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A novel dodecanuclear chromium(III) cage: structural control by choice of leaving group

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The synthesis and structural characterisation of a novel metal polyhedron is reported, involving chromium(III) and isobutyrate; comparison of this product with those obtained using different carboxylates suggests that the leaving group—which can be carboxylate, water or both—strongly influences the structure found.

Recent research on paramagnetic cages has been stimulated by the discovery of 'single molecule magnetism',[1,4] *i.e.* cages which have an energy barrier to reorientation of their magnetisation which is sufficiently high that at low temperature magnetisation is lost slowly when an external magnetic field is removed. We have been looking at new routes to high nuclearity cages, and found that heating small cages to high temperatures in an inert atmosphere can lead to oligomerisation.[5–7] Here we report a further reaction which gives a quite new metal polyhedron, but also which indicates that choice of carboxylate can control the structure of the resulting cage.

Reaction of $Cr(NO_3)_3 \cdot 9H_2O$ (0.050 mol) with $K(O_2CCHMe_2)$ (0.175 mol) in H_2O (100 cm^3) at *ca.* 80 °C gives a blue precipitate (> 90% yield) which is soluble in Pr^iOH. Analysis of this solid suggests formation of an oxo-centred chromium triangle, $[Cr_3O(O_2CCHMe_2)_6(H_2O)_3](NO_3)$ **1**.† Heating this precipitate at 400 °C under a stream of N_2 for 5 min gives a dark green solid which can be recrystallised from a mixture of $Pr^nOH–CH_2Cl_2$ to give green blocks suitable for X-ray study in 7 days. The yield of crude material is 84%. IR spectroscopy and elemental analysis confirm the crude and recrystallised compounds are identical.

Structural analysis‡ reveals a cage of stoichiometry $[Cr_{12}O_8(OH)_4(O_2CCHMe_2)_{16}(HO_2CCHMe_2)_4]$ **2** (Fig. 1). The cage consists of three face-sharing Cr_4O_4 heterocubanes, with the two terminal cubanes capped by further chromium centres attached to the external μ_4-oxides. The central cubane, containing Cr(3), Cr(4), Cr(5) and Cr(6), is held together exclusively through four μ_4-oxides [O(3), O(4), O(5) and O(6)]. These oxides have an unusual geometry, with one Cr–O–Cr angle *ca.* 164°, and five further Cr–O–Cr angles at between 90 and 101°. Therefore these four-coordinate oxygens have a 'saw-horse' geometry, rather than tetrahedral. This geometry may be found

