

Editorial

# Molecular Magnets

Maria Bałanda \*  and Magdalena Fitta Institute of Nuclear Physics Polish Academy of Sciences, Radzikowskiego 152, 31-342 Krakow, Poland;  
magdalena.fitta@ifj.edu.pl

\* Correspondence: maria.balanda@ifj.edu.pl

Received: 28 February 2019; Accepted: 4 March 2019; Published: 6 March 2019



Molecular magnetism is an interdisciplinary research area, which deals with design, synthesis and physical characterization as well as the theoretical modeling of molecular materials showing acquired properties. The features that distinguish molecular magnets from traditional magnetic materials are: low-density, transparency to electromagnetic radiation, and sensitivity to external stimuli such as light, pressure, temperature, chemical modification or magnetic/electric field. Furthermore, molecular magnetism offers an exceptional collection of materials of various magnetic dimensionality: from 0D single-molecule magnets and 1D single-chain magnets, regarded as molecular nanomagnets due to slow relaxation and bistability at low temperatures, through 2D molecular layers, to 3D coordination polymers showing the collective ordering of magnetic moments below the critical temperature  $T_c$ . Research into molecule-based materials, both theoretical and experimental became more intense at the end of 20th century and has concentrated on (i) low dimensional materials, motivated by their potential applicability in high-density magnetic storage or nanoscale devices and (ii) on “functional” materials, strongly responding to change in external parameters, that may be used in sensors of a different type. This Special Issue shows the rich palette of the properties of magnetic molecular materials and presents current work on this interesting and important topic. The issue contains four review articles and also includes the results by the authors, as well as original contributed papers.

Molecular magnets involve well-localized magnetic moments, which make them the perfect playground for the investigation of intriguing phenomena and testing theoretical models. The interplay of spatial anisotropy of the exchange coupling and the intrinsic or magnetic-field induced spin anisotropy were discussed in the two-dimensional magnetic models by Orendáčová et al. [1]. In this excellent review, authors provide a concise introduction of the development of the theory and numerical approaches aimed at the description of low-dimensional magnetism. The main body of this paper presents a thorough study of the ground state and finite-temperature properties of the  $S = \frac{1}{2}$  models interpolating between the quantum Heisenberg antiferromagnetic chain and the rectangular spin lattice. The effect of the possible inter-layer exchange coupling resulting in the stabilization of the 3D long-range order is also discussed. Some physical consequences following from the characteristics of the underlying model are evidenced by reporting consistent experimental data on magnetic and calorimetric properties of low-dimensional Cu(II) based metal-organic magnets.

A complete understanding of the mechanisms of the magnetic interaction in molecular magnets requires advanced calculations such as proposed by Brumfield and Haraldsen in [2]. Based on the Heisenberg spin-spin exchange model, the general relationships for the quantum energy levels, the spin states for isosceles spin trimmers of spins equal  $\frac{1}{2}$  up to  $5/2$  are provided. Dependence on heat capacity, magnetic susceptibility on temperature, and the corresponding inelastic neutron scattering structure factors have been determined. As stated by the authors, results of the calculations could help with the general analysis and characterization of magnetic molecule-based systems.

The influence of external pressures on the structural and magnetic properties of molecular magnets has been reviewed by Zentkova and Mihalik [3]. The underlying mechanisms of the effect are presented on the example of  $\text{Cr}(\text{CN})_6$ -based Prussian blue analogues (PBs)— $\text{TM-Cr}(\text{CN})_6$  and

K-M-Cr(CN)<sub>6</sub>, where TM = Mn, Ni, Co, Cr, and M = Mn, Ni. After reviewing the sensitivity of PBs to external stimuli and the high potential of PBs for applications, the authors describe the super-exchange interaction between the metallic ions and give an analysis of the pressure effect in case of predominated ferromagnetic, ferrimagnetic as well as mixed ferro–ferromagnetic interactions. Results of structural, magnetic and Raman spectra measurements at pressures of up to GPa for different analogues are shown. The paper clearly explains the reason of various pressure-induced T<sub>c</sub> change observed for subsequent samples under study. The pressure effect on magnetic properties was also checked for hexacyanometalate-based nanoparticles and core–shell heterostructures.

Similar to other magnetic materials, molecular magnets also exhibit a magnetocaloric effect (MCE). The review of the magneto-thermal properties of octacyanometallate-based and molecular magnets showing the different types of crystal architecture is presented by Fitta et al. [4] MCE study was performed for 3D and 2D coordination polymers and the high spin cluster built with [Nb<sup>IV</sup>(CN)<sub>8</sub>] or [W<sup>V</sup>(CN)<sub>8</sub>] molecular blocks. The results were obtained by means of two experimental methods, i.e., calorimetry and magnetometry. Moreover, the study of a new effect-rotating magnetocaloric effect (RMCE) in two 2D molecular magnets was presented. Dependence of MCE on temperature and on the value of the magnetic field was tested. It was found that the Ni<sub>9</sub>[W(CN)<sub>8</sub>]<sub>6</sub> cluster compound has a potential for cryogenic magnetic cooling. Conclusions related to MCE scaling and critical behavior in some systems under study were also included.

