Polymeric two- and three-dimensional transition-metal complexes comprising supramolecular host-guest systems

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Based on a synthetic strategy, extended anionic, homo- and bimetallic oxalato-bridged transition-metal compounds with two- (2D) and three-dimensional (3D) connectivities can be synthesized and crystallized. Thereby, the choice of the templating counter ions will determine the crystal chemistry. The aim of this synthetic, supramolecular approach is to exploit host-guest solids, where each component contributes its own physical characteristics. The two entities could behave independently, resulting in composite properties, or they may interact in a synergistic way, potentially leading to new physical phenomena.

Complexes de métaux de transition comportant des systèmes du type 'host-guest'. A l'aide d'une stratégie de synthèse, il est possible d'obtenir et de faire cristalliser des composés comportant un réseau anionique homo- et bi-métallique à ponts oxalates, présentant des structures bi- (2D) ou tri-dimensionnelles (3D). Ainsi, le choix des contreanions jouant un effet template, détermine-t-il la structure obtenue. Cette approche synthétique et supramoléculaire permet l'étude des composés 'host-guest', où tous les composants apportent au solide leurs propres caractéristiques physiques. Les deux entités peuvent se comporter de manière indépendante d'un point de vue des propriétés physiques du solide, ou bien interagir et créer une synergie qui donne lieu à de nouveaux phénomènes physiques.

With this report on two- (2D) and three-dimensional (3D) molecular networks, emphasis is placed on the description of the topological aspects of specific host-guest systems that are assembled with transition-metal ions, linked through bis-chelating oxalate ligands and templated through the action of appropriate counter-ion complexes. Thereby, the fundamental structural and electronic factors that need to be controlled are the size, shape, rigidity and topology, as well as the electronic relationship of the constitutant molecular entities. For host-guest systems, these factors taken together constitute the phenomenon of host-guest complementarity.[1]

Currently, the object of our studies in the field of supramolecular host-guest chemistry is to explore a new class of multi-property materials. In particular, we are interested in the design and study of the physical properties of molecular assemblies exhibiting spontaneous magnetization below a certain critical temperature T_c.[2–13] Now, what will be really appealing in these molecular compounds is not only that they behave as classical solid state magnets, but also that they may exhibit a completely new physics. Consequently, it is aimed to design compounds in which the magnetic properties are combined with other physical properties, in particular photophysical properties, possibly in a synergistic way.[10–14]

Supramolecular networks based on coordination chemistry

Basic principles of specific 2D and 3D network configurations

The challenge in the field of supramolecular chemistry is the control of both molecular and supramolecular structures with preferably extended two-dimensional or three-dimensional motifs. In the case of coordination compounds, a high structural organisation is ensured through multiple binding sites of transition-metal ions, which may lead to a higher dimensional architecture of extended inorganic networks. Thus, the overall topology is strongly influenced by the coordination algorithm of the linking metal ions as well as by the choice of the bridging ligand system.

In this respect the oxalate ion, $C_2O_4^{2-}$, is well-known to be an attractive ligand, because its ambidentate coordinating ability enables the construction of homo- and bimetallic chain and layer structures, and even the formation of three-dimensionally connected transition-metal frameworks.[2–7] In the following, we will discuss some basic ideas that are relevant for the understanding of the corresponding two- and three-dimensional framework topologies. In fact, both structure types are formally composed of $[M^{z+}(ox)_3]^{(6-z)-}$ building blocks, whereby each of these units represents a three-connected point (see Fig. 1). These building blocks, which are predestined to create extended network motifs, may polymerise in principle in two ways. Thereby, one alternative leads to a 2D honeycomb layer compound, whereas in the other possible arrangement, an infinite 3D structure is formed. In the former case, building blocks of different chirality are alternately linked and consequently, the bridged metal ions are confined to lie within a plane, as illustrated in Fig. 1 (*left*). Consequently, a layered structure motif will result. In contrast, as depicted in Fig. 1 (*right*), assembling building blocks of the same chiral configuration will lead to a 3D framework structure.

