Multifunctional coordination compounds: design and properties

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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 that have a predictable order and useful solid-state properties. Hence, it is in the realm of supramolecular chemistry to follow a strategy for synthesizing materials that combine a selected set of properties, for instance from the areas of magnetism, photophysics and electronics. As a possible approach, host–guest solids that 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 in detail about their structural properties and their multifunctional characteristics in the area of molecular magnetism and photophysics.

Keywords: coordination compounds; network compounds; oxalate complexes; molecular magnetism; energy transfer

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, until 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 (Zaworotko 1997; Zimmerman 1997; Desiraju 1996; Lehn 1995).

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. 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 (figure 1). Starting with a detailed discussion about the structural topology of this supramolecular coordination compound, we will subsequently present some experimental results in the areas of magnetism and
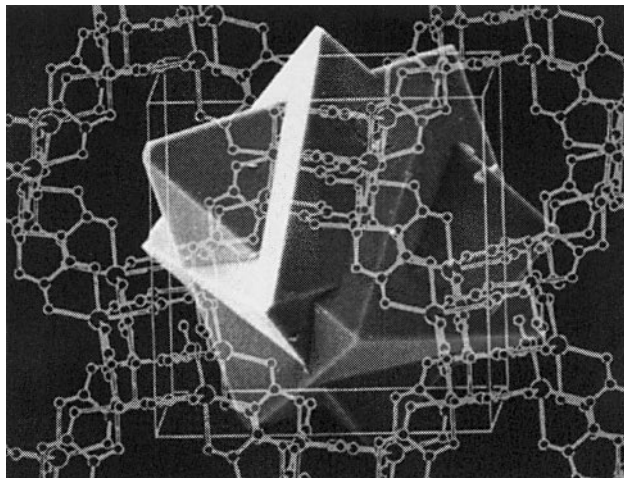
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Figure 1. Single crystal of a chiral three-dimensional molecular network compound
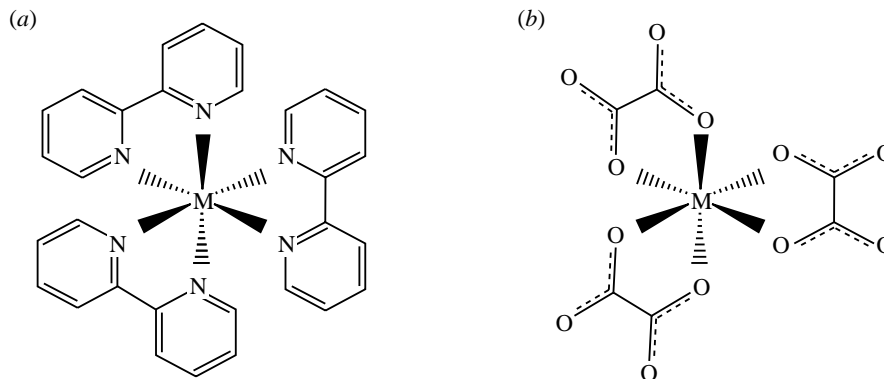with transition metals as spin carriers.

Figure 2. 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
centre.

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 coor-
dination solids based on transition-metal oxalates, which, typically, behave as host–
guest compounds with different lattice dimensionalities (Schmalle *et al.* 1996; Pellaux
et al. 1997; Decurtins *et al.* 1993, 1994*a, b*, 1996*b*). Thereby, the idea of a reasonable
strategy looks simple: mix metal ions with a preference for a particular coordina-
tion 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
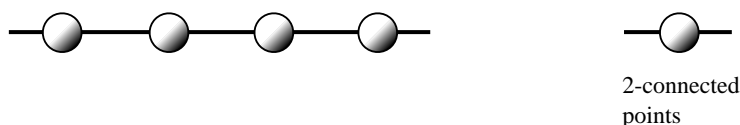
2-connected
points

Figure 3. An atom or a molecular complex forming two bonds comprises
a structural unit for a one-dimensional compound.

on the robustness of some coordination subunits and of the supramolecular motif as a whole. Figure 2 depicts two preorganized transition metal complexes that act as mutually complementary molecular partners. Due to their specific coordination properties and their similar size and shape, they are predisposed on one hand to act as template molecules and on the other to form extended two- and three-dimensional 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 (Wells 1984) that will determine the connectivity and structural dimensionality for many of these molecular assemblies, ranging from infinitely extended one-dimensional to three-dimensional motifs (compare figures 3–5). 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 form one-dimensional molecular chains (figure 3). Analogously, as illustrated in figure 4, the formation of two-dimensionally 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.

Along this line, extended three-dimensionally 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 5 shows that, in each case and very strictly, distinct three-dimensional lattice types are created. Most interestingly, the subunits that will form a 3-connected three-dimensional 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 10 points.

