FEATURE ARTICLE
Kasper S. Pedersen, Jesper Bendix and Rodolphe Clérac
Single-molecule magnet engineering: building-block approaches
Single-molecule magnet engineering: building-block approaches†

Kasper S. Pedersen,*abc Jesper Bendix*cd and Rodolphe Clérac*ab

Tailoring the specific magnetic properties of any material relies on the topological control of the constituent metal ion building blocks. Although this general approach does not seem to be easily applied to traditional inorganic bulk magnets, coordination chemistry offers a unique tool to delicately tune, for instance, the properties of molecules that behave as “magnets”, the so-called single-molecule magnets (SMMs). Although many interesting SMMs have been prepared by a more or less serendipitous approach, the assembly of predesigned, isolatable molecular entities into higher nuclearity complexes constitutes an elegant and fascinating strategy. This Feature article focuses on the use of building blocks or modules (both terms being used indiscriminately) to direct the structure, and therefore also the magnetic properties, of metal ion complexes exhibiting SMM behaviour.

1. Introduction

Single-molecule magnets (SMMs), i.e. paramagnetic molecules exhibiting a magnet behaviour,‡ of intrinsic molecular origin in the absence of a magnetic order, have received considerable attention in chemistry, physics and materials science since their discovery in the early 1990s. The main interest arose from the possible applications of SMMs in data storage, quantum computing§ and molecule-based spintronics devices. Even if SMMs have not yet been employed for practical applications, their underlying physics and chemistry have a much broader perspective. For instance, these “nanomagnets” and related molecular magnetic complexes serve as simple models for understanding more complex magnetic materials (extended 1D, 2D or 3D networks, large aggregates, ...). Moreover, significant advancements in nanostructuring and deposition of single molecules

Kasper S. Pedersen (b. in 1986, Allerød, Denmark) completed his studies in Inorganic Chemistry under the supervision of Prof. J. Bendix at the University of Copenhagen. From early in his studies he worked with Dr P. L. W. Tregenna-Piggott (**) in Switzerland on spectroscopic studies of SMMs by inelastic neutron scattering. Currently, he is pursuing a PhD in the groups of Prof. J. Bendix and Dr R. Clérac. His current research interests include synthesis and investigations of molecule-based magnetic materials based on heavier transition elements and f-elements as well as spectroscopic investigations.

Jesper Bendix (b. in 1965, Copenhagen, Denmark) received his PhD at the University of Copenhagen under the supervision of Prof. C. E. Schäffer in 1998. Following post-doctoral stays in Mülheim, Germany with Prof. K. Wieghardt, at Caltech, USA, with Prof. H. B. Gray, at the University of Utah with Prof. J. S. Miller, and in Berne, Switzerland, with Dr P. L. W. Tregenna-Piggott (**), he returned to Copenhagen where he is currently heading the section for inorganic chemistry. His current research focuses on synthesis as well as electronic and structural studies of molecule-based magnetic materials and on the electronic structure of high-valent metal centres.
allowed the studies on individual SMMs and to probe their intrinsic magnetic properties outside the crystal lattice.\textsuperscript{10,11} These detailed studies of the SMM properties include the seminal observation of slow relaxation\textsuperscript{12} and quantum tunnelling\textsuperscript{13} of magnetization of magnetically isolated molecules covalently grafted to surfaces. Furthermore, studies of SMMs in solution,\textsuperscript{14,15} as well as nanostructured on surfaces,\textsuperscript{10,11,16,17} in junctions,\textsuperscript{18} films,\textsuperscript{19} porous materials\textsuperscript{20} or in multi-dimensional coordination networks have been undertaken.\textsuperscript{21–23}

Key to the possible applications of molecular magnetic systems is a thorough understanding of the design pathways towards specific structural motifs and the understanding of the related magnetic properties of the constituent molecular entities. SMMs can be roughly divided into two classes: mononuclear and polynuclear complexes. Mononuclear SMMs have only been reported in recent years with the first example being the $[\text{Ln(pc)$_3$}]^-$ ($\text{Ln} = \text{Dy}^{	ext{III}}, \text{Tb}^{	ext{III}}, \text{H}_2\text{pc} = \text{phthalocyanine}$) “double-decker” complexes.\textsuperscript{26} After this ground-breaking discovery, a multitude of mononuclear lanthanide\textsuperscript{27–38} and more recently, several 3d metal ion complexes behaving as SMMs have been reported.\textsuperscript{39–45,46–48} Additionally, SMM behaviour in photo-excited spin-crossover complexes has very recently also been reported.\textsuperscript{49,50} Common to the majority of these systems, the slow-relaxation of magnetization arises due to a strong uniaxial magnetic anisotropy of the paramagnetic metal ion. The second class of SMMs encompasses polynuclear, exchange coupled complexes in which the constituent metal ions may be transition metal ($n_d$, $n = 3$ to 5) ions, lanthanides/actinides ($n_f$, $n = 4, 5$), or both. The SMM signature was reported for the first time in a dodecanuclear $[\text{Mn}_{12}]$ complex that is the archetypal example of an exchange-coupled polynuclear SMM.\textsuperscript{1,2,51,52} This family of SMMs can be further sub-divided into two classes based on the employed synthetic approach. The synthesis of the first sub-class proceeds via a concerted association of metal ions through bridging ligands and with capping ligands to prevent polymerisation. The bridging ligands, most commonly oxide, hydroxide, alkoxides or phenolates obtained by deprotonation in the reaction medium, give pathways for magnetic exchange interactions between the constituent metal ions in the final polynuclear complex. The vast majority of SMMs have been obtained by this more or less serendipitous method\textsuperscript{53} and pivotal studies, which have paved the way for the current understanding of SMM physics (e.g. quantum tunneling of magnetization, QTM,\textsuperscript{44} and quantum coherence\textsuperscript{55}), were discovered in such systems. Alternatively, the synthetic approach towards the second sub-class of polynuclear SMMs makes use of presynthesized molecular building-blocks, which are able to associate directly in solution. In that respect, two kinds of precursors exist, namely $\text{M} - \text{L}$ ligand donors and $\text{M}'$ ligand acceptors, which react and form $\text{M} - \text{L} - \text{M}'$ motifs.

The remaining and non-trivial question is now: how to define a building-block and to understand how the structure of the building-blocks influences the final polynuclear complex topology and eventually the magnetic properties? If these questions can be satisfactorily answered, SMMs can be tailored to specific applications by chemical design. In this Feature article, we review the recent efforts to design SMMs using building-block approaches. Instead of a comprehensive review of the vast literature, we have been selective and discuss several explanatory examples of different uses of building-blocks with various bridging ligands.

In most of the cases, the observation of an SMM behaviour is attributed to the presence of a large spin ground state ($S_T$) and a strong easy-axis magnetic anisotropy.\textsuperscript{56} The large spin ground state is secured by the magnetic superexchange mechanism, which couples constituent spin centres ($S_i$), more or less strongly as described by the phenomenological Heisenberg–Dirac–van Vleck (HDvV) spin-Hamiltonian:

$$H = -2 \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$$

(1)

where $J_{ij}$ is the interaction parameter representing ferro- or antiferro-magnetic interactions (positive and negative values, respectively) between the $i$th and $j$th spins.\textsuperscript{§} In simple systems (like most of the 3d-based SMMs), the magnetic anisotropy, commonly referred to the (axial) zero-field splitting (ZFS) of the resulting ground state spin, $S_T$, is described by $D_S S_T^2$ where $S_T$ projects $S_T$ on the quantization ($Z$) axis with the eigenvalue of $M_T$ and $D$ is the anisotropy parameter arising as a tensorial sum of single-ion contributions of the intrinsic local anisotropy of the metal ion units.\textsuperscript{56} Commonly, the single ion anisotropy mainly originates from the orbital angular momentum of excited states, which is mixed into the ground state by second-order spin–orbit coupling.\textsuperscript{56} For $D < 0$, an energy barrier ($\Delta$) of $D S_T^2$ (for integer $S_T$) or $\Delta = D(S_T^2 - 1/4)$ (for half-integer $S_T$) separates

\textsuperscript{§} Alternative Hamiltonian conventions (as a matter of personal taste) such as $- \sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$ or $\sum_{i<j} J_{ij} \hat{S}_i \cdot \hat{S}_j$ are often found in the literature and a special attention to the employed definition should be given when comparing parameter values. Throughout this Feature article, we will consistently adopt the definition given in eqn (1).