As a next step, simple topological rules will be applied in order to define the number of building blocks that are needed to build closed circuits, hence, extended framework motifs. Fig. 2 illustrates the way that two dimeric subunits may be combined to form the planar honeycomb network.

In an analogous manner, it can easily be seen from Fig. 3, that two tetrameric subunits are needed to build closed circuits composed of ten metal centers, which in sum define the three-dimensional decagon framework structures. Such tetrameric subunits are necessary because only four three-connected points ($Z = 4$) combined together will have the six free links necessary to build the 3D net. Identically oriented links repeat at intervals of ($Z + 1$) points, so that circuits of

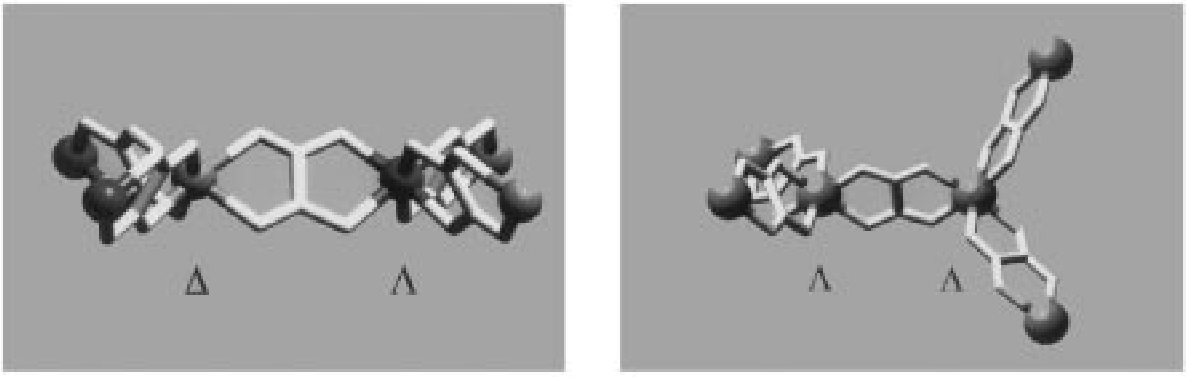

Fig. 1 Chiral $[M^{z+}(ox)_3]^{(6-z)-}$ building blocks assembled with (*left*) alternating chiral configuration and (*right*) equal chiral configuration

$2 \cdot (Z + 1)$ points are formed. Thus, 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.

The chiral 3D host-guest system

In this paragraph, the discussion about the structural aspects of the 3D network system will be continued and in particular the features of the host-guest chemistry will be taken into account. Specifically, for the design of the actual chiral 3D supramolecular host-guest system, the mutual interaction of two distinct, complementary molecular units or coordination entities will be necessary. In the present case, as illustrated in Fig. 4, these are the above described anionic, tris-chelated transition-metal oxalato complexes $[M^{z+}(ox)_3]^{(6-z)-}$ that form the host system and the cationic, tris-chelated transition-metal diimino complexes, for instance $[M(bpy)_3]^{2+/3+}$, bpy = 2,2′-bipyridine, which plays the role of the guest compounds.

A short characterisation of the key structural elements shows that both coordination compounds gain enhanced stability from the chelate effect, which in turn is expressed in their specific molecular topology. As a further consequence of this $[M(L \wedge L)_3]$-type of connectivity, each coordinated metal