In the actual case of this report, the molecular subunits are anionic tris-chelated transition-metal oxalato complexes $[M^{z+}(ox)_3]^{(6-z)-}$, where $ox = C_2O_4^{2-}$ (see figure 2b). Therefore, as a consequence of this $[M(L^\wedge L)_3]$ type of connectivity, each coordinated metal ion represents a chiral centre 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
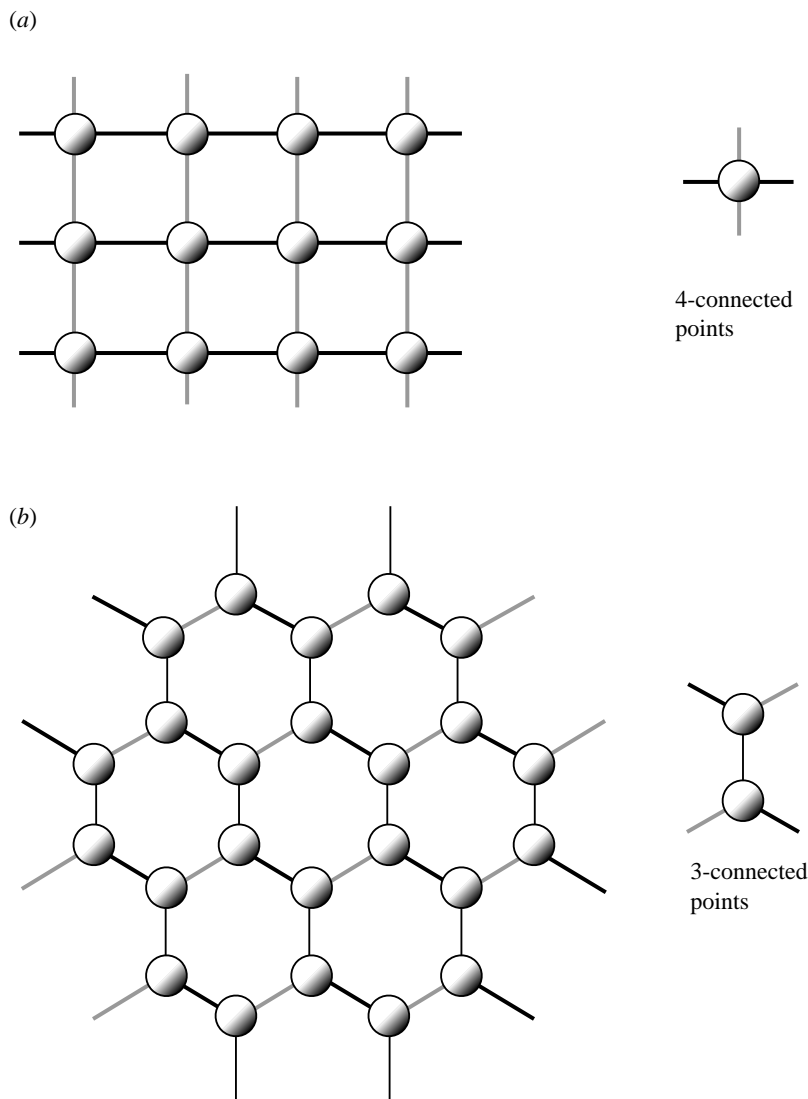
(*a*)

4-connected points

(*b*)

3-connected points

Figure 4. (*a*) An atom or a molecular complex forming four bonds comprises a structural unit for a two-dimensional compound. (*b*) The repeat unit consists of a pair of 3-connected points.

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 figure 6. Consequently, a layered structure motif will result. In contrast, as also depicted in figure 6, an assembling of building blocks of the same chiral configuration will lead to a three-dimensional framework structure. It remains to apply the topological rules described above in order to define the number of 3-connected subunits that are needed to build closed circuits, hence, extended framework motifs. Figure 7 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 figure 8 that two tetrameric subunits are
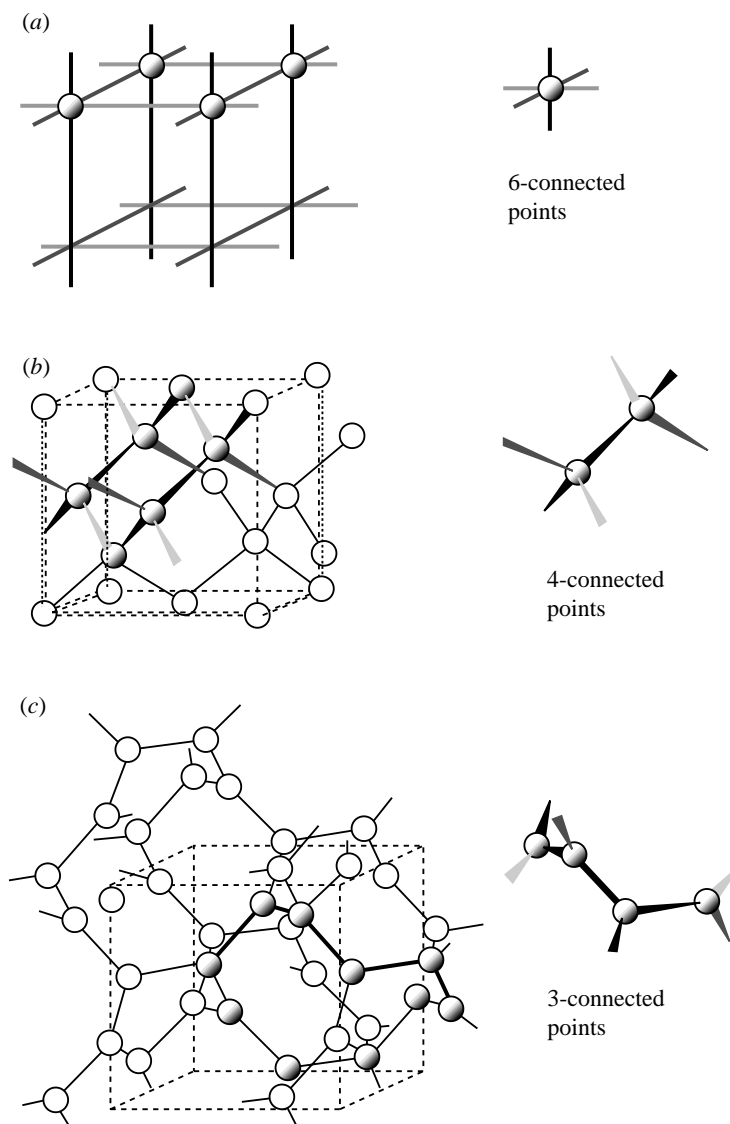
(*a*)

