

Molecular-based magnets: an epilogue

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This Royal Society Discussion Meeting provided an overview and sampling of some of the exciting current developments in the rapidly growing area of molecule-based magnets. Clearly, as only a few of the multitude of groups studying aspects of the technologically important topic were represented, and time, as it is always in short supply, was not available for the speakers to cover many topics, the audience received a taste of the field. Hence, a variety of overview references to reviews are provided (Gatteschi 1994; Kahn 1993; Kinoshita 1994; Miller & Epstein 1994, 1995*a, b*; Coronado *et al.* 1996; Turnbull *et al.* 1996).

Magnetic materials prepared from molecules, not atoms or ions, have enabled the establishment of a diverse new class of magnets with magnetic ordering temperatures well above room temperature. As a class, molecule-based magnets are anticipated to exhibit a plethora of technologically important attributes that include modulation/tuning of properties via organic chemistry methodologies, compatibility with polymers for composites, low density, flexibility, transparency, low temperature processibility, insulating, solubility, high coercivity, high strength, low environmental contamination, biocompatibility, high magnetic susceptibilities and permeabilities, high magnetizations, low magnetic anisotropy, semiconducting behaviour, etc. Many of these non-magnetic characteristics are not available with conventional atom-based magnets.

Molecular-based magnets have indeed been prepared with critical temperatures ranging from 0.2 to 400 K, with the purely organic magnets, i.e. those with spins solely residing in the p-orbital, having the lowest T_c , i.e. *ca.* $0.2 < T_c < 1.48$ K. Compounds with spins only residing in d-orbitals have a broad range of T_c up to 372 K for a new material reported first reported at this Discussion Meeting (Hatlevik *et al.* 1999). Materials with spins residing in both p- and d-orbitals also have a broad range of T_c up to 400 K. Likewise, examples of molecular-based magnets exhibit a broad range of coercivity spanning from low values (*ca.* 0 Oe) associated with soft magnets to several teslas associated with hard magnets (Kurmoo, this issue; Miller *et al.*, unpublished research).

To achieve magnetic ordering, it is mandatory that unpaired electrons are present and their number and coupling dictate the resultant magnetic behaviour. As emphasized by several speakers, the couplings are a consequence of the three-dimensional structure motif and although an *a priori* understanding of the structure–magnetic property relationship is strongly desired, it is increasingly clear that this is complex and so far elusive. Nonetheless, it is a high priority for researchers in the area. Structural motifs documented to stabilize magnetic ordering can be zero (isolated molecules and ions), one (linear chain), two (layers), or three dimensional (networks).

In addition to complex structures, the diversity of magnetic behaviours is bewildering. Within this broad class of materials, ferromagnets, ferrimagnets, antiferromagnets, canted antiferromagnets (or weak ferromagnets), metamagnets, spin glasses, spin frustration, spin flops, as well as the exciting new area of high spin 'small' clusters, some of which are 'single' molecule magnets have been reported. In the area of high spin clusters, the one with the largest spin state, $S = 39/2$, was reported for the first time at this Discussion Meeting (Hashimoto & Ohkoshi, this issue).

Materials that combine magnetic properties with other properties are envisioned to lead to new technologically important materials. In this regard, photomagnetic behaviour was discussed (Hashimoto & Ohkoshi, this issue) and spin crossover materials were touched upon. The former is a rapidly growing embryonic area, while the more mature latter area still has many exciting aspects that will fuel continued studies worldwide.

All emerging research areas have issues that need to be addressed. As a consequence of growth by diverse research groups worldwide (each with differing backgrounds, e.g. synthetic organic, organometallic, main group, and coordination chemistry, as well as physical organic and inorganic chemistry, not to ignore physical chemistry, condensed matter physics, materials science, etc.), language problems arise that impede communication and progress. It behoves all participants in this field to devote some time both to define and clarify the terms they use as well as learn the terms of others.

Issues from a more technical perspective include three-dimensional structure control, identification of structure function relationships, and control of anisotropy. Identification of structure cannot be overemphasized. Akin to the study of biologically important systems, it is necessary to understand and control the primary, secondary, and tertiary structures. Structure determination, particularly by neutron diffraction, at the temperatures at which the magnetic phenomena and transitions occur is the Holy Grail. As challenging as this is, progress in this area should be targeted. The availability of CCD detectors has enabled the structure determination of increasingly smaller crystals and this should provide an impetus to the development of structure-function relationships. Nonetheless, disorder persists as a problem and improved methods need to be developed to unravel complex disorder. The growth of larger crystals will simplify, in some cases, the structure determination by X-ray diffraction, but more importantly will enable important single crystal neutron diffraction studies as well as anisotropic magnetic (EPR and magnetization) and optical measurements. Probing of the local magnetic properties should be a highly placed agenda item and muon spin resonance is being used more and more to provide information in this regard.

Perhaps in a decade, another Royal Society Discussion Meeting on this topic can be convened, and I trust enormous progress will have been made with many fascinating new and totally unexpected results being reported.

References

- Coronado, E., Delhaès, P., Gatteschi, D. & Miller, J. S. (eds) 1996 *Molecular assemblies to the devices*. NATO Advanced Studies Workshop, E321. Kluwer.
- Gatteschi, D. 1994 *Adv. Mat.* **6**, 635.
- Hatlevik, Ø., Buschmann, W. E., Zhang, J., Manson, J. L. & Miller, J. S. 1999 *Adv. Mat.* **11**, 914.

- Kahn, O. 1993 *Molecular magnetism*. New York: VCH.
- Kinoshita, M. 1994 *Jap. J. Appl. Phys.* **33**, 5718.
- Miller, J. S. & Epstein, A. J. 1994 *Angew. Chem. Int. Ed.* **33**, 385.
- Miller, J. S. & Epstein, A. J. 1995a *Chem. Eng. News* **73**(40), 30.
- Miller, J. S. & Epstein, A. J. (eds) 1995b *Molecule-based magnets*. *Mol. Cryst. Liq. Cryst.* **271–274**.
- Turnbull, M. M., Sugimoto, T. & Thompson, L. K. (eds) 1996 *Molecule-based magnetic materials*. ACS Symp. Ser., 644.

