Magnetically ordered molecule-based assemblies†

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The development of molecules and assemblies of molecules exhibiting technologically important bulk properties, such as magnetic ordering, is an important worldwide research focus. Organic- and molecule-based magnets have been discovered and several families have been reported with magnetic ordering temperatures exceeding room temperature and as high as ~125 °C. Examples of both hard and soft magnets have been reported with coercivities as high at 27 000 Oe (and exceeding commercially available magnets) have been reported. Several examples are based on the radical anion of tetracyanoethylene, $S = 1/2$ [TCNE]$^{•-}$. The include ionic zero-dimensional (0-D) [FeCp*$_2$]$^{•+}$[TCNE]$^{•-}$ (Cp* = pentamethylcyclopentadienide), 1-D [MnTPP]$^+$[TCNE]$^{•-}$ [TPP = meso-tetraphenylporphinato] coordination polymers, and 3-D extended network structured M[TCNE]$_x$·ySolvent (M = V, Mn, Fe, Co, Ni, Dy). This Perspective focuses on work in our laboratory that will be discussed at the Dalton Discussion 9 meeting entitled "Functional Molecular Assemblies." In addition to the overview of TCNE-based organic magnets, the targeted design, preparation, and chemical as well as magnetic characterization of a new family of magnets based on $S = 3/2$ mixed-valent [Ru$^{II/III}_2$(O$_2$CR)$_4$]$^+$ (R = Me, Bu^t) is described. In particular [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] prepared from aqueous media possess two interpenetrating cubic lattices and magnetically orders at 33 K. In contrast, [Ru$_2$(O$_2$CBu^t)$_4$]$_3$[Cr(CN)$_6$] forms a 2-D layered lattice and orders at 37.5 K. Both exhibit hysteretic behavior, however, this is quite anomalous for the former cubic lattice. This as well as other anomalous magnetic behaviors is attributed to the presence of the second interpenetrating lattice.

Introduction

Magnets are exceptionally important materials with a myriad of expanding uses that their annual worldwide sales is $2 × 10^9$,[1] and growing at 10% per annum.[2] As a consequence, improvement of the properties of magnets as well as identifying new properties, in particular in combination with other technologically useful phenomena, is an important goal of contemporary materials research.[3]

As with most traditional materials,[4] conventional magnets (e.g. Fe, Fe$_3$O$_4$, CrO$_2$) are atom based with d-(or f-) orbital-based spin sites and have extended network bonding in three dimensions. Their insolubility and need for energy-intensive metallurgical fabrication methods is due to their extended network structures. With our discovery[5] that organic-based magnets can be prepared, the expectation arises that more generally molecule/polymer-based magnets should have improved solubility and processing comparable to conventional polymers. Molecule-based magnets are expected to have one or more of the properties listed in Table 1 and hence may be important materials for future generations of electronic or photonic and/or so-called 'smart' devices.[6] This is particularly timely due to the enhanced emphasis on reduced energy consumption and environmental-friendly processing and materials disposal. Also, combinations of properties, such as

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Table 1 Attributes of organic and molecule-based magnetic assemblies

High, magnetic susceptibilities and magnetizations	Semiconductivity
Bistability [≥2 'stable' states (weakly/strongly magnetic)]	Low density
Transparency	Biocompatibility
Fabrication/processibility at low temperature	Redox activity
Large polarizabilities	Magnetostrictive response
Optical changes (linear and/or nonlinear)	Magneto-optic response
Modulation/tuning of properties *via* organic chemistry	Flexibility
Low environmental contamination	Solubility

magnetic ordering that is controlled by irradiation of light[7] or optical transparency,[8] that are not currently achievable may be important in future generation applications.

Molecule-based magnets possess distinctly different structure types with respect to conventional atom-based magnets, and offer the opportunity for new phenomena, as well as combinations of properties not observed for classical magnets. For example, the first organic-based ferromagnet, *i.e.* ionic, noncovalent-bonded 'zero-dimensional', organic-solvent soluble [FeCp*$_2$]$^{•+}$[TCNE]$^{•-}$ (Cp* = pentamethylcyclopentadienide; TCNE = tetracyanoethylene) would not have been predicted to exhibit bulk ferromagnetic behavior based upon the prevailing conventional understanding of magnetism. This is due to the large nonbonded distances between spins.[9,10] Likewise, we later discovered that [MnTPP]$^+$[TCNE]$^{•-}$ [TPP = *meso*-tetraphenylporphinato], a soluble 1-D coordination polymer,[9a,11] which would not have been predicted to magnetically order due to its low dimensionality, as occurs.