Rodolphe Cléralc (b. in 1971, Versailles, France) received his PhD at the University of Bordeaux 1 under the supervision of Prof. C. Coulon in 1997. After a short post-doctoral stay in the group of Prof. O. Kahn (ICMCB, Bordeaux), he joined Prof. K. R. Dunbar’s group at Michigan State University (East Lansing, Michigan, USA) in 1998 and in 1999, he moved with Dunbar’s group to Texas A&M University (College Station, Texas, USA) where he collaborated with Prof. F. A. Cotton. In 2000, he established his research group (Molecular Materials & Magnetism) at the Centre de Recherche Paul Pascal (CNRS) interested in the synthesis and physical properties of molecular materials.
the $M_S = \pm S_T$ ground states. Recently, a few examples of mononuclear systems exhibiting $D > 0$ were reported to exhibit SMM properties; however, the underlying physics is still in debate.\(^{57-60}\) An energy diagram of an SMM with an easy-axis anisotropy ($D < 0$) is schematized in Fig. 1.\(^{61}\) The energy span of the $S_T = 4$ manifold resulting from ferromagnetic coupling of $S = 2$ rare earth ions ranges from $M_S = \pm 4$ to $M_S = 0$ of $J/k_B = 25.5$ K.\(^{61}\) By application of a magnetic field, one of the two “wells” can be stabilized and thereby selectively populated due to the Zeeman energy $\mu_B g_S H M_S$ (with the field applied along the quantization, $Z^*$ axis). When the polarizing field is removed, the system is magnetized and out of equilibrium. In a thermally activated regime where the relaxation is due to spin–phonon interaction, the magnetization of the system follows an exponential decay: $M(t) = M(Z) \times \exp(-t/\tau)$. This expression also defines the relaxation time, $\tau$, that obeys a thermally activated behaviour, i.e. the Arrhenius law: $\tau(T) = \tau_0 \exp\left[\frac{D}{k_B T}\right]^2$. The magnitude of the energy barrier, $D$, and the pre-exponential factor, $\tau_0$, which is related to $\tau_0$, the nature of the spin–phonon interaction,\(^{62}\) are the characteristic parameters commonly reported for an SMM. Most of the time, an experimental “effective” barrier ($\Delta_{\text{eff}}$) smaller than the expected one ($\Delta$, on the basis of $S_T$ and $D$) is obtained due to quantum tunnelling of magnetization (QTM) through the potential barrier via excited $M_S$ states.\(^{63}\) Indeed this is the case of the above example (Fig. 1) for which the observed energy barrier ($\Delta_{\text{eff}}$) extracted from ac susceptibility measurements is only 16 K, which is much lower than the calculated value (25.5 K). However, application of a small dc field (800 Oe) puts the $\pm M_S$ levels out of resonance and thereby increases $\Delta_{\text{eff}}$ to 23 K. The QTM is governed by non-diagonal terms entering into the Hamiltonian, giving rise to a mixing of $M_S$ states. In the vast majority of the characterized SMMs, the symmetry is lower than axial and the anisotropy part of the spin Hamiltonian to second order reads $\tilde{H} = D(S^2 + \frac{1}{2}S(S + 1)) + E(S^2 - \frac{1}{2}S^2)$ where $|E| \leq \frac{1}{2}|D|$. The $E$ term has the effect of mixing the $M_S$ states differing by $\Delta M_S = \pm 2$. In some cases, this anisotropy description might not be sufficient to explain the relaxation and thus higher order terms, despite their small parameter values, have to be taken into account.\(^2\)

For the reasons stated above, the maximization of both $D$ and $S_T$ seems crucial for the successful preparation of SMMs. synthetically, it has been proven very difficult to obtain a large $S_T$ ground state by ferromagnetic interactions whilst simultaneously perfectly aligning anisotropy axes of each magnetic site. The largest SMM reported to date is an aesthetic $\{\text{Mn}^{III}_{12}\}$ nanoscopic wheel which, despite its high nuclearity, exhibits only a relatively small spin ground state of $\sim 6$ and a modest energy barrier of 18 K.\(^{63}\) The largest $S_T$ is found in a ferromagnetically coupled mixed-valence $\{\text{Mn}^{II}_{2},\text{Mn}^{III}_{12}\}$ complex exhibiting a record $S_T = 83/2$ ground state but no SMM properties are observed due to an almost perfect compensation of the $\text{Mn}^{III}$ local anisotropy tensors.\(^{64,65}\) One of the successes in the realm of polynuclear SMMs has been a family of $\{\text{Mn}_{14}\}$ complexes, some of which exhibit an energy barrier higher ($\Delta_{\text{eff}}/k_B = 86.4$ K for $\{\text{Mn}^{III}_{11}\text{O}_2\text{Et-sao}_{11}\text{O}_2\text{CPh}[\text{Me}_{11}]_{11}\text{EtOH}_{11}\}}$, Et-saoH$_3$ = 2-hydroxyphenylpropanone oxime) than the celebrated $\{\text{Mn}_{12}\}$ SMM ($\Delta_{\text{eff}}/k_B = 61$ K).\(^{1,66,67}\) Indeed targeting very large spin ground states in pursuit of effective SMMs is not necessarily the most fruitful approach since the overall anisotropy decreases as $S_T \rightarrow 3$, leading to a SMM energy barrier almost independent of $S_T$ for sufficiently large $S_T$ values.\(^{68-70}\) Recently, $M$ vs. $H$ hysteresis loops at unprecedented temperatures (up to 14 K, 0.9 mT s$^{-1}$) have been reported for dinuclear lanthanide complexes bridged by the exotic paramagnetic N$_2$ radical,\(^{71,72}\) and a record anisotropy barrier for polynuclear SMMs of more than 600 K was observed for a $\{\text{Dy}_{14}\}$ hexanuclear complex.\(^7\) Particularly in the latter case, these promising results rely rather on the strong single-ion magnetic anisotropy of the lanthanide ions than on the spin ground state of the molecule. However, the use of spin architectures employing multiple spin centres remains a viable route to prepare individual molecules with interesting

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\[^{1}\] In this context, the experimental estimation of $J_{\text{eff}}$ by assuming a pure thermally activated process at the highest available temperatures may be inappropriate in some cases as recently demonstrated independently by Sorace, Dreiser and co-workers.\(^{77-78}\)
magnetic properties, while simultaneously exploiting and optimizing the existing knowledge of preparative coordination chemistry. Importantly, this also constitutes the most realistic approach towards a good understanding of the interaction of magnetic molecules (irrespective of their nuclearity) with extended structures, e.g. surfaces.

2. Topological control

The rational synthesis of polynuclear metal complexes using a bottom-up approach based on building blocks or modules is by no means a new idea nor restricted to magnetic systems. However, due to the intimate relationship between structure and magnetic properties, this approach is particularly relevant for polynuclear magnetic systems. In order for the building blocks to be able to direct or template the desired structure of a polynuclear system some prerequisites need to be fulfilled to avoid the synthesis of non-expected products that might be thermodynamically favored. One of the most important aspects is to consider modules with a sufficient degree of robustness to maintain their structure-directing abilities under the assembly conditions. This somewhat vague property reflects the relative nature of the robustness concept in connection with synthesis, balancing ligand exchange kinetics between the different precursors and with the harshness of the conditions required for the assembly of the targeted polynuclear system.

A second prerequisite for the building blocks to function as structure directing entities is a built-in preference for a specific coordination geometry at metal centers as well as at the bridging ligands. Octahedral coordination is predominant for the transition metal ions, and this is especially true for the kinetically robust systems. For a bridging ligand, the simplest conceivable geometry is to linearly connect two metal ions. This is true for the ubiquitous cyanide bridges, but also to quite some extent for fluoride, but not for oxide, when acting as bridging ligands. This tendency is supported by the histograms of Fig. 2 showing the crystallographically determined M–N ≡ C angle (where M is a transition metal ion) and, for comparison, the M–F/O–M’ angles in unsupported fluoride/oxide-bridged molecules and networks. The relative numbers are striking and reflect the extensive scientific work in cyanide chemistry. Consequently, M–N ≡ C–M’ motifs with robust octahedral metal ions, which are reminiscent of the Prussian blue compounds, are frequently used to design polynuclear complexes. Many molecular species obtained from building blocks of different denticities can be conceptually considered as fragments of a three-dimensional Prussian blue structure.

The robustness of a given building block can derive from either the metal center (e.g. the most robust ones being d3 and diamagnetic low-spin d6 metal ions) or from the use of polydentate, and possibly, rigid ligands. Due to the limited choice of d3 or d6 systems, the use of polydentate ligands is the most efficient approach to enforce robustness and additionally to allow further geometrical preferences based on ligand design. Considering a set of different metal ions, which are reminiscent of the Prussian blue compounds, 76,77 the synthetic point of view, it is also useful to note that a less intuitive definition of the building block concept considers a metal-free bridging ligand as a building block directing the geometry of the whole system by its robust structure. This definition significantly widens the modular description but allows for a unified view encompassing common polynuclear topologies directed by the ligand structure. This last aspect is well illustrated by the large number of ring structures obtained using bridging carboxylate ligands. Indeed, the vast majority of the reported SMMs also falls in this extended definition and will not be included in this article; instead the reader is directed to excellent reviews by Aromi, 7, Winpenny, 79 Christou, 80 Tang, 81 and Powell 82 for a detailed discussion of SMM topologies and their molecular control by ligand design.

In the context of molecule-based magnetism, the bridging ligand, in addition to guiding the structure, also needs to be compact enough to mediate efficient magnetic interactions. From the synthetic point of view, it is also preferable to choose bridging ligands with moderate basicity. Bridging ligands that are too reactive would limit the range of possible partners and conditions (e.g. solvents) since their structural integrity may be compromised, emphasizing further the relative nature of the robustness concept.

