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Single-molecule magnets: Uranyl steps in the ring

Polly L. Arnold*

EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[*]Corresponding author; email: polly.arnold@ed.ac.uk

Abstract

Uranium and manganese cations have been combined in a wheel-shaped supramolecular assembly that retains its magnetic spin state after the external field is removed, with a high barrier to its relaxation. This cluster supports recent predictions of the usefulness of the actinides in single-molecule magnetic devices.

Main text

The linear uranyl dication, $[\text{UO}_2]^{2+}$ — the most prevalent of the uranium salts, both in the laboratory and the environment — is inert owing to a very strong covalent *trans*- UO_2 bonding and oxo groups that show little propensity to behave as Lewis bases. Single electron reduction of this ion, however, forms a monocationic uranyl ion $[\text{UO}_2]^+$ that is also linear and strongly bonded but exhibits greater oxo Lewis basicity and thus greater reactivity. In recent years, this $5f^1 [\text{O}=\text{U}=\text{O}]^+$ monocation has featured in a variety of stable oxo-functionalised uranyl complexes^{[1],[2]}, prompting the search for extended supramolecular structures based on oxo-coordination. Marinella Mazzanti and co-workers have now described in *Nature Chemistry* the self-assembly of this uranyl monocation with Mn^{II} species into a $\{\text{U}_{12}\text{Mn}_6\}$ supramolecular wheel that behaves as a single-molecule magnet at low temperatures^[3].

Molecules that behave as magnets are those that, after being magnetized under an external magnetic field, require a significant energy input to reverse their magnetisation. This behaviour is of molecular origin — very different from the magnetisation that arises in bulk materials owing to the long-range ordering of the magnetic moments of metal centres. Single-molecule magnets attract much attention as they hold the promise to address the demands of modern information technology: magnetic systems consisting of one, or only a few, magnetic molecules would provide the ultimate miniaturisation.

The magnetisation and relaxation behaviour of single-molecule magnets of *d*-block metal compounds is well understood. For over two decades, chemists have been making molecules that can retain their magnetisation for several years at very low temperatures (below around 5 K). Above these temperatures, however, the magnetisation is lost — either by thermally activated spin-relaxation or by quantum tunnelling mechanisms — preventing their practical use. Recent results have suggested that *f*-block metal ions may be able to address this issue^{[4],[5]}. Polynuclear *3d–5f* complexes in particular may combine the best of both worlds: the spin characteristics of *3d* metals with the anisotropy of *f* centres, yet with the added benefit that the *5f* orbitals extend further than their *4f* counterparts.

The strategy of Mazzanti and colleagues relies on the self-assembly of $5f^1$ $[\text{U}^{\text{V}}\text{O}_2]^+$ complexed with a chelating ligand (ethylene-bis(salicylimine), ‘salen’) with $3d^5$ $\text{Mn}^{\text{II}}(\text{NO}_3)_2$. Slow diffusion of the two species led to the crystallization of a giant wheel structure that comprises twelve U^{V} and six Mn^{II} cations. The key interaction that holds the wheel together is the ‘cation–cation interaction’ (CCI) between the uranyl oxo groups and the manganese cations (Figure 1X). This type of interaction was originally described for interactions between actinyl ions of uranium’s heavier and more radioactive congeners, neptunium and plutonium. Here CCIs with both $5f^1$ and $5f^2$ cations pose problems in a real-world situations, as they induce the formation of unwanted clusters in nuclear waste processing solutions.

In fact, it is a triangular, mixed-valence cluster $\{\text{Np}^{\text{VI}}\text{O}_2\text{Cl}_2\} \{\text{Np}^{\text{V}}\text{O}_2\text{Cl}(\text{thf})_3\}_2$ held together by CCIs that was the first example of a polymetallic transuranic complex displaying both slow relaxation of the magnetisation and interactions between *5f* centres^[6].

