

The Exploitation of Versatile Building Blocks for the Self-Assembly of Novel Molecular Magnets

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Received March 20, 2001; accepted March 21, 2001

IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

Using molecular building blocks to self-assemble lattices supporting long-range magnetic order is currently an active area of solid-state chemistry. Consequently, it is the realm of supramolecular chemistry that synthetic chemists are turning to in order to develop techniques for the synthesis of structurally well-defined supramolecular materials. In recent years we have investigated the versatility and usefulness of two classes of molecular building blocks, namely, *tris*-oxalato transition-metal (M. Pilkington and S. Decurtins, in “Magnetoscience—From Molecules to Materials,” Wiley-VCH, 2000), and octacyanometalate complexes (Pilkington and Decurtins, *Chimia* 54, 593 (2001)), for applications in the field of molecule-based magnets. Anionic, *tris*-chelated oxalato building blocks are able to build up two-dimensional honeycomb-layered structural motifs as well as three-dimensional decagon frameworks. The discrimination between the crystallization of the two- or three-dimensional structures relies on the choice of the templating counterions (Decurtins, *Chimia* 52, 539 (1998); Decurtins *et al.* *Mol. Cryst. Liq. Cryst.* 273, 167 (1995); *New J. Chem.* 117 (1998)). These structural types display a range of ferro, ferri, and antiferromagnetic properties (Pilkington and Decurtins, in “Magnetoscience—From Molecules to Materials”). Octacyanometalate building blocks self-assemble to afford two new classes of cyano-bridged compounds namely, molecular clusters and extended three dimensional networks (J. Larionova *et al.*, *Angew. Chem. Int. Ed.* 39, 1605 (2000); Pilkington *et al.*, in preparation). The molecular cluster with a $\text{Mn}^{\text{II}}\text{Mo}^{\text{V}}$ core has the highest ground state spin value, $S = 51/2$, reported to-date (Larionova *et al.*, *Angew. Chem. Int. Ed.* 39, 1605 (2000)). In the high-temperature regime, the magnetic properties are characterized by ferromagnetic intracluster coupling. In the magnetic range below 44 K, the magnetic cluster signature is lost as possibly a bulk behavior starts to emerge. The three-dimensional networks exhibit both paramagnetic and ferromagnetic behavior, since the magnetic properties of these materials directly reflect the electronic configuration of the metal ion incorporated

into the octacyanometalate building blocks (Pilkington *et al.*, in preparation). For both the oxalate- and cyanide-bridged materials, we are able to manipulate the magnetic properties of the supramolecular assemblies by tuning the electronic configurations of the metal ions incorporated into the appropriate molecular building blocks (Pilkington and Decurtins, in “Magnetoscience—From Molecules to Materials,” *Chimia* 54, 593 (2000)). © 2001 Academic Press

Key Words: molecule-based magnets; supramolecular chemistry; *tris*-oxalato building blocks; cyanometalates; extended networks; molecular clusters.

1. INTRODUCTION

For more than two-thousand years man's fascination with magnets has been historically recorded. Around the 11th Century, the Chinese found that a steel needle stroked with “lodestone” (Fe_3O_4) became magnetic and furthermore, when this needle was freely suspended, it pointed north-south. Hence the magnetic compass was invented and its discovery soon spread to Europe. Indeed, Columbus made good use of this technology when he made his famous voyage across the Atlantic Ocean. At several points in history the field of magnetism has experienced a revival, the first of which came in the 17th Century when William Gilbert, physician to Queen Elizabeth I of England, proposed that the Earth itself was a magnet, with its magnetic poles some distance away from its geographic ones. Gilberts initial experiments and observations regarding the magnetic behavior of iron resulted in the preparation of the first man-made magnet.