The discovery of bulk magnetism in molecular and polymeric solids has stimulated worldwide interest with numerous groups participating.[12] The growing worldwide interest in molecule-based magnets has led to many advances in the development of new materials as well as understanding the spin coupling mechanisms. Progress in these areas is summarized in recent reviews[9,10] with important contributions from many groups worldwide. The history of organic- and molecule-based magnets is also available.[13]

Several models have been invoked for achieving ferromagnetic spin coupling ($J > 0$).[9c] They can be summarized as: (1) spins in orthogonal orbitals in the same spatial region (*i.e.* Hund's rule); (2) configuration interaction (CI) of (a) degenerate states (first-order perturbation theory), *i.e.* 'double exchange' solely for delocalized mixed-valent systems, and (b) ferromagnetic nondegenerate states (second- order perturbation theory); and (3) dipole–dipole through-space coupling not involving orbital overlap. Additionally, antiferromagnetic coupling ($J < 0$) between alternating spin sites each with a different number of spins can lead to a ferrimagnet.[9c,14] Furthermore, due to the complexity of molecular systems, combinations of these mechanisms are likely operative. The literature has other names associated with these mechanisms, *e.g.* superexchange is classified as CI of nondegenerate states, *etc.* However, a CI model invoked for several systems has been shown to have some conceptual flaws.[15] Hence, due to space constraints, the details of mechanisms will not be discussed herein, but they can be found in reviews.[9c,10]

As a consequence of the growing worldwide discoveries, the understanding of magnetic phenomena has enjoyed a renaissance as it is being expanded in part by contributions from molecule-based chemistry. These include the discovery (1) of bulk ferro- and ferrimagnets based on organic/molecular components[9,16,17] with critical temperatures exceeding room temperature;[9,10,18] (2) of

Prussian blue structured, room temperature magnets;[19–22] (3) that clusters in high, but not necessarily the highest, spin states with a large magnetic anisotropy and negative zero field splitting have a significant relaxation barrier that traps magnetic flux enabling a single molecule/ion (cluster) to act as a magnet at low temperature (*i.e.* single molecule magnet);[23] (4) of materials exhibiting large, negative magnetizations;[24] (5) that spin-crossover materials can have large hysteretic effects above room temperature;[25] (6) of photoinduced magnetism;[7,26,27b] (7) of electrochemical[24d,27] modulation of the magnetic behavior; (8) of the Haldane conjecture[28a] and its realization;[28b,c] (9) of valence tautomers exhibiting spin crossover,[29] (10) of Spin Peierls transitions;[30] (11) of single chain magnets;[31] (12) of spin ladders;[32] and (13) high spin organic molecules.[33] Also, (14) giant[34] and (15) colossal[35] magnetoresistance effects observed for 3-D network solids might be observed for molecule-based magnets. We recently realized magnetoresistance effects for our room-temperature V[TCNE]$_x$ ($x \sim 2$) film magnet.[36]

The essential components of any molecule-based magnet are molecules or ions possessing unpaired electron spins. While necessary it is insufficient as these spins must couple sufficiently strongly to enable magnetic ordering to occur. Furthermore, the coupling must be uncompensated, else antiferromagnetic ordering occurs. Antiferromagnetic ordering *per se* is interesting and perhaps more so than ferromagnetic ordering and while the subject is of on ongoing academic interest, it is not of technological interest and it is not the focus of the worldwide efforts to study molecule-based magnets. Achievement of sufficiently strong antiferromagnetic or ferromagnetic coupling to enable formation of either a ferri- or ferromagnet, respectively, is challenging and more of an art than of a science. It is the focus of this Dalton Perspective to provide the results of several successful assemblies of magnetically ordered materials with special emphasis of work in our laboratory. Our laboratory refers to successful on-going collaborations with Arthur J. Epstein and his group at The Ohio State University, in addition to many delightful and productive collaborations with a multitude of talented scientists worldwide.[37]

Metallocene-based magnets

In an effort to make a new molecule-based metal decamethyl-ferrocene, Fe^{II}Cp*$_2$, was reacted with 7,7,8,8-tetracyano-*p*-quino-dimethane (TCNQ) and two phases of [Fe^{III}Cp*$_2$]$^{•+}$[TCNQ]$^{•-}$ were prepared. One phase was characterized to be a metamagnet; *i.e.*