Here, the U^{V} uranyl cation both provides the desirable magnetically anisotropic $5f^1$ electron, and forms a sufficiently strong CCI to allow the wheel to form. Indeed, particularly strong magnetic coupling between *4f* and *5f* centres^[2], as well as between two U^{V} cations, has already been demonstrated through uranyl oxo groups.

The magnetic behaviour reported in the present wheel however is much more interesting in terms of quantum computing applications and — for a few reasons — much more difficult to quantify. Perhaps the main reasons are that the wheel forms as an insoluble crystal, and from so many components. These prevent magnetic dilution experiments to determine if long-range magnetic fields of the ions interfere with the single molecule’s own magnetism. Molecular separations of 40–50 Å are usually necessary to rule out the possibility of inter-

molecular weak ferromagnetic interactions. An alternative to measuring a frozen, dilute solution is to co-crystallise the species with an isostructural diamagnetic analogue — for example, replace its Mn^{II} centres by Zn^{II} ones — but the nature of the self-assembly process precludes the use of mixtures in the synthesis. Furthermore, the researchers also note that diamagnetic candidate metals have not yet afforded the same clustering geometries as their Mn^{II} counterparts. The fact that suitable intermolecular distances cannot be achieved makes the results harder to interpret and model.

Figure 1. A range of the possible CCI-type interactions enable the use of uranium(v) as a supramolecular building block. a, Increasingly common CCI motifs for uranyl as a result of single electron reduction, and the competing interaction with manganese. b, an additional tris(uranyl) coordination node focused around Mn^{II} . c, The $\text{Mn}(\text{II})$ is sufficiently Lewis acidic to outcompete the inter-uranyl CCIs, while a more traditional uranyl dimerization in the equatorial plane, and *cis*-Mn coordination combine to control the geometry of the $\{\text{U}_{12}\text{Mn}_6\}$ supramolecular wheel.

Another problem arises from the sheer size of the wheel. It is difficult for computational chemists to extract meaningful electronic structure data even from dinuclear uranium complexes, due to the large number of

electrons and orbitals. Exploring all the possible electronic transitions within this wheel are thus beyond the capabilities of modern computational methods.

Yet, this supramolecular wheel is very enticing. Perhaps most pleasing is the use of the uranyl monocation to build magnetic structures aligned through its highest symmetry axis. The ions in lanthanide and lower oxidation state uranium magnets^[7] described previously have no geometrical preference. Although care should be applied in assuming that the primary symmetry and magnetic anisotropy axes are superimposable^[8], the complementary use of the axial oxo and equatorial ligand binding sites in U^v uranyl to mediate coupling could be used to construct interesting new molecules.

A notable challenge that the experimental data highlights here is that a full characterisation of the magnetic structure of the complex is currently beyond the technologies available to us. Should we wait for the techniques and computers to catch up? Surely the best course to achieve real progress is instead to target the most challenging molecules we can, and remain careful in our interpretation as we learn the complexities of new systems. And there will no doubt be many more intriguing compounds to come.

References

- [1] Schnaars, D. D., Wu, G. & Hayton, T. W. *Inorg. Chem.* **50**, 9642–9649 (2011).
- [2] Arnold, P. L., *et al.* *Angew. Chem., Int. Ed. Engl.*, **50**, 887–890 (2011)
- [3] Mougel, V. *et al.* *Nature Chem.* **4**, XX–XX (2012)
- [4] N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, *J. Phys. Chem. B.*, **108**, 11265–11271 (2004)
- [5] Karotsis, G. *et al.* *J. Am. Chem. Soc.* **132**, 12983–12990, (2010).
- [6] N. Magnani *et al.* *Phys. Rev. Lett.*, **104**, 197202–197205 (2011)
- [7] J. D. Rinehart, Meihaus, K. R. & Long, J. R. *J. Am. Chem. Soc.*, **132**, 7572–7573 (2010).
- [8] Cucinotta, G. *et al.*, *Angew. Chem., Int. Ed.* **51**, 1606–1610 (2012).