An essential aspect in engineering building blocks is to provide intrinsic magnetic characteristics essential to contribute to the final magnetic properties. To obtain SMMs, the building blocks usually contribute with Ising-like magnetic anisotropy or a large spin but other interesting additional properties like photomagnetism or luminescence can also be implemented. Building blocks may come as either homoleptic complexes, for which the cyanide (see Section 3) and oxalate (see Section 4) complexes are the most common, or as heteroleptic systems for which a large variety of ligand combination have been employed with a strong predominance of cyanide-based complexes. For the heteroleptic systems, the coordination sphere of the octahedral complexes, which can be cis-/trans- or fac-/mer-stereoisomers, directs towards different polynuclear structures.
The polymerization of building block units into multidimensional structures is a common synthetic problem for chemists who want to engineer molecular objects. In most cases, the successful synthesis of polynuclear complexes involves precursor units with strongly directional coordination abilities, which must be assisted by an appropriate choice of capping ligands. This choice is by no means trivial. First, the capping ligands often provide the solubility requirements for the subsequent assembly. Furthermore, the nature of the capping ligand may have dramatic structure-directing properties imposed by second coordination sphere interactions and packing effects. On the other hand, coordination polymers of SMMs are certainly another interesting research area that has led to magnetically interesting systems such as single-chain magnets (SCMs).

Indeed, some SCM systems can be considered as one-dimensional polymers of SMM repeating units, allowing the modelling of the complex dynamics of Ising-type SCMs, on the basis of the known properties of the isolated SMMs.

3. Cyanide-based precursors

By far, the cyanide-based homo- or heteroleptic precursors are the most ubiquitous building blocks that have been used to design SMMs, high-spin or simple magnetic molecules (“0D”), extended magnetic networks such as chains (1D), sheets (2D) and three-dimensional (3D) lattices. Shatruk, Avendano and Dunbar reviewed comprehensively the chemistry of polynuclear cyanidometallates in 2009 and herein we will focus mainly on results obtained since. To quote these authors: “The shape adopted by the cyanide-bridged core in these clusters is dictated by the topology of the available coordination sites”. This sentence describes precisely what will be the theme of the following paragraphs.

The interest in cyanide-based SMMs is in direct line with the famous Prussian blue and its analogues, which have been intensively studied, in particular by the groups of Girolami, Verdaguer, and Miller. In these systems, an experimental and detailed theoretical understanding of the magnetic interaction through bridging cyanide ligands has been achieved in relation to the involved metal ions and structural/geometrical parameters. This knowledge of the exchange mechanisms was fundamental in order to engineer cyanide-encompassing molecular analogues with tailor-made magnetic properties. The popularity of the cyanide ion was also boosted by the availability of the cyanide ion was also boosted by the availability of homoleptic cyanidometallate building blocks was a trigonal bipyramidal (TBP) complex, \([\text{Cr}^{III}(\text{CN})_6]^{3-}\) with a close-to-octahedral \([\text{Cr}^{III}(\mu-\text{CN})_{12}]^{6-}\) central core. Ferromagnetic Ni\(^{II}\)-Cr\(^{III}\) coupling interactions \((J_{\text{Ni-Cr}}/k_B = +12.1 \text{ K})\) give rise to an \(S_T = 15/2\) ground state. Even though Ni\(^{II}\) often possesses strong magnetic anisotropy, the proximity of the complex to octahedral symmetry is expected to significantly decrease the overall magnetic anisotropy and hence only a very small anisotropy barrier was found \((\Delta_{\text{eff}}/k_B \approx 6 \text{ K, } \tau_{\text{p}} = 1.1 \times 10^{-11} \text{ s})\). The first established SMM incorporating a cyanidometallate building block was a trigonal bipyramidal (TBP) complex, \([\text{Mn}^{III}(\text{tmphen})_3][\text{Mn}^{III}(\text{CN})_{12}]\) (2, tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) reported by Dunbar and co-workers. Herein, each of three facially-oriented cyanide ligands of the \([\text{Mn}(\text{CN})_{12}]^{3-}\) moiety links to a \([\text{Mn}(\text{tmphen})_3]^{2+}\) unit as depicted in Fig. 3. Since the Mn\(^{III}\) magnetic anisotropy is negligibly small, the presence of a spin-relaxation barrier arises due to anisotropic Mn\(^{III}\)-Mn\(^{III}\) exchange interactions through the bridging cyanides induced by the unquenched orbital angular momentum of the low-spin Mn\(^{III}\) \((t_{2g}^6)\) in octahedral symmetry (vide infra). In 3d metal ions, the orbital angular momentum is generally quenched by the presence of a low-symmetry ligand field. However, in systems incorporating hexacyanidometallates the main perturbation of the d-orbitals arises from the strong octahedral ligand field and thereby leaves the orbital angular momentum unquenched to a large extent even in polynuclear complexes with a low overall symmetry. Dunbar and co-workers reported other TBP
complexes but none showing SMM properties, while on the other hand, some of them showed remarkable spin-crossover and photomagnetic behaviour.\textsuperscript{111,115}

The groups of Long, Miyasaka and Clérac reported similar trinuclear \{Mn\textsuperscript{III}Fe\textsuperscript{II}Mn\textsuperscript{III}\} SMMs in which two Mn\textsuperscript{III} Schiff-base (SB) complexes “sandwich” a trans-bridging [Fe(CN)\textsubscript{6}]\textsuperscript{3–} moiety.\textsuperscript{67,116,117} In these compounds, the co-axial orientation of the Mn\textsuperscript{III} ZFS tensors and the ferromagnetic Mn–Fe interaction \(J_{\text{Mn-Fe/Ka}} = +6.5\) K both contribute to the SMM behaviour.\textsuperscript{116} (NET\textsubscript{4})\{Mn\textsubscript{3}(rac-salmen)\textsubscript{2} (MeOH)\textsubscript{2}Fe\textsubscript{II}Fe\textsubscript{II}(CN)\textsubscript{6}\} \(3\) \( (\text{rac-salmen})^2 = \text{rac}(\text{methylenylene)bis(salicylideneiminate, Fig. 4})\) has the higher spin-relaxation barrier \((A_{\text{eff/0}}/k_B)\) of \(14\) K \((t_0 = 2.5 \times 10^{-7}\) s).\textsuperscript{88,117,118}