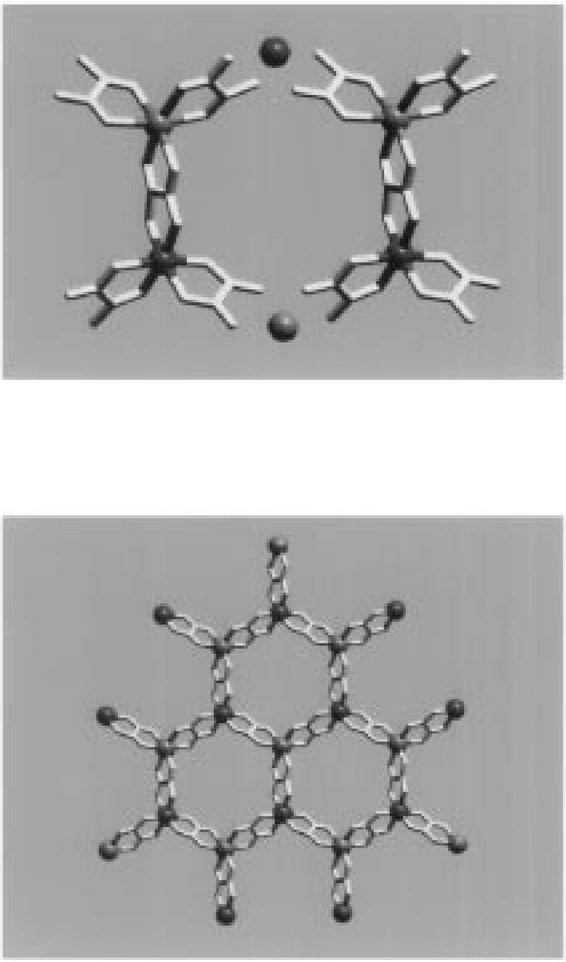

Fig. 2 (*Top*) Two dimeric units of the alternating chirality type are necessary to form a closed hexagon ring; (*bottom*) the resulting planar network motif.

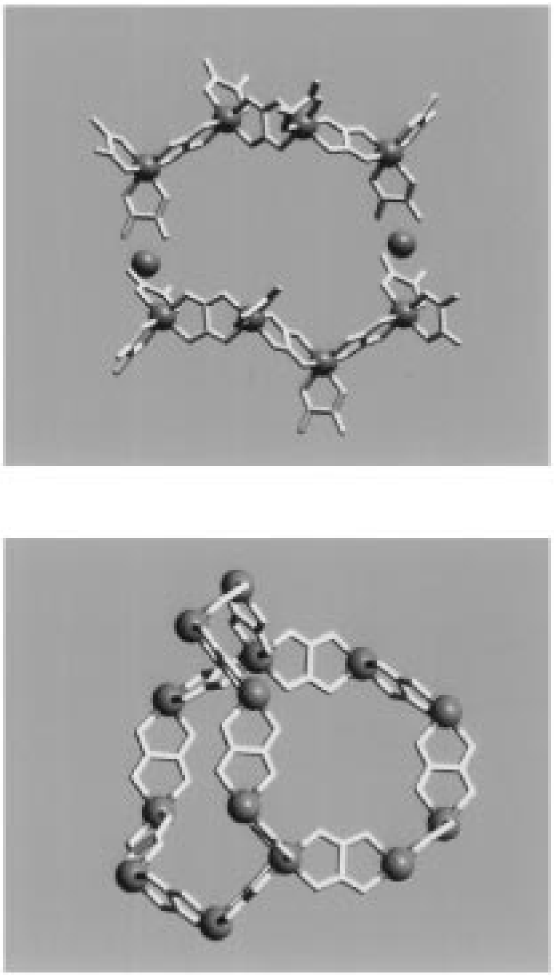

Fig. 3 (*Top*) Two tetrameric units of the same chirality type are necessary to form a closed decagon ring; (*bottom*) a fragment of the 3D, chiral framework

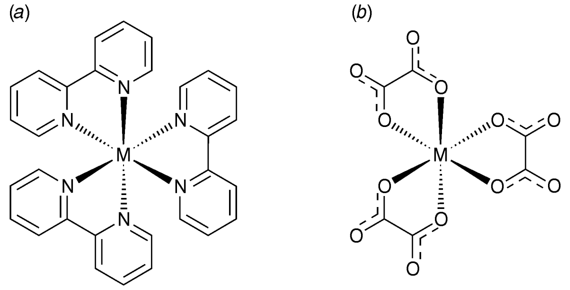

Fig. 4 Schematic representations of the two chiral (the Λ-isomers are shown) preorganized (*a*) cationic and (*b*) anionic coordination entities

ion represents a chiral center with D_3 point-group symmetry, showing either Δ- or Λ-helical chirality. Furthermore, the chelation mode of the transition-metal ions determines unambiguously the shape and rigidity of these preorganised complexes, inasmuch as the specific configuration leads to the typical three-bladed propeller geometry.