6-connected
points

(*b*)

4-connected
points

(*c*)

3-connected
points

Figure 5. (*a*) An atom or a molecular complex forming six bonds comprises a structural unit for a three-dimensional compound. (*b*) The repeat unit consists of a pair of 4-connected points, leading to a three-dimensional (6,4) network. (*c*) The repeat unit consists of a tetramer of 3-connected points, leading to a three-dimensional (10,3) network.

needed to build closed circuits composed of 10 metal centres, which, in sum, define the chiral three-dimensional 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 crystal-lization conditions for each specific material. In the actual case of these tris-chelated transition metal oxalato complexes, the discrimination between the formation and crystallization of either a two-dimensional or a three-dimensional framework struc-
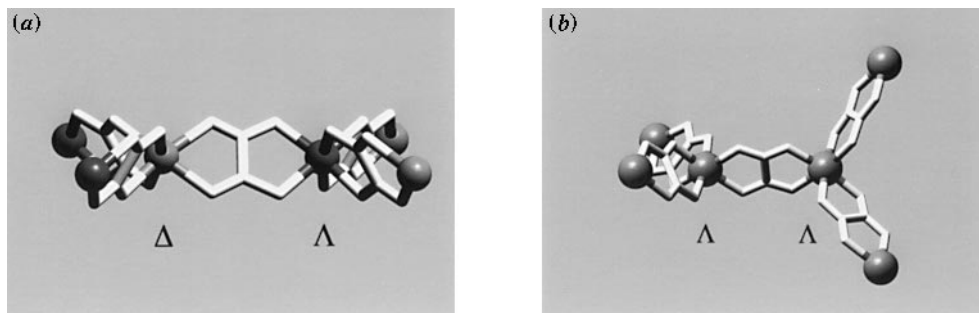
Figure 6. Chiral $[M^{z+}(ox)_3]^{(6-z)-}$ building blocks assembled with
(*a*) alternating chiral configuration, (*b*) equal chiral configuration.
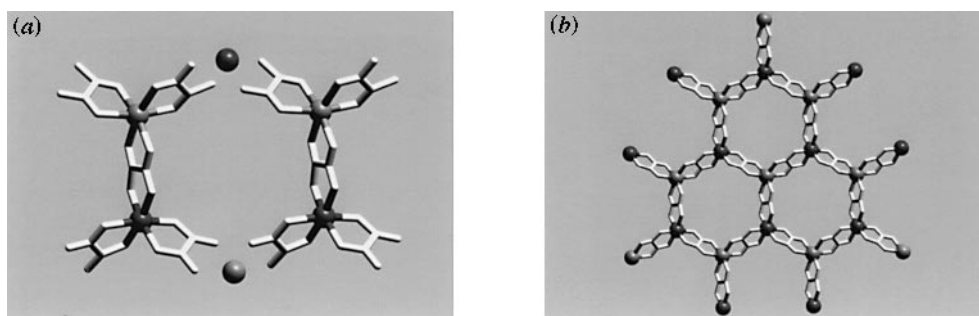

Figure 7. (*a*) Two dimeric units of the alternating chirality type are necessary to form a
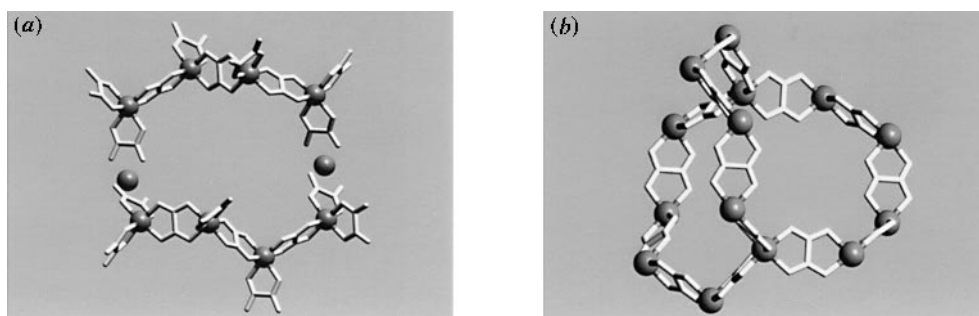closed hexagon ring; (*b*) the resulting planar network motif.