The \{Mn(SB)\}\textsuperscript{2+} complexes are widely used modules to design SMMs due to the relatively strong magnetic anisotropy originating from the ZFS of the Mn\textsuperscript{III} \( (d^4)\) metal ion in tetragonal ligand fields imposed by the Jahn–Teller (JT) elongation.\textsuperscript{119} A comprehensive discussion of the \{Mn(SB)\}\textsuperscript{2+} chemistry can be found in ref. 120 and some SMM highlights are presented in the next sections. Using the synthetic approach developed for 3 with different central hexacyanometallate moieties, an isostructural series of SMMs has been described based on [Cr(CN)\textsubscript{6}]\textsuperscript{3–} \( (4\), \(121 [Fe(CN)\textsubscript{6}]\textsuperscript{3–} \( (5\), \(122 [Ru(CN)\textsubscript{6}]\textsuperscript{3–} \( (6), \(123 \) and [Os(CN)\textsubscript{6}]\textsuperscript{3–} \( (7) \) building blocks, “sandwiched” between two [Mn\textsuperscript{III}(5-Brsalen)- (MeOH)]\textsuperscript{2+} \((5\)-Brsalen\textsuperscript{2+} = ethylene-bis(5-bromosalicylideneiminate)\textsuperscript{[iminato]}) units. The molecular structure of the \[Mn_2(5-Brsalen)_2(MeOH)_2C_0\textsubscript{6}H_2O\] \( \text{M(CN)}\textsubscript{6}\textsuperscript{3–}\) unit is very close to that found in K[Mn\textsubscript{3}(5-Brsalen)\textsubscript{3} (H\textsubscript{2}O)\textsubscript{2}M(CN)\textsubscript{6}]\textsubscript{2}H\textsubscript{2}O\textsuperscript{116,118} but the presence of NET\textsubscript{4}\textsuperscript{+} counterions and methanol capping ligands on Mn\textsuperscript{III} ligands leads to more magnetically isolated complexes and unquestionable SMM properties. From the viewpoint of the detailed understanding of the magnetic properties, 4 is the simplest system to analyse due to the orbitally non-degenerate ground state of the [Cr(CN)\textsubscript{6}]\textsuperscript{3–} building block. The Mn\textsuperscript{III}, Cr\textsuperscript{III} interaction is anti-ferromagnetic, thereby giving rise to an \(S_T = 5/2\) ground state with a spin-relaxation barrier due to the intrinsic magnetic anisotropy provided by the Mn\textsuperscript{III} sites. A detailed study of this SMM combining magnetic measurements, frequency-domain Fourier-transform THz-EPR spectroscopy and inelastic neutron scattering (INS) was reported to gain insight into the low-lying energy states of 4.\textsuperscript{124} Specifically, the analysis of both spectroscopic and magnetic data led to the following set of parameters: \(J_{\text{Mn-Cr/Ka}} = +6.90\) K and \(D/k_B = -5.25\) K. A similar analysis of the isostructural complex 8, incorporating diamagnetic [Ir(CN)\textsubscript{6}]\textsuperscript{3–}, yielded \(D_{\text{Mn/Cr}}/k_B = -5.35\) K and \(E_{\text{Mn/Kb}} = +0.30\) K demonstrating that the intrinsic properties of the \{Mn(SB)\} unit are unaltered.\textsuperscript{124} Complex 4 displays clear frequency-dependent maxima in the out-of-phase component of the dynamic (ac) susceptibility with an SMM energy barrier of 18 K \((t_0 = 2 \times 10^{-8}\) s), which is slightly lower than the spectroscopically determined value of 26 K. This observation might be the result of QTM via the first excited state located at 18 K \((M_S = \pm 3/2; S_T = 5/2)\). In 5–7, the theoretical treatment is more complicated as the exchange interactions become largely anisotropic as a result of the first-order orbital angular momentum quantum state within the ground \(2^T_{2g}(nd^9)\) term \((O_{tb})\).\textsuperscript{114,125–127} The transformation properties of the orbital angular momentum operator, \(\hat{L}\), leads to non-zero matrix elements, \(\langle \Gamma |\hat{L}| \Gamma' \rangle\), only for \(\Gamma = 2^S\text{Tr} 1^T_{2g} \| 2^S\text{Tr} 1^T_{2g}\) or \(2^S\text{Tr} 1^T_{2g} \| 2^S\text{Tr} 1^T_{2g}\).\textsuperscript{128} Importantly, the orbital contributions to the superexchange mechanism render the HDV Hamiltonian inapplicable.\textsuperscript{114,125} For \(2^T_{2g}(nd^9)\), the strong coupling of the fictitious \(l = 1\) orbital momentum associated with a T term and the \(S = 1/2\) spin momentum, lifts the 6-fold degeneracy giving a lower-lying \(E_{1^T_{2g}}\) Kramers doublet \( (j = 1/2)\) of the octahedral double group \((O_{tb})\).\textsuperscript{128} Taking 7 as an example, the simultaneous modelling of the dc susceptibility, magnetization, INS and frequency-domain Fourier-transform EPR spectra by means of a nearest neighbour spin-Hamiltonian yielded the following principal component parameters \(J_{xx}/k_B = 13(1)\) K, \(J_{yy}/k_B = -25(1)\) K and \(J_{zz}/k_B = 24(1)\) K.\textsuperscript{129} The averaged parameters show an increase in the values extracted for the isostructural complex 6,
incorporating [Ru(CN)₆]³⁻, corroborating the common theorem that descending in a transition metal group gives rise to an increase in the magnetic interaction due to increasingly diffuse magnetic orbitals.⁴⁴,⁹⁵,¹¹⁰ The energy separation between the ground j = 1/2 doublet and j = 3/2 state is given by \( \frac{2}{\sqrt{3}} \zeta_{nl} \) where \( \zeta_{nl} \) is the one-electron spin–orbit coupling parameter. \( \zeta_{nl} \) scales dramatically with the atomic number and is approximately 700 and 4000 K for Fe and Os, respectively.¹³¹ When [M(CN)₆]³⁻ building blocks are parts of a polynuclear complex, the symmetry is no longer octahedral and low-symmetry ligand field effects become often of importance. For the [Os(CN)₆]³⁻ unit that exhibits a strong ligand field of \( \Delta_{0}/K_B \approx 56,000 \) K (\( \approx 39,000 \) cm⁻¹),¹⁰⁶ small ligand field effects are unlikely to alter the j = 1/2 ground state or induce significant quantum mixing as the separation from the j = 3/2 state is quite large: \( \frac{2}{\sqrt{3}} \zeta_{Os(III)} \approx 6000 \) K. For lighter atoms such as Fe(III) in a [Fe(CN)₆]³⁻ environment, small ligand field effects are able to mix j = 3/2 into the ground state. Using the angular overlap model, Tregenna-Piggott et al. estimated the \( \frac{2}{\sqrt{3}} \zeta_{Fe(III)} \) energy splitting of a [Fe(CN)₆]³⁻ trans-bridging unit to yield three Kramers doublets at 0, 850 and 1450 K.¹¹⁶ The intrinsic complicated magnetic properties of the [Fe(CN)₆]³⁻ and [Mn(CN)₆]³⁻ building blocks and their unexplored [V(CN)₆]³⁻ and [Ti(CN)₆]³⁻ analogues, make them less predictable – but fascinating – magnetic modules to design SMMs.¹³² Interestingly, \( \Delta_{eff} \) for complexes 5 to 7 was found to increase upon descending in the group 8 of the periodic table, emphasizing the promising and largely unexplored properties of 4d and 5d metals in the quest for new SMMs.¹³³

Related to the above systems based on [Mn(SB)⁺] units, a “T-shaped” SMM, [Mn(III)(salen)(EtOH)][Fe(III)(CN)₆] (9, Fig. 4c) was also reported (salen²⁻ = N,N'-ethylene-bis(salicylideneiminate)).¹³⁴ The nearly perpendicular orientation of the Mn(III) JT axes reduces the overall magnetic anisotropy and the complex has a smaller energy barrier than the related system 3. When the assembly of [Mn(SB)⁴⁺] and [Cr(CN)₆]³⁻ is pursued to its logical end, a heptanuclear complex is formed, [Cr(μ-Cl)]²⁺Mn(III)₆(salen)₆⁻(EtOH)₆ (10).¹¹⁹ For this complex, the nearly complete cancellation of D by the almost perpendicular JT axes results in the absence of SMM behaviour. The [Cr(CN)₆]³⁻ module was also combined with an S = 2 Fe(III) ion placed in a macrocyclic pentadentate ligand yielding a linear ferromagnetically \( (J_{Fe-Cr}/K_B = 5.41 \) K) coupled \{Fe(II)Cr(III)\} complex (11, \( \{[Fe(3,5-tol)(H₂O)]_2[Cr(CN)_6][ClO₄]_2\}3H₂O; LN₃O₂ = 3,12,18-triazia-6,9-dioxabicyclo[12.3.1]octadeca-1(18),14,16-tiene) with a large \( \Delta_{eff} = 44.3 \) K (\( \tau_0 = 1.4 \times 10^{-9} \) s).¹³⁵ The magnetic anisotropy in this SMM originates from the hepta-coordinated Fe(II) (S = 2) unit (see Scheme 1m) for which \( \Delta_{Fe/KB} \) amounts to \( \approx 6.7 \) K.

Glaser et al. extended the hexacyanometallate approach by exploiting phloroglucinol-derived [=1,3,5-trihydroxybenzene] salen ligands to synthesize a heptanuclear [Mn(III)₆Cr(III)] SMM (12, Fig. 5, \( \{[talen(II)₆Mn(III)₂][Cr(III)₆](MeOH)₆(CH₂CN)₆][SPh₄]₃\}4CH₂CN·2Et₂O; \( H₄talen(II) = 2,4,6-tris-[1-2-(3,5-di-tert-butylsalicylaldimino)-2-methylpropylimino]-1,3,5-trihydroxybenzene] \) exhibiting an effective barrier of 25.4 K.¹³⁶,¹³⁷ The main difference of this system from 10 lies in a trigonal distortion of the octahedral geometry resulting in a non-cancellation of the magnetic anisotropy and thereby in the observation of the SMM behaviour.¹³⁷ Fitting of the \( J \tau \) vs. \( T \) data at high temperatures allowed an estimation of \( J_{Mn-Cr} \) at about \( \approx 7.2 \) K with \( S_F = 21/2 \). This value is close to the one found for 4 despite the more linear Mn–N–C angle of 160–162° in 12. The synthesis of \( C_3 \) symmetrical SMMs is particularly appealing as the QTM is commonly governed by the rhombic \( E \) term that vanishes in the trigonal symmetry. Nevertheless, higher order terms of the anisotropy allowed in the \( C_3 \) symmetry might still govern the QTM despite their small values. Exchanging [Cr(CN)₆]³⁻ by
[Fe(CN)₆]³⁻ affords the analogous {Mn³⁺Fe²⁺} complex showing weak characteristics of SMM behaviour. However, substituting for [Os(CN)₄]³⁻ yields [Mn³⁺Os²⁺] with stronger anisotropy and slower relaxation of the magnetization due to anisotropic Mn³⁺–Os²⁺ exchange interactions.

Recently, the same group reported an analogous {Ni⁴⁺Mn⁴⁺} complex encompassing a central low-spin [Mn(CN)₆]³⁻ module ([[(talenBu)[(Mn⁴⁺MeOH)]₄]₂{Mn³⁺CN[CN]₆}]lact₂.10.5MeOH, 13, lact = lactate). Thanks to the lactate counterions that favour the occurrence of hexagonal and cubic packing, the {Mn⁴⁺Mn⁴⁺} complex adopts an S₆ crystallographic symmetry. Notably, a trigonal distortion of [Mn(CN)₆]³⁻ does not quench the effective l = 1 orbital angular momentum but the spin–orbit coupling leads to a nonmagnetic ground state for the j = 0 [Mn(CN)₆]³⁻ central unit. Despite the “blocked” exchange pathway through the essentially diamagnetic [Mn(CN)₆]³⁻ unit (at low temperature), the {Mn⁴⁺Mn⁴⁺} complex exhibits an unusual double M vs. H hysteretic behaviour. The weak intra-[talenBu]Mn⁴⁺–Mn⁴⁺ antiferromagnetic interactions stabilize an S = 2 intermediate spin state for both {talenBu}Mn⁴⁺ units, which interact weakly ferromagnetically leading to an S₄ = 4 ground state. Slow dynamics of this ground state is observed around zero-dc field but above 3.4 T, zero-field excited spin states become the lowest in energy giving rise to the second hysteresis loop.

