COMMUNICATION

Structural, magnetic and DFT studies of a hydroxide-bridged {Cr8} wheel

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Structural, magnetic and theoretical studies of an octanuclear chromium(III) wheel are reported, containing hydroxide and pivalate bridges.

There is much interest in the literature in the synthesis and properties of wheels of 3d-metals as possible models for infinite chain systems,[1] and some suggestions that related compounds could be used as Qubits for quantum computing.[2] There are several examples of wheels with chromium.[3] One such compound is $[CrF(O_2CCMe_3)_2]_8$ **1**.[3a,b] Here we report the hydroxide analogue of this molecule and compare the magnetic properties of the two.

$[Cr(OH)(O_2CCMe_3)_2]_8$ **2** is synthesised by heating a solution of chromium nitrate (28 mmol) in water (50 ml) with sodium pivalate (58 mmol) at 40 °C. Subsequent filtration and dissolution in MeCN–diethyl ether solutions give a purple microcrystalline solid which analyses well† for **2**·4H$_2$O. Deep purple crystals suitable for X-ray diffraction were obtained by vapour diffusion of MeCN into toluene with a yield of crystals of 5%.

Diffraction studies‡ shows the compound crystallises with one molecule in the asymmetric unit, and with a regular octagonal structure with the bridging OH pointing into the centre of the ring (Fig. 1). The pivalate moieties are arranged in two conformations, firstly in a plane about the edge of the ring and secondly in an alternating fashion above and below the ring. The Cr–O distances in the wheel are unexceptional. The other hydroxide bridged {Cr8} wheels are $[Cr(OH)(O_2CPh)_2]_8$, which was made in very low yield *via* heating a chromium triangle,[3c] and a similar structure with chlorobenzoate which co-crystallises with a Cr triangle.[5] We can also make this

benzoate bridged ring reliably by the route described here, which suggests that the pyrolysis step described previously[3c] was unnecessary.

The ES-MS of **2** in acetone gave a signal at *m/z* 2204, probably due to the molecular ion plus one H$_2$O and one sodium. The UV-vis spectra of both **1** and **2** in diethyl ether show three bands, a charge transfer band at 217 nm, and two d–d transitions at 409 and 570 nm for **2** and at 426 and 610 nm for **1**. The result of this difference is that **1** is deep green while **2** is deep purple.

The magnetic susceptibility, χ_m, of **2** has been studied from 2 to 320 K (Fig. 2).§ There is a steady decrease in $\chi_m T$ as the temperature falls, demonstrating that the coupling between Cr(III) centres is antiferromagnetic and the ground state is $S = 0$. The room-temperature value of $\chi_m T$ (13.7 cm^3 K mol^{-1}) is a little below the value calculated for eight $S = 3/2$ centres and $g = 1.99$ (calc. 14.9 cm^3 K mol^{-1}).
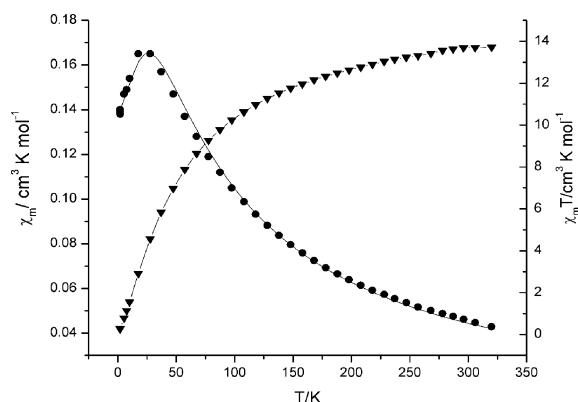

Fig. 2 Plot of χ_m and $\chi_m T$ *vs. T* for **2**. Circles: measured χ_m; triangles, measured $\chi_m T$; solid line: fit as described in text.

The coupling constant (J) for the Cr–Cr magnetic interaction was found by treating the wheel as an infinite chain using the Fisher approximation (eqn. (1)):[6]

$$\chi_m = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{1+u}{1-u} \qquad (1)$$

where $u = \coth[JS(S+1)/kT] - [kT/JS(S+1)]$.

This gave a value for J as -10.1 cm^{-1} (Fig. 2). This value for J is comparable with literature values for similar compounds.[3c,e]

Previous work[7] has shown that DFT calculations using the hybrid B3LYP functional with Ahlrich's TZV basis set implemented on Gaussian 98/03,[8] provides good estimates of magnetic exchange. We have therefore used this technique to compare the exchange in **1** and **2**.

Dinuclear model complexes of **1** and **2**, and variants, have been used to calculate exchange coupling constants, with water added as a terminal ligand (Table 1). The computational
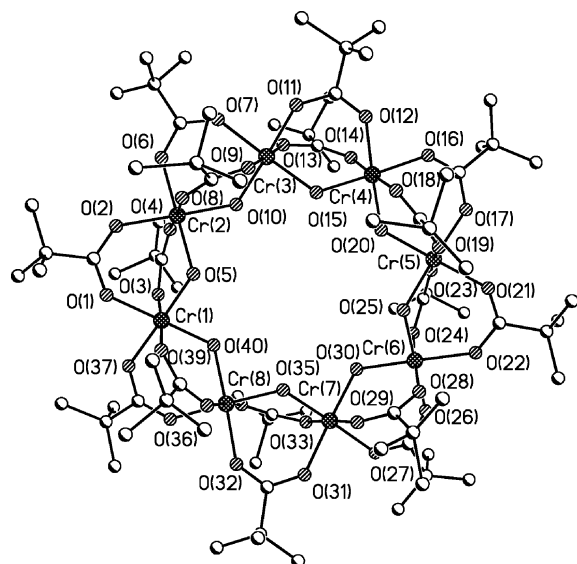

Fig. 1 Structure of **2**. Bond length ranges (Å): Cr–O (piv) 1.952–1.985, Cr–O (hydroxide) 1.932–1.953. Bond angle ranges (°): *cis* at Cr 86.1–94.0, *trans* at Cr 176.1–179.5°. Av. esds: 0.007 Å, 0.3°.