Traditionally, magnetic materials were prepared using high-temperature metallurgical methods and they share the generic attributes of being *atom-based*, having *d*- or *f*-orbital spin sites, and possessing extended network magnetic

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“bonding” in at least two-dimensions. In recent years however, the preparation of novel magnetic materials *via* molecular chemistry (6) has now become an active and exciting field of research and as a consequence, magnetism is currently experiencing a renaissance since it is being expanded by contributions from both organometallic and organic chemistry (7). The development of molecule-based magnets from molecular building blocks is therefore a multidisciplinary field involving the combined efforts of synthetic organic and inorganic chemists, physical chemists, physicists, and material scientists working at the frontiers of solid-state chemistry. Furthermore, efforts in this area are strongly driven by the microelectronics industry since single-molecular magnets represent the ultimate in miniaturization (8).

In recent years, the field of molecule-based magnets has greatly benefited from the large advances made in the field of supramolecular chemistry. Indeed, molecular magnetism itself can be considered to be supramolecular in its nature, since it results from the collective features of components bearing free spins and on their arrangement in organized assemblies (9). The engineering of molecular magnetic systems thus requires the search for paramagnetic species and their arrangement in suitable supramolecular architectures so as to induce spin coupling and alignment.

2. OXALATE BUILDING BLOCKS

The most general function of supramolecular chemistry, e.g., of host-guest chemistry is to organize molecules (3, 10). One possible approach to the design of crystalline solids is to use preorganized molecules, e.g., transition-metal com-

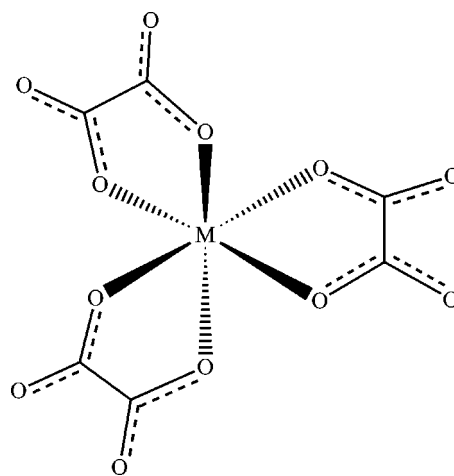


FIG. 2. Molecular building blocks, namely anionic, *tris*-chelated transition-metal oxalato complexes, $[M^{z+}(\text{ox})_3]^{(6-z)-}$; $\text{ox} = \text{C}_2\text{O}_4^{2-}$. As a consequence of this type of connectivity, each coordinated metal ion represents a chiral center with D_3 point group symmetry, showing either Δ or Λ -helical chirality.

plexes, since a high structural organization can be ensured through the multiple binding of transition-metal ions, giving rise to a variety of extended inorganic networks in one, two, or three dimensions, see Fig. 1.

The emphasis here lies in the design of the ligands together with the choice of the metal ions since the overall topology of the network is strongly influenced by the coordination algorithm of the linking metal ions as well as by the choice of the bridging ligands (3).

In recent years, we have shown that it is possible to develop a strategy for the self-assembly of supramolecular systems based on transition-metal oxalates, which typically behave as host/guest compounds with different lattice dimensionalities (1, 3, 10). All of these classes of structure are formally composed of metal-oxalate building blocks, see Fig. 2, and these compounds display a range of magnetic properties, since it is well known that the oxalate bridge is a good mediator of both antiferromagnetic and ferromagnetic interactions between paramagnetic metal ions. When oxalate-based subunits of the same chiral