With respect to the aim of attaining a high level of organisation, both molecular entities exhibit a complementary functionality. The anionic, tris-chelated oxalato complexes are able to build up the above defined extended polymeric host system, whereas the cationic complexes act as templates to initiate the formation and finally the crystallization of the three-dimensionally, covalently connected open framework. Fig. 5 shows a stereoview of this network topology that forms the 3D host system.

As it was deduced in the former paragraph, the topological principle implies that for the 3D case, only subunits of the same chirality are assembled. Consequently, the uniform anionic 3D-network-type topology with stoichiometries like $[M^{II}_2(ox)_3]_n^{2n-}$ or $[M^IM^{III}(ox)_3]_n^{2n-}$ ($M^{II/III}$ = transition-metal ions and M^I = Li, Na) 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 that are present in the crystalline state of these 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 stoichiometry. Thereby, the $2n$ metal ion centers occupy special sites with a three-fold symmetry axis.

Furthermore, extended helical geometries are encountered through the three-dimensional repetitive assembling of subunits with helical chirality. Thus, the framework structure may alternatively be seen as composed of either right-handed (Λ-chirality) or left-handed (Δ-chirality) helices with a 4_1, 4_3 or 2_1 arrangement, running in three perpendicular directions while simultaneously being covalently bound to each other. Fig. 6 exhibits such a helical strand extending parallel to a screw axis.

In addition, the chiral, cationic tris-chelated guest complexes fit perfectly into the elaborate pattern of vacancies. Within the channel system they occupy the n available chiral sites with point symmetry 32 ($P4_332/P4_132$) or 3 ($P2_13$). At least for the former case, the molecular D_3 point group symmetry of the guests is fully retained. In analogy to a 'lock-and-key effect', a Δ-Δ or Λ-Λ pairing in the chirality of the host framework and the guests is observed.

One of the main attractions in studying these 3D extended network compounds is the fact that the synthetic route allows for a large variation of the metal ions, mainly within the first-row transition-metal series but also extendable to Ru, Os and

