

Forum

Preface for the Forum on Molecular Magnetism: The Role of Inorganic Chemistry

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Molecular magnetism is a rapidly expanding field of research whose central theme is the design and study of magnetic molecules and materials with tunable properties. In the early stages of the field, which began to take shape in the 1980s, much of the effort was directed at the pursuit of molecule-based magnetic solids that order at high temperatures. These materials are basically of two types: those based on tetracyanoethylene (TCNE)¹ and those based on cyanide.² As the field rapidly evolved over the past two decades, exciting new challenges appeared on the horizon, including the use of building block approaches for the preparation of complex multifunctional magnetic materials, the fabrication of nanosized magnetic molecules and other nanostructures that exhibit quantum effects, and, the ultimate frontier, viz., the realization of practical applications. In all of these developments, inorganic chemistry, and, in particular, coordination chemistry, plays a principal role.

The purpose of this Forum issue is to highlight recent progress and perspectives in this diverse field and to underscore the influence of inorganic chemistry on an important area of materials science. A common thread that runs throughout research in molecular magnetism of metal ions is the application of classical coordination chemistry concepts as mapped out 150 years ago by the father of modern coordination chemistry, Alfred Werner. Given that Prussian Blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$, the first coordination compound and first molecule-based magnetic solid, was discovered in 1704 by the Berlin artist Diesbach,³ it is remarkable that, some 300 years later, we are only beginning to realize the enormous potential of cyanide materials and other magnetic coordination compounds. Indeed, Andreas Ludi, who dubbed Prussian Blue “The Inorganic Evergreen” in an article published in *Journal of Chemical Education* in 1981,⁴ was more visionary than he could have realized when he wrote those words. It is a privilege to follow in the footsteps of Alfred Werner and many other luminaries in the field of coordination chemistry, who have made countless seminal contributions to magnetism in the areas of synthetic inorganic and bioinorganic chemistry, theory, and spectroscopy, essential tools for magnetochemists in the year 2009.

Current trends in molecular magnetism revolve around two main classes of materials, viz., multifunctional magnetic materials and molecular nanomagnets. *Multifunctional materials* hold promise for the realization of technologically important properties previously thought to be possible only with atom-based inorganic solids (e.g., magnetic ordering combined with conductivity, superconductivity, or ferroelectricity). An extensive class of magnetic materials of this type falls into the category of *switching magnetic materials*. The

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magnetic properties for these types of molecular solids are tuned by the application of external stimuli (light, pressure, temperature, guest solvent molecules, etc.). Archetypes of switching magnetic materials are spin-crossover compounds⁵ and magnets based on Prussian Blue analogues for which temperature-, light-, and pressure-induced switching have been demonstrated.⁶ Another class of intriguing optomagnetic materials at the forefront of synthetic efforts in molecular magnetism is chiral magnets, wherein the interplay of chirality and ferromagnetism can result in the observation of novel physical properties such as magnetochiral dichroism.⁷

Other important multifunctional materials based on inorganic building blocks are those exhibiting a coexistence of two properties, viz., *dual-function materials*. These materials are hybrids generally formed by two independent molecular networks, wherein each network furnishes distinct physical properties. A remarkable example of such a system is one in which molecular magnetism is combined with conductivity.⁸ Examples of these materials are those composed of a cationic conducting network [typically based on tetrathiafulvalene (TTF)-type organic molecules] and anionic metal complexes that serve as the magnetic component. Notable achievements in this area are the discovery of paramagnetic molecular metals and superconductors in the 1990s and the discovery of ferromagnetic molecular metals in 2000.⁹ Importantly, the interplay between conductivity and magnetism has given rise to novel properties, for example, the observation of field-induced superconductivity.¹⁰ A major frontier to conquer in the future is the design of a material with the coexistence of superconductivity and ferromagnetism.

The topic of *molecular nanomagnets* is of paramount importance in the field.¹¹ This assertion is amply supported by the increasing number of publications that regularly appear in this journal devoted to the study of single-molecule magnets (SMMs). These molecular materials exhibit slow

paramagnetic relaxation of the magnetization at low temperatures and display magnetic hysteresis analogous to that observed in bulk magnets.¹² Arguably, even more fascinating is the fact that they show evidence of quantum effects.¹³

Most SMMs are polynuclear metal complexes whose structures consist of a magnetic cluster of exchange-coupled transition-metal ions protected by a shell of ligands, but an entirely different paradigm for molecular nanomagnets was unearthed with the discovery of single-ion lanthanide SMM complexes.¹⁴ This innovation represents a crucial step in the miniaturization of nanomagnets, namely the fact that a single anisotropic magnetic ion in an axial crystal-field environment is a sufficient condition for the establishment of a thermal barrier for reversing magnetization and for observing quantum tunneling effects. A fast-developing, related area is that of single-chain magnets,¹⁵ which are essentially one-dimensional analogues of SMMs. These “magnetic nanowires” are exciting new materials that, in principle, have the capability of giving rise to higher blocking temperatures for molecular paramagnets.

