# Experimental spin density in the high spin ground state of the Fe$_8$pcl cluster

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## Abstract

The induced spin density was determined by polarised neutron diffraction in the $S = 10$ ground state of [(tacn)$_6$Fe$_8$O$_2$(OH)$_{12}$]Br$_{4.3}$-(ClO$_4$)$_{3.7}$ · 6H$_2$O, Fe$_8$pcl, which differently from the bromide analogous, Fe$_8$Br$_8$, presents a centre of symmetry. The relative spin arrangement is in agreement with the model proposed from classical magnetic measurements and with the previous spin density study in the noncentrosymmetrical Fe$_8$Br$_8$ compound. The experimental spin populations on the iron atoms are in good quantitative agreement with calculations using exact diagonalisation of the exchange Hamiltonian with experimental $J$ values obtained from magnetic susceptibility measurements on Fe$_8$Br$_8$. This determination confirms that the spin density determination provides a valuable evaluation of the relative strengths (and sign) of the intracluster magnetic interactions and that the dissymmetry observed on the spin populations in the Fe$_8$Br$_8$ compound with respect to quasi-D$_2$ symmetry of the molecular frame was an artefact due to the data refinement method for non centrosymmetrical structures.
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## 1. Introduction

Magnetic molecular clusters formed by a relatively large number of strongly interacting transition metal ions and characterised by a large Ising type magnetic anisotropy, constitute the so-called single molecule magnets [1]. Since the nanometric size of the clusters is intermediate between simple paramagnetic molecules and a bulk material, they present coexistence of both quantum and classical magnetic behaviours.

The Fe$_8$Br$_8$ cluster, {[(tacn)$_6$Fe$_8$O$_2$(OH)$_{12}$]Br$_7$ · H$_2$O}-[Br · 8H$_2$O], (with tacn = 1,4,7-triazacyclononane) [2], has attracted special attention in recent years as displaying pure quantum tunnelling of the magnetisation [3]. Another interesting feature is the strong magnetic anisotropy of the cluster, although each Fe$^{III}$ ion ($S = 5/2$) is individually isotropic. The structure of the cluster consists of eight Fe$^{III}$ ions linked by oxo and hydroxo bridges. The four central iron(III) lie on a plane and are bridged by two μ$_3$-oxo groups to give a well known butterfly topology observed in other tetranuclear clusters [4]. The other four iron(III) centres are connected to the central ions by 12 μ$_2$-hydroxo groups. A model with six spin up and two spin down iron ions was proposed to describe the spin configuration of the magnetic ground state $S = 10$, resulting from the competition

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between various intra-cluster antiferromagnetic interactions [5]. In order to determine without any ambiguity the distribution of the spins in the ground state, the magnetisation density was determined by polarised neutron diffraction in the $Fe_8Br_8$ cluster, which crystallises in the acentric space group $P1$ [6]. The magnetisation density map, reconstructed by the Maximum of Entropy method applied to noncentrosymmetric structures [7], confirmed that six ions carry spins parallel to the applied field, which are the two body ions of the butterfly configuration and the four peripheral ions, while the ions of the middle of the wings carry opposite spins. However, the spin density map strongly deviates from the $D_2$ symmetry which can be assumed from the molecular framework of the central iron oxide core: indeed the spin populations on Fe1′ [4.79(22) $\mu_B$] and Fe2′ [2.34(26) $\mu_B$] are very different as well as the populations on Fe3′ [−1.94(31) $\mu_B$] and Fe4′ [−4.91(32) $\mu_B$] (for the metal ions labelling see Fig. 1).

In order to check if the asymmetry of the spin distribution in $Fe_8Br_8$ is significant or only due to an artefact related to the particular case of a noncentric space group, the magnetisation density in the $Fe_8$ core was determined on a recently synthetised centrosymmetric derivative of $Fe_8$, $Fe_8$pcl [8]. This cluster of formula [(tacn)$_6$Fe$_8$O$_2$(OH)$_{12}$]Br$_{4.3}$(ClO$_4$)$_{3.7}$·6H$_2$O, presents nearly the same central core as $Fe_8Br_8$, but owns a centre of symmetry, and crystallises in the centrosymmetrical space group $P2_1/c$. The molecular structure of the $Fe_8$ core is represented in Fig. 1. There are four iron sites in the asymmetrical unit: Fe1 on the body of the butterfly, Fe2 at the extremities of the wings and peripheral iron atoms Fe3 and Fe4 connected to the sides of the wings. The magnetic properties of $Fe_8$pcl are very similar to those of $Fe_8Br_8$ with a $S = 10$ spin ground state as well [8].