Figure 8. Two tetrameric units of the same chirality type are necessary to form a
closed decagon ring. (*b*) A fragment of the three-dimensional chiral framework.

ture 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 two-dimensional 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 two-dimensional honeycomb networks that are interleaved by the templating cations. Although these two-dimensional compounds are not chiral, they express a structural polarity due to the specific arrangement of the templating cations (see figure 9). These organic cations, which are located between the anionic layers, determine the
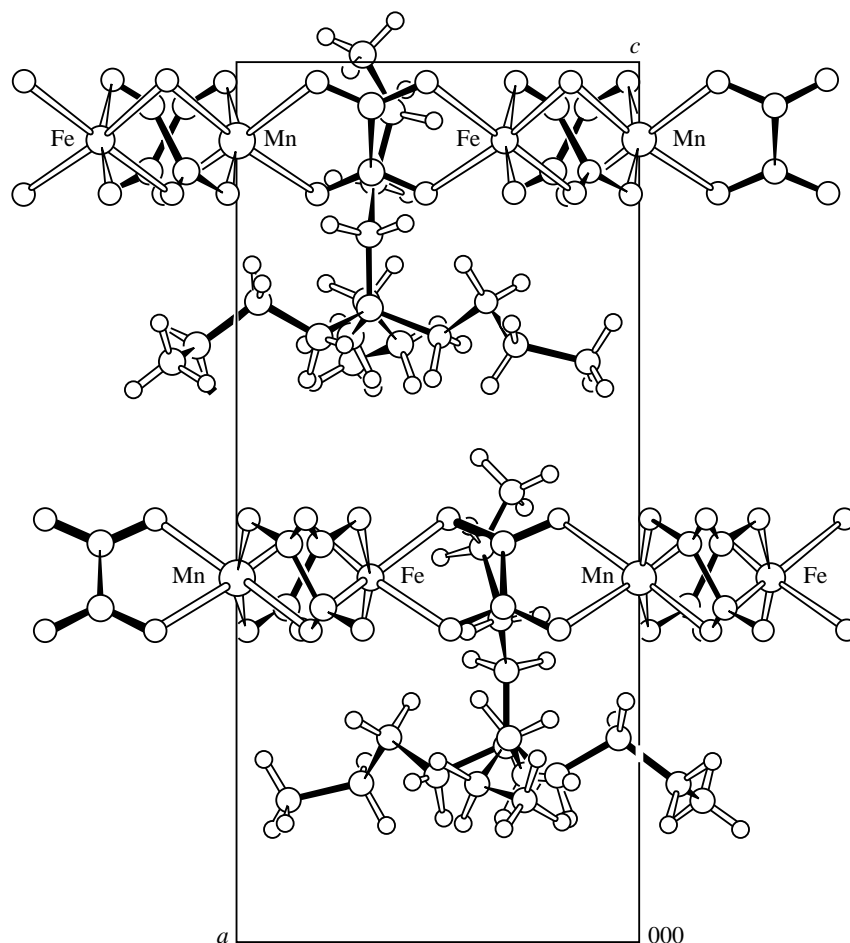
Figure 9. [010] projection of $\{[N(n\text{-}C_4H_9)_4][Mn^{II}Fe^{III}(C_2O_4)_3]\}_n$.

interlayer separations. From single-crystal X-ray studies, these distances have been determined to have 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, respectively (Decurtins *et al.* 1994*a*; Pellaux *et al.* 1997; Mathonière *et al.* 1996).

Remarkably, the cationic tris-chelated transition-metal diimine complexes,

$$[M(bpy)_3]^{2+/3+}$$
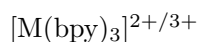
(see figure 2*a*), act as templates for the formation and crystallization of the three-dimensional decagon framework structures. As outlined above, the topological principle implies that, for the three-dimensional case, only subunits of the same chiral configuration are assembled. Consequently, the uniform anionic three-dimensional network type with stoichiometries like