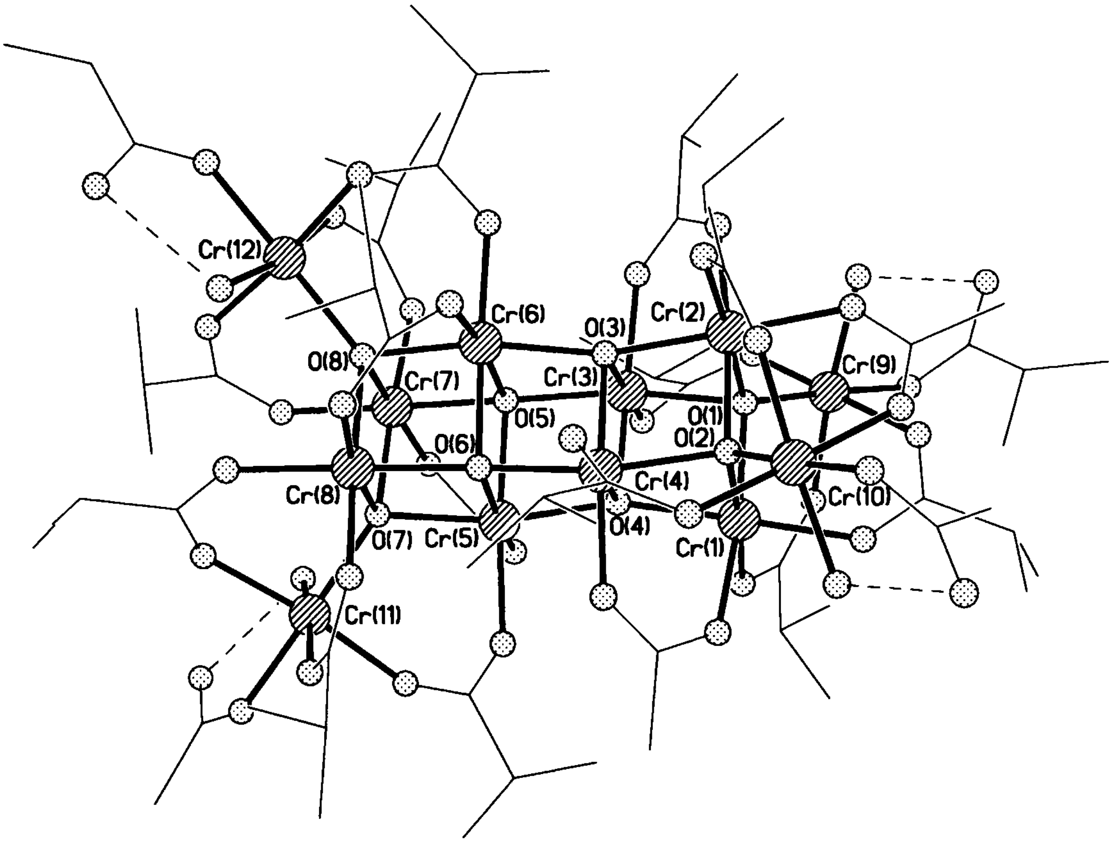

Fig. 1 The structure of **1**. The H-bonds between OH and protonated carboxylates are shown as dashed lines (see text). Bond length ranges: Cr–O(μ_4-O) 1.947–2.050, Cr–O(O_2CR) 1.943–1.997, Cr–O(OH) 1.966–1.986 Å. Av. esd. 0.008 Å. Bond angle ranges: *cis* O(μ_4-O)–Cr–O(μ_4-O) 78.8–89.3, *trans* O(μ_4-O)–Cr–O(μ_4-O) 163.7–166.1, *cis* O(μ_4-O)–Cr–O(O_2CR) 89.1–103.0, *trans* O(μ_4-O)–Cr–O(O_2CR) 169.6–179.2, *cis* O(O_2CR)–Cr–O(O_2CR) 81.7–90.8, *trans* O(O_2CR)–Cr–O(O_2CR) 173.0–173.9, *cis* O(OH)–Cr–O(μ_4-O) 92.6–93.4, *cis* O(OH)–Cr–O(O_2CR) 87.5–91.5, *trans* O(OH)–Cr–O(O_2CR) 170.1–171.4°. Av. esd. 0.4°.

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because this central Cr_8O_8 fragment can be considered to be a fragment of the NaCl structure.

The μ_4-oxides involved in the external heterocubanes have a more regular geometry, approximating to tetrahedral. The two Cr atoms in the face that is shared with the central heterocubane are each bridged to one of the two external Cr atoms [either Cr(1) and Cr(2) or Cr(7) and Cr(8)] by 1,3-bridging carboxylates. The final four Cr atoms [Cr(9), Cr(10), Cr(11) and Cr(12)] are found attached to the μ_4-oxides, and these are each further attached to the centre triple-cubane by bridging carboxylates. Two of these carboxylates bridge to Cr centres at the exterior of the triple-cubane [*e.g.* between Cr(9) and Cr(1)], and one bridges to a Cr centre in the shared-face [*e.g.* between Cr(9) and Cr(5)].

The chromium sites therefore fall into three groups. All are six-coordinate with regular octahedral geometries, but they vary in the groups attached to them. The Cr sites in the central cubane are each bound to four μ_4-oxides and two oxygen donors from carboxylate bridges. The Cr sites at the exterior of the triple-cubane are each bound to three μ_4-oxides and three O-atoms from carboxylates. The Cr sites capping the tricubane are each bound to one μ_4-oxide, three oxygens from bridging carboxylates and two terminal groups that can be described as a hydroxide and a HO_2CCHMe_2 group, or a water molecule and a $^{-}O_2CCHMe_2$. As there is a strong H-bond (O···O 2.47 to 2.53 Å) between these two groups, the exact description is perhaps unimportant.

