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Powder Neutron Diffraction in an Applied Magnetic Field: A Novel Tool for Transition Metal Chemistry

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We report a new, simple type of powder neutron diffraction experiment which gives the size, direction, and location of spin moments in the ground state of the relatively complex transition metal cluster compound $[Mn_{12}O_{12}(CD_3COO)_{16}(D_2O)_4]\cdot 2CD_3COOD.4D_2O$, **1**. Spin density is seen not only on the manganese sites but also on the bridging ligands.

The study of the three dimensional distribution of the magnetization, using polarized neutron diffraction (PND), has provided very detailed accounts of some systems, giving insight, for instance, into covalence and magnetic exchange pathways.[1] This experiment is, however, time-consuming and generally requires large single crystals, although powder PND experiments have occasionally been performed.[2] PND also requires an accurate, neutron diffraction, crystal nuclear structure.

A simpler experimental method for examining the spatial arrangement of magnetization in a molecule is to measure the difference between the neutron diffraction patterns from a paramagnetic powder with and without a strong magnetic field present. The resultant difference pattern should be due almost entirely to magnetic scattering. This simple concept has not been implemented before because no suitable equipment has been available. The IRIS facility, at the ISIS spallation neutron source, Rutherford Appleton Laboratory, Chilton, U.K., is probably unique in that a cryomagnet can be installed on a high-resolution neutron powder diffractometer that has good neutron flux and is suitable for the observation of large *d*-spacings. This opens up the possibility of obtaining a set of magnetic diffraction intensities from a strongly magnetized paramagnetic complex in less than 24 h.

Experiments at zero magnetic field on powdered materials with spontaneous magnetic order are common. They show the utility of neutron diffraction from materials such as anitiferromagnets in determining relative magnetization orientations *between* molecules.[3] However, it is our aim to investigate details of the magnetization distribution *within* a molecule, and any spontaneous magnetic ordering only complicates the interpretation (other than for the very rare, simple ferromagnetic case).

As a first trial of the technique we considered transition metal cluster compounds because they are an area of active general interest. Other applications are in hand. PND is generally not helpful in cluster chemistry, because large crystals are generally unavailable, and chemists would like information on the magnetization distribution in many molecules whose ground states are often poorly defined by existing experimental data. An example is the Mn_8Fe_4 cluster complex isomorphous to **1**.[6] **1** was chosen for our initial study because it is an exception in that X-ray diffraction, EPR, bulk magnetic susceptibility and magnetization, and inelastic neutron scattering experiments convincingly define a model for the magnetic ground state of the crystal.[7] Thus this material can provide a proving experiment on a material close in kind to a large area of potential use for this technique. There are 44 unique atoms in the unit cell, with three independent manganese sites and a molecular volume of 1858 Å^3.[8] The molecule has 4-fold symmetry with four Mn(IV) and eight Mn(III) sites which are linked into an Mn_{12} cluster by bridging oxo and carboxylate ligands. The ground state is $M_s = \pm 10$ with g *ca.* 1.9, in which all eight Mn(III) spin moments have been modeled with moments aligned parallel to

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(1) Recent examples are: (a) Best, S. P.; Figgis, B. N.; Forsyth, J. B.; Reynolds, P. A.; Tregenna-Piggott, P. L. W. *Inorg. Chem.*, in press. (b) Ressouche, E.; Boucherle, J.-X.; Gillon, B.; Rey, P.; Schweizer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3610; (c) Figgis, B. N.; Reynolds, P. A.; Cable, J. W. *J. Chem. Phys.* **1993**, *98*, 7743.

(2) (a) Herren, F.; Ludi, A.; Gudel, H. U.; Givord, D.; Day, P. *Helv. Chim. Acta* **1980**, *63*, 148; (b) Ritter, C. *J. Phys.: Condensed Matter* **1989**, *1*, 2765.

