

## Editorial for the Virtual Issue on Quantum Molecular Magnets

The meteoric rise of molecular magnetism as a central topic in the field of inorganic chemical research over the past 2 decades is readily apparent by the steadily increasing number of papers appearing on the topic in chemistry and physics journals. Included under the umbrella of subjects in this burgeoning field are paramagnetic molecules and one-dimensional chains of molecules that can be magnetized at low temperatures, referred to as “single-molecule magnets” (SMMs) and “single-chain magnets” (SCMs) or, more generally, as “quantum molecular magnets” (QMMs). The seminal discovery responsible for the explosion of recent activity in low-dimensional magnets is the finding that the mixed-valence  $\text{Mn}_4^{\text{IV}}\text{Mn}_8^{\text{III}}$  dodecanuclear molecule  $[\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 2\text{CH}_3\text{COOH}\cdot 4\text{H}_2\text{O}$  (known as  $\text{Mn}_{12}$ -acetate) behaves as a tiny bar magnet at low temperatures.<sup>1</sup> The magnetic dipole behavior is a consequence of an energy barrier for reversing the magnetization derived from the combination of a large spin and strong easy-axis anisotropy, which means that the molecule is easily magnetized along one preferred direction. The early recognition that  $\text{Mn}_{12}$ -acetate exhibits exotic quantum as well as classical magnetic properties<sup>2,3</sup> ignited new interest in magnetochemistry worldwide and set the stage for a new era of collaborative research between chemists and physicists, the eventual aim of which is to achieve bona fide device applications, especially in the areas of molecular spintronics and quantum computing.<sup>4</sup>

Since publication of the seminal papers that appeared in the early-to-mid-1990s, interest in SMMs has been nothing short of astounding. Over the course of the past 2 decades, the quest for SMMs with enhanced properties, fueled by the interplay of synthesis and theory, has gradually evolved into increasing sophistication in the design of SMMs including those based on heavier transition metals (as opposed to 3d elements) as well as the lanthanide and actinide elements. The field has blossomed into a topic of amazing diversity and promise.

A second key discovery in the area of Quantum Molecular Magnets occurred one decade after SMMs were introduced to the scene, namely, the existence of a new type of molecule-based magnet that became known as a Single Molecule Magnet.<sup>5</sup> The SCM family of compounds exhibits slow paramagnetic relaxation below certain blocking temperatures similar to the behavior of SMMs in a phenomenological sense, but the origin of the behavior is quite different. This point notwithstanding, the two types of QMMs share common design issues, and it is natural that the chemistry of SMMs and SCMs would develop hand-in-hand. Indeed, recent efforts to merge the two areas by using SMMs as building blocks for weakly coupled chains of SMMs and new generations of SCMs have produced fascinating results.

Given that the topic is deeply rooted in coordination chemistry principles, it should not come as a surprise that one of the leading international journals for reporting findings in this area is the American Chemical Society journal *Inorganic Chemistry*. Other ACS journals such as the *Journal of the American Chemical Society* and the *Journal of Physical Chemistry*

have also published numerous papers on the topic of QMMs, and it is these three journals that are highlighted in this inaugural joint virtual issue (<http://pubs.acs.org/page/vi/2012/quantum-molecular-magnets.html>). A Forum issue on molecular magnetism was published in 2009 in *Inorganic Chemistry*, but the array of topics covered was much broader than the current focus on QMMs. In this virtual issue, we showcase papers on this subject from the recent literature (2011 and 2012) by making them available online in a single collection along with their synopses for comprehension by the nonspecialist. These 23 papers are organized in the issue in such a way so as to demonstrate ongoing trends and new directions in the field.

The issue begins with papers that demonstrate how to design new types of SMMs and SCMs and materials based on them. The interesting report by the groups of Kubo, Yamashita, and their co-workers describes the use of  $\text{Mn}^{\text{III}}$  complexes in combination with a conducting nickel dithiolate compound to create a hybrid material that behaves as a semiconductor and also a SMM at different temperatures.<sup>6</sup> This research merges two very different areas of inorganic research and is a fine example of the diversity of the research in the field. The following paper by Kong, Long, and co-workers explores another intriguing application of molecular nanomagnets, namely, the magnetocaloric effect (MCE), which is a large temperature change in a material triggered by a magnetic field.<sup>7</sup> In this paper, the authors combine nickel and cobalt ions with gadolinium ions to produce very large polynuclear complexes that exhibit the largest MCE for 3d/4f compounds reported to date with the dysprosium derivatives behaving as SMMs. In the next paper,<sup>8</sup> Hong and co-workers use  $\text{Mn}^{\text{III}}$  Schiff base cations as linkers for octacyanotungstate(V) anions to form a 3d/5d bimetallic compound that exhibits SCM behavior as well as a separate magnetically ordered regime, highlighting the fact that dual properties are possible. An example of the use of preformed clusters as building blocks for magnetic chains comes from the group of Escuer and co-workers, who report a mixed-valence tetranuclear compound with azido and oximate bridges.<sup>9</sup> The result is a ferromagnetically coupled SCM composed of high-spin  $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$  units. In these aforementioned papers, a common theme is the fact that  $\text{Mn}^{\text{III}}$  chemistry, which has been important in the field since its inception, continues to offer opportunities for exciting new materials.