In this paper, we report the experimental determination of the induced spin density in the cluster [(tacn)$_6$Fe$_8$O$_2$-(OH)$_{12}$]Br$_{4.3}$(ClO$_4$)$_{3.7}$·6H$_2$O in the spin ground state at 2 K under a magnetic field of 7 T and the comparison with that one previously obtained for the $Fe_8Br_8$ cluster.

## 2. Experimental

### 2.1. Polarised neutron diffraction

The interest of polarised neutron diffraction is that it enables to determine the magnetic structure factors, which are the Fourier components of the magnetisation density, even in the case of very weak magnetism. The magnetic structure factors are vectorial quantities. Assuming that the spin density can be written as a sum of atomic spin densities localised on the atoms characterised by a magnetic form factor $f_m^i(\mathbf{K})$, the magnetic structure factors can be expressed as a sum over the atoms $i$ in the cell:

$$\vec{F}_M(\mathbf{K}) = \Sigma_i \vec{m}_i f_m^i(\mathbf{K}) e^{i\vec{K}\vec{r}_i} \tag{1}$$

where $\vec{m}_i$ is the induced moment on atom $i$.

In the case of a centric space group, the expression of the flipping ratio for a Bragg reflection with scattering vector $\mathbf{K}$, is

$$R(\mathbf{K}) = \frac{F_N^2 + 2F_N F_M^{\perp z} + F_M^{\perp 2}}{F_N^2 - 2F_N F_M^{\perp z} + F_M^{\perp 2}} \tag{2}$$

where $F_N$ is the nuclear structure factor, $F_M$ is the magnetic structure factor, $F_M^\perp$ its component perpendicular to the scattering vector and $F_M^{\perp z}$ is the component of $F_M^\perp$ along the $z$ direction (i.e. parallel to the magnetic field and to the neutron polarisation direction).

This expression is valid only if the induced moments $\vec{m}_i$ on atoms in different crystallographic sites are collinear [9]. This is not the case for the $Fe_8$pcl compound which exhibits a large magnetic anisotropy [8]. The unit cell contains two cluster molecules, A and B, which are not parallel to each other as shown by the view of the crystallographic cell along the $a$ direction in Fig. 2. The directions of local anisotropy of each of the two clusters in the unit cell can be obtained by assuming the principal axes of the anisotropy tensor with respect to the central core are the same as those accurately determined by single crystals HF-EPR measurements for the $Fe_8Br_8$ cluster [10]. The angle between the easy axes of clusters A and B is about 58° while the two intermediate axes are almost perpendicular to each other. Therefore, the induced moments on the two cluster molecules in the cell are not collinear in a general case and the components of the magnetic moments induced along the magnetic field are not necessarily equal.
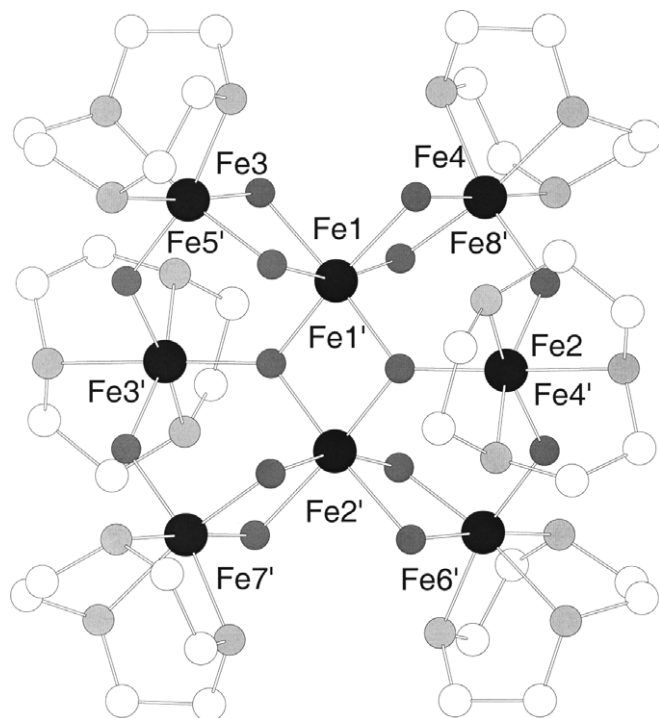


Fig. 1. Molecular structure of the central core [(tacn)$_6$Fe$_8$O$_2$(OH)$_{12}$]$^{8+}$ in $Fe_8$pcl. Iron ions are in black, oxygen in medium grey, nitrogen in light grey, carbon in white. The labelling scheme (Fe1′–Fe8′) for $Fe_8Br_8$ is reported below the labelling scheme for $Fe_8$pcl (Fe1–Fe4).