Fe^{II}Cp*$_2$ TCNQ   TCNE
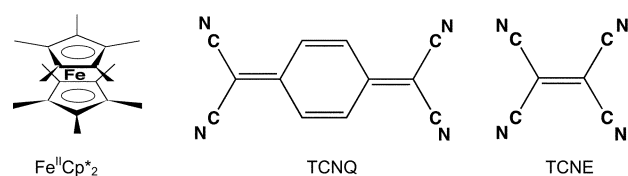
it had an antiferromagnetic ground state, but above a critical field, H_{cr}, of 1.3 kOe, had a transition to a ferromagnetic-like state.[38–40] The metamagnet phase possesses a 1-D chain motif with alternating $S = 1/2$ [Fe^{III}Cp*$_2$]$^{·+}$ cations and $S = 1/2$ [TCNQ]$^{·-}$ anions (Fig. 1). This unexpected observation of magnetic ordering, albeit antiferromagnetic,[13b,37] led to a new approach for stabilizing the ferromagnetic ground state, i.e., increasing the magnetic coupling (J) via increasing the spin density of the spin-bearing anion and using a smaller anion that might get closer to the cations enabling stronger coupling. TCNQ is nominally twice the size of TCNE and hence the spin density of TCNE is twice that of TCNQ. Hence, substitution of TCNQ with tetracyanoethylene (TCNE) was identified. Subsequently, [Fe^{III}Cp*$_2$]$^{·+}$[TCNE]$^{·-}$ was designed, synthesized, and subsequently characterized to be a bulk ferromagnet with an ordering temperature, T_c, of 4.8 K, and a coercivity, H_{cr}, of 1 kOe at 2 K.[5]
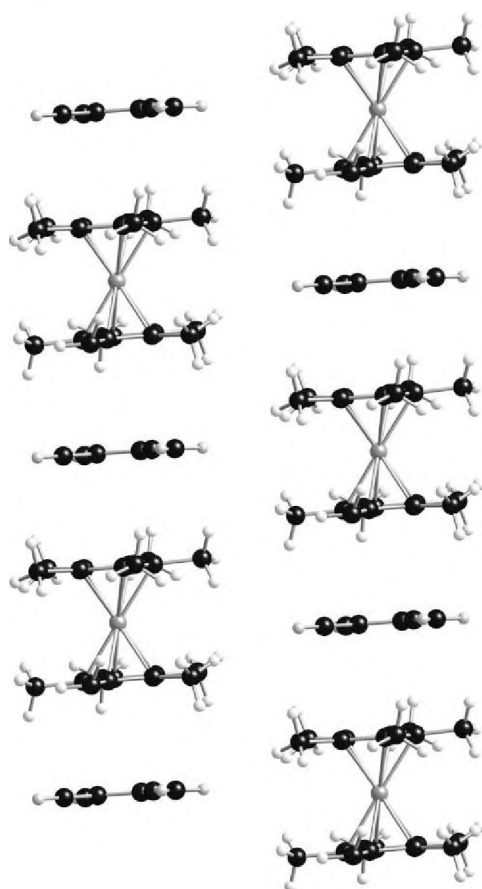

Fig. 1 Structure of ferromagnetically coupled out-of-chain segments of 1-D chains of [FeCp*$_2$][TCNE] with alternating [FeCp*$_2$]$^-$ and [TCNE]$^{·-}$ units.[5b]

With the discovery of [Fe^{III}Cp*$_2$]$^{·+}$[TCNE]$^{·-}$ as the first organic-based magnet[5] in addition to its detailed characterization of its physical and magnetic properties, many related materials were synthesized. These new materials were based on substitution of pendant groups on the cyclopentadienyl ring, expansion of the ring, substitution of iron with other metal ions, and replacement of the TCNE with alternative electron acceptors, most notably with TCNQ. [Fe^{III}Cp*$_2$]$^{·+}$[TCNE]$^{·-}$ and [Fe^{III}Cp*$_2$]$^{·+}$[TCNQ]$^{·-}$ (M =

Cr, Mn, Fe) magnetically order with ordering temperatures, T_c, that increase as M = Mn > Fe > Cr for both TCNE and TCNQ, and the T_c values for the TCNE-based salts exceed that to the TCNE-based magnets. Aspects of these studies are summarized elsewhere.[9c,41–43]

