

Molecular magnets

Can we create permanent magnets which are light, transparent and bio-compatible?

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The polarised hot neutron diffractometer D3



Conventional permanent (ferro)magnets, made of transition metals and rare-earths like iron and neodymium, are everywhere: in cars, kitchen gadgets, telephones, computers, and so on. Indeed, they generate the second largest cash flow in the global economy. Now, the market for magnetic devices is set to widen further, thanks to the creation of magnets made from molecular compounds.

Molecular magnets have many useful additional properties: lightness, transparency, solubility, magneto-optical properties (using light to change the magnetic state), and biocompatibility. They also offer the opportunity of being able to 'tune' the transition temperature at which the material becomes ferromagnetic – by tweaking the chemical structure. These molecular compounds will not only extend the use of permanent magnets but also open the way to a novel class of information storage systems.

The first ferromagnetic molecular compound – decamethylferrocenium tetracyanoethylene – was discovered in 1986; its transition temperature was only 4.8K. Since then, huge progress has been made and room-temperature molecular magnets are now quite common. An example is a magnet consisting of a complex metal compound – a hexacyanometallate $L^p[M(CN)_6]^{q-}$, where L and M are transition-metal ions. The electronic structure of this compound is well understood, so it is possible to tune its magnetic properties. Another example is the low-temperature magnet based on clusters of manganese atoms, Mn_{12} acetate, which can exist in a variety of subtle magnetic states that can be controlled by an applied magnetic field.

In the conventional compounds based on metals, the magnetic moments (which arise from the spins of unpaired electrons) are well localised on the metal atoms, with only a small part of the 'spin density', or magnetisation, transferred onto the groups of atoms attached to the metal. The distribution of the magnetisation is thus just the sum of contributions of individual magnetic atoms within the molecule.

In the case of a molecular compound, however, the situation is completely different. The unpaired electron responsible for its magnetism sits in a molecular orbital built up from the orbitals of the atoms constituting the

molecule. This means that the magnetisation tends to be smeared out across the molecule, though perhaps concentrated on certain atoms.

A uniquely sensitive probe

Polarised neutron diffraction is the only technique sensitive enough to investigate the magnetisation. Neutrons themselves have a magnetic moment, and polarised beams of neutrons (with spins aligned in the same direction) are a unique probe of magnetic behaviour. Measuring the magnetisation distribution across a molecule reveals precious information on the nature of the molecular orbitals responsible for the magnetism, the interactions with neighbouring molecules in the solid, as well as the chemical bonding and how the electron spin is spread out and oriented. This allows us to test the underlying theories of molecular bonding and magnetism, and create new magnetic materials with predicted properties. ■

Figure 1 shows the spin density in the first genuine organic ferromagnet synthesised, the β phase of *para*-nitrophenyl nitronyl nitroxide (transition temperature 0.6K). Most of the spin density lies on the O-N-C-N-O group of atoms of the nitronyl nitroxide fragment; the contours reveal that the unpaired electron responsible for magnetism is mostly situated on the oxygen and nitrogen, but when on the central carbon atom it reverses its spin direction, giving a negative spin density

Figure 2 shows what happens to the spin density in a similar molecule, $CuCl_2(NitPh)_2$, (the phenyl groups are not shown) when a transition metal like copper is present. The spin density is positive on the nitroxides (NO) and negative on the copper. The lack of magnetisation on the oxygen nearest the copper shows that the spin distribution in the nitronyl nitroxide has been completely upset by the magnetic interaction with the copper

