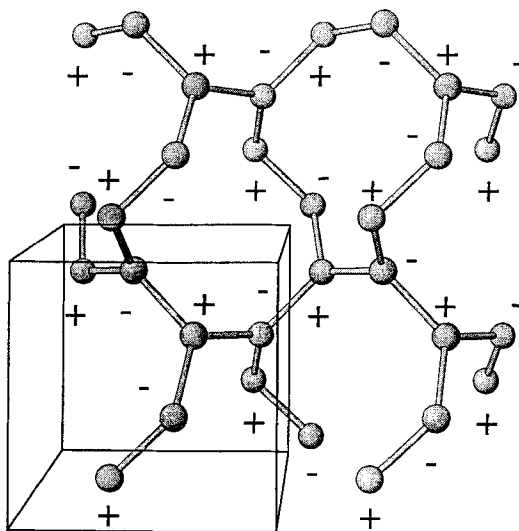


FIGURE 11 Scheme of the antiferromagnetic, collinear configuration of the magnetic moments originating from the Mn^{2+} ions, which constitute the chiral, 3D network compound

Figure 11 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 behaviour is in accordance with the typical isotropic character of the Heisenberg ion Mn^{2+} .

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.

MULTIFUNCTIONALITY: PHOTOPHYSICS

In this section we will comment on some observations of excitation energy-transfer processes 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.^{6,22,23}

Figure 12 illustrates these energy-transfer processes schematically with different host/guest stoichiometries, and particularly one can point out that chemical variation and combination of metal ions of different valencies in the oxalate-backbone as well as in the tris-bipyridine cation offer unique opportunities for studying a large variety of photophysical phenomena. Naturally, the sensitiser can be incorporated into the oxalate-backbone or the tris-bipyridine cation, either in low concentration as dopant, at higher concentration in mixed crystals, or fully concentrated in neat compounds.

As an example of the energy-transfer processes, Fig. 13 shows the luminescence spectra of three representative compounds. For instance, if Al^{3+} is replaced by Cr^{3+} , the $[\text{Ru}(\text{bpy})_3]^{2+}$ luminescence from the spin-forbidden MLCT transition is completely quenched and the sharp luminescence bands characteristic for the zero-field components of the ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition of octahedrally coordinated and trigonally distorted Cr^{3+} are observed at $14,400\text{ cm}^{-1}$. This is a clear indication for very efficient energy-transfer from the initially excited $[\text{Ru}(\text{bpy})_3]^{2+}$ to $[\text{Cr}(\text{ox})_3]^{3-}$. However, not only acceptors on the oxalate-backbone may quench the $[\text{Ru}(\text{bpy})_3]^{2+}$ luminescence. Replacing a fraction of the $[\text{Ru}(\text{bpy})_3]^{2+}$ by $[\text{Os}(\text{bpy})_3]^{2+}$ results in luminescence from $[\text{Os}(\text{bpy})_3]^{2+}$ and a quenching of the $[\text{Ru}(\text{bpy})_3]^{2+}$ luminescence, too. Indeed, the energy-transfer to $[\text{Os}(\text{bpy})_3]^{2+}$ is even more efficient than to $[\text{Cr}(\text{ox})_3]^{3-}$.

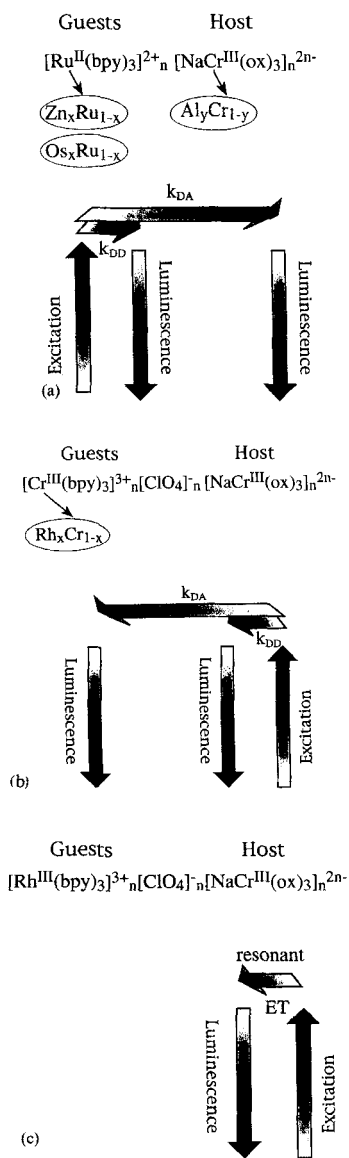


FIGURE 12 Schematic representation of energy-transfer processes for different stoichiometries; (a) excitation into the guest system; (b) and (c) excitation into the host system