Table 1 DFT calculated coupling constants for different model complexes.

Model		J/cm^{-1}
A	$[Cr_2(OH)(O_2CCMe_3)_2(H_2O)_6]^{3+}$	-22
B	$[Cr_2F(O_2CCMe_3)_2(H_2O)_6]^{3+}$	-13
C	$[Cr_2O(O_2CCMe_3)_2(H_2O)_6]^{2+}$	$+9$
D	$[Cr_2(OH)(O_2CMe)_2(H_2O)_6]^{3+}$	-24
E	$[Cr_2(OH)(H_2O)_8]^{5+}$	-11

approach is based on the work of Alvarez and co-workers,[9] and the conclusions broadly support those of published correlations in dinuclear Cr(III) complexes.[10] The calculation of J predicts the correct sign for model **A** compared to the experimental value, however there is a discrepancy between the absolute values (-10 *vs.* -22 cm^{-1}). Replacement of the OH bridge by F, (**B**), changes J to -13 cm^{-1}, while deprotonation to give oxide (**C**) gives a ferromagnetic exchange if the Cr–O bond length were unchanged. Varying the substituents on the bridging carboxylate has no significant influence on J (*e.g.* compare **A** and **D**). Replacing the carboxylate with water (**E**) makes the exchange less antiferromagnetic. This suggests that the super-exchange paths through hydroxide and carboxylate are both anti-ferromagnetic.

The disagreement between the measured value for **2** and model **A** implies that a numerical estimate of J requires a calculation performed on the full structure. This may be because the models assume one exchange interaction at each Cr centre, while the structure has two interactions at each site around the wheel. As evidence for this argument, Lippard and co-workers have reported a dimer, $[Cr_2(OH)(O_2CH)_2(H_2O)_6]^{3+}$, with an exchange of -22.4 cm^{-1}.[11]

The calculations predict that deprotonation of the hydroxide would give a ferromagnetic exchange interaction. This is not seen experimentally for Cr(III) dimers.[12] Therefore the orbitals that contribute to superexchange through the oxide/hydroxide bridge have been examined in more detail to explain the discrepancy. For a $\{Cr_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2\}$ core the magnetic exchange is a direct competition between two paths: (**a**) ($d_{yz}|p|d_{yz}$) and (**b**) ($d_{z^2}|p|d_{xz}$). The former favours antiferromagnetic exchange while the latter (the so called "crossed pathway") contributes to the ferromagnetic component; π–π interactions are more significant than σ–σ in this case.[13]

The interaction (**b**) is the more sensitive to the nature of the O-bridge. Protonation of the oxide should reduce the spin density, and hence weaken (**b**). However (**b**) is also sensitive to the Cr–O distance. For $\{Cr_2(\mu\text{-}O)(\mu\text{-}O_2CR)_2\}$ the Cr–O bond is usually around 1.85 Å; protonation leads to the distance increasing to *ca.* 1.94 Å. Chemically we cannot separate the influence of bond lengthening from addition of a proton. However we can calculate the relative influence using DFT. In model **A** the Cr–O(hydroxide) distance was set as 1.94 Å (from **2**) and gives a weak antiferromagnetic interaction; if we do the same calculation (model **C**) for Cr–O(oxide) without altering the Cr–O distance the interaction is weakly ferromagnetic. The broken-symmetry DFT calculations enable the spin densities on the "O" centre to be calculated for both the $S = 0$ and $S = 3$ states. For **A** the value is -0.006 for both spin states (assuming positive spin density at Cr for the high spin state). For **C** the values are -0.013 and 0.054, respectively. The small and negative spin density on the hydroxide bridge weakens the ferromagnetic interaction (**b**); thus (**a**) is dominant and **A** (and **2**) show antiferromagnetic exchange. The positive spin density on the oxide group in the high-spin form of **C** supports spin delocalisation being the dominant mechanism for exchange rather than spin polarisation.

DFT calculations are valuable in investigating the mechanism for exchange interactions. A common practice is for fragments to be extracted from a large structure to speed calculation. The observation here is that while this does not invalidate trends calculated, it might change absolute values.

Acknowledgements

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† Anal. Calc. (found) for $C_{80}H_{152}O_{40}Cr_8$: C 44.3 (43.0), H 7.1 (7.3)%.

‡ Crystal data for $C_{80}H_{152}O_{40}Cr_8$: monoclinic, space group $P2_1/c$, $a = 25.081(4)$, $b = 17.012(3)$, $c = 30.995(5)$ Å, $\beta = 109.617(3)°$, $V = 12458(4)$ Å^3, $M = 2170$, $Z = 4$, $\lambda = 0.71073$ Å, $\mu = 0.738$ mm^{-1}, $T = 293(2)$ K, reflections used = 25455 ($R_{int} = 0.1152$), $R1 = 0.0839$ (for 9817 data with $I > 2\sigma(I)$).

Data collection, structure solution and refinement used SHELXTL.[4] Full details have been deposited and will be published later. CCDC reference number 233922. See http://www.rsc.org/suppdata/dt/b4/b404031g/ for crystallographic data in CIF or other electronic format.

§ Variable temperature magnetic measurements on **2** in the region 1.8–325 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 100 G field. The data have been adjusted for the diamagnetism of the sample using Pascal's constants.

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