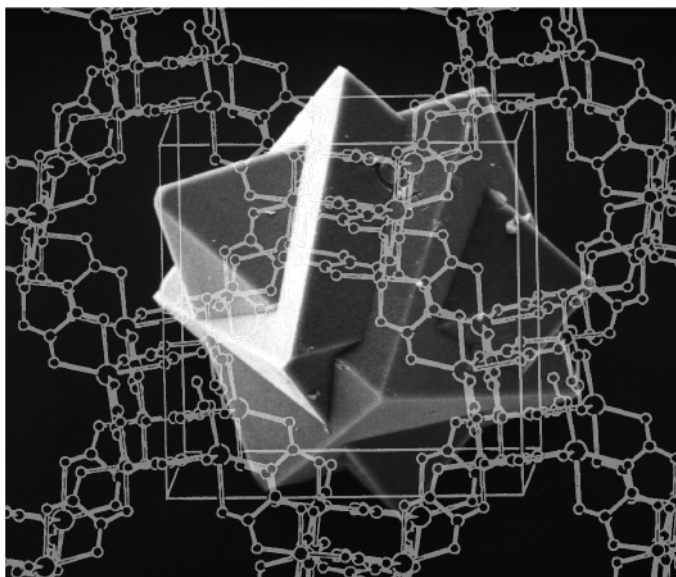


FIG. 1. A single crystal of a chiral 3D molecular network compound assembled from oxalate building blocks with transition-metal ions as spin carriers (3).

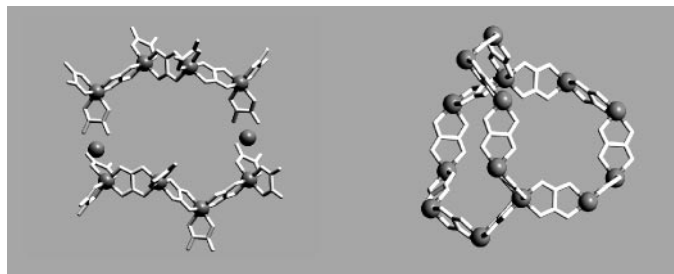


FIG. 3. Left, two tetrameric units of the same chirality result in the formation of a closed decagon ring. Right, a fragment of the 3D chiral framework (3).

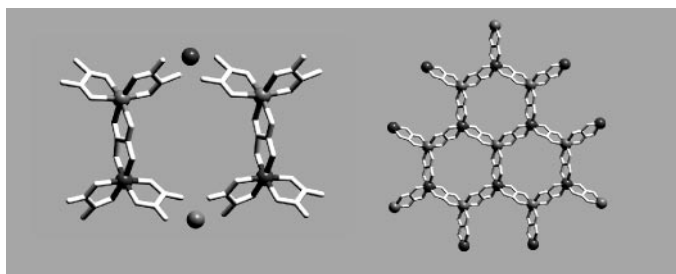


FIG. 4. Left, two dimeric units of alternating chirality result in the assembly of a closed hexagon ring. Right, the resulting planar network motif (3).

configuration are assembled in the presence of cationic *tris*-chelated transition-metal diimine complexes, anionic three-dimensional decagon frameworks are obtained, see Fig. 3. If, however, building blocks of different chirality are alternatively linked, the bridged metal ions are confined to lie within a plane as illustrated in Fig. 4, and a layered motif will result (3).

We have established that the discrimination between the formation and crystallization of either two- or three-dimensional anionic frameworks with analogous network stoichiometries depends on the choice of the templating counterions. Cationic *tris*-chelated transition metal diimine complexes $[M(\text{bpy})_3]^{2+/3+}$, *bipy* = 2,2'-bipyridine, act as templates for the formation and crystallization of the three-dimensional decagon framework structures and then assume the role of guest compounds by occupying the voids in the framework, see Fig. 5.

In contrast, other types of cations, e.g., $[\text{XR}_4]^+$ ($X = \text{N}$, P , $\text{R} = \text{phenyl}$, *n*-alkyl) initiate the growth of two-dimen-