Unlike [Fe^{III}Cp*$_2$][TCNQ], [Fe^{III}Cp*$_2$][TCNE] can be solvated to form [Fe^{III}Cp*$_2$][TCNE]·S (S = MeCN, EtCN, etc.) with a similar structure as [Fe^{III}Cp*$_2$][TCNE].[5b] Using the maximum in the in-phase 10 Hz ac $\chi'(T)$ data as the blocking temperature, T_f, the magnetic behavior of [FeCp*$_2$][TCNE]·S was determined.[44] The T_f, of [FeCp*$_2$][TCNE] was previously reported to be 5.1 K,[45] 0.3 K greater than its 4.8 K T_c. The $\chi'(T)$ and $\chi''(T)$ components of the ac susceptibility for [FeCp*$_2$][TCNE] and [FeCp*$_2$][TCNE]·MeCN are identical with a 4.96 K T_f based upon the maximum in the 10 Hz ac $\chi'(T)$ data. The $\chi'(T)$ and $\chi''(T)$ of [FeCp*$_2$][TCNE]·S (S = MeCN) significantly differs, however, from that observed for [FeCp*$_2$][TCNE]. The T_f, is substantially reduced to 2.87 K, and a frequency dependence based figure of merit for glassy behavior increases over 30-fold indicating extensive disorder and glassiness. Similar results are observed for solvated [FeCp*$_2$][TCNE]·S (S = EtCN, PrCN, PhCN, 1,2-C$_6$H$_4$Cl$_2$, NCC$_4$H$_8$CN). In contrast use of S = THF unexpectedly increases T_f to 5.50 K.[44] This increase is attributed to a pressure induced by the THF that does not occur for the nitrile-based solvents. The T_f for [FeCp*$_2$][TCNE] is pressure dependent and increases by ~0.22 K kbar^{-1} ($P < 14$ kbar).[45] hence, the THF solvent induces ~2.5 kbar of pressure.

M[TCNE]$_x$-based ferrimagnets

Bis(benzene)vanadium(0), V^0(C$_n$H$_n$)$_2$, is structurally related to FeCp*$_2$, and isoelectronic to MnCp*$_2$, and reaction of it with TCNE led to the discovery of V(TCNE)$_x$·yS ($x \sim 2$; $y \sim 1/2$), the first room-temperature organic-based magnet ($T_c \sim 400$ K).[18] Subsequently this magnetic material was also prepared via the reaction of TCNE and V^0(CO)$_6$.[46] Utilization of volatile V^0(CO)$_6$ and TCNE precursors led to the development of a chemical vapor deposition (CVD) route to solvent-free thin films of the V[TCNE]$_x$ magnet that also exhibited enhanced air stability.[47] X-Ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies reveal that vanadium is present as V^{II} and is coordinated by six nitrogens with V–N distances of 2.076 Å at 10 K (Fig. 2).[48]
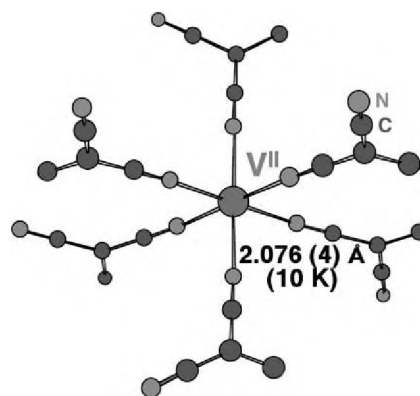

Fig. 2 Local structure around each V^{II} site V(TCNE), deduced from XANES and EXAFS studies.[48]

V[TCNE]$_x$ is an amorphous, disordered material with a small coercive field, H_{cr}, < 1 Oe at room temperature and 7.4 Oe at 5 K.[49] Furthermore, it is a magnetic semiconductor with a room temperature conductivity of ~10^{-4} S cm^{-1}, and magnetotransport studies indicate that electrons in valence and conducting bands are spin polarized, suggesting 'spintronic' applications.[50] Magnets of M(TCNE)$_x$·yS (M = Mn,[51] Fe,[51,52] Co,[51] Ni,[51,53] Gd;[54] x ~ 2; y ~ 1/2) composition, solid solutions of V$_x$M$_{1-x}$(TCNE)$_y$·yS (M = Fe,[55] Co,[56] Ni;[53] x ~, y ~ 1/2) composition, and magnets based upon TCNQ[57] have also be prepared.

