Turning up the heat: synthesis of octanuclear chromium(III) carboxylates

Ian M. Atkinson,[b] Cristiano Benelli,[c] Mark Murrie,[a] Simon Parsons[a] and Richard E. P. Winpenny*[a]

[a] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*
[b] *School of Molecular Science, James Cook University, Queensland 4811, Australia*
[c] *Department of Chemistry, University of Florence, Via Maragliano 77, 50144 Florence, Italy*

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Two new octanuclear Cr(III) carboxylate complexes are reported illustrating a temperature dependent route to high nuclearity species.

A vast amount of research is currently focused on the investigation of magnetic exchange interactions in polynuclear assemblies and more specifically upon molecules which possess high spin ground states. Although the use of carboxylate ligands has proved a rich source of high nuclearity complexes for both manganese[1] and iron[2] similar studies with chromium(III) carboxylates have thus far been much more restricted. This is probably due to the relative kinetic inertness of Cr(III) and the inherent stability of the low nuclearity complexes—in particular oxo-centred Cr(III) triangles—once formed. Further reaction of $\{Cr_3O\}$ units has so far only produced $\{Cr_4O_2\}$ cores[3] despite the fact that these units can be thought of as building blocks in the formation of larger structures for Mn[1] and Fe.[2] The most significant exception is a report of a dodecanuclear Cr cage with pivalate ligands, formed by heating an ill-defined material of stoichiometry '$[Cr(OH)(O_2CCMe_3)_2]$' under an inert atmosphere.[4] We now report that this reaction is applicable to other carboxylates and other metals, and that the topology of the resulting cages can be controlled by temperature. We also show that electrospray mass spectrometry (ESMS) is an excellent tool for demonstrating nuclearity of such cages in solution.

Reaction of $Cr(NO_3)_3\cdot 9H_2O$ (0.050 mol) with KO_2CPh (0.178 mol) in H_2O (500 cm^3) at *ca.* 80 °C gives a blue precipitate in $>90\%$ yield which has solubility in several organic solvents. ESMS† of this material dissolved in CH_2Cl_2–MeOH indicates a structure based on a typical oxo-centred $\{Cr_3O\}$ unit $[Cr_3O(O_2CPh)_6(H_2O)_2(OH)]$ **1**: *m/z* (% intensity) found (calc.) = 950.7 (67%) (951.7, M$^+$). Higher *m/z* peaks assigned as MeOH adducts with consistent isotopic splitting patterns are also seen. Unfortunately whether **1** is trimeric or contains oligomers of trimers is not certain.

Complex **1** undergoes complicated thermal rearrangements upon heating. Heating **1** at 210 °C *in vacuo* for 2 h caused elimination of H_2O yielding a pale green–blue powder. Extraction with CH_2Cl_2 followed by slow evaporation of the solution over a period of seven months at ambient temperature gave crystals of $[Cr_8(OH)_8(O_2CPh)_{16}]$ **2** (yield *ca.* 15%).‡ The structure of **2** (Fig 1)§ reveals eight octahedrally coordinated Cr atoms linked by eight bridging hydroxides and sixteen 1,3-bridging O_2CPh ligands forming a sixteen membered ring. The hydroxide ligands line the cavity in the centre of the 'wheel' pointing alternately slightly above and below the Cr_8 ring. Eight of the O_2CPh ligands bridge Cr atoms around the outside of the 'wheel' almost in-plane with the wheel, while the remaining eight ligands bridge alternately above and below the ring at an angle of *ca.* 90° forming two hydrophobic pockets.

The wheel may be formed in small amounts from the thermolysis and crystallise slowly, however the ESMS of the crude green–blue powder formed after thermolysis shows the predominant species present to be of similar mass to oxo-centred triangles, but with the MeOH adducts having greater relative intensity compared with **1** than in the spectra prior to heating. The balance of evidence is that heating to 210 °C disrupts the triangular units of **1**, probably by driving off terminally coordinated water, with **2** forming during crystallisation. ESMS of redissolved crystals of **2** did not show any significant peaks due to polynuclear species.

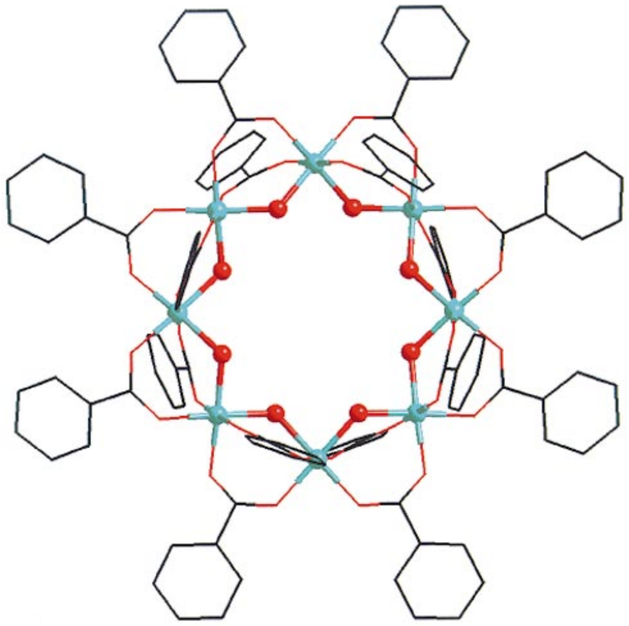

Fig. 1 The structure of **2**. Bond length ranges: Cr–O(benzoate) 1.925–2.002, Cr–O(hydroxide) 1.930–1.969 Å (av. esd 0.013 Å). Bond angle ranges: *cis* at Cr 84.5–95.6, *trans* at Cr 175.2–179.5° (av. esd 0.6°) (Cr, blue; O, red, μ-OH ball, other O atoms line; C, black lines).