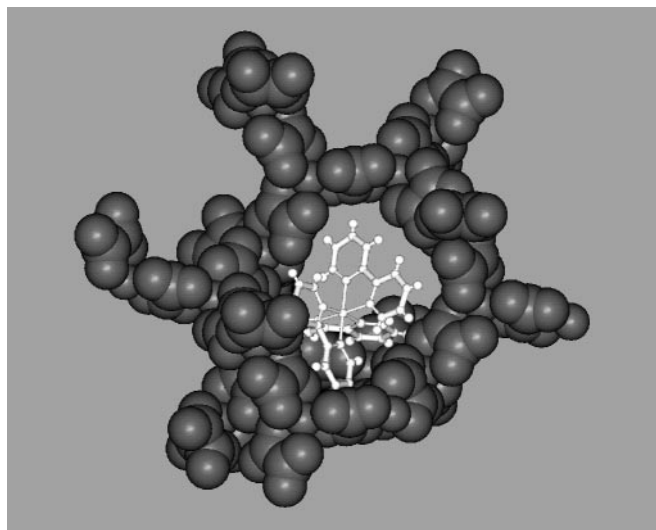


FIG. 5. A chiral 3D host/guest compound of stoichiometry $[\text{MII}(\text{bpy})_3][\text{M}^{\text{I}}\text{M}^{\text{III}}(\text{C}_2\text{O}_4)_3]_n$. Only one guest molecule is shown within the chiral framework.

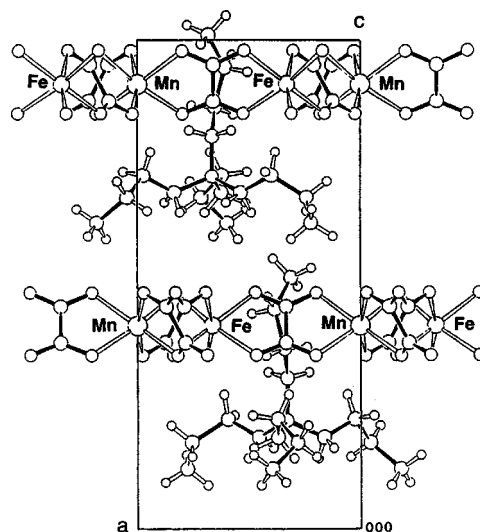


FIG. 6. $[010]$ Projection for the compound of stoichiometry $\{[\text{N}(n\text{-C}_4\text{H}_9)_3]_n[\text{Mn}^{\text{II}}\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3]_n\}$. The structure consists of anionic 2D honeycomb networks that are interleaved by templating cations (3).

sional honeycomb networks that are then interleaved by the templating cations as shown in Fig. 6 (3). Depending on the metal ions incorporated into these frameworks, the near-neighbor exchange may be ferro- or antiferromagnetic, leading to either bulk ferro-, ferri-, or antiferromagnetic behavior (1).

3. PRUSSIAN-BLUE-TYPE BUILDING BLOCKS

An alternative class of functional supramolecular materials is the three-dimensional network architectures self-assembled from cyanide ligands and metallic centers that carry a magnetic moment. Since the μ -cyanide linkages permit an interaction between paramagnetic metal ions, cyanometalate building blocks have currently found useful applications in the field of molecule-based magnetism (8, 11). Many of these compounds are closely related to Prussian blue (12), a mixed-valent cyanoferrate of stoichiometry $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot 15\text{H}_2\text{O}$. Substitution of Fe^{III} and Fe^{II} by other ions M' and M leads to a series of analogues whose structural topology is face-centered cubic, see Fig. 7. When paramagnetic metal ions are used, compounds with a range of magnetic properties have been reported since the linear $-M'-\text{N}\equiv\text{C}-M-$ sequence permits an interaction between paramagnetic metal ions.