Tetraphenylporphinatomanganese(II)-based magnets

In addition to the above TCNE-based magnets, metallomacrocycle based magnets typified [MnTPP][TCNE]·2PhMe (H$_2$TPP = *meso*-tetraphenylporphyrin) [1 = MnTPP] were reported[58] and subsequently discovered to order as ferrimagnets.[9a,11] This large family of magnets all are soluble 1-D coordination polymers possessing [TCNE]$^{•-}$ bonding to and bridging between two Mn(III) ions (Fig. 3). These materials are ferrimagnets resulting from the antiferromagnetic coupling of the S = 2 Mn^{III} with S = 1/2 [TCNE]$^{•-}$ with critical temperatures, T_c, ranging from 3.5 to 28 K.[9a,59] Furthermore, at low temperature they exhibit complex magnetic behaviors that include spin glass behavior, and large coercivities in the range of 27 kOe (Fig. 4).[60]

[Ru$_2$(O$_2$CR)$_4$]$^+$-based magnets

The design and subsequent synthesis of a specific structural motif with specific physical properties is a holy grail for chemists and materials scientists. In this vein we targeted a new family of molecule-based magnets utilizing D_{4h}, paddle wheel-structured ruthenium acetate, Ru$_2$(O$_2$CMe)$_4$, 2. Complex 2 as 2$^-$ has one vacant coordination site per Ru to build an extended structure, and has as a σ^{2}π^{4}δ^{2}δ*^{1}π*^{2} S = 3/2 valence electronic configuration,[61,62] and hence, three unpaired electron spins that are essential, but not sufficient, for achieving magnet ordering. To simply balance the charge, anionic [Cr(CN)$_6$]$^{3-}$ was selected due to its six cyanides being able to bond to six [Ru$_2$(O$_2$CMe)$_4$]$^-$ moieties to form a charge compensated 3-D network structure. Thus, the structure of [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] was anticipated to be cubic with a ~ 13.3 Å, as well as magnetically order.
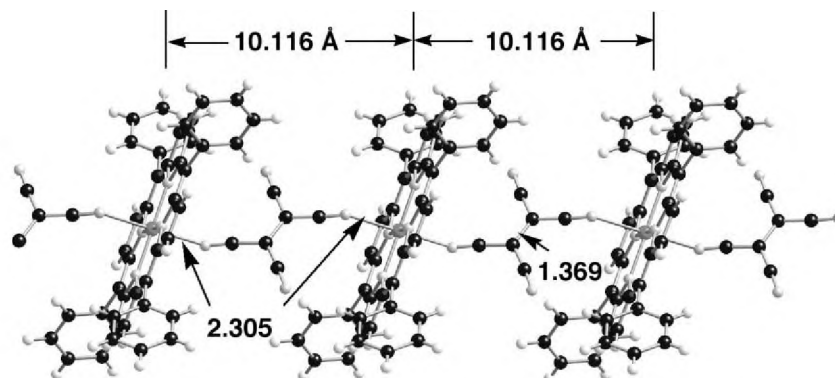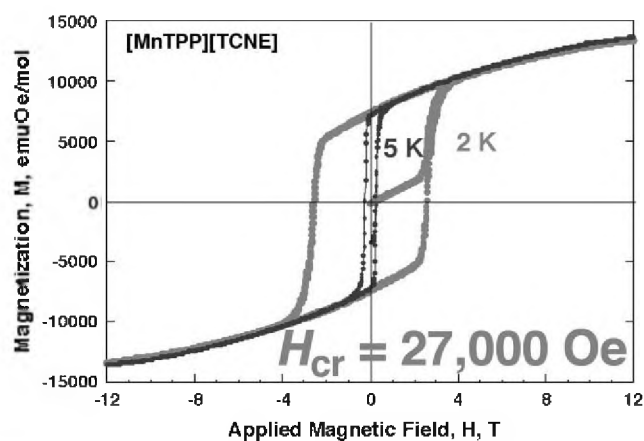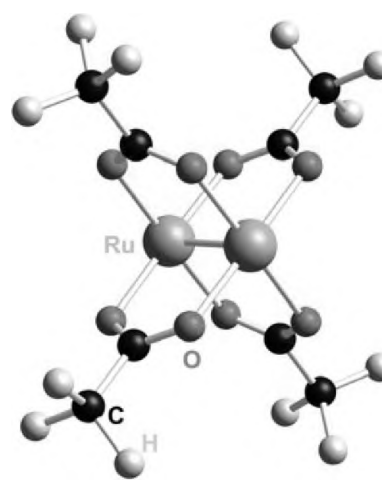
Fig. 4 2 and 5 K hysteresis loops (±12 T) observed for [MnTPP][TCNE]·2PhMe.

