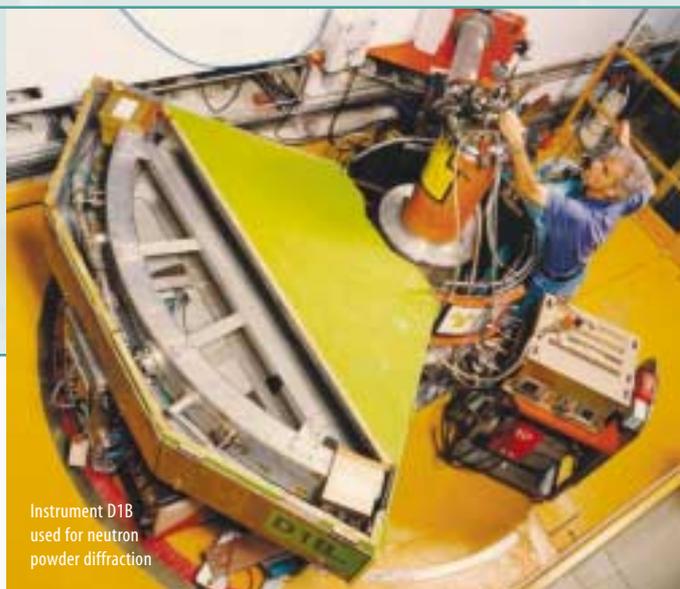


# Molecules seize the moment

Molecules with unpaired electrons offer a new type of magnetic material

>> DANTE GATTESCHI



Instrument D1B used for neutron powder diffraction

**M**agnets based on molecular building blocks have the potential to produce materials with novel characteristics of both theoretical and practical interest. The advantages of molecular magnets are that they can be altered by fine-tuning their structure chemically, they are soluble in organic solvents so can be processed easily, and they may interact with light in a technologically useful way. One intriguing application is in the new field of quantum computing which relies on encoding information in superposed quantum states.

Contrary to classical magnets, where the magnetisation density is localised on the atoms of metallic lattices, in molecular magnets the density may be spread across several of the constituent atoms. It is often difficult to understand the magnetic interaction without a detailed knowledge of how this magnetisation density is distributed. Here, polarised neutron diffraction techniques (p. 6) provide the most significant results.

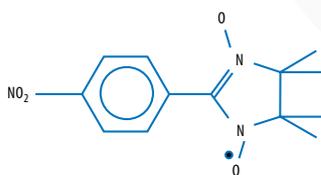
## Organic magnets

The first materials investigated in this way were organic molecules containing a nitrogen-oxygen single bond carrying an unpaired electron – a nitroxide radical (to be magnetic, molecules must have unpaired electrons). Normally, radicals are very reactive, as the unpaired electron tries to seek a mate to form a stable chemical bond, but the radical can be stabilised by protecting the nitroxide bond with surrounding bulky groups of atoms. The first genuine ferromagnet made, with no metal atoms, is shown in figure 1 – although it was magnetic only below 0.6K. It contains a six-membered carbon ring (a benzene ring) attached to a nitrogen with attendant two oxygens (a nitro group). Polarised neutron studies showed that the unpaired spin density is not limited to the nitroxide bonds but actually spreads through the benzene ring to the nitro group. The nitro group of one molecule can then couple ferromagnetically with the nitroxide group of a neighbouring molecule. This arrangement is shown in figure 2. The measured spin density confirms this and agrees well with theoretical predictions.

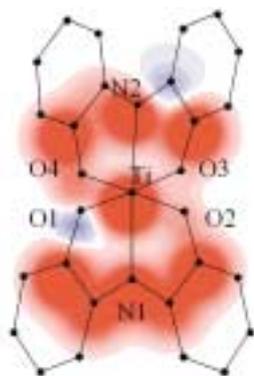
Another fascinating class of magnetic molecules contain metal ions bound to flat, ringed organic structures called semiquinones, which again have an

unpaired electron. When bound to a nonmagnetic titanium ion ( $Ti^{4+}$ ), they generate moderately strong ferromagnetic coupling. Figure 2 shows a beautiful example, with two semiquinone-based structures attached to the titanium so that their planes are perpendicular to each other. The unpaired electrons responsible for the magnetism are smeared out in orbitals above and below the rings. We still do not understand how they couple ferromagnetically: the smeared-out orbitals could overlap directly; or the unpaired electrons could couple through the intervening orbitals of the metal ion. Polarised neutron data suggest that the latter is the case, as unpaired spin density is observed on the titanium atom.

Clusters of metal atoms bound in a molecular framework to create ‘single molecule magnets’ have also generated enormous interest. As described on p.6, the magnetic spins of the metal atoms can combine in complex ways. One of the first single molecule magnets discovered was a cluster of eight iron ions bridged by oxide and hydroxide ions – basically a fleck of rust enclosed in a flower-like organic structure. Magnetic measurements showed that the total spin of the molecule is 10. This suggests that since each iron atom has five unpaired electrons (spin 1/2 each, so total 5/2), six iron atoms must have their spins up (spin 15) and two must have their spins down (spin 5). Polarised neutron analysis of the magnetisation density as in figure 3 confirms this arrangement. ■

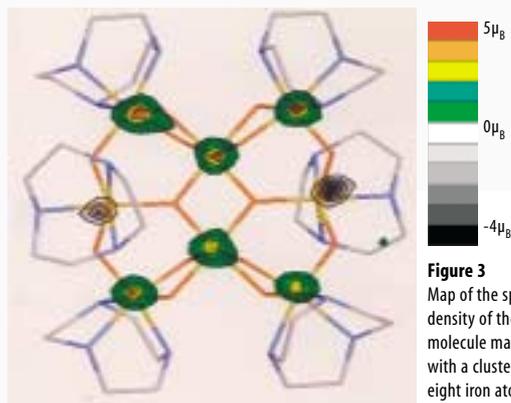


**Figure 1**  
A nitroxide-based organic magnet



**Figure 2**  
Map of the spin density of a titanium semiquinone radical-ion

KEY  
Red: positive spin density  
Blue: negative spin density



**Figure 3**  
Map of the spin density of the single molecule magnet with a cluster of eight iron atoms