Among the cyanide-based SMMs, the {Re⁴⁺Mn⁴⁺} complex [14; ([PY₅Me₂]₄Mn⁴⁺Re(CN)₇)(PF₆)₅]-6H₂O; PY₅Me₂ = 2,6-bis(1,1-bis(2-pyridyl)ethyl)pyridine] based on the pentagonal bipyramidal [Re⁴⁺CN(CN)₇]⁻ module stands apart with a large barrier of 47 K (τ₀ = 2.4 × 10⁻⁸ s). This system, depicted in Fig. 3, incorporates bulky ([PY₅Me₂]₄Mn⁴⁺)₂⁺ units (Scheme 10), which limit the nuclearity of the complex. At first look, the presence of an SMM behaviour in 14 seems surprising as the magnetic anisotropy of Mn⁴⁺ is well-known to be very weak and ZFS is obviously meaningless for S = 1/2 systems like [Re⁴⁺CN(CN)₇]⁻. Indeed, the (NBu₄)₃[Re(CN)₇] precursor exhibits a strongly anisotropic g tensor with g₁ = 3.66 and g₃ = 1.59 (from X-band EPR) reflecting the unquenched orbital angular momentum of the ⁴E₄⁻(d) ground state in the idealized D₅h symmetry. Therefore, the strong magnetic anisotropy of 14 is likely due to anisotropic Re⁴⁺–Mn⁴⁺ exchange interactions, which have been described for isoelectronic [Mo(CN)₆]³⁻–Mn⁴⁺ systems in the frame of the superexchange theory. Similar complexes with [Ni⁴⁺Re⁴⁺] (15; ([PY₅Me₂]₄Ni⁴⁺Re(CN)₇)(PF₆)₅) and (16; ([PY₅Me₂]₄Cu₄Re(CN)₇)(PF₆)₅) cores also exhibit slow relaxation of the magnetization although with significantly reduced J₄Re⁴⁺. While Δeff/k₀ = 24 K and τ₀ = 1.4 × 10⁻⁷ s for 15, only a small frequency dependence of a non-zero γ(T) with ν ≤ 1.5 kHz was observed for 16 suggesting a much smaller Δeff. The potentially interesting magnetic properties of the [Mo(CN)₆]³⁻ module incorporated into molecular systems have been studied by Dunbar, Wang and co-workers. The first complex incorporating this moiety was [Mo₃{Ni₃}₃{H₂O}₈][{Mo(CN)₄}₈{Mn(L₉)}₈{Mn(L₉)}₈{H₂O}₈]xH₂O (L₉ = 2,13-dimethyl-3,6,9,12,18-pentaazaacyclo-12,3,13-triadeca-1(18),2,12,14,16-pentaene). This {Mn⁴⁺Mo⁴⁺} (18) complex exhibits a large spin ground state (S₄ = 31), but instead of possessing SMM properties, it shows a 3D ferrimagnetic ordering at low temperature.

Very recently, the same group reported on three trinuclear MnIII–MoIV(CN)₇–MnIII complexes where L is a pentadentate ligand. In particular, the quasi-linear Mn⁴⁺–MoIV(CN)₇–Mn⁴⁺ complex, {Mn[Li₂MeO]₂[H₂O]}[Mo(CN)₇]·6H₂O (19, Li₂MeO = 2,6-bis(3,6-diazahex-2-ened-2-yl)pyridine, Fig. 4d), exhibits clear SMM properties with Δeff/k₀ = 58.5(4) K and τ₀ = 2.0(3) × 10⁻⁸ s. These characteristics make this complex the current record holder in terms of Δeff for cyanide-based SMMs. Additionally, this system exhibits a large M vs. H hysteresis loop at low temperatures with a coercive field of 2.0 T (with a 0.05 T s⁻¹ sweeping rate) at 1.8 K. Octacyanidometallates are known for W⁴⁺, Mo⁴⁺, Nb⁴⁺ and Re⁴⁺ metal ions. The incorporation of these units into coordination networks and their resulting magnetic properties have been the topics of reviews by Sieglocha and co-workers.

Using these octacyanidometallate building blocks, Dunbar and co-workers isolated TBP complexes similar to the ones described earlier (2, Fig. 3, left), [Ni⁴⁺(tmphen)₃][W₆V(CN)₉] (20), but no M vs. H hysteresis loop was observed down to 40 mK. Only a few reports on SMMs based on [M₃(CN)₇]³⁻ building blocks (M = Mo⁴⁺, W⁴⁺, Re⁴⁺) (S = 0) have been reported. These include polynuclear complexes with stoichiometries such as [Ni⁴⁺Mo⁴⁺] (21, S₄ = 12; [Ni[Ni(bpy)(H₂O)]₈{Mo(CN)₇}]·12H₂O, 151; Ni⁴⁺W₆V₆] (22, S₄ = 12; [Ni[Ni(bpy)(H₂O)]₈{W(CN)₆}]·23H₂O, 152,153) and site-substituted Re⁴⁺ analogues [{Co₃(CH₃OH)₄}_{24}{W(CN)₆}{[Re(CN)₆]}]·xCH₃OH·yH₂O, 23,155 but only thin evidence of slow magnetic relaxation has been observed. Another family of heterometallic systems encompass mixed 3d–5d–4f species incorporating paramagnetic octacyanometallates,156–159 some of which exhibit SMM behaviour. Herein, the 3d–4f back-bone is based on bicompartimental Schiff-base ligands derived from o-vanillin and diamine ligands, which accommodate a Cu²⁺ ion in a salen-type environment.162,163 With the phenolates and the methoxy groups, this unit constitutes a chelating metallo-ligand for lanthanide ions, which, subsequently, may coordinate the octacyanometallate by either the Cu²⁺ or the Ln³⁺ ion.

**Heteroleptic cyanidometallates**

Detailed reviews of the use of di- and tri-cyanidometallate precursors in the design of polynuclear systems have recently been published by Wang et al.164,165 Using these modules, the first indications of SMM behaviour in a cyanide-bridged system was found in a {Mo⁴⁺Mn⁴⁺} complex [24; K[Me₃tacn]MnMo(CN)₈(CIO₄)]₄; Me₃tacn = N,N,N',N'-trimethyl-1,4,7-triazacyclononane] incorporating fac-[Mo⁴⁺(Me₃tacn)(CN)₈] units.166 Each of these modules coordinates through only one cyanide ligand to the central Mn⁴⁺ ion leading to an approximately prismatic structure (Fig. 6). The intra-complex Mo⁴⁺–Mn⁴⁺ antiferromagnetic interactions (Jₙ₉-Mo/k₀ = -9.6 K) yield an S₄ = 13/2 spin ground state. Fitting of the M vs. H/T data revealed an Ising-type magnetic anisotropy of D/k₀ = -0.47 K.

Notably, the isostructural {Cr⁴⁺Mn⁴⁺} (25; K[Me₃tacn]Cr₃Mn₃(CN)₈(CIO₄)]₄) complex did not exhibit SMM properties,167 likely due to a stronger magnetic anisotropy exhibited by the Mo⁴⁺ unit over the Cr⁴⁺ building block. For d⁷ ions (t₂g), like Mo⁴⁺, in an axially perturbed ligand field, the magnetic anisotropy is primarily induced by the mixing of the A₂g(t₃₂g) ground
state with the excited $^4T_2g(O_h)$ state via spin–orbit coupling.\textsuperscript{168} If only this mixing is taken into account, the $D$ parameter scales as $\tilde{\zeta}_{\text{nl}}^2$. For 3d$^3$ metal ions such as V$^{3+}$, Cr$^{3+}$ and Mn$^{4+}$ for which the spin–orbit coupling is relatively weak, this second-order contribution to the magnetic anisotropy is often negligible, whereas this effect becomes important for 4d and 5d transition metal ions.

The $\text{trans-[ReCl}_4$(CN)$_2$]$_2$$^{2-}$ building block reported by Long and co-workers is another interesting example of a heteroleptic cyanide-based 5d metal ion module.\textsuperscript{169} This building block is unique in the sense of being the sole example of a paramagnetic mixed halide–cyanide complex. In addition, it offers both strong magnetic anisotropy as well as effective mediation of metal ions.

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(31; [MnCl]4[Re(triphos)(CN)3]4) SMM and polymeric systems based on this module. The structure of the parent complex, 31, is a molecular cube as depicted in Fig. 8. Other divalent metal ions such as FeII, CoII, NiII and ZnII have been incorporated into analogous systems, but only the MnII complex was shown to be an SMM (Δeff/kB = 13 K, τo = 3.25 × 10−7 s).192

The static magnetic properties are dominated by the antiferromagnetic interactions between ReIII (S = 1/2) and MnII (S = 5/2) spins but a detailed analysis of the experimental magnetic data becomes highly complicated due to orbital contributions to the magnetic exchange mechanism and a large temperature independent paramagnetism (TIP) of the ReIII ion.193

Glaser and co-workers extended their strategy of molecular recognition with triple-salen ligands by exchanging [Cr(CN)6]3− with fac-[CrIII(Me3tacn)(CN)3]3− with fac-[CrIII(Me3tacn)(CN)3] module to coordinate only one {MnIII 32}triple-salen moiety; [((pzTp)Fe(CN)3]4[Co(tpe)]4] (32) and [((pzTp)Fe(CN)3]4[Ni(tpe)]4] (33). For this system, the χ″(T) data only show weakly frequency-dependent onsets of peaks between 1.8 and 2.5 K suggesting a lower spin-relaxation barrier than in the {MnIII, CrIII} complex (12, Δeff/kB = 25.4 K) as expected when lowering the spin ground state from S = 3/2 to 1/2 (32).