2, Ru$_2$(O$_2$CMe)$_4$

[Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] was formed from the reaction of [Ru$_2$(O$_2$CMe)$_4$]Cl and K$_3$[Cr(CN)$_6$] in water.[63] As anticipated [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] exhibits a cubic (Fig. 5), 3-D extended structure, however, being body centered it possesses a second interpenetrating lattice (Fig. 6). This structure was confirmed from the
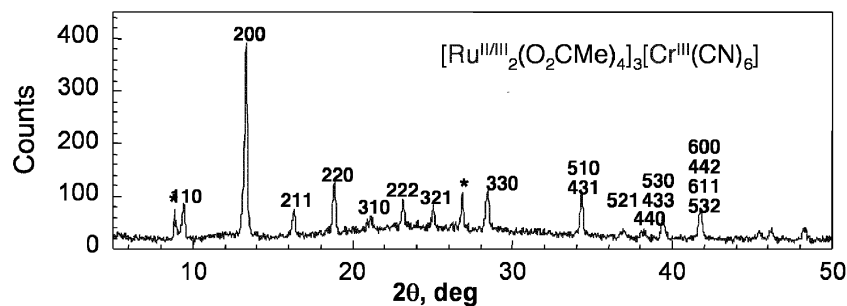
Fig. 3 Segment of a typical 1-D ···[MnTPP]$^+$[TCNE]$^{•-}$··· coordination polymer showing [TCNE]$^{•-}$ *trans*-μ-N-σ-bonding uniformly to [MnTPP]$^+$ (1).[11]

Fig. 5 Body centered cubic (bcc) X-ray powder diffraction pattern ($a = 13.34$ Å) for aqueous-prepared [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$].
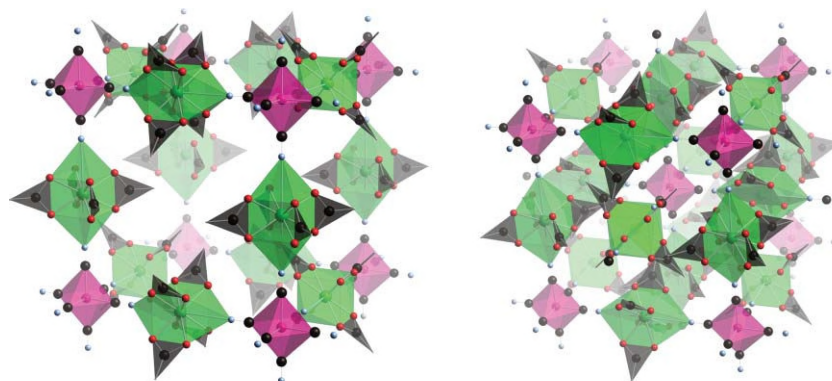
Fig. 6 Single, noninterpenetrating [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] cubic lattice (a), and the observed interpenetrating [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] cubic lattices (b). Reprinted with permission of the copyright owner.[64]

Reitveld analysis of the synchrotron powder X-ray diffraction data and density measurements.[63] More importantly, the temperature dependent effective moment, $\mu_{\text{eff}}(T)$ of [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] decreases with decreasing temperature upon cooling from room temperature to ~100 K in accord with the expectation of single ion magnetic behaviors for the $S = 3/2$ Cr(III) site and the three $S = 3/2$ diruthenium sites with strong zero-filed splitting, *i.e.*, the lower curve in Fig. 7. Below 100 K, $\mu_{\text{eff}}(T)$ increases dramatically with decreasing temperature suggestive of the onset of magnet ordering (upper curve), which is observed to occur *via* other measurements at 33 K.[63]
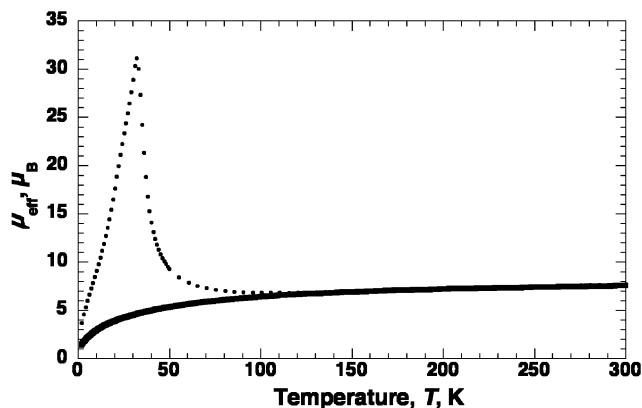

Fig. 7 $\mu_{\text{eff}}(T)$ of [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] that is in accord with the paramagnetic behavior of three $S = 3/2$ diruthenium sites with strong zero field splitting (below ~100 K), and $S = 3/2$ Cr(III) sites (lower curve) above ~100 K.