The next two papers illustrate the increasing concentration of work in the area of lanthanide-based QMMs. Murray and co-workers discovered a noteworthy example of atmospheric  $\text{CO}_2$  fixation in chemistry that leads to the formation of hexanuclear lanthanide molecules with a trapped carbonate ligand.<sup>10</sup> Interestingly, both the terbium and gadolinium derivatives are SMMs. In a collaborative piece of work by Chibotaru, Powell, Lan, Roesky, and co-workers, the authors make use of a ligand that contains three pockets for metal ions to bind.<sup>11</sup> When the

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ligand is bound to a single dysprosium ion, the complex is a SMM whose behavior can be switched off by incorporating paramagnetic  $\text{Mn}^{\text{II}}$  ions in the other two binding sites. Such experiments contribute important information to our understanding of how to control the behavior of SMMs for future applications.

As in any field, theory is crucial for the advancement of our understanding of QMMs. Density functional theory and valence-bond configuration methods have been applied by Atanasov, Delley, Neese, and co-workers to gain insight into the correlation of exchange coupling with structural parameters.<sup>12</sup> Their calculations on triangular  $\{\text{Mn}^{\text{III}}_3\text{O}\}$  SMMs are in good agreement with experimental data, and the authors conclude that ferromagnetic interactions occur via a spin-polarization mechanism. Importantly, the findings can be extrapolated to other SMMs and will aid chemists in their pursuit of new SMMs.

The next group of papers in the issue serves as an excellent illustration of how fundamental chemistry is being used to advance the understanding of QMMs. The work is dedicated to the important topic of how organic supporting groups on a SMM can be tuned to enhance the properties of SMMs. The separation of individual SMMs affects their ability to remain in a magnetized state, and sufficient isolation from each other is critical if surface-functionalized SMMs are to be feasible for high-density information storage. Hendrickson and co-workers tackled the issue of decreasing *intermolecular* magnetic interactions by equipping small cationic manganese dicubane SMMs with bulky peripheral ligands by using large tetraphenylborate anions.<sup>13</sup> The strategy was successful because, indeed, a reduction in the influence of nearest-neighbor SMMs on the single-molecule response of each individual molecule was documented. The paper by Holmes, Cl  rac, and co-workers is dedicated to another mission: to demonstrate how ligands in the same family, in this case tris(pyrazolyl)borates, can be used to influence the symmetry of complexes based on iron(III) tricyano building blocks and cause drastic differences in the magnetic properties.<sup>14</sup> Steric effects were found to control the spatial arrangement of the individual building units and the direction as well as alignment of anisotropy axes of the metal ions. Such *intramolecular* structural tweaking is at the heart of how chemists contribute to the advancement of many fields, including this one.

Another main theme that is emerging in SMM research is the study of mononuclear rather than polynuclear complexes. In the first of this group of papers, Misra and Goswami report computational work on octahedral  $\text{Cr}^{\text{III}}$  complexes with the conclusion that axial  $\pi$ -donor ligands lead to an "easy-plane" anisotropy, whereas  $\pi$ -acceptors promote "easy-axis" anisotropy.<sup>15</sup> Such predictions are highly useful for experimentalists in choosing ligand sets for the desired axial magnetic anisotropy required for SMM properties. In the vein of seeking SMM behavior in small-spin mononuclear transition-metal complexes that exhibit significant anisotropy,  $\text{Co}^{\text{II}}$  is becoming a popular target. Murugesu, Richeson, and co-workers studied the ligand substituent effects on the geometrical distortion of square-pyramidal  $\text{Co}^{\text{II}}$  complexes in order to tune the anisotropy arising from spin-orbit coupling, which directly influences the SMM properties.<sup>16</sup> Romero and co-workers are also pursuing mononuclear SMMs, but in their work highlighted in this issue,<sup>17</sup> the focus is on the lanthanide family. A radical nitronyl nitroxide, rather than typical closed-shell ligands, was used to prepare a new type of neutral SMM of  $\text{Tb}^{\text{III}}$ . A unique type of

SMM with only a single metal atom is being studied by Koga and Karasawa, who employ a phenylpyridyl ligand equipped with a diazomethane group to prepare  $\text{Co}^{\text{II}}$  complexes, which, upon irradiation, produce 2p-based carbene radicals that couple to the 3d spins to produce in situ SMMs.<sup>18</sup> This is a clever approach to using external stimuli, in this case light, to turn on the magnetic bistability of a molecule. In the final paper on this topic, Almeida and co-workers report a rare example of an actinide SMM based on  $\text{U}^{\text{III}}$  with tris(pyrazolyl)borate and bipyridine ligands.<sup>19</sup> The 5f elements are relatively undeveloped in this field but their stronger anisotropy and more covalent interactions make them even more potentially interesting targets for QMMs than the lanthanides, and we are sure to see more of these compounds in the near future.