$$[M_2^{II}(ox)_3]_n^{2n-}, \quad [M^I M^{III}(ox)_3]_n^{2n-} \quad \text{or} \quad [M^{II} M^{III}(ox)_3]_n^{n-}$$
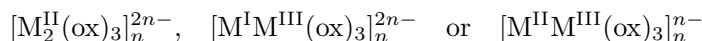
is chiral, as it is composed of $2n$ centres exhibiting the same kind of chirality. Naturally, this chiral topology is in line with the symmetry elements that are present in
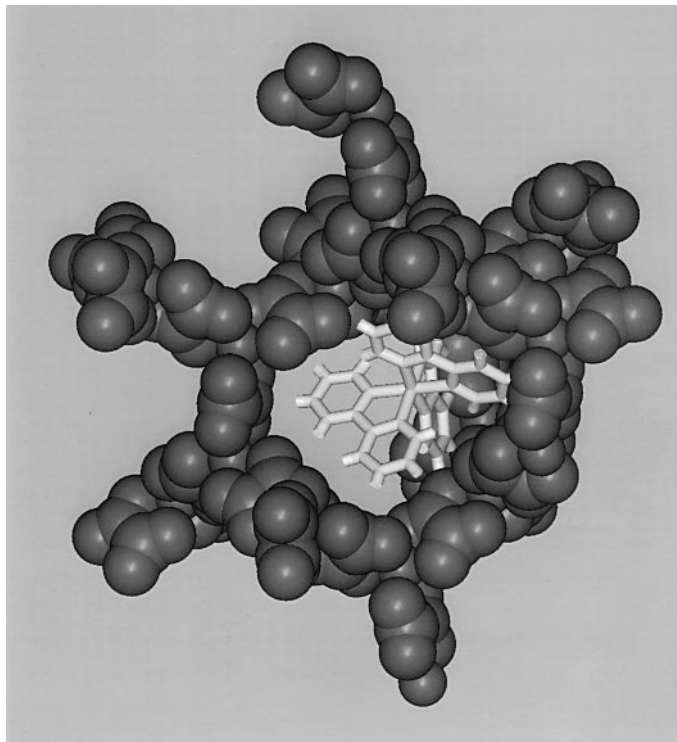
Figure 10. The three-dimensional host–guest compound. Only one
guest molecule is shown within the chiral framework.

the crystalline state of the three-dimensional 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 bi-metallic stoichiometries. Thereby, the $2n$ metal ions occupy special sites with a threefold symmetry axis. Figure 10 depicts a view of the three-dimensional host–guest assembly.

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

3. Multifunctionality: molecular magnetism

The magnetic properties of molecule-based materials have become an important focus of scientific interest in the last few years (Miller & Epstein 1994, 1995; Kahn 1993; Ferlay *et al.* 1995), whereby the search for molecule-based ferromagnets that order at or above room temperature is a major driving force moving this field (Ferlay *et al.* 1995). 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.* as early as 1967 (Wickman *et al.* 1967). This compound, a chlorobis(diethyldithio-carbamato)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 centres 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, supra-molecular functions like energy- and charge-transfer processes can benefit from these properties; and

(iii) the collective features of components bearing free spins may result in supra-molecular assemblies exhibiting molecule-based magnetic behaviour, 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 ferromagnetic 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 three-dimensional lattice.

Naturally, if the compounds assume a two-dimensional 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 (Kahn 1993). Naturally, in search for an answer to the second question, effort has to be made to investigate the magnetic ordering behaviour of the above-described two-dimensional and three-dimensional systems.

Along this line, a successful molecular design of two-dimensionally extended metal-complex magnets that are based on trioxalatochromium(III) building blocks (see figure 2b) has been reported in Tamaki *et al.* (1992). Within a series of layered oxalate-bridged bi-metallic compounds, ferromagnetic ordering behaviour has been shown to occur at temperatures below 14 K. Since then, a variety of analogous two-dimensional bi-metallic assemblies, also with mixed-valency stoichiometries, have been prepared and characterized (Mathonière *et al.* 1994, 1996; Nuttall *et al.* 1995; Carling *et al.* 1996). Overall, many of these layered compounds exhibit ferromagnetic, ferrimagnetic or antiferromagnetic long-range ordering behaviour, and, in some cases, they show evidence for at least short-range interactions.

In contrast with the large body of experimental results that 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 two-dimensional systems, a three-dimensional molecular network compound will be chosen for a brief discussion.

Thus, we briefly report on neutron diffraction experiments, performed on a three-dimensional polycrystalline sample with stoichiometry

$$[Fe^{II}(d_8\text{-bpy})_3]_n^{2+} \ [Mn_2^{II}(ox)_3]_n^{2n-},$$
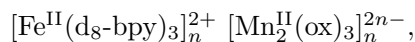
with the goal of determining the magnetic structure of this helical supramolecule in the antiferromagnetically ordered phase, thus, below $T_N = 13$ K (Decurtins *et al.* 1996a). The existence of this magnetically ordered phase has formerly been suggested from magnetic DC-susceptibility measurements, 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 (Decurtins *et al.* 1994b). 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 from 30 K to 1.8 K. Figure 11 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
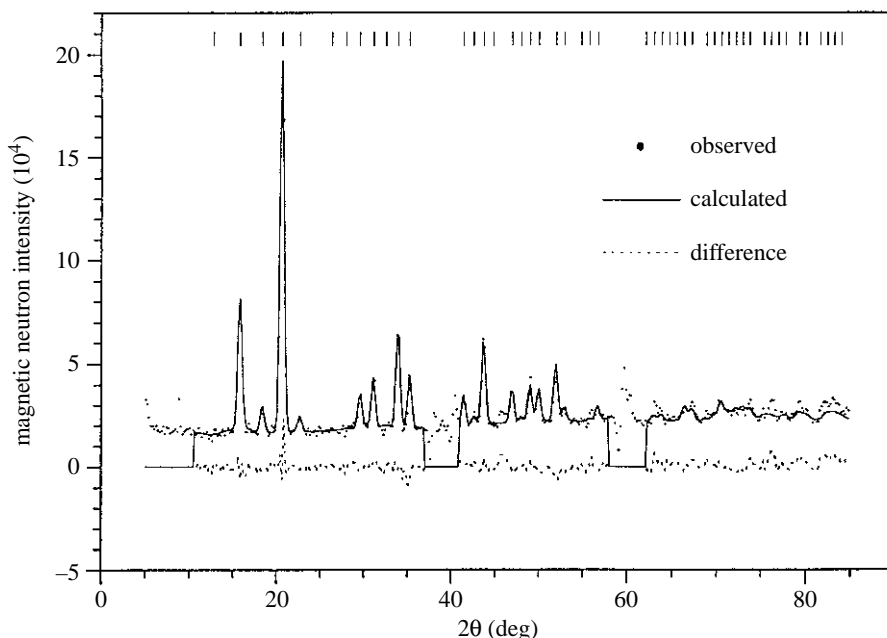
Figure 11. Observed (difference $I(1.8\text{ K}) - I(30\text{ K})$), calculated and difference magnetic neutron-diffraction patterns of a polycrystalline sample of $[\text{Fe}^{\text{II}}(\text{d}_8\text{-bpy})_3]_n^{2+}$ $[\text{Mn}_2^{\text{II}}(\text{ox})_3]_n^{2n-}$.

