Insights into single molecule magnetism from charge and spin density studies

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Single-molecule magnets (SMM) are special molecules, which are able to preserve an induced magnetization after the removal of an external magnetizing field, but in contrast to the domains that explain magnetism in bulk ferromagnets, the magnetic properties in SMMs have a purely molecular origin. Such tiny magnets are naturally in high demand as they have potential technological applications in e.g. spin-based electronics. It is known that these materials rely on significant magnetic anisotropy to function, and this is exactly what is caused by orbital angular momentum, either directly from the ground state or from mixing-in from excited states. Within the last decade or so, lanthanide-based SMMs have been found to offer promising candidates for this purpose.[1] However, recently also compounds based on cheap and earth-abundant metals such as iron have been found to be useable by clever engineering of the ligand field. In this talk, I will outline three of our recent results based on diffraction studies of SMMs.

Firstly, the best mononuclear transition metal-based SMM so far discovered which combines two unusual features of an iron complex, namely two-coordinate Fe(I),[2] $[Fe(C(SiMe_3)_3)_2]^-$ (left Figure). This complex has a record high effective relaxation barrier (U = 226(4) cm^{-1}). It had been suggested that the low coordination number and the low oxidation state combine to give a very weak ligand field with the d_{z^2}-orbital lowest in energy of the *d*-orbitals. To study this we have modeled the experimental electron density of this compound, as well as its di-valent analogue, and use these to discuss the molecular magnetic properties.[3] *Secondly*, we have studied the 4f electron density in a Dy-based SMM and compared that with the calculated density underlying the suggestions for improving magnetic anisotropy by Rinehart & Long.[4] *Finally*, I will show how polarized neutron single crystal data can lead to quantitative knowledge of the local susceptibility tensor.[5]

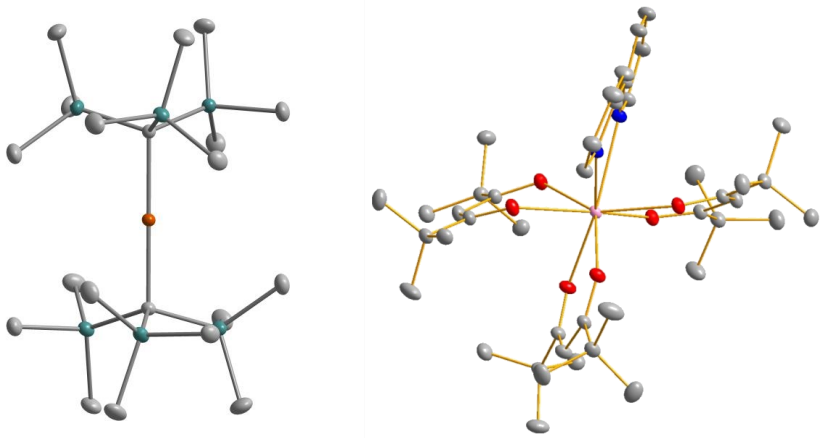

Figure ORTEP drawings of (left) the $[Fe(C(SiMe_3)_3)_2]^-$ anion obtained from 100 K X-ray data measured on a $[K(crypt\text{-}222)][Fe(C(SiMe_3)_3)_2]$ (crypt-222 = 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo [8.8.8]hexacosane), and (right) $Dy(2,2'\text{-bipyridine})(t\text{-Bu-acac})_3$. The atoms are depicted as 50 % probability ellipsoids. Pink, orange, blue, red, petrol blue and grey refer to dysprosium, iron, nitrogen, oxygen, silicon and carbon, respectively. Hydrogen atoms have been omitted for clarity.

[1] See, for example: K. R. Meihaus and J. R. Long, *J. Am. Chem. Soc.* **2013**, *135*, 17952-17957.
[2] J. M. Zadrozny, D. J. Xiao, M. Atanasov, G. J. Long, F. Grandjean, F. Neese and J. R. Long, *Nat. Chem.* **2013**, *5*, 577-581.
[3] M. K. Thomsen, A. Nyvang, J. P. S. Walsh, P. C. Bunting, J. R. Long, F. Neese, M. Atanasov, A. Genoni and J. Overgaard, *J. Amer. Chem. Soc.* **2018**, *submitted*.
[4] C. Gao, A. Genoni, S. Gao, A. Soncini, S.-D. Jiang and J. Overgaard, *Nat. Chem.* **2018**, *under review*.
[5] E. A. Klahn, C. Gao, B. Gillon, A. Gukasov, X. Fabreges, R. O. Piltz, S. Jiang and J. Overgaard, *Chem. Eur. J.* **2018**, 10.1002/chem.201803300.

Curriculum Vitae - Jacob Overgaard

Personal details:

Born October 13, 1974 in Struer, Denmark. Lives now in Risskov with my wife and two daughters.

Academic degrees:

2015: **Doctor of Science** awarded by Aarhus University for a thesis entitled "*Applications of electron density studies in molecular and solid-state sciences*".

2001: **PhD** in Chemistry from Department of Chemistry, Aarhus University.

Scientific career:

2010-current: Senior Researcher at the Department of Chemistry, Aarhus University.

2005-2010: Staff crystallographer, Aarhus University

2004: Postdoc, based at Aarhus University, focused on the use of synchrotron radiation.

2001-2004: Postdoctoral Research Fellow at School of Chemistry, University of Sydney.

Teaching & Supervision experience:

- Teacher in Chemical Crystallography. (2007 - now); Structural Chemistry I (1/3 load; 2017 -); Inorganic Chemistry II (1/3 load; 2018 -)
- Lab responsible, first year General Chemistry (2016 -)
- Course responsible, first year Introduction to Chemistry Research practical course (2016 -).
- Current research group (2018): 3 Project, 1 MSc, 2 PhDs, 2 postdocs.
- Educated 10 BSc, 2 MSc, 4 PhD's (3 as co-supervisor).

Miscellaneous:

International Collaborators: Strong personal ties with the groups of Profs Chilton and Winpenny (University of Manchester); Profs Maheswaran, Rajaraman and Murugavel (IIT Bombay); Prof Jones and Murray (Monash University) and Soncini (Melbourne); Prof Long (UC Berkeley).

Oral presentations: Invited speaker at more than 20 international conferences and meetings.

Reviewer: Reviewer for ACS, RSC, Angew Chem, and IUCr journals, as well as proposal reviewer for Australian Research Council and member of scientific review committees for large facilities, such as ANSTO, Australia and ORNL, Oak Ridge, USA.

Board Membership: Member and Treasurer of the Executive Committee of the European Crystallographic Association, elected in 2018.

Bibliometric data:

Web of Science, September 22, 2018: 124 publications with h-index 28.