Characterisation of a dodecanuclear chromium(III) cage with an $S = 6$ ground state

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Neutron diffraction, magnetic susceptibility and EPR spectroscopic studies of a dodecanuclear chromium cage are reported which show the molecule has an $S = 6$ spin ground state; this is the highest spin ground state known for a cage of this metal.

Research on high nuclearity paramagnetic cages has recently led to the discovery of single molecule magnets,[1–4] *i.e.* complexes which show hysteresis in magnetisation *versus* external field response which is of a molecular origin. The initial discovery was in a dodecanuclear mixed-valent manganese(III)/(IV) cage stabilised by carboxylate ligands.[1] Our interest in the area led us to examine a report of a mixed valent chromium cage,[5] of formula $[Cr_{12}O_{12}(O_2CBu^t)_{15}]$, where many of the features of the Mn_{12} single molecule magnets are present, at least in principle.

The synthesis is unusual, but straightforward. Reaction of $Cr(NO_3)_3{\cdot}9H_2O$ (0.050 mol) with $K(O_2CBu^t)$ (0.178 mol) in H_2O (500 cm^3) at *ca.* 80 °C gives a blue precipitate (90% yield) which is soluble in several organic solvents. Heating this precipitate at 400 °C under a stream of N_2 for 1 h eliminates HO_2CBu^t, yielding a dark green solid which analyses well for $[Cr_{12}O_{12-x}(OH)_x(O_2CBu^t)_{15}]$; electrospray mass spectrometry† of a CH_2Cl_2–MeOH solution of this solid indicates that the only significant species present in solution is $[Cr_{12}O_{12-x}(OH)_x(O_2CBu^t)_{15}]$. The yield of this compound is 77%. Very large green crystals could be grown by slow evaporation of an *n*-propanol solution of this material.

Initially we performed an X-ray structure determination of these crystals,‡ which revealed a dodecanuclear chromium cage, based on a centred-pentacapped-trigonal prism (Fig. 1). The complex has crystallographic D_3 symmetry, with the central Cr [Cr(1)] at the junction of the C_3 and C_2 axes, the Cr atoms [Cr(2) and symmetry equivalents (s.e.)] capping the triangular faces on the C_3 axis, and the Cr centres [Cr(3) and s.e.] capping the rectangular faces on the C_2 axes of the cage. Only the Cr atoms [Cr(4) and s.e.] at the vertices of the trigonal prism are in general positions. The cage is held together by μ_4-oxides [O(1) and s.e.], which bridge between the central Cr site, and one each of the vertex, triangular face-capping and rectangular face-capping sites; six μ_3-oxygens [O(2) and s.e.], which each bridge between two vertex sites and a cap on a rectangular face, and fifteen O_2CBu^t groups, which each bridge a Cr···Cr vector in a 1,3-bridging mode. Examination of the structure revealed that all Cr sites had similar bond lengths and angles; there was no sign of mixed valency which would lead to a charge imbalance if the apparent formula of $[Cr_{12}O_{12}(O_2CBu^t)_{15}]$ is correct. We therefore examined the alternative explanation, that some of the bridging oxide units were protonated, by performing a single crystal neutron diffraction study.‡

The presence of O_2CBu^t as the carboxylate ligand is not ideal for a neutron study, especially as all the methyl groups are disordered. However, the study unambiguously shows the presence of a half-weight hydrogen atom attached to the μ_3-O-atoms [O(2) and s.e.]. The formula should therefore be corrected to $[Cr_{12}(O)_9(OH)_3(O_2CBu^t)_{15}]$ **1**, and all Cr sites are Cr(III).

The magnetic properties of the cage remain interesting. Susceptibility studies§ reveal a double maxima in the $\chi_M T$ *vs.* T plot (where χ_M is the molar susceptibility) (Fig. 2). The low temperature maximum, at *ca.* 10 K, has a value of 21.6 cm^3 K mol^{-1}, consistent with an $S = 6$ ground state (χ_M calculated for $g = 1.99$ is 20.8 cm^3 K mol^{-1}), and the presence of the higher temperature maximum suggests a complicated ordering of the higher energy spin states. The complexity of the structure makes modelling this behaviour difficult, however further characterisation of the spin ground state comes from multifrequency EPR studies. At low temperature, and all frequencies studied (24, 34, 90, 180 GHz), a complex multiplet is observed (Fig. 3). The 90 GHz spectrum in Fig. 3(b) can be simulated¶ with the spin-Hamiltonian parameters: $S = 6$, $g_{zz} = 1.965$, $g_{xx} = g_{yy} = 1.960$, $D = +0.088$ cm^{-1}, $E = 0$ (where D and E are the axial and rhombic zero-field splitting parameters respectively) [Fig. 3(c)]. Simulations with other values for S result in significantly poorer fits with the experimental spectra. It is unusual to