The problem of preventing decay of the magnetization for SMMs in the absence of a field due to fast quantum tunneling in SMMs is a critical one, and chemistry aimed at controlling this phenomenon is being devised, including pioneering work by the Christou group. In the paper featured here,<sup>20</sup> Christou and co-workers prepared a tetramer of small triangular  $\text{Mn}_3$  SMMs by using dioximate ligands, which serve as covalent tethers that allow for weak magnetic coupling, as evidenced by the shift in the tunneling event from zero field in the hysteresis loop due to exchange bias from the local fields generated by the nearby SMMs acting on one another. In a similar vein, Kataev, M  ller, Meyer, and co-workers observed exchange bias behavior in linear molecules based on the  $[\text{Mn}^{\text{III}}_2\text{Ni}^{\text{II}}_3(\mu\text{-O})_8]$  unit that exhibit SMM behavior with hysteresis loops that are shifted above and below zero field depending on whether the weak intermolecular interactions are ferromagnetic or anti-ferromagnetic in nature, respectively.<sup>21</sup> Given that the molecules are robust, the intramolecular coupling is fairly strong, and the periphery can be modified, one can envisage the deliberate construction of new one-dimensional magnetic compounds including SCMs based on them. Following on the theme of SMMs whose tunneling at zero field is suppressed is the paper by Tang, Zhang, Chibotaru, and co-workers, who report another case of exchange bias that involves an asymmetric  $\text{Dy}^{\text{III}}_2$  molecule that exhibits both a normal regime of SMM behavior originating from each individual dysprosium site and a second type of SMM response that is due to the exchange interactions between the two dysprosium sites.<sup>22</sup> The weak interaction is a desirable feature because it leads to a barrier for relaxation that is three times larger than that of the individual dysprosium SMMs. Finally in this group of papers is a unique approach to forming SMMs from weak interactions reported by Miyasaka and co-workers, who reacted mononuclear  $\text{Mn}^{\text{III}}$  complexes with Keggin-type polyoxometalates, the result of which is different types of Coulombic aggregates including  $\text{Mn}_2$  SMMs.<sup>23</sup>

As the topic of SMMs has evolved, a natural direction for the research to take has been to immobilize them on surfaces for potential device applications. The three papers in this group provide excellent examples of approaches and techniques that are important for chemists to learn and use in order to be able to harvest the quantum properties of the molecules, which requires them to be manipulated outside their crystalline form. Moro, Forment-Aliaga, and co-workers report on their work in this area in which  $\text{Mn}_{12}$  SMMs were attached to gold surfaces that have been functionalized with sulfonate or carboxylic acid groups, which are being used to prevent direct interaction of the SMMs with the surface.<sup>24</sup> Although the redox properties of the  $\text{Mn}_{12}$  molecules are preserved when assembled with the

acid-based gold self-assembled monolayer, the magnetic properties are, nonetheless, perturbed, which is likely due to the fact that the SMMs need to be further decoupled from each other to fully retain the properties of the individual molecules. In the next paper,<sup>25</sup> Cornia and co-workers elucidate the spin structure of a Fe<sub>4</sub>-type SMM that retains its memory on a gold surface by using X-ray magnetic circular dichroism (XMCD) to probe an isomorphous surface-bound Fe<sub>3</sub>Cr analogue; the results indicate that the ferrimagnetic nature of the original Fe<sub>4</sub> SMM leading to an  $S = 5$  ground state is retained on the surface. Amabilino, Veciana, and co-workers report the surface chemistry of the well-known terbium(III) phthalocyanine double-decker SMM, which forms well-organized rectangular two-dimensional nanocrystals on highly oriented graphite as determined by atomic force microscopy and scanning tunneling microscopy (STM).<sup>26</sup> The results of XMCD studies confirm that the lanthanide molecules retain their SMM properties in close contact with a graphite surface.