The need for higher ordering temperatures has provided the driving force for several research teams to probe in detail the nature of the $M'-\text{N}\equiv\text{C}-M$ interactions in the Prussian blue family of compounds. In 1995, Verdager and co-workers were able to increase the Curie temperature and overcome the room-temperature barrier with a Prussian blue structured $\text{V}[\text{Cr}(\text{CN})_6]_{0.86} \cdot 2.8\text{H}_2\text{O}$ compound that orders at $T_c = 315 \text{ K}$ (13). This compound is a complex

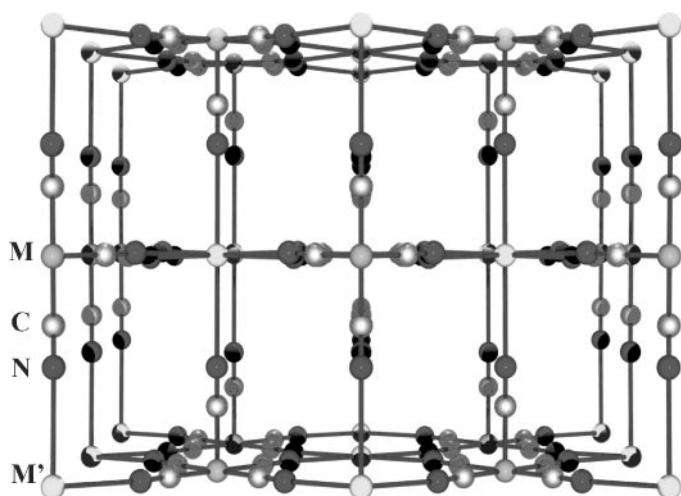


FIG. 7. Three-dimensional cubic structure of an idealized Prussian blue analogue.

nonstoichiometric mixed valent material and in contrast to molecule-based magnets or materials in general, the preparative procedure dictates the properties. As a consequence, several more complex, air-stable related materials with T_c values up to 372 K have been recently prepared in collaboration with other research groups (14, 15). Extending this synthetic approach further, Olivier Kahn and co-workers investigated the versatility of the $[M(CN)_7]^{n-}$ precursor for the self-assembly of novel magnetic materials (16). The result was a new class of heptacyanometalate magnetic materials, namely a two-dimensional compound of stoichiometry $K_2Mn_3(H_2O)_6[Mo(CN)_7]_2$ as well as two phases (alpha and beta) of a three-dimensional compound of stoichiometry $Mn_2(H_2O)_5Mo(CN)_7$. All three compounds exhibit a long-range ferromagnetic ordering along with a field-induced spin reorientation (16).

4. OCTACYANOMETALATE BUILDING BLOCKS

Since Prussian blue chemistry is currently enjoying an active revival (11), our group is currently exploring the closely related octacyanometalate building block $[M(CN)_8]^{n-}$, where M is a transition-metal ion, for the self-assembly of novel supramolecular coordination compounds. We have recently structurally and magnetically characterized a novel cyanide-bridged high-spin molecular cluster of stoichiometry $[Mn^{II}\{Mn^{II}(MeOH)_3\}_8(\mu-CN)_{30}\{Mo^V(CN)_3\}_6] \cdot 5MeOH \cdot 2H_2O$, prepared by the self-assembly of $[Mo^V(CN)_8]^{3-}$ building blocks together with divalent metal ions (4). The cluster comprises 15 cyano-bridged metal ions, namely 9 Mn^{II} ions ($S = \frac{5}{2}$) and 6 Mo^V ions ($S = \frac{1}{2}$), giving a total of 51 unpaired electrons within the cluster. The $Mo^V-CN-Mn^{II}$ geometry is such that the atoms are all linked to form an aesthetically pleasing

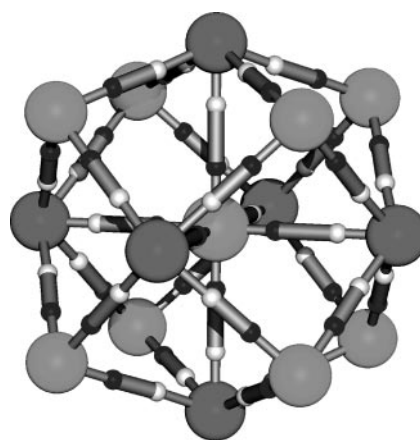


FIG. 8. Representation of an idealised $[Mn_9^II(\mu-CN)_{30}Mo_6^V]$ cluster core. The light gray spheres represent Mn^{II} ions and the dark gray spheres represent Mo^V ions and the bonds between them represent μ -cyano ligands (4).

topological pattern in which the polyhedron spanned by the peripheral metal ions is closest in geometry to a rhombic dodecahedron, see Fig. 8. Furthermore, in parallel studies Hashimoto and co-workers have also reported the synthesis of a Mn_9W_6 cluster with an analogous structural topology (17).