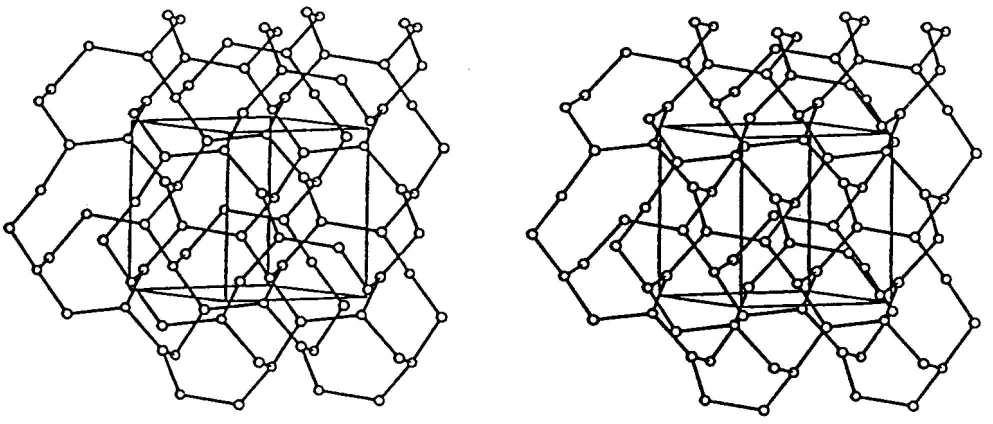

Fig. 5 Stereoview of the 3-connected 10-gon (10,3) network topology

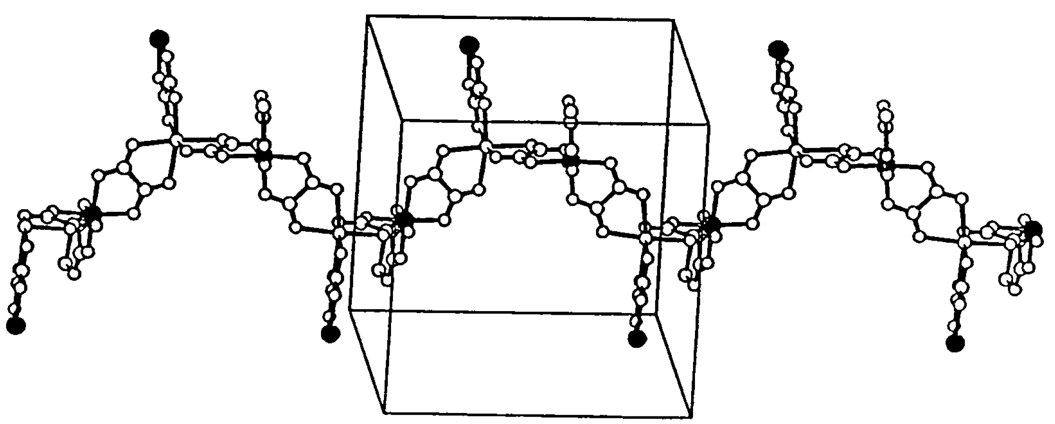

Fig. 6 View of a helical strand along a 2_1 axis from a $[M^IM^{III}(ox)_3]_n^{2n-}$ type compound

Rh ions, for example, in case of the templating cationic complexes. Thus, an overall stoichiometry of $[\mathrm{M^{II}(bpy)_3}]_n^{2+}$ $[\mathrm{M^{II}_2(ox)_3}]_n^{2n-}$ results.

Interestingly, $[\mathrm{M^{III}(bpy)_3}]^{3+}$ cations also may act as templates for the 3D network formation. In this case the additional charge is compensated through the incorporation of anions like $\mathrm{BF_4^-}$.

The honeycomb layer compounds

The anionic tris-chelated oxalato complexes may also form infinitely extended sheets of hexagonal symmetry. According to the argumentation of the preceeding paragraph, the discrimination between the formation and crystallization of either a 2D or a 3D supramolecular host-guest system with analogous network stoichiometries relies on the choice of the templating counter ion. In particular, $[\mathrm{XR_4}]^+$, (X = N, P; R = phenyl, *n*-propyl, *n*-butyl) cations initiate the growth of 2D sheet structures containing $[\mathrm{M^{II}M^{III}(ox)_3}]_n^{n-}$, network stoichiometries.[2–4] Fig. 7 shows two projections of a sector from a 2D honeycomb layer compound.

As noted above, in contrast to the chiral 3D network compounds, the 2D framework topology implies an assembly of coordination entities with alternating chirality between nearest neighbouring centres. Although these 2D compounds are not chiral, they express a structural polarity due to the specific arrangement of the templating cations [see Fig. 7(*b*)]. These organic cations, which are located between the anionic layers, determine on the one hand the interlayer separation, which typically shows values in the range of 8–9 Å, but on the other hand also determine the molecular packing arrangement of the solids, hence the resulting space group, for instance *R*3*c* for $[\mathrm{P(Ph)_4}]^+$, $[\mathrm{N(Pr)_4}]^+$ and *P*6$_3$ for $[\mathrm{N(Bu)_4}]^+$.

Supramolecular functions

Molecular-based magnetism and photophysics

In this section, only a brief account will be given of the topic of supramolecular functions. One of the fundamental end uses of these specific supramolecular frameworks lies in the field of molecular magnetism. Clearly, where major break-throughs must be expected in the field of molecular magnetism is in the association of properties that are not met in traditional magnets, for instance if photophysical properties are associated with magnetic phase transitions.