When prepared from acetonitrile, the reaction of [Ru$_2$-(O$_2$CMe)$_4$]Cl and [NEt$_4$]$_3$[Cr(CN)$_6$] forms [Ru$_2$(O$_2$CMe)$_4$]$_3$-[Cr(CN)$_6$]·xMeCN, and although amorphous based on the observed density it is anticipated to possess a primitive cubic structure with the MeCN solvent filling the void space.[63] [Ru$_2$-(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$]·xMeCN also magnetically ordered at 34.5 K as a ferrimagnet.

Both [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] and [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$]·xMeCN exhibit magnetic hysteresis, $M(H)$. The hysteresis loop observed for [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$]·xMeCN is typical for a magnet and it has a coercivity at 5 K of 1670 Oe, Fig. 8.[63] In contrast, [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] exhibits an anomalous constricted hysteresis loop depicted in Fig. 8. Hence, [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] with the second, interpenetrating lattice exhibits an unusual shape, which saturates to a 30% larger value at high applied magnetic fields, and a coercivity of 470 Oe. The genesis of the unusual behavior is attributed to the presence of the interpenetrating lattices of [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] and is the focus on ongoing work. Nonetheless, it represents a rare example of physical properties dramatically different and dependant upon the presence of the second interpenetrating lattice.[65]

The zero field cooled-field cooled (ZFC-FC) temperature-dependent magnetization data, $M(T)$, for MeCN-made [Ru$_2$-(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] is typical for a magnet as upon cooling it coincides until a bifurcation point, T_b, is reached. Below T_b the ZFC data substantially drops in value while the FC data continues to increase, Fig. 9. However, ZFC data for water-made [Ru$_2$(O$_2$CMe)$_4$]$_3$[Cr(CN)$_6$] coincides with the FC data with decreasing temperature. This again is attributed to the presence of the second interpenetrating lattice.
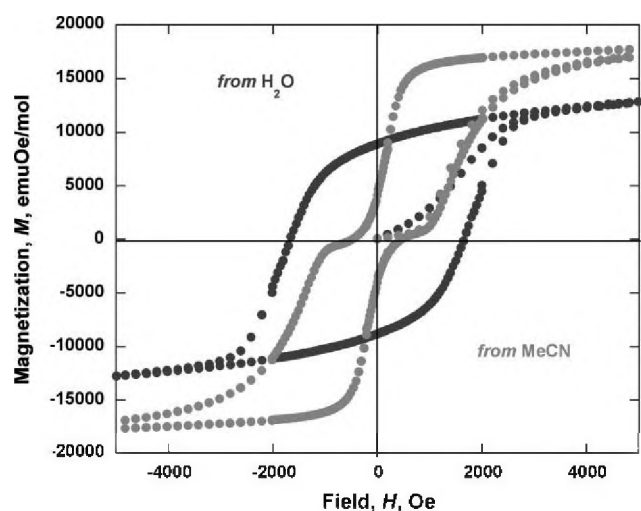
Fig. 8 Hysteresis, $M(H)$, for the $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]\cdot x$MeCN magnet with a single lattice prepared, and the $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ magnet with a second interpenetrating lattice.
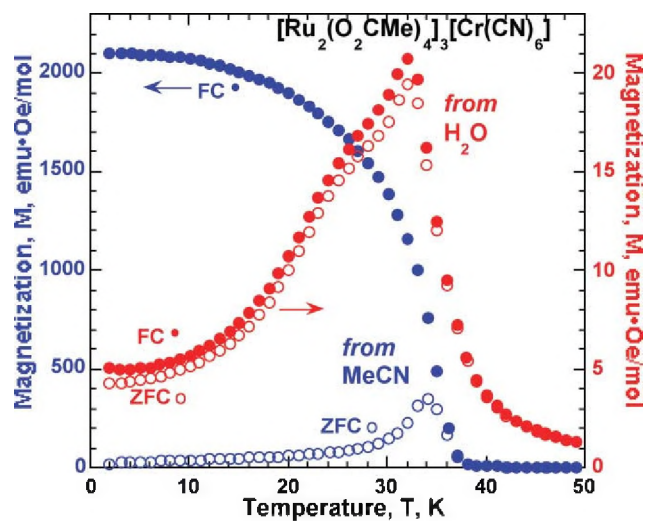
To eliminate the possibility of formation of the cubic lattice without the second interpenetrating lattice the acetate (methyl group) was substituted by pivolate (*tert*-butyl group).[66] Modeling of the shape and void volume and by the isosurface method[67] indicated that both cubic lattices were stable, Fig. 10. Hence, due to the larger *tert*-butyl group $[Ru_2(O_2CBu^t)_4]_3[Cr(CN)_6]$ was anticipated to form a cubic, noninterpenetrating lattice. Nonetheless, Yoshioka *et al.*[68] reported that $[Ru_2(O_2CBu^t)_4]_3[M(CN)_6]\cdot 2H_2O$ (M = Co, Fe) formed an extended layered (2-D), not cubic (3-D) network structure.