The groups of Holmes, Oshio and Zuo reported {FeIII, NiII} molecular cubes exhibiting SMM properties.195–199 All the reported examples are based on cyanido-based FeIII modules with tris(pyrazol-1-yl)borate,181 the FeIII–NiII interaction is magnetic bistability controlled by an intra-molecular electron transfer and two different redox configurations: i.e. the paramagnetic {FeIII, CoII} and diamagnetic {FeII, CoIII} states.

From a strategic point of view, the nearly cubic structure of the previously described SMMs does not appear to be the ideal geometry to obtain SMM properties (due to a near compensation of magnetic anisotropy tensors). Therefore, researchers have been trying to reduce the {FeIII, NiII} cubes into less-symmetrical smaller fragments like defect cubanes, squares and trinuclear complexes. Interestingly, the use of facial tricyanido modules also stabilizes molecular square SMMs with alternating FeIII and NiII,181,182,184,202–205 or CuII metal ions.206

In these FeIII–NiII systems illustrated by [Tp*Fe(CN)3]2−/[Ni(DMF)4]2−,207 [Tp*Fe(CN)3]2−/[Ni(DMF)4]2−,207 [Tp*Fe(CN)3]2−/[Ni(DMF)4]2−,207 [Tp*Fe(CN)3]2−/[Ni(DMF)4]2−,207 the FeIII–NiII interaction is ferromagnetic with JNi–Fe coupling constants up to +10.1 K,208 giving rise to an S = 3 ground state. It was argued that the distortion of the NiII coordination sphere does not significantly alter the SMM properties suggesting that orbital contributions from the S = 1/2 FeIII module is the main origin of the SMM properties in these molecular FeIII–NiII squares.207 Their effective magnetic bistability was reported.200 Recently, Oshio and co-workers reported a mixed-valence cube complex Na[(Tp)4FeIII4FeII2(CN)12NiII4(L)4]3(OTf)12 incorporating a redox-active ligand: \( L = \alpha\text{[4'-methyl-4,5-dimethylthio-tetrathiafulvalene-5'-thio]-}[\text{tris-2,2,2-(1-pyrazolyl)-ethoxy}]-p-xylene \). Unfortunately this complex, which was not structurally characterized, only exhibits a small frequency-dependent increase of the \( \chi''(T) \) data between 1.8 and 3 K.199

An analogous [FeII, CoII] cube complex, [[(pzTp)Fe(CN)3]4[Co(tpe)]4] (35) incorporating the tach (1,3,5-triaminocyclohexane) capping ligand was synthesized by Long and co-workers but no slow relaxation of magnetization was reported.200

Fig. 8 Molecular structures of 31 (left) and 33 (right) cubes. Colour codes: Re, marine; Ni, turquoise; Fe, orange; Mn, pink; Cl, green; P, yellow; N, pale blue; C, grey.

Fig. 9 Molecular structures of 37 (top, left), 38 (top, right) and 42 (bottom, right) in the FeIII–CoII, FeIII–FeII state obtained at T = 100 K. Colour codes: Ni, turquoise; Co, purple; Fe, orange; O, red; N, pale blue; C, grey.
SMM energy gaps are relatively moderate with the largest reported value being $A_{\text{eff}}/k_B = 29.0(4)$ K.\textsuperscript{202}

Defect square ($\text{Fe}^{\text{III}/\text{II}}$) SMMs were also obtained, for example by reaction of (NET$_3$)[$(\text{pzTp})\text{Fe}^{\text{II}}(\text{CN})_3$] with Ni$^\text{II}$ and bpy (38, [(pzTp)Fe(CN)$_3$]$^{2+}$[Ni(bpy)$_2$]$^{2+}$]H$_2$O; bpy = 2,2'-bipyridine.$^{183}$ Interestingly, this complex shown in Fig. 4 exhibits a clear SMM signature by ac susceptibility measurements despite the small $S_f = 2$ ground state induced by the intra-complex ferromagnetic interactions ($J_{\text{Fe-Ni}}/k_B = 7.0(2)$ K). In the absence of a static dc field, the energy barrier is about 12.0 K ($t_o = 4 \times 10^{-7}$ s) that increases up to 20.6 K ($t_o = 2 \times 10^{-8}$ s) in a small dc field (2000 Oe). Such trinuclear SMMs can be seen as building-modules for larger molecular ($\text{Fe}^{\text{III}/\text{II}}$)$_n$ structures where $n = 2$ or 3. Although not synthetically assembled from pre-isolated trinuclear precursors, an exo-cyclic ($\text{Fe}^{\text{III}/\text{II}}$) SMM (39; [(Tp$^\text{Me}$)Fe(CN)$_3$]$^{2+}$[Ni(DMF)$_2$]$^{2+}$4DMF·H$_2$O; Tp$^\text{Me}$ = tris(3,4,5-trimethylpyrazole)borate) and a fused system of exo-cyclic squares ($\text{Fe}^{\text{III}/\text{II}}$)$_4$ (40; [(Tp$^\text{Me}$)Fe(CN)$_3$]$^{2+}$[Ni(MeOH)$_2$]$^{2+}$[Ni(MeOH)]$_2$·3H$_2$O·8MeOH) have been reported.$^{208}$ In these two complexes, the Ni$^\text{II}$ sites connect three [(Tp$^\text{Me}$)Fe(CN)$_3$]$^{2+}$ modules. Their remaining positions are occupied by rather labile solvent molecules, which do not apply any particular geometrical constraints on the coordination sphere. The energy barriers for these ($\text{Fe}^{\text{III}/\text{II}}$)$_n$ SMMs are slightly higher than for the trinuclear parent complex, 38, with $A_{\text{eff}}/k_B = 15.6$ K and 17.7 K in zero-dc field and 26 K and 24.5 K in 1500 and 600 Oe for 39 and 40, respectively.

The use of the same Fe$^{\text{III}}$ module, [(Tp$^\text{Me}$)Fe$^{\text{III}}$(CN)$_3$]$^{2+}$, and geometrically constraining the Ni$^\text{II}$ coordination sphere by the tetradentate tren ligand (tren = tris(2-aminoethyl)amine), leaving only two cis-positions accessible, leads to an octanuclear ($\text{Fe}^{\text{III}/\text{II}}$)$_4$ complex (41; [(Tp$^\text{Me}$)Fe(CN)$_3$]$^{2+}$[Ni(tren)]$_4$[ClO$_4$]$_4$·7H$_2$O·4MeCN)$^{185}$ Its complicated molecular structure can be viewed as an “unwrapped” version of the ($\text{Fe}^{\text{III}/\text{II}}$)$_4$ cube. This low-symmetric complex exhibits one of the largest effective energy barriers (33 K) for any cyanide-based 1st row transition metal SMM.

As previously mentioned for a {Fe$^\text{IV}$Co$_4$} cube complex,\textsuperscript{201} a few examples of molecular ($\text{Fe}^{\text{III}/\text{II}}$)[($\text{Fe}^{\text{III}/\text{II}}$)$_2$] squares have been reported\textsuperscript{209–215} to exhibit photo- and thermally-assisted intramolecular charge transfer similar to the effect observed in three-dimensional Fe/Co Prussian Blue analogues.$^{27}$ The principle of this phenomenon is based on the reversible interconversion of diamagnetic [Fe$^{\text{II}}$(μ-CN)Co$^{\text{III}}$]$^{2+}$ pairs into paramagnetic [Fe$^{\text{III}}$(μ-CN)Co$^{\text{II}}$]$^{2+}$ pairs by light irradiation and thermal energy. Very recently, SMM properties in a photo-induced state, clear frequency-dependent $\chi''(T)$ peaks were observed, suggesting that this complex was the first photo-switchable SMM. The associated spin-reversal barrier was estimated at about 26 K in a static field of 500 Oe.

In contrast to the fac-tricyanido systems, mer-tricyanido modules have received much less attention.$^{217–222}$ mer-Tricyanido complexes are well-known especially for iron$^{[m]}$ as illustrated by the [Fe$^{\text{III}}$(bpca)(CN)$_3$]$^{-}$ (bpcaH = bis(2-pyridylcarboxyl)amine),$^{223}$ and [Fe$^{\text{III}}$(pcq)(CN)$_3$]$^{-}$ (pcqH = 8-(pyridine-2-carboxamido)quinoline) building blocks.$^{217,224}$ As for the trans-dicyanido modules (vide supra), these units are favoring one-dimensional assembly unless steric constraints from the other building blocks impose otherwise.

To the best of our knowledge, no SMMs incorporating these mer-tricyanido building blocks have been reported so far.