Two new oxime-based cationic [Mn<sub>6</sub>]<sup>2+</sup> complexes, synthesized and characterized structurally and magnetically, are presented by Rojas-Dotti et al. [5]. A ground state spin value of both systems is S = 12. In these compounds the slow relaxation of magnetization occurs, which is consistent with the single-molecule magnet (SMM) behavior. Moreover, the energy barrier for the relaxation of magnetization determined for one of the considered compounds is the highest reported so far for cationic oxime-based [Mn<sub>6</sub>]<sup>2+</sup> systems. As mentioned by the authors, such a type of the cationic SMM can be used as precursors of new multifunctional magnetic materials through the incorporation of anionic species that bring for instance conductivity or luminescence to the final material.

Example of the interesting solvatomagnetic compound based on [Cu(cyclam)]<sup>2+</sup> and [W(CN)<sub>8</sub>]<sup>3-</sup> building blocks is presented by Nowicka et al. in [6]. The removal of water molecules from the ladder-chain crystal structure of the compound during the dehydration process leads to the modification of the geometry of the bonds, and finally to the single-crystal-to-single-crystal structural transformation. The noticeable change of magnetic properties was observed and reflected in switching the predominant intra-chain interactions from ferromagnetic in a hydrated compound to antiferromagnetic in an anhydrous sample. The dehydration process is not fully reversible, probably due to the formation of intra-chain hydrogen bonds.

An important group of molecular magnets are purely organic molecular materials, as they show electric conductivity and non-trivial magnetic properties. New examples of organic magnetic materials are presented by Pinkowicz et al. [7]. The paper reports the synthesis, crystal structures and magnetic characterizations of a series of six dioxothiadiazole-based radical compounds. Structurally, the presented compounds are formed by alternating cation–anion layers or chains of π-conjugated molecules. Magnetic data reveal weak antiferromagnetic interactions between the radical anions. Magnetic interaction pathways between pairs of radical anions are justified by the presence of C-H N hydrogen bonds. Authors discuss the influence of the structural differences on the magnetic properties of the radical salts under the study.

Finally, research on the π-d interacting magnetic molecular superconductor κ-(BETS)<sub>2</sub>FeX<sub>4</sub> (X = Cl, Br) studied by means of an angle-resolved heat capacity is reviewed by Fukuoka et al. [8]. The π-d interacting systems consisting of organic donor molecules and counter anions containing magnetic ions, are of interest due to the cooperative phenomena between conducting electrons and localized spins, leading to unique magnetic and transport properties. The experimental method used enables high accuracy investigations of the anisotropy of the magnetic heat capacity against the in-plane magnetic field. Instrument applicable to tiny single crystals of molecular magnetic materials was constructed

by the authors of the article. Uncommon crossover from a 3D magnetic ordering to a 1D magnet was observed at the field parallel to the  $a$  axis, while the superconducting transition temperature also showed a remarkable anisotropy against the in-plane magnetic field. These valuable results point to the influence of the 3d electron spins on the superconducting state of the  $\pi$  electron system.

**Acknowledgments:** Guest editors appreciate all the authors of the articles for sending their works. They hope the content of this special issue presents a comprehensive report on the current work on molecular magnets and will be interesting for the readers.

## References

1. Orendáčová, A.; Tarasenko, R.; Tkáč, V.; Čižmár, E.; Orendáč, M.; Feher, A. Interplay of Spin and Spatial Anisotropy in Low-Dimensional Quantum Magnets with Spin 1/2. *Crystals* **2019**, *9*, 6. [[CrossRef](#)]
2. Brumfield, A.; Haraldsen, J.T. Thermodynamics and Magnetic Excitations in Quantum Spin Trimers: Applications for the Understanding of Molecular Magnets. *Crystals* **2019**, *9*, 93. [[CrossRef](#)]
3. Zentkova, M.; Mihalik, M. The Effect of Pressure on Magnetic Properties of Prussian Blue Analogues. *Crystals* **2019**, *9*, 112. [[CrossRef](#)]
4. Fitta, M.; Peřka, R.; Konieczny, P.; Bařanda, M. Multifunctional Molecular Magnets: Magnetocaloric Effect in Octacyanometallates. *Crystals* **2019**, *9*, 9. [[CrossRef](#)]
5. Rojas-Dotti, C.; Moliner, N.; Lloret, F.; Martínez-Lillo, J. Ferromagnetic Oxime-Based Manganese(III) Single-Molecule Magnets with Dimethylformamide and Pyridine as Terminal Ligands. *Crystals* **2019**, *9*, 23. [[CrossRef](#)]
6. Pacanowska, A.; Reczyński, M.; Nowicka, B. Modification of Structure and Magnetic Properties in Coordination Assemblies Based on  $[\text{Cu}(\text{cyclam})]^{2+}$  and  $[\text{W}(\text{CN})_8]^{3-}$ . *Crystals* **2019**, *9*, 45. [[CrossRef](#)]
7. Pakulski, P.; Arczyński, M.; Pinkowicz, D. Bis(triphenylphosphine)iminium Salts of Dioxothiadiazole Radical Anions: Preparation, Crystal Structures, and Magnetic Properties. *Crystals* **2019**, *9*, 30. [[CrossRef](#)]
8. Fukuoka, S.; Fukuchi, S.; Akutsu, H.; Kawamoto, A.; Nakazawa, Y. Magnetic and Electronic Properties of  $\pi$ -d Interacting Molecular Magnetic Superconductor  $\kappa$ -(BETS) $_2$ FeX $_4$  (X = Cl, Br) Studied by Angle-Resolved Heat Capacity Measurements. *Crystals* **2019**, *9*, 66. [[CrossRef](#)]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).