(3) (a) Byrne, J. *Neutrons, Nuclei and Matter*; Institute of Physics: Bristol, U.K., 1994. (b) *Chemical Crystallography with Pulsed Neutrons and Synchrotron X-rays;* Carrondo, M. A., Jeffrey, G. A., Eds.; NATO ASI Series, Riedel: Dordrecht, The Netherlands, 1987.

(4) These crystals are magnetically anisotropic so an initial zero-field pattern was taken, the field then raised to 3.0 T twice, and a second pattern taken. This and further patterns taken at intervals enable us to determine the extent of crystallite realignment in the magnetic field.

(5) Reynolds, P. A.; Fullagar, W. K.; White, J. W.; Cookson, D. Unpublished results.

(6) Schake, A. R.; Tsai, H. L.; Webb, R. J.; Folting, K.; Christou, G.; Hendrickson, D. N. *Inorg. Chem.* **1994**, *33*, 6020.

(7) (a) Caneschi, A.; Gatteschi, D.; Sessoli, R.; Barra, A. L.; Brunel, L. C.; Guillot, M. *J. Am. Chem. Soc.* **1991**, *113*, 5873; (b) Hennion, M.; Mirebeau, I.; Sessoli, R.; Caneschi, A. Presented at the International Conference on Neutron Scattering, Sendai, Japan, 1994; paper P-3-B-51; (c) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. *Nature* **1993**, *365*, 141.

(8) Lis, T. *Acta Crystallogr.* **1980**, *B36*, 2042.

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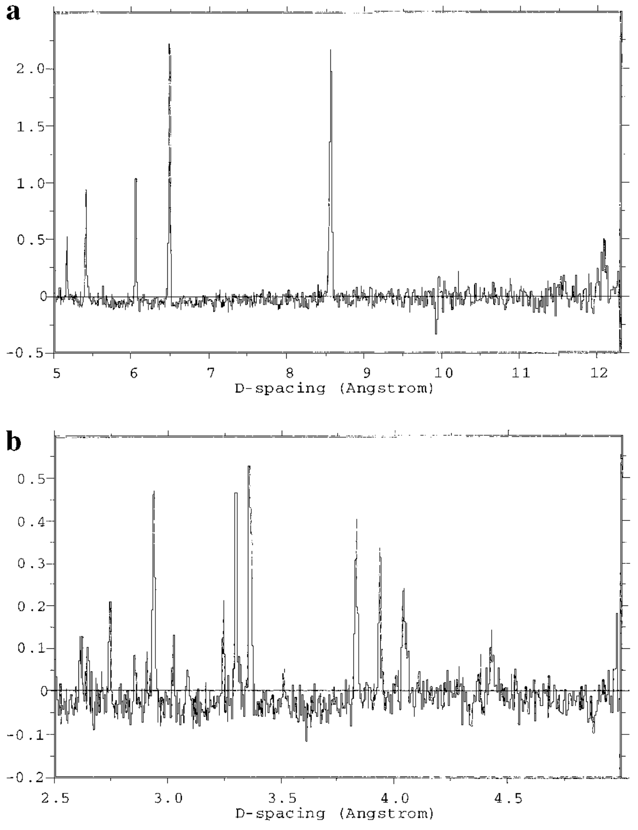

Figure 1. Difference between the neutron diffraction patterns from **1** at 1.5 and 0 Tesla: (a) *d*-spacing from 5 to 12.3 Å; (b) *d*-spacing from 2.5 to 5 Å.

the crystal *c* axis and the four Mn(IV) moments aligned antiparallel. The first excited state lies higher by ca. 10 cm^{-1}.

We obtained several 8 h diffraction patterns on IRIS at applied magnetic fields of 0 (several times, alternate runs), 1.5, 3, and 5 T, using a 4 *g* sample of a powder of **1** at 4 K.[4] An X-ray powder pattern from this sample was obtained at the ANBF beamline on the Photon Factory synchrotron at Tsukuba, Japan, which confirmed the identity and purity of the compound.[5]

The difference between the zero-field, nuclear, diffraction pattern and the pattern at 1.5 T is shown in Figure 1 down to a *d*-spacing of 2.5 Å. The difference pattern has only positive peaks, and it has a different intensity distribution from the nuclear-only pattern. This is a strong indication that the difference pattern consists of peaks due to magnetic scattering. From this difference pattern we find, by peak fitting, significant magnetic scattering intensities for 38 separate, resolved Bragg peaks with a best $\sigma(I_{obs})/I_{obs}$ of 0.03.