The structure of **2** is new, but related to previous cages built of cubanes. The nearest relation is an octanuclear triple-cubane of cobalt(III), reported by Christou and coworkers,[10] which lacks the final four capping atoms. Three octanuclear cages, featuring Cr,[6] Fe[11] and Co,[12] contain a heterocubane capped on the μ_4-oxides. **2** combines features from both these previous structural types. There are also some similarities between **2** and Ni_{11} and Mn_{18} cages we have reported previously, which also feature face-sharing heterocubanes.[13]

It appears that the structure of **2** is largely maintained in solution. Two peaks, due to mono- and di-cationic species, dominate the electrospray mass spectrum.§ The mono-cationic species, at *m/z* 2351.4, can be assigned as $(\mathbf{2} - 2\,HO_2CCHMe_2 - 2H_2O)^+$ (calc. 2353.7), while the dication at *m/z* 1160.1 matches $(\mathbf{2} - 2\,HO_2CCHMe_2 - 2OH - 2H_2O)^{2+}$ (calc. 1159.8). Remaining peaks in the spectrum have less than 10% of the intensity of these peaks.

The reaction to form **2** gives quite different cages if the carboxylate present is benzoate[6] or pivalate (trimethylacetate).[7] As the yields are very good (approaching 90%) for all cages, it is worth discussing the difference in these three examples. For benzoate, assuming a stoichiometric reaction, a balanced equation for the reaction at 400 °C would give:

$$8\,[Cr_3O(O_2CPh)_6(H_2O)_2(OH)] \rightarrow 3\,[Cr_8(\mu_4\text{-}O)_4(O_2CPh)_{16}] + 20\,H_2O$$

This implies exclusive loss of water on heating. A balanced equation for the reaction involving pivalate is:

$$4[Cr_3O(O_2CCMe_3)_6(H_2O)_2(OH)] \rightarrow [Cr_{12}(\mu_4\text{-}O)_9(\mu_3\text{-}OH)_3(O_2CCMe_3)_{15}] + 9\,HO_2CCMe_3 + 4H_2O$$

This is mainly loss of carboxylic acid on heating, with some loss of water. The reaction which gives **2**, is intermediate between these two extremes:

$$4[Cr_3O(O_2CCHMe_2)_6(H_2O)_2(OH)] \rightarrow [Cr_{12}(\mu_4\text{-}O)_8(OH)_4(O_2CCHMe_2)_{16}(HO_2CCHMe_2)_4] + 4H_2O + 4HO_2CCHMe_2$$

It is noticeable that for benzoate, which has the lowest pK_a (4.19) of the three carboxylates, water is lost and the carboxylate is retained, while for both pivalate (pK_a 5.03) and isobutyric acid (pK_a 4.84) a mixture of acid and water are lost. This gives us a hypothesis to examine to see if further chromium cages with new metal polyhedra can be made from this simple route. It also implies an unusual means of influencing the structure of a cage by the pK_a of the leaving group.

Magnetic studies of **2** are disappointing.¶ The room temperature value of $\chi_m T$ (where χ_m is the molar magnetic susceptibility) of 18.1 emu K mol^{-1}, is below that expected for 12 non-interacting Cr^{III} centres (22.3 emu K mol^{-1}, for g = 1.99). This value indicates moderately strong antiferromagnetic exchange between metal centres. This is confirmed by the steady fall in $\chi_m T$ down to 25 K, where the value is 7.2 emu K mol^{-1}. Below 25 K the fall is more rapid, and at the lowest temperature studied (1.8 K) the cage is almost diamagnetic.

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Notes and references

† Satisfactory elemental analyses were obtained for all compounds reported.

‡ *Crystal data* for $C_{80}H_{148}Cr_{12}O_{53}\cdot 3.5CH_2Cl_2$. **2**: triclinic, $P\bar{1}$, a = 16.770(5), b = 17.049(6), c = 24.405(9) Å, α = 88.12(3), β = 85.11(3), γ = 69.756(15)°, V = 6523(4) Å^3, M = 2755.15, Z = 2, T = 150.0(2) K, $R1$ = 0.0975. Data collection, structure solution and refinement were performed using programs DIRDIF[8] and SHELXL-97.[9] Only Cr and O atoms were refined anisotropically, and there is a disordered solvent region in the structure. CCDC 182/1559. See http://www.rsc.org/suppdata/cc/b0/b001140l/ for crystallographic files in .cif format.

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

¶ 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. Diamagnetic corrections for sample holders and samples were applied to the data.

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