the increase of the intensities corresponds to a propagation vector $\boldsymbol{K} = \boldsymbol{0}$, 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 $T_{\text{N}} = 13(0.5)$ 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 $x = 0.649\,07$. 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 $P4_332/P4_132$ (Sikora 1994). 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 $M_{\text{S}} = g\mu_{\text{B}}NS$, where S is the spin quantum number, N the Avogadro number and g the electron g-factor. Thus, a gS 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.

Figure 12 shows the pattern of the magnetic structure within the three-dimensional manganese(II) network. Despite the three-dimensional helical character of the framework structure incorporating the magnetic ions, a two-sublattice antiferromagnetic spin arrangement has been proven to occur, hence, no helimagnetic structure has
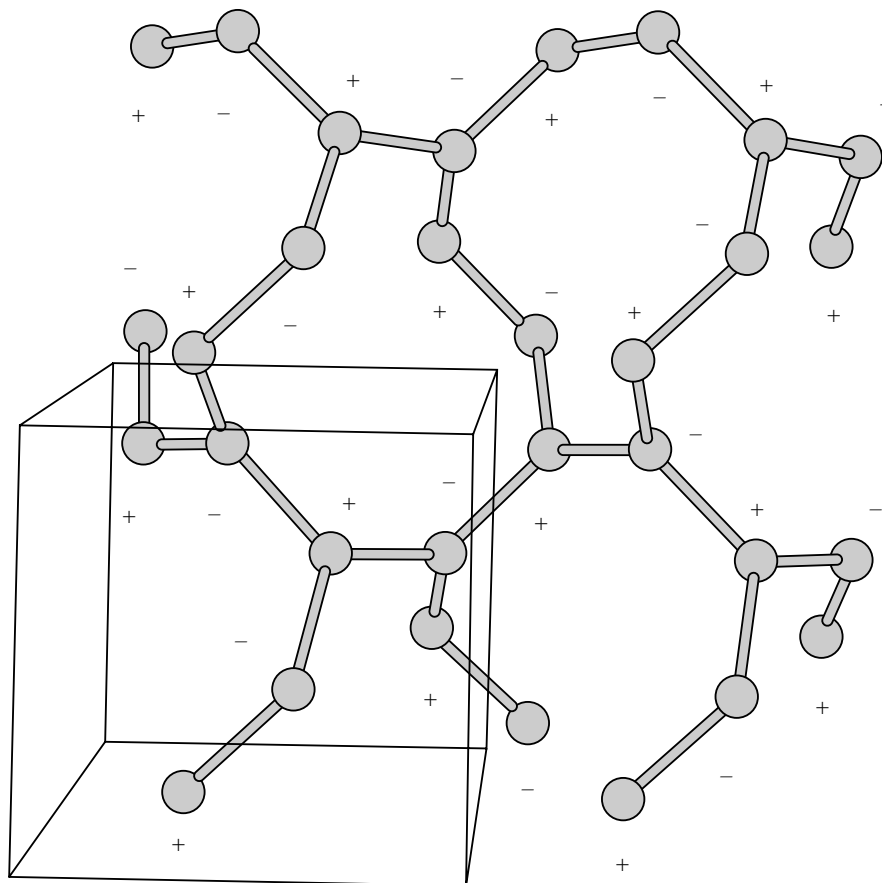
Figure 12. Scheme of the antiferromagnetic collinear configuration of the magnetic moments originating from the Mn^{2+} ions, which constitute the chiral three-dimensional network compound.