Generally, any synthetic strategy aimed at designing molecular magnets has to answer the questions (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;[12] therefore, it has been widely used to construct polynuclear compounds in the search for new molecular-based magnets. In the search for an answer to the second question, effort has been given to the investigation of the magnetic ordering behaviour of the above described 2D and 3D systems. In this respect, the neutron scattering technique has been especially successful for the elucidation of the magnetic structures of the ordered phase below T_c.[9] In addition, polarized neutron diffraction and the determination of spin density distributions are other sophisticated methods that are in use, however, for further discussions, the interested reader will be referred to the literature,[8–13] where the current state-of-the-art in the area of molecular magnetism can be found.

With respect to the search for an additional, synergistic property that could be combined with the molecular magnetic function, it is also aimed to exploit the photophysical behaviour of these molecular frameworks. Thereby, chemical variation and combination of metal ions of different valencies in the oxalate backbone as well as in the tris-bpy cation offer unique opportunities for studying a large variety of photophysical processes, such as light-induced electron transfer and excitation energy transfer in the solid state. In general, the sensitiser can be incorporated into the oxalate backbone, such as a $[\mathrm{Cr^{III}(ox)_3}]^{3-}$ entity, or as a guest cation, in the form of the ubiquitous photosensitiser $[\mathrm{Ru(bpy)_3}]^{2+}$ for example.[6,14] Naturally, many other combinations can be envisaged and ongoing studies aim to reveal the exciting photophysical behaviour of these host-guest systems.

Conclusions

The results of this report show a concept for the synthesis of 2D and 3D molecular 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. Furthermore, helical chirality adds a fascinating aspect to the supramolecular architectures.

Ongoing studies focus on similar concepts with the aim to produce new multiproperty materials with original molecular architectures, using all the possibilities of molecular synthesis,

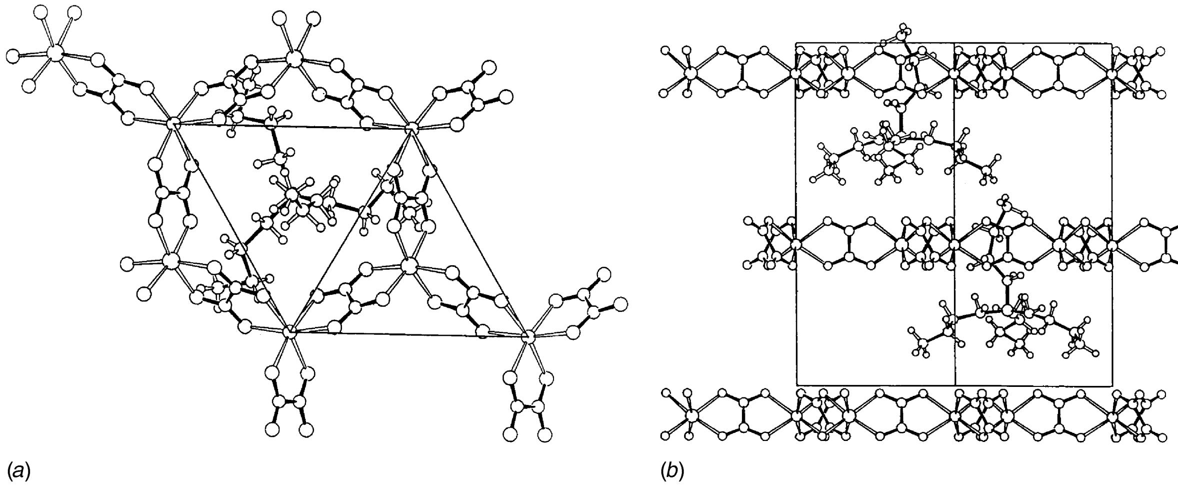

Fig. 7 Sector from the $\{[\mathrm{N(Bu)_4}][\mathrm{Mn^{II}Fe^{III}(ox)_3}]\}$ layer compound (*a*) [001] projection; (*b*) [110] projection

and then to investigate the synergy between coupled physical properties.

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