The magnetic properties of the Mn_9Mo_6 cluster above 44 K are characterized by ferromagnetic intracluster coupling, which finally leads to an $S = 51/2$ ground state spin. In contrast to other high-spin clusters, this compound does not exhibit the typical phenomena of molecular hysteresis and slow quantum tunneling at low temperatures. In this case, a competitive interplay of intra- and intercluster interactions leads to a very interesting magnetic regime. Unfortunately, a modeling of the magnetic data below 44 K, where bulk magnetic ordering seems to arrive, is not possible since this new situation has not been dealt with theoretically so far. Further experiments are needed before we can move forward in our understanding and interpretation of the magnetic data in the low-temperature regime. It seems, however, reasonable to suggest that dipole-dipole interactions could contribute to the intercluster coupling since these interactions will become increasingly important with increasing S state values of high-spin clusters. Interestingly, in contrast to these observations, antiferromagnetic intracluster interactions are reported for the Mn_9W_6 cluster, which give rise to a smaller ground state spin value of $S = 39/2$ (17).

The cluster topology essentially reflects the preferred coordination geometry of the metal ions concerned, and we have had recent success in the preparation of several variations of this cluster, substituting Mo^V in the octacyanometalate building block for W^V , and Mn^{II} for other divalent metal ions such as Co^{II} or Ni^{II} (2, 18).

One of the most interesting features of molecular-based materials is the way in which the magnetic properties may be transformed by quite small and subtle variations in molecular chemistry. Working along these lines, we have recently investigated the effects of changing the oxidation state of the metal in the octacyanometalate building block moving from M^V to M^{IV} , ($M = \text{Nb}, \text{Mo}, \text{W}$) (2, 5). Hence, reaction of the appropriate octacyanometalate building block with an M^{II} salt afforded in all cases crystalline compounds that have been shown by single-crystal X-ray analysis to be cyano-bridged extended three-dimensional networks with a general stoichiometry of $[M^{IV}\{\mu\text{-CN}\}_4M^{II}(\text{H}_2\text{O})_2\}_2]$ (5). All compounds crystallize in the tetragonal space group $I4/m$, with one M^{IV} ion sitting on the crystallographic four-fold axis and a M^{II} ion, together with two coordinating water molecules occupying a crystallographic mirror plane. Figure 9 illustrates the molecular structure of the three-dimensional compound of stoichiometry $[\text{W}^{IV}\{\mu\text{-CN}\}_4\text{Fe}^{II}(\text{H}_2\text{O})_2\}_2]$. The network comprises W^{IV} ions, which are connected to nearest neighbor Fe^{II} ions through cyanide bridges in a three-dimensional grid-like arrangement. The Fe^{II} ions are in an octahedral environment, bonded to four nearest neighbor W^{IV} ions; two axial water molecules complete the six-fold coordination.