$[Ru_2(O_2CBu^t)_4]_3[Cr(CN)_6]\cdot 2H_2O$ was prepared and is isomorphous to the layered, 2-D structure previously reported,[65] Fig. 11. Furthermore, as well magnetically orders at 37.5 K and exhibits a conventionally shaped hysteresis loop and normal zero field cooled/field cooled behaviors, albeit the coercive field is quite large (*i.e.* 20 000 Oe).[64] Thus, replacement of an alkyl group with another alkyl group has a profound effect on the resultant structure.

Fig. 9 Typical ZFC and FC $M(T)$ data as observed for MeCN-made $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ ($\bigcirc$,$\bullet$) and for H$_2$O-made $[Ru_2(O_2CMe)_4]_3[Cr(CN)_6]$ ($\bigcirc$,$\bullet$).
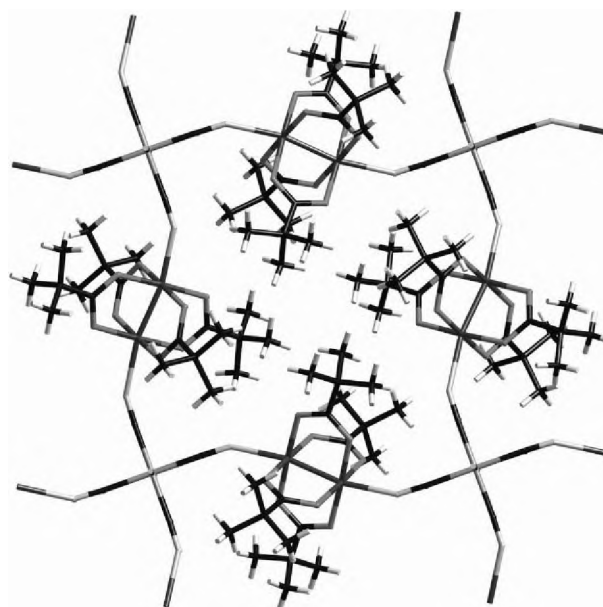
Fig. 11 Top view of layered (2-D) $[Ru_2(O_2CBu^t)_4]_3[Cr(CN)_6]$ (top).
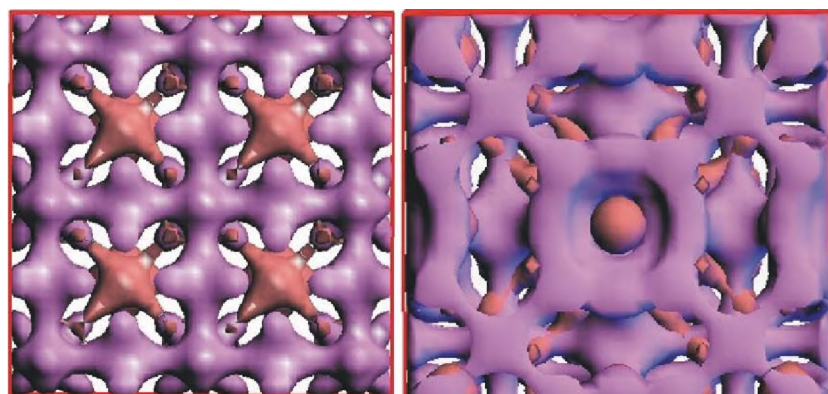
Fig. 10 Calculated void space (pink) for noninterpenetrating $[Ru_2(O_2CR)_4]_3[Cr(CN)_6]$ (purple) [R = Me (left); *tert*-Bu (right)]. Reprinted with permission of the copyright owner.[64]

Conclusion

Several families of molecule-based magnets have been prepared in our laboratory as well as in other laboratories worldwide. The anomalous hysteresis and, zero field cooled-field cooled temperature-dependent (ZFC/FC) magnetization for cubic $[Ru_2(O_2CMe)_4]_3[Cr(CN)_n]$ deviate from typical magnetic behaviors and the genesis is under continuing study. Nonetheless, these anomalies are attributed to the presence of the second interpenetrating lattice. The study of molecule-based magnets continues to fascinate chemists worldwide.

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