We have fitted the observed magnetic diffraction intensities at 1.5 T using a modification of the program ASRED,[9] which calculates magnetic structure factors for a series of single crystal orientations and, from these, produces powder-averaged magnetic intensities using a Dollase−March preferred orientation parameter.[10] We model the magnetization density in the cluster as a set of spherical densities located on various atom sites with coordinates estimated from ref 5. We have used the 3d radial extent on the Mn(IV) site (Mn(1) in crystal structure) and the two independent Mn(III) sites (Mn(2) and Mn(3)). We also used the 2p extent on bridging oxo and carboxylate ligand atoms. Approximate molecular symmetry and the limited experimental resolution allows us to reduce the bridging populations to only four independent parameters: three for the carboxylate (labeled C(1)OO etc.) and one for the oxo units O(2) and O(3). The O(1) and ligated water sites are not clearly separated from the Mn site at this resolution.

The *R* factors of the fit are high ($R(I) = 0.34$ and $R_w(I) = 0.12$[11]) as a result of the amplification of the relative errors by the subtraction process. However, we obtain a χ^2 value of 1.3. We have not corrected for a number of possible sources of systematic error, such as absorption. Refinements using the 3 and 5 T runs do not differ significantly from the 1.5 T data, apart from a slight increase in the orientation parameter. For most crystal orientations the magnetization is saturated at 1.5 T. In agreement with previous theory, the Mn(IV) site has a moment of −2.2(3) spins opposed to and less than those of the two Mn(III) sites of 4.0(4) and 4.0(2). The directions of the moments on these sites are closely tied to the crystal *c* axis. This is clearly shown by the observation of zero magnetic intensities for the 002 and 004 reflections. This is an Ising-like arrangement. An isotropic Heisenberg Mn−Mn coupling Hamiltonian gives $\chi^2 = 3.2$, which represents a very significant degradation in fit. This shows that the technique can usefully differentiate between possible model Hamiltonians.

These data also clearly show that a model of coupled Mn−Mn ions is inadequate. The metal site populations, 2.2 for Mn(IV) and 4.0 for Mn(III), are much larger than values expected for the octahedrally coordinated ions, of 1.5 and 2.0 spins respectively. There is a substantial, generally negative, spin density on the bridging ligands. We obtain O(2) = O(3) = −1.0(2), C(1)OO = −0.5(8), C(3)OO = 2.0(5), and C(5)OO = C(7)OO = −1.4(2). These values are significant: if we constrain the spin to Mn sites only, we obtain $\chi^2 = 2.2$. This augmentation of spin differences within the molecule is traditionally described as resulting from “spin polarization” and is a manifestation of electron−electron correlation effects. However, we have suggested that in the approximation of unrestricted Hartree−Fock theory this augmentation may be more transparently associated with greater covalence in the minority-spin than in the majority-spin molecular orbitals. We have called the effect “differential covalence”.[12]

We conclude that this type of powder neutron diffraction experiment can rapidly give useful information about the spin distribution in quite large paramagnetic molecules where knowledge of the crystal structure is incomplete. This may be of interest to chemists as a semiroutine technique when bulk magnetization measurements are inconclusive. However, the limited number and accuracy of reflection intensities mean that it cannot provide the fine detail that is available from a single-crystal PND experiment, particularly, the shape of the spin density at the individual centers.

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Supporting Information Available: List of observed and calculated magnetic diffraction intensities from the 1.5 T data and figures showing total diffraction patterns at 0 and 1.5 Tesla (3 pages). Ordering information is given on any current masthead page.

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