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 three-dimensional 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. Multifunctionality: photophysics

In this section, we will comment on some observations of excitation energy-transfer processes within the three-dimensional 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
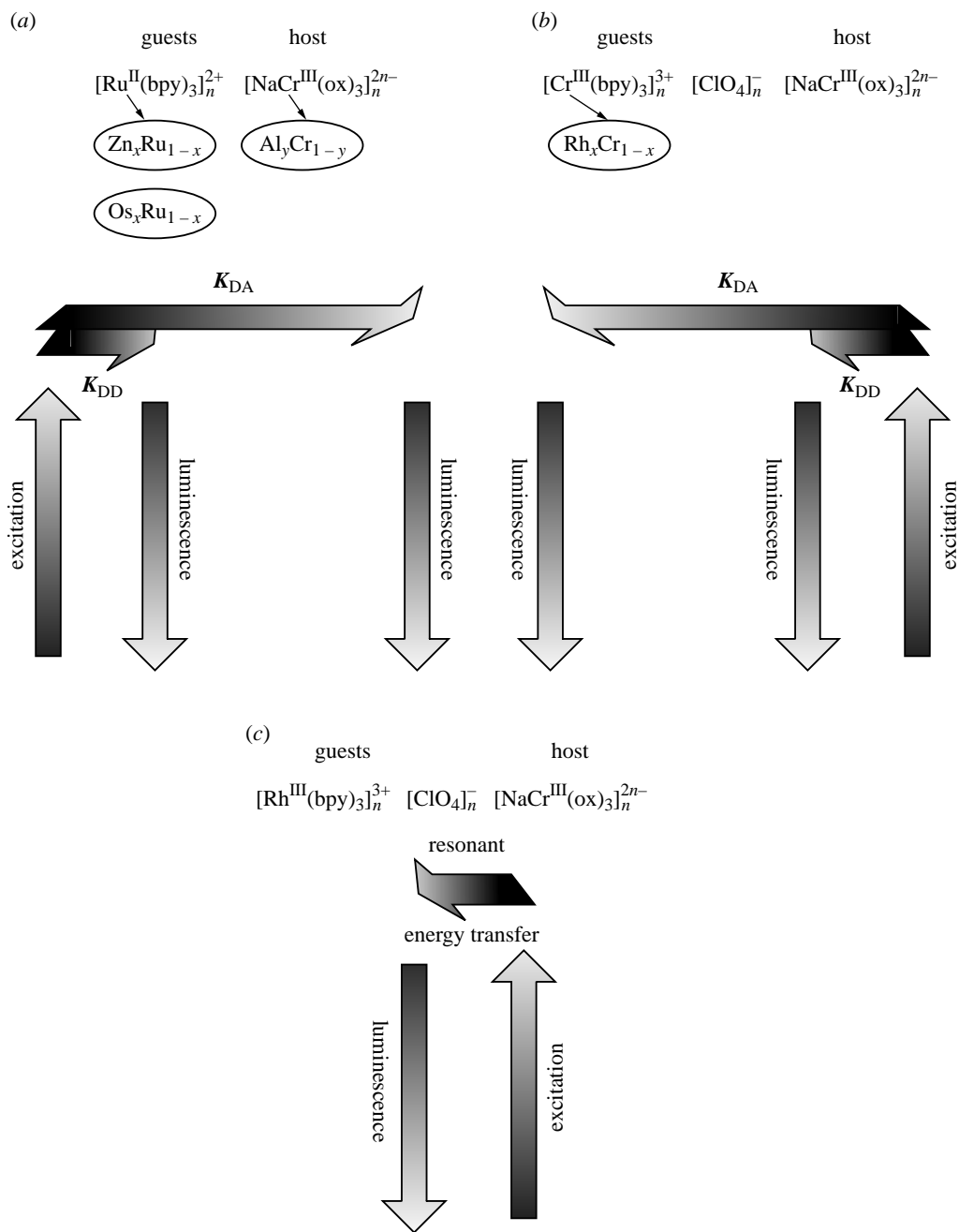
(a)

guests   host

$[Ru^{II}(bpy)_3]_n^{2+}$ $[NaCr^{III}(ox)_3]_n^{2n-}$

Zn_xRu_{1-x} Al_yCr_{1-y}

Os_xRu_{1-x}

(b)

guests   host

$[Cr^{III}(bpy)_3]_n^{3+}$ $[ClO_4]_n^-$ $[NaCr^{III}(ox)_3]_n^{2n-}$

Rh_xCr_{1-x}

K_{DA} K_{DA}

K_{DD} K_{DD}

excitation   luminescence   luminescence   luminescence   luminescence   excitation

(c)

guests   host

$[Rh^{III}(bpy)_3]_n^{3+}$ $[ClO_4]_n^-$ $[NaCr^{III}(ox)_3]_n^{2n-}$

resonant

energy transfer

luminescence   excitation

Figure 13. Schematic representation of energy-transfer processes for different stoichiometries: (*a*) excitation into the guest system; (*b*) and (*c*) excitation into the host system.

host as well as within the guest system (Decurtins *et al.* 1996*b*; Hauser *et al.* 1996; von Arx *et al.* 1996).