The final two papers in the virtual issue represent important new directions in the field. Wang, Gao, and co-workers report organometallic SMMs based on Dy<sup>III</sup> and Ho<sup>III</sup>, which they refer to as “single-ion magnets” or SIMs. In these compounds, there is a single metal center, with the only coligands being carbon-based, C<sub>5</sub>Me<sub>5</sub><sup>-</sup> and cyclooctatetraene.<sup>27</sup> These neutral sandwich molecules are cousins of the Ln(phthalocyanine)<sub>2</sub> double-decker SMMs, which are also neutral, a fact that may provide an advantage over coordination complexes for placement onto surfaces because of their increased solubility and volatility, provided that they are sufficiently robust.

The final paper by Evans, Long, and co-workers reports dinuclear lanthanide complexes supported by a highly reduced dinitrogen ligand, namely, the radical N<sub>2</sub><sup>3-</sup> bridging ligand, which engenders unprecedented strong coupling between 4f metal-based spins.<sup>28</sup> The Tb<sup>III</sup>, Ho<sup>III</sup>, and Er<sup>III</sup> analogues exhibit slow relaxation indicative of SMM behavior, with the terbium derivative displaying exceptionally high blocking temperatures and hysteresis at temperatures as high as 14 K, which makes it the hardest SMM magnet known to date. The results reported in this paper represent more than an incremental advance in the field and presages many more “quantum leaps” in the field of quantum molecular magnetism to come!

The papers in this virtual issue attest to the fact that, molecular magnetism is a dynamic and adaptable field. The major challenge in the 1990s was the design and study of molecule-based magnets with increasing critical temperatures, but this situation has evolved into the design of multifunctional materials, with the coexistence or coupling of properties and of SMMs and SCMs exhibiting quantum effects. Moreover, far from the early days of seeking ever larger spin-state molecules as potential SMMs, the current trend is to study magnetic relaxation and quantum effects in smaller molecules with low or modest ground-state spin values. In all of these achievements, chemistry, and in particular coordination chemistry, has played a central role. Although it was not possible to highlight all of the remarkable milestones in the past few years with these 23 papers, it can be said that molecular magnetism has expanded into many new scientific and technological areas related to nanomagnetism and even biomedicine. In the former case, the possibilities offered by multifunctional magnetic materials and magnetic molecules are becoming a main focus of interest in the nascent field known as molecular spintronics, the aim of which is to detect spins in molecules in response to an external stimulus for device applications including computer logic and

memory storage. In this scenario, the goal is not only to prepare crystalline materials exhibiting multifunctionality but rather to process these stimuli-responsive magnetic materials as thin films, with the aim of integrating them into devices whose properties can be tuned by application of not only a magnetic field but also other physical stimuli (light, pressure, electric field, etc.). This research requires expertise beyond coordination chemistry including solid-state, organic/organometallic, and surface and interfacial chemistry, which are often used simultaneously for the elaboration of molecule/substrate hybrids.

The ultimate goal of this research in the long term is to reduce the size of future devices to a single molecule in order to increase the efficiency and speed and to take advantage of the quantum effects of the SMMs and SCMs for their use in quantum computing. Such a dream is prompting chemists working in molecular magnetism to collaborate with communities working in molecular electronics, surface nanoscience, and scanning probe microscopy. Some recent breakthroughs include the anchoring on surfaces of SMMs exhibiting magnetic hysteresis, the discovery of mononuclear SMMs (also known as SIMs) generally based on 4f but recently also 3d metal ions, the anchoring and organization of the QMMs on surfaces for potential use as qubits, the fabrication of nanodevices based on single molecular nanoparticles exhibiting thermally or electrically induced spin switching and bistability near room temperature, and the prospect of using electric fields or currents to control the spin state of a magnetic molecule.

In summary, the possibilities are limitless, and it is a stimulating exercise to predict future trends in this area. From a chemical point of view, one can envisage the combination of traditionally separated fields of chemistry: development of complex architectures exhibiting multifunctional properties; the trend from growing crystals to developing functional films and the preparation of magnetic materials with reduced dimensionality (a single chain, a single layer, a single nanoparticle, or a single molecule); deposition of these nano-objects on surfaces/interfaces with a nanometer accuracy. From the physical point of view, the future must include the use of state-of-the-art techniques to interrogate the magnetic properties in a reduced number of magnetic centers, with the final aim being to manipulate a single spin. In this vein, the use of a stimulus different from the magnetic field to control the spin state of a system is required; in particular, one can use an electric field with gates or STM tips that undergo fast switching (approximately picoseconds) and can be applied on the nanoscale. From the applied point of view, there is great promise in using the above systems as active components of new spintronic devices, in quantum computing as qubits, and in biomedicine as new theragnostic agents. As “blue-sky” as these concepts sound, they represent realistic directions in which research in the area of QMMs is headed in only two decades since its inception, when the first example of a coordination compound with a magnetic memory effect was realized!

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## ■ AUTHOR INFORMATION

### Notes

Views expressed in this editorial are those of the author and not necessarily the views of the ACS.

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