Despite the structural similarities, the change in electronic ground state moving along the periodic table from

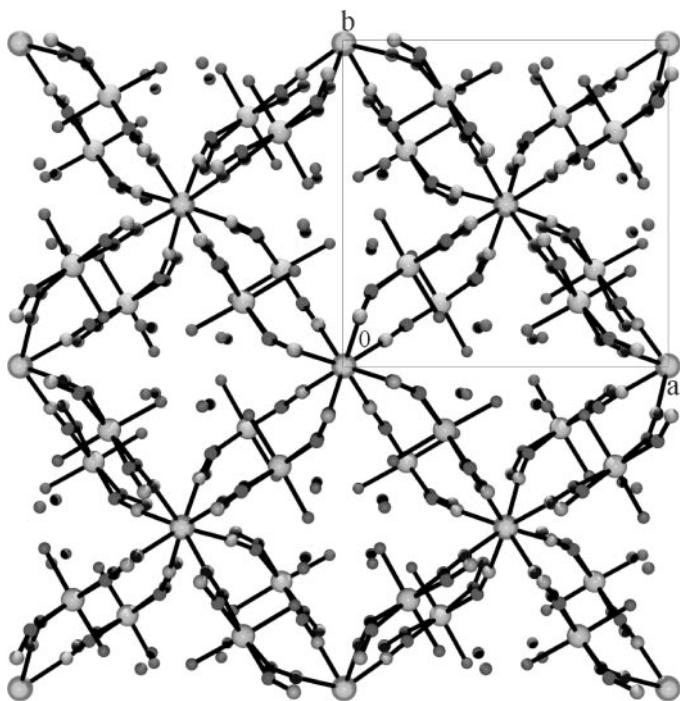


FIG. 9. Structure of the 3D $[\text{W}^{IV}\{\mu\text{-CN}\}_4\text{Fe}^{II}(\text{H}_2\text{O})_2\}_2]$ network viewed down the crystallographic four-fold axis. Axial-coordinated water molecules, as well as free solvent waters, occupy the channels of the network and are involved in H-bonding interactions.

Nb^{IV} to Mo^{IV} and W^{IV} confers two different classes of magnetic properties on these compounds. The networks incorporating diamagnetic Mo^{IV} or W^{IV} metal ions are paramagnetic. However, Nb^{IV} represents a d^1 electronic configuration; hence a paramagnetic metal center and, accordingly, the three-dimensional phases of the networks that incorporate $[\text{Nb}^{IV}(\text{CN})_8]^{4-}$ building blocks all show bulk magnetic behavior (5). Ongoing studies focus on the elucidation of the magnetic structures of this new class of three-dimensional materials (19), as well as detailed structural studies to develop a straightforward concept for the synthesis of new materials from cyanometalate building blocks, having a predictable structural order and a useful set of solid-state properties.

SUMMARY

At the turn of the second millennium, the traditional field of magnetism is once again experiencing a revival as molecule-based magnets have started to emerge over recent years (7, 20). Progress in this area has been strongly influenced by the interdisciplinary effort of several research groups, including that of the late Olivier Kahn, whose vision it has been to use molecular complexes as “bricks” for the construction of supramolecular lattices supporting long-range magnetic order (6). One of the major challenges still facing synthetic chemists working in this area is to find a strategy to control the self-assembly of molecular “bricks” in an ordered manner, so that the resulting supramolecular compound has the desired structure, stability, and physical properties. In order to address this problem, we have investigated the versatility of two classes of molecular building blocks, namely octacyanometalates and transition-metal oxalates for the self-assembly of molecule-based magnetic materials with predetermined solid-state structures. This research has yielded a novel cyano-bridged molecular cluster with the highest ever ($S = 51/2$) ground state spin and ferromagnetic ordering at low temperatures (4), as well as a range of new two- and three-dimensional extended networks exhibiting a wide range of ferro-, ferri-, and antiferromagnetic properties (1, 2).

Dimensionality, chirality, transparency, and processability are several important properties currently under investigation in the field of molecule-based magnets (21). The flexibility of the supramolecular approach enables chemists to design and assemble molecular lattices in which two or more physical properties are combined, e.g., superconductivity with long-range magnetic order. As a consequence, many of these materials may exhibit properties never previously associated with molecular materials or traditional magnets; hence, the field of magnetism will continue to grow and develop as the search for new molecule-based materials, together with the development of new technologies, provides us with new challenges in the future.

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