Another important objective in the field is the fabrication of magnetic molecules as nanostructures (thin films, nanoparticles, nanorods, etc.) and in the organization of these magnetic molecules and “nanoobjects” on surfaces. Mounting theoretical and experimental evidence lends considerable justification for this area of research, as it is becoming increasingly more obvious that immense and virtually unexplored possibilities exist for molecular nanomagnets in spintronics, quantum computing, and medicine. Until recently, *spintronics* has been almost exclusively the realm of conventional inorganic metals and semiconductors. Molecular electronics emerged several decades ago as a new approach for complementing and even supplanting conventional inorganic electronics when technology transforms to the nanoscale. In this context, a natural evolution of molecular electronics is that of using magnetic molecules as well as molecule-based magnetic materials as components for new spintronic devices.¹⁶ The two major trends in this new area are the design of molecular analogues of inorganic spintronic

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structures and single-molecule spintronics. For the former application, molecular magnetic conductors may prove to be useful, and, in fact, several materials have already been shown to exhibit interesting spintronic properties, for example, giant negative magnetoresistance.¹⁷ There are two challenging goals in this area, namely, to raise the operating temperatures at which these phenomena occur and to prepare the materials as organized thin films and multilayers. For the second application—single-molecule spintronics—it is noted that this nascent field has almost exclusively focused on theoretical proposals and speculations. Very few examples of charge transport through SMMs and other magnetic molecules have been reported thus far.¹⁸ These measurements are at the very early stage, and many problems, which are intrinsic to the molecules (such as their chemical stabilities when they are deposited on a metallic surface) need to be solved to obtain reliable results. A second concern is that of controlling, as much as possible, the positioning of the magnetic molecules on surfaces.¹⁹ Efforts are underway that employ both the “bottom-up” and “top-down” approaches as well as combinations of the two in order to control the position and the orientation of the molecule with nanoscale accuracy for applications such as information storage or quantum computing.²⁰

Other applications of molecular nanomagnets under consideration are magnetic cooling (such as magnetic refrigerants) due to the large magnetic entropy variations related to the high-spin value of the SMMs.²¹ In biomedicine, magnetic nanoparticles, mostly in the form of metal oxides, have been shown to be useful as contrast agents in magnetic resonance imaging and in the hyperthermic treatment of tumors, to mention only two major achievements.²² In this vein, magnetic nanoparticles based on molecules, particularly cyanide compounds, are gaining considerable ground. The prospect of being able to fine-tune the properties is a major driving force behind this line of research.

The evolution of molecular magnetism from simple molecular species to complex architectures with remarkable new properties in nanomagnetism and to more intricate multifunctional materials with applications in molecular spintronics, medicine, and other related areas reflects the extraordinarily multidisciplinary nature of the field. Indeed, the collaborations between chemists and physicists that were absolutely essential for the development

of magnetochemistry in general have expanded to include research in surface and materials science and engineering, medicine, biochemistry, and biophysics.

Articles that cover all aspects of the aforementioned topics are represented in this Forum issue dedicated to molecular magnetism. On the subjects of molecule-based magnets and exchange interactions, two papers discussing the magnetic exchange between actinides, as well as between d transition metals and lanthanides, are reported by Long et al. and Andruh et al., respectively. Advances in magnetostructural chemistry of the decamethylferrocenium—TCNE ferromagnet, a classic material in the history of the field, are presented by Stephens, Miller, and co-workers. Recent developments in the pursuit of magnetic molecules and molecular nanomagnets are highlighted in several papers: Clerac, Miyasaka, Yamashita, and Julve describe magnetic materials known as single-chain magnets, and the group of Thompson et al. discuss the use of polytopic ligands for the elaboration of magnetic grids. The design of new molecular nanomagnets formed by cluster-type complexes is reported in two independent papers. Approaches outlined by Oshio and Powell in their paper involve the preparation of a wide variety of iron-based molecular wheels, and Christou describes how he and his group are exploiting azide ligands in manganese SMM chemistry. The application of polyoxometalate chemistry to the design of SMMs based on mononuclear lanthanide complexes is reported by Coronado and co-workers. The topic of multifunctional materials is represented by articles describing spin-crossover metal—organic frameworks based on cyanide complexes by Real et al. and the overview written by Mathonière, Verdagner, Sieklucka, and co-workers on photo-magnetic phenomenon in clusters and extended molecule-based magnets. Structural modulation of the spin dynamics in a family of SMMs based on trinuclear manganese clusters is detailed by the groups of Hendrickson and Hill. Finally, the important issue of the fabrication of nanostructures of molecular magnets is addressed in the paper of Malah, Catala, and co-workers, who report advances in magnetic nanoparticles based on coordination compounds, and the article authored by Gatteschi, Sessoli, Cornia, and co-workers, who describe the organization and addressing of magnetic molecules on surfaces, a topic that has risen to the forefront very quickly in recent years and will doubtless continue to be at the heart of much new research in the future.²³

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