### 4. Non-cyanide based precursors

Undoubtedly, cyanide remains the coordination chemist’s favourite bridging ligand in the quest for new SMMs and functional materials. The cyanide-based complexes often possess three essential properties: (i) integrity in solution, (ii) relatively linear bridging modes between metal ions (Fig. 2) and (iii) a redox-activity that does not alter the complex structure. None of these properties are indeed exclusive to the cyanide-based building blocks, and magnetic modules based on other type of bridging groups should be considered in the design of SMM systems.

**Halide and pseudo-halide based modules**

Although a few examples of SMMs with chloride bridges have been reported,$^{225}$ no examples assembled from modules can be said to exist. Building-block examples based on pseudo~halid~ates (other than cyanides) including azide and (iso)thiocyanate are also extremely rare$^{216,227}$ and no examples of SMMs synthesized by a modular approach have been reported. Gao, Lau and co-workers reported the mer-[Ru$^{\text{III}}$(nap)(N$_2$)$_2$]$^{+}$ module (H$_2$nap = N-salicylidene-o-aminophenol) but its reaction with Ni$^{\text{II}}$ or Co$^{\text{II}}$ afforded polynuclear complexes incorporating diamagnetic Ru$^{\text{II}}$ ions.$^{228}$ Isoelectronic three-atom ligands such as cyanate, thiocyanate or azide have been used to prepare complexes of paramagnetic transition metal ions but no SMM systems incorporating these modules have been prepared so far. Remarkably, relatively strong exchange interactions have been observed in Ni$^{\text{II}}$–SCN–Cr$^{\text{III}}$ and Ni$^{\text{II}}$–SCN–Mo$^{\text{III}}$ linkages but SMMs incorporating such units have not been reported.$^{226}$

At this stage of this Feature article, it is natural to wonder if the modular approach can use a single atom as a magnetic bridge to design SMMs. An obvious choice would be oxide or hydroxide based building blocks but they are not easy to...
employ due to the strong basicity of most paramagnetic complexes. In principle, a reasonable approach could involve complexes with metal ions in a high oxidation state, which should have less basic oxide, or, eventually, nitride complexes. Only two examples of SMMs incorporating oxide-based modules have been reported, but both involve diamagnetic ReIV metal ions.229,230 Building blocks based on fluoride as the potential bridging ligand to synthesize magnetic materials are also largely unexplored.231–236 Being isoelectronic to oxide, the incorporation of fluoride is not obvious. In addition to its basicity, the oxide group has the tendency to form non-linear bridges (Fig. 2) between two or more metal ions making it less appealing as the bridging ligand. These two effects appear less pronounced for fluoride. Several mononuclear 3d metal ion fluoride complexes are known and commonly fluoride leads to linear or almost linear bridges.237 The main synthetic problem of these fluoride complexes arises from the inherent lability of many fluoride complexes. However, this issue can be overcome by using, for instance, kinetically robust CrIII fluoride complexes,238 or by enforcing robustness with selected auxiliary ligands as discussed earlier. Being a “hard” ligand, fluoride has a strong preference for “hard” metal ions such as lanthanides. Further discussions about the controlled design of 3d–4f SMM systems with fluoride-based modules will be presented in the last paragraph of this section dedicated to lanthanide and actinide based building-blocks. We recently reported (PPh4)2[ReF6]2H2O (43) incorporating a close-to-octahedral [ReF6]3− anion to exhibit slow relaxation of the magnetization.60 This interesting module in 43 has a large zero-field splitting of $D/k_B = ±34.0$ K and $|E|/k_B = 3.7$ K as determined from inelastic neutron scattering and high-field EPR spectroscopy.60 The strong magnetic anisotropy combined with the ability to bridge several metal centres make homoleptic fluoride-complexes, such as [ReF6]3−, interesting, but completely unexplored modules for SMMs.

Oxalate-based modules

Trisoxalatometallate(III), [M(ox)3]3−, have been widely employed for assembling magnetic materials.238 This interest is motivated by the strong preference of the oxalate group to bridge two metal ions in a double-chelate fashion. However, the propensity of the [M(ox)3]3− unit to form extended systems makes these precursors less suitable to design SMMs, unless sterical constraints imposed by capping ligands are introduced on the acceptor metal ions. This problem can also be overcome by turning to heteroleptic oxalate systems with an appropriate choice of capping ligands. For instance, an interesting ReVIII module, [ReVIIICl4(ox)]3−, has been reported.239 The d10-configuration of the ReIV ion gives a kinetically robust and hydrolytically stable building block. In combination with NiIII metal ions, a propeller-shaped [NiIIReIV]3 complex ([NBu4][NiCl4(ox)])[44, Fig. 10] is formed.240,241 Modelling of the $\gamma T$ vs. $T$ data gave a ferromagnetic NiII–ox–ReIV interaction ($J_{Re-Ni/k_B}$) of $±12$ K. It is interesting to note that the field dependence of the magnetization for the (PPh4)2[ReCl4(ox)] precursor reveals a strong magnetic anisotropy that has been estimated at $D/k_B ≈ 86$ K.239 Notably, Martinez-Lillo et al. recently reported NBu4+ salts of [ReCl4(ox)]3− and [ReBr4(ox)]3−, to display SMM properties in small dc fields.242 For 44, an out-of-phase $\chi''$ signal was clearly visible in zero dc field, but under 2000 Oe, the spin-relaxation slows down as expected in presence of significant QTM. In a recent communication, the same authors reported a [GdIIIReIV]4 four-bladed propeller ([NBu4]5[Gd[ReBr4(µ-ox)]4(H2O)]H2O), but no slow relaxation of the magnetization was observed.243 So far, the only example of SMM behaviour in a 3d transition metal oxalate complex is [[CrIII(bpy)(ox)]3CoIII(Me2phen)]4H2O (45; Me2phen = 2,9-dimethyl-1,10-phenanthroline) that is obtained by the reaction of the [CrIII(bpy)(ox)]3− module with CoIII in the presence of the Me2phen ligand. Only an onset of $\chi''(T)$ peaks is observed above 1.8 K, suggesting SMM properties and a small energy barrier.244

Acceptor modules

Some of the most commonly used modules to design SMMs are acceptor type units made of a MnIII ion and a Schiff base (SB) ligand (see e.g. Scheme 1j). Polynuclear complexes based on these Schiff base complexes [abbreviated {Mn(SB)}+] have been reviewed by Miyasaka et al.120 and along this Feature article we have already shown several examples of SMMs incorporating these units (Fig. 4, 5 and 7). The Schiff base ligands are often tetradentate to the MnIII site occupying equatorial positions and allowing the two remaining apical positions to be accessible for further coordination for example with a cyanide group.88,116–119,121–123 The {Mn(SB)}+ units constitute a class of very useful modules for SMM synthesis due to their relatively strong magnetic anisotropy reflected in a large negative value of $D$ estimated up to $−6$ K.124,245 In solution, the mononuclear {Mn(SB)}+ unit is in equilibrium with an “out-of-plane” dinuclear form (Scheme 1k) in which the phenolate oxygens bridge two {Mn(SB)}+ moieties along the JT axes.120 Depending on the structural parameters, the MnIII–MnIII interaction through the bis-phenolate oxygens in this dinuclear module is often ferromagnetic in nature due to an accidental orthogonality of the d$z^2$ orbital occupied by one electron and the empty d$e_g$ orbital of the other MnIII centre. Due to this ferromagnetic interaction, that leads to an $S_T = 4$ spin ground state, and the covalent ZFS MnIII tensors, the [MnIII(saltmen)2(ReO4)]3 complex (46; saltmen2+ = N,N′-(1,1,2,2-tetramethylethylene)bis(salicylideneiminate)) was found to be an SMM (Fig. 1).61 Since then,
several other \{Mn_{2}(SB)\}_{2}^{2+} SMMs have been reported.246,247 These out-of-plane \{Mn_{2}(SB)\}_{2}^{2+} building blocks have also been employed extensively to obtain photomagnetic chains,248 SCM\textsuperscript{s}\textsuperscript{44,87–89} and two-dimensional networks by assembly with appropriate modules.22,249–252

The terminal labile positions of the \{Mn\textsuperscript{III}(SB)\}_{2}^{2+} module can be decorated by other building blocks, for instance the \{Mn\textsuperscript{II}-(5-Rsaltmen)\}_{2}\{Ni(pao)\}_{2}(phen)\textsuperscript{2-} (DCNQI)\textsuperscript{2-} core (52).257 The Mn\textsuperscript{II}-radical interaction is antiferromagnetic (J\textsubscript{Mn-Mn/KB} < -23 K) and much stronger than the ferromagnetic Mn\textsuperscript{III–Mn}\textsuperscript{III} interaction (J\textsubscript{Mn-Mn/KB} > +20 K) leading to an S\textsubscript{g} = 3 ground state. The ac susceptibility measurements reveal the SMM properties of these complexes with frequency-dependent in-phase and out-of-phase components (\nu\textsubscript{ac} \leq 1.5 kHz, T \geq 1.8 K) as well as a sweep rate dependence of the M vs. H hysteresis at 0.4 K.

Beside the \{Mn(SB)\}_{2}^{+} modules, similar acceptor building blocks to design SMMs are relatively rare and only a few other examples, which have already been described in the previous paragraphs, are shown in Scheme 1(l–o). Recently, mononuclear transition metal complexes with “unconventional” coordination numbers and geometries have been reported to display SMM properties due to a very strong magnetic anisotropy.40,46,258 This new category of mononuclear SMMs is currently the topic of a very competitive subject with a rapidly growing number of published systems.39–48,259 It sounds reasonable to think that in the close future some of these complexes could be employed as acceptors or, in some cases, donor modules to design new polynuclear SMMs with remarkable characteristics.