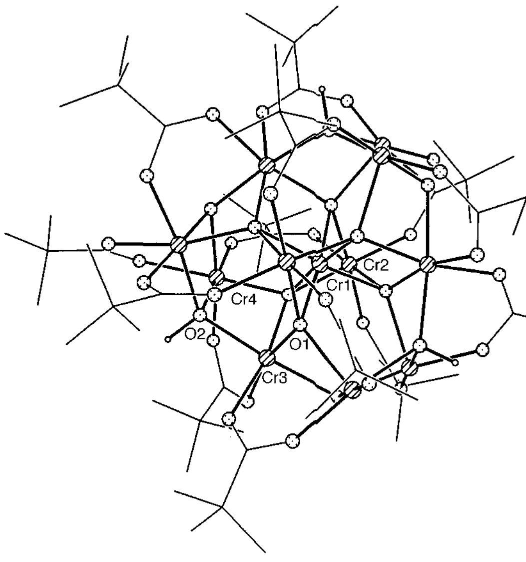

Fig. 1 The structure of **1**. Bond lengths (Å): Cr(1)–O(1) 1.980, Cr(2)–O(1) 1.994, Cr(2)–O(1B) 1.982, Cr(3)–O(1) 2.022, Cr(3)–O(2) 1.971, Cr(3)–O(1C) 1.988, Cr(4)–O(1) 1.987, Cr(4)–O(2) 1.971–1.978, Cr(4)–O(carboxylate) 1.93–1.959 (av. esd. 0.003). Bond angle (°) ranges: *cis* at Cr(1) 81.46–102.4, *trans* at Cr(1) 174.38, *cis* at Cr(2) 80.77–99.14, *trans* at Cr(2) 176.78, *cis* at Cr(3) 76.96–98.94, *trans* at Cr(3) 167.47–174.2, *cis* at Cr(4) 78.5–102.75, *trans* at Cr(4) 165.3–179.39 (av. esd. 0.7). (Cr atoms, shaded; O atoms, regular dots; C atoms shown as lines).

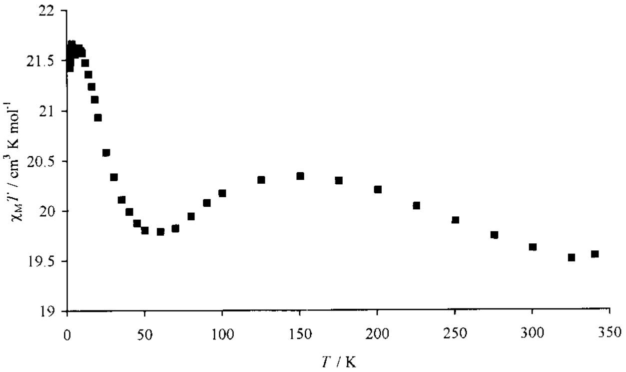

Fig. 2 Plot of $\chi_M T$ *vs.* T for **1**, measured with a 1000 G field.

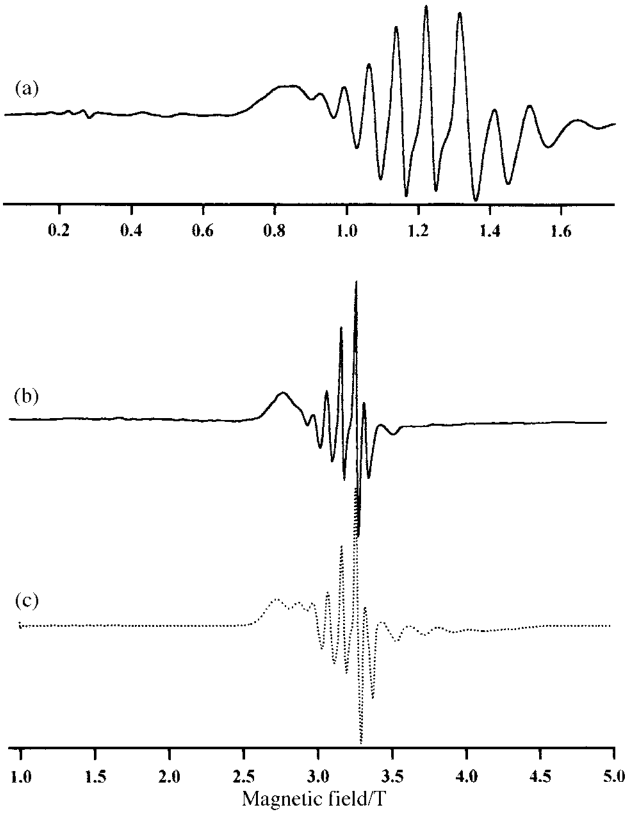

Fig. 3 EPR spectra of a powdered sample of **1** at (a) 34.11 GHz and 10 K, (b) 89.21 GHz and 5 K, (c) simulation of the 89.21 GHz spectrum using parameters given in the text.

observe such detail in spectra of high spin state cages.[9] The sign of D was determined by examining depopulation effects in spectra recorded at 180 GHz, between 20 and 2.8 K.

The cage is therefore the highest spin Cr cage known. Unfortunately the sign of D indicates that it will not be a single molecule magnet. Further studies of the cage will include a polarised neutron study which we hope will give the spin structure of the ground state of the cage directly.

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Notes and references

† Electrospray mass spectra were obtained on a Finnegan LCQ spectrometer with the sample dissolved in CH_2Cl_2 which was added to MeOH prior to injection into the spectrometer.

‡ *Crystal data* for $C_{75}H_{138}Cr_{12}O_{42}\cdot 4.5H_2O\cdot C_3H_8O$ **1**: rhombohedral, space group $R32$, a = 18.3867(11), c = 36.034(6) Å, V = 10550(2) Å^3, M = 2477.0, Z = 3 (the molecule lies on a 32 site), T = 150.0(2) K, $R1$ = 0.0649. Data collection, structure solution and refinement were performed using programs DIRDIF[6] and SHELXL-97.[7] Neutron data were collected at 150 ± 1 K on the SXD instrument at the ISIS spallation neutron source using the time-of-flight Laue diffraction method.[8] The intensities of 5093 observed reflections were extracted and reduced to structure factors using standard SXD procedures,[8] which gave a merged data set comprising 1048 unique reflections. CCDC 182/1183.

§ Variable-temperature magnetic measurements on **1** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules. A diamagnetic correction for the sample holder was applied to the data.

¶ The simulation requires the line-width of the $2S$ allowed transitions to vary with the M_s states according to a power series $\Delta B = A + BM_s + CM_s^2$. The spectra were fitted with A = 400 G for z and 270 G for xy lines, B = 0 and C = 50 G.

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