     Figure 13 illustrates these energy-transfer processes schematically with different
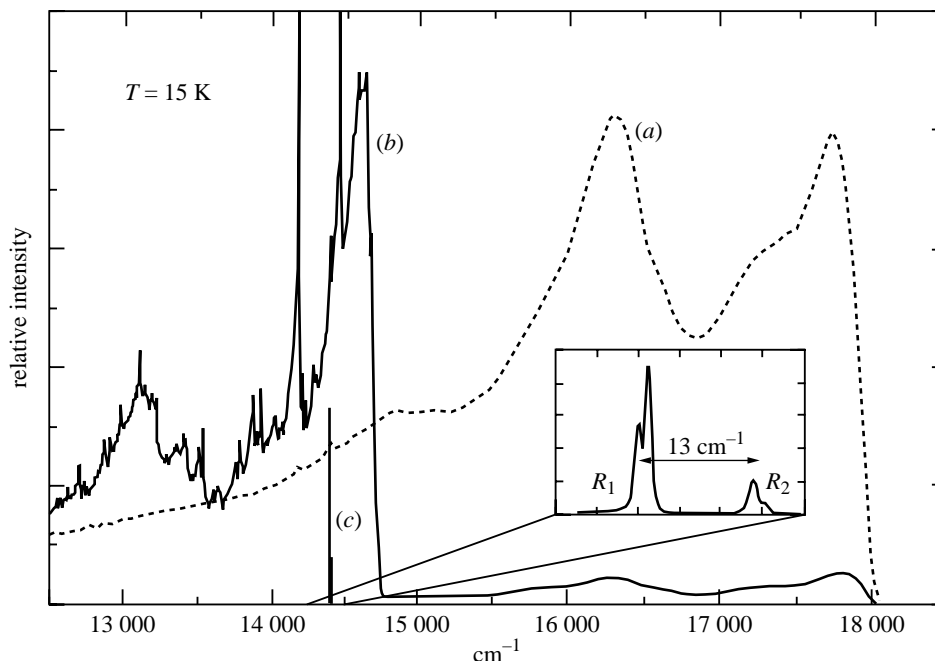
Figure 14. Luminescence spectra at $T = 15$ K of (a) $[Ru(bpy)_3][NaAl(ox)_3]$; (b) $[Ru_{1-x}Os_x(bpy)_3][NaAl(ox)_3]$, $x = 1\%$; (c) $[Ru(bpy)_3][NaCr(ox)_3]$; $\lambda = 476$ nm.

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 sensitizer 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, figure 14 shows the luminescence spectra of three representative compounds. For instance, if Al^{3+} is replaced by Cr^{3+}, the $[Ru(bpy)_3]^{2+}$ luminescence from the spin-forbidden MLCT transition is completely quenched, and the sharp luminescence bands characteristic for the zero-field components of the $^2E \rightarrow {}^4A_2$ transition of octahedrally coordinated and trigonally distorted Cr^{3+} are observed at $14\,400$ cm^{-1}. This is a clear indication of very efficient energy transfer from the initially excited $[Ru(bpy)_3]^{2+}$ to $[Cr(ox)_3]^{3-}$. However, not only acceptors on the oxalate backbone may quench the $[Ru(bpy)_3]^{2+}$ luminescence. Replacing a fraction of the $[Ru(bpy)_3]^{2+}$ with $[Os(bpy)_3]^{2+}$ results in luminescence from $[Os(bpy)_3]^{2+}$ and a quenching of the $[Ru(bpy)_3]^{2+}$ luminescence too. Indeed, the energy transfer to $[Os(bpy)_3]^{2+}$ is even more efficient than to $[Cr(ox)_3]^{3-}$.

Alternatively, as shown schematically in figure 13b, irradiating into the spin-allowed $^4A_2 \rightarrow {}^4T_2$ absorption band of $[Cr(ox)_3]^{3-}$ from the host system results in intense luminescence from the ^2E state of $[Cr(bpy)_3]^{3+}$ within the guest system, again demonstrating a rapid energy-transfer process (Decurtins *et al.* 1996b). Finally, according to figure 13c, the stoichiometry $[Rh(bpy)_3]_n^{3+}[ClO_4]_n^-[NaCr(ox)_3]_n^{2n-}$ allows

us to study the energy transfer within the R_1 line of the ^{2}E state of Cr^{3+}. In that case, from a fluorescence-line-narrowing experiment, clear evidence for a resonant energy-transfer process could be gained (Hauser *et al.* 1996; von Arx *et al.* 1996).

5. 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 two-dimensional and three-dimensional 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 behaviour. Overall, we are looking for synergistic properties within this class of multifunctional materials.

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Discussion

M. Verdaguer (*Laboratoire de Chimie Inorganique et Matériaux Moléculaires, Université Pierre et Marie Curie, Paris, France*). Professor Decurtins has shown an impressive number of chiral three-dimensional systems.

Was the synthesis and the crystallization performed with racemic or resolved reactants?

Starting with racemic reactants, were 50/50 mixtures of A and B enantiomers obtained? Was enantiomeric excess in the crystallization observed in some cases? I am aware of such a possibility with some systems.

Were Λ or Δ, three-dimensional systems, obtained at will starting with Λ or Δ resolved reactants?

S. Decurtins. The synthesis and crystallization has been performed with racemic reactants.

We only investigated the solid-state products in that respect by means of single-crystal X-ray diffraction experiments. This means that either one of the enantiomeric forms are observed, since the crystallization leads to a distinct enantiomeric form for each crystal.

I think the outcome is obvious, and, in any case, one gets at will three-dimensional single crystals, each one with a distinct chirality.