Lanthanide and actinide based building-blocks

Obtaining a topological control of coordination architectures with f-block elements is notoriously difficult due to their high coordination numbers and the lack of ligand field stabilization. Indeed the coordination geometries are mainly governed by the sterical hindrances of the [metal-(ligands] and crystal packing effects.260 In addition, even very weak ligand field perturbations may have a significantly strong influence on the SMM properties.38,261–263 Despite the obvious downsides from the viewpoint of the chemical design, lanthanide-based complexes have received an immense attention in recent years as they have served as key ingredients in several high barrier 3d–4f or pure 4f SMMs.71,72,264–266 Although the observation of SMM properties in most lanthanide complexes is inherently related to the ligand field of the isolated lanthanide ion,262,263,267,268 effects of even small ligand field perturbations and exchange interactions have shown to be of crucial importance in the observation of magnetization slow dynamics.38,269 For these reasons, the molecular design of lanthanide-based SMMs requires the ligand field of the lanthanide ions to be as preserved as possible. This is clearly not an easy task even if the use of multi-dentate chelating ligands or other particularly rigid ligands, with or without functional groups susceptible to bridge adjacent magnetic centers, might be an approach to explore. Recently, Murugesu and Long reported COT-based Er and Dy SMMs (COT = cycloocta-1,3,5,7-tetraenediide), which exhibit M vs. H hysteresis loops at temperatures of up to 10 K (for [Er(COT)\textsuperscript{3+}] with a field sweep rate of 0.78 mT s\textsuperscript{-1}). Indeed such rigid complexes appear to be promising modules for higher-nuclearity systems.26 Although serendipitous approaches have

![Fig. 11](image-url) Structure of 47 (left) and 51 (right). For 51, the apical Mn–\cdot\cdot\cdot O separations are very long (3.081(2) Å) and concomitantly is the Mn\textsuperscript{III–Mn}\textsuperscript{III} interaction only weak (J\textsubscript{Mn-Mn/KB} = +1.7(1) K).
been use extensively to synthesize 4f metal ion based SMMs, lanthanide building blocks do exist and the modular strategy has also been applied successfully to a limited number of systems. A very common building block is the [Dy(hfac)\(_3\)] complex (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate). The two coordinated water molecules are easily replaced either by azotropically distillation or directly in the synthesis of polysynuclear complexes. Lanthanide-based SMM complexes are reported with coordinating nitronyl nitroxide radicals, organic linkers and transition metal complexes. As an illustration, the trinuclear fluoride-bridged SMM (57), [Dy(hfac)\(_3\)](H\(_2\)O)\(_2\)CrF\(_2\)(py)\(_2\)Dy(hfac)\(_3\)](NO\(_3\)], is obtained from the assembly of trans-CrF\(_2\)(py)\(_2\)&& and [Dy(hfac)\(_3\)](H\(_2\)O)\(_2\]) modules. The magnetization dynamics was too fast to be able to observe a \(\chi''\) maximum (with \(\nu_{ac} \leq 1.5\) kHz), but muon-spin rotation spectroscopy reveals a small energy barrier of about 4.2 K (\(\tau_0 = 5.3(4) \times 10^{-8}\) s). In addition, the study of 57 by X-ray magnetic circular dichroism allowed a direct estimation of the nature and magnitude of the exchange interaction.

This information can hardly be obtained from bulk magnetic measurements and is therefore, generally, not known for lanthanide SMMs.

Actinide based complexes are gaining an increasing attention in the SMM community due to their strong magnetic anisotropy, like lanthanide ions, but also because they offer the possibility of stronger exchange interaction due to the less localized 5f orbitals over the 4f orbitals of the lanthanides. Until now, actinide SMMs are known only for U and Np systems. But most of the few published studies have been dedicated to mononuclear U\(^{IV}\) systems for which it was recently argued that the SMM properties are intrinsic to the trivalent uranium centre. A single example of a mononuclear Np\(^{IV}\) system has been reported: neptunocene, [Np(COT)\(_2\)] (58). Only two examples of exchange coupled polysynuclear uranium SMMs are reported so far. The first one reported by Liddle and co-workers is an inverted-sandwich arene-bridged diuranium(III) species that shows a frequency dependent ac susceptibility signal below 4 K (\(\tau_0 = 3(2) \times 10^{-8}\) s). In addition, the study of 57 by X-ray magnetic circular dichroism allowed a direct estimation of the nature and magnitude of the exchange interaction.

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reported so far \([\{[\text{TP}]\text{Dy}_2(\mu-\text{ox})\}_2\text{CH}_3CN\cdot\text{CH}_2\text{Cl}_2]\). Interestingly, the SMM barrier of 55 (52 K) is higher than for the exchange coupled complex 56 that corroborates the argumentation given by Sessoli and co-workers for 53 and 54. Wippeny and co-workers have elegantly used Cr\(^{III}\) “horsehoe” modules to obtain mixed chromium(III)–lanthanide(III) complexes but none of them were reported to be SMMs. Bendix’s group has recently demonstrated the possibility of controlling to some extent the topology of lanthanide-based complexes using fluoride bridges. The strong preference of fluoride to stabilize linear bridges seems to dictate the polysynuclear complex arrangement. For instance, cis-difluoro, trans-difluoro and fac-trifluoro complexes can form linear rod-like, square-like and pyramidal molecular systems, respectively, which show SMM properties for some of them. As an illustration, the trinuclear fluoride-bridged SMM (57), [Dy(hfac)\(_3\)](H\(_2\)O)\(_2\)CrF\(_2\)(py)\(_2\)Dy(hfac)\(_3\)](NO\(_3\)], is obtained from the assembly of trans-CrF\(_2\)(py)\(_2\)&& and [Dy(hfac)\(_3\)](H\(_2\)O)\(_2\]) modules. The magnetization dynamics was too fast to be able to observe a \(\chi''\) maximum (with \(\nu_{ac} \leq 1.5\) kHz), but muon-spin rotation spectroscopy reveals a small energy barrier of about 4.2 K (\(\tau_0 = 5.3(4) \times 10^{-8}\) s). In addition, the study of 57 by X-ray magnetic circular dichroism allowed a direct estimation of the nature and magnitude of the exchange interaction.

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magnetization of this complex was studied using the ac technique leading to an 140-K energy barrier.\textsuperscript{50,295}

5. Conclusions and perspectives

Combining relevant and interesting physical properties in a controlled manner in the same material is an important topic for modern chemists. In particular, the engineering of new multifunctional materials associating magnetism with e.g. photo-activity, electro-activity, porosity, conductivity or other properties controlled by an external stimuli, are being currently targeted by many research groups. Potentially, coordination chemistry provides the necessary tools for designing such new materials in rational and methodical approaches. However, the development of the preparative coordination chemistry is still behind the organic chemistry and consequently, it remains difficult for coordination chemists to design and synthesize, at will, polynuclear metal ion complexes or coordination polymers. Inspired from the protective groups in organic chemistry that direct the reactivity in particular positions, coordination chemists increase their structural control on the final material by using precursors with reduced degrees of freedom. Along this line, the used building-blocks are often carrying capping or strongly coordinating ligands to be able to direct the coordination properties and the final assemblies. Nevertheless, it is important to keep in mind that serendipitous self-assembly reactions have provided many systems of crucial importance to the development of the field of molecular magnetism and that the limitations of the modular approach with respect to structural design of polynuclear complexes are still important.

By creating complicated structures in a hierarchical fashion, the preparative coordination chemist can rely on an existing understanding of the first and second coordination sphere complexities and the well-understood relative robustness of coordination complexes. Furthermore, this modular strategy offers an efficient transfer of the metal ion properties, imposed by the first coordination sphere, to extended structures. Thus, this approach allows us to control not only the spatial arrangements, but also the electronic structure of complicated systems. In this context, many combinations of metal ion modules and bridging ligands are unexplored to design new molecule-based magnetic materials including SMMs and related materials.

In parallel with the use of known building-blocks, the quest for new magnetic modules should not be forgotten as they constitute the basis of this synthetic strategy. In particular, it would be very interesting to exploit the recent examples of mononuclear SMMs and photo-switchable SMMs as modules for higher nuclearity SMM-based architectures. As evidenced in this Feature article by the current limited number of modules used to elaborate SMMs, chemists should continue to develop this step-by-step approach in concert with more serendipitous syntheses, which have led, and will also lead, to many magnetically interesting systems without clearly identified building-block precursors. However, we believe that the described modular synthetic strategy, that efficiently used the existing knowledge of coordination chemistry, offers the best chances to premeditate and control the physical properties of the resulting coordination structures.

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Notes and references

This is a page from a scientific journal article. The content includes references to various scientific works, likely discussing the chemistry of cyano complexes of transition metals and related phenomena. The text is dense and technical, typical of scientific research publications. The references cited are from a variety of sources, spanning different years and journals, indicating a comprehensive review or discussion on the topic. The article appears to be discussing the chemistry of cyano complexes and their magnetic properties, as inferred from the context and the cited references.