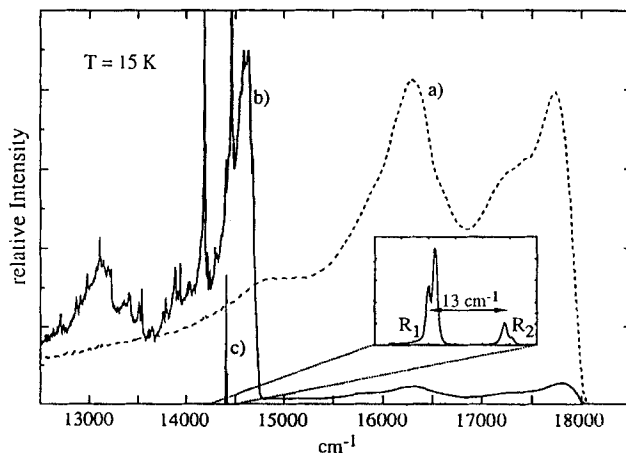


FIGURE 13 Luminescence spectra at $T = 15$ K of (a) $[\text{Ru}(\text{bpy})_3][\text{NaAl}(\text{ox})_3]$; (b) $[\text{Ru}_{1-x}\text{Os}_x(\text{bpy})_3][\text{NaAl}(\text{ox})_3]$, $x = 1\%$; (c) $[\text{Ru}(\text{bpy})_3][\text{NaCr}(\text{ox})_3]$; $\lambda = 476$ nm

Alternatively, as schematically drawn in Fig. 12(b), irradiating into the spin-allowed $^4\text{A}_2 \rightarrow ^4\text{T}_2$ absorption band of $[\text{Cr}(\text{ox})_3]^{3-}$ from the host system results in intense luminescence from the ^2E state of $[\text{Cr}(\text{bpy})_3]^{3+}$ within the guest system, again demonstrating a rapid energy-transfer process.⁶ Finally, according to Fig. 12(c), the stoichiometry $[\text{Rh}(\text{bpy})_3]^{3+}_n[\text{ClO}_4]^-_n[\text{NaCr}(\text{ox})_3]^{2n-}_{2n}$ allows us to study the energy-transfer within the R_1 line of the ^2E state of Cr^{3+} . In that case, from a fluorescence line narrowing experiment, clear evidence for a resonant energy-transfer process could be gained.^{22,23}

SUMMARY

Nowadays, the synthetic chemists have turned their attention to an ambitious architectural goal — 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 2D 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.

Acknowledgments

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References

1. M. J. Zaworotko, *Nature* **386**, 220 (1997).
2. S. C. Zimmerman, *Science* **276**, 543 (1997).
3. S. Decurtins, H. W. Schmalle, P. Schneuwly and H. R. Oswald, *Inorg. Chem.* **32**, 1888 (1993).
4. S. Decurtins, H. W. Schmalle, H. R. Oswald, A. Linden, J. Ensling, P. Gütllich and A. Hauser, *Inorg. Chim. Acta* **216**, 65 (1994).
5. S. Decurtins, H. W. Schmalle, P. Schneuwly, J. Ensling and P. Gütllich, *J. Am. Chem. Soc.* **116**, 9521 (1994).
6. S. Decurtins, H. W. Schmalle, R. Pellaux, P. Schneuwly and A. Hauser, *Inorg. Chem.* **35**, 1451 (1996).
7. H. W. Schmalle, R. Pellaux and S. Decurtins, *Z. Kristallogr.* **211**, 533 (1996).
8. R. Pellaux, H. W. Schmalle, R. Huber, P. Fischer, T. Hauss, B. Ouladdiaf and S. Decurtins, *Inorg. Chem.* **36**, 2301 (1997).
9. A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1984).
10. *Proceedings of the IV International Conference on Molecule-Based Magnets*, Molecular Crystals and Liquid Crystals, J. S. Miller and A. J. Epstein, Eds. (Gordon & Breach, London, 1995, Vols. 271–274).
11. O. Kahn, *Molecular Magnetism* (VCH, Weinheim, 1993).
12. J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* **33**, 385 (1994).
13. S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Nature* **378**, 701 (1995).
14. H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull and F. R. Merritt, *Phys. Rev.* **155**, 563 (1967).
15. H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.* **114**, 6974 (1992).
16. C. Mathonière, S. G. Carling, D. Yusheng and P. Day, *J. Chem. Soc., Chem. Commun.* 1551 (1994).
17. C. J. Nuttall, C. Bellitto and P. Day, *J. Chem. Soc., Chem. Commun.* 1513 (1995).
18. C. Mathonière, C. J. Nuttall, S. G. Carling and P. Day, *Inorg. Chem.* **35**, 1201 (1996).
19. S. G. Carling, C. Mathonière, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.* 1839 (1996).

20. S. Decurtins, H. W. Schmalke, R. Pellaux, R. Huber, P. Fischer and B. Ouladdiaf, *Adv. Mater.* **8**, 647 (1996).
21. W. Sikora, PC-program MODY in Collected abstracts of a "Workshop on Magnetic Structures and Phase Transitions," Krakow, Poland (1994).
22. A. Hauser, H. Riesen, R. Pellaux and S. Decurtins, *Chem. Phys. Lett.* **261**, 313 (1996).
23. M. E. von Arx, A. Hauser, H. Riesen, R. Pellaux and S. Decurtins, *Phys. Rev. B* **54**, 15800 (1996).