Heating **1** at 400 °C under a stream of N_2 for 1 h eliminates more H_2O, yielding a dark green solid. Extraction with CH_2Cl_2 followed by addition of Pr^{n}OH (1 : 3, v/v) gave crystals of $[Cr_8O_4(O_2CPh)_{16}]$ **3** after 7 d in 70% yield.‡ The structure of **3** (Fig. 2)§ shows a distorted $\{Cr_4O_4\}^{4+}$ cubane core where each μ_4-oxide bridges to a further Cr atom creating a larger Cr_4 tetrahedron. The structure can also be considered to be formed from two orthogonal distorted $\{Cr_4O_2\}$ butterfly units and has non-crystallographic T_d symmetry. Twelve of the sixteen O_2CPh ligands link the cubane Cr atoms to the outer Cr atoms while four of the O_2CPh ligands are found in the unusual bidentate bridging mode capping the final two coordination sites on the outer Cr atoms. This coordination leads to the outer Cr sites being considerably more distorted from octahedral geometry than the Cr atoms of the central cubane. The Cr–O bond lengths to these chelating benzoates are also longer, which suggests these groups may be substituted which might allow new chemistry to be performed at these sites. Peaks in the ESMS are seen, both prior to crystallisation and for pure **3**, at *m/z* (% intensity) found (calc.) = 1232.3 (27%) [1231.9, $(\mathbf{3} + 2Na)^{2+}$]; 1220.1 (31%) [1220.4, $(\mathbf{3} + Na)^{2+}$]; 1088.1 (100%) [1087.8, $(\mathbf{3} - 2\ O_2CPh)^{2+}$]. In contrast to **2** therefore, we can conclude that **3** is present in solution, and is the major product of the thermolysis.

The Cr(III) starting materials are perfectly set up to promote oligomerisation *via* conversion of coordinated H_2O to hydrox-

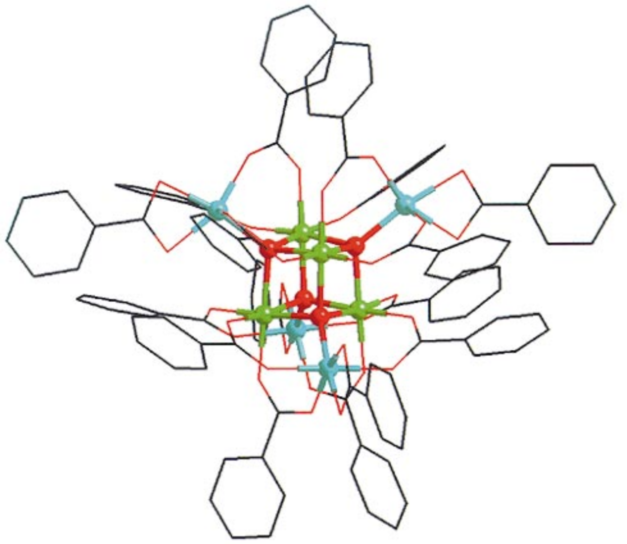

Fig. 2 The structure of **3**. Bond length ranges: Cr–O(1,3-bridging benzoate) 1.927–1.985, Cr–O(chelating benzoate) 2.009–2.056, Cr–O(oxide) 1.966–2.039 Å (av. esd 0.008 Å). Bond angle ranges: *cis* at Cr (metal atoms of central cubane) 81.7–99.1, *trans* at Cr(cubane) 172.8–179.7, *cis* at Cr (outer metal atoms) 64.7–109.4, *trans* at Cr (outer metal atoms) 154.9–74.2° (av. esd, 0.3°) (Cr atoms of central heterocubane, green; outer Cr, blue; O, red, μ_4-O ball, other O atoms line; C, black lines).

ide or oxide bridges rather than relying upon the serendipitous formation of such bridges in solution reactions. Furthermore, controlling the temperature of these rearrangement reactions permits isolation of different nuclearity products and we believe this route is applicable to other metals. IR and elemental analysis strongly suggests that the iron analogue of **3** can be made by the same route. The structure of **3** is also very similar to a mixed-valent Co cage, made by an entirely different route, with benzoate ligands which has been reported by Christou *et al*.[9] No other cages containing this metal-array have been described.

Preliminary magnetic measurements on both **2** and **3** indicate antiferromagnetic exchange between the Cr centres. The susceptibility data¶ for **2** could be modelled with one exchange parameter, $J = 12.0$ cm^{-1}; while for **3** two exchange terms were required: $J_1 = 2.1$ cm^{-1}, and represents the exchange between Cr atoms within the central heterocubane (green in Fig. 2), while $J_2 = 3.4$ cm^{-1}, models the exchange between the central Cr atoms and the outer tetrahedron. The latter model is not ideal at present, but the fit is sufficiently good to be satisfied that these exchange parameters are broadly correct.

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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.

‡ Satisfactory elemental analyses were obtained for **2** and **3**.

§ *Crystal data*: for $C_{106}H_{84}Cr_8O_{40}\cdot 1.5CH_2Cl_2$ **2**: monoclinic, space group $C2/c$, $a = 24.219(7)$, $b = 23.534(7)$, $c = 23.318(10)$ Å, $\beta = 95.37(5)°$, $V = 13232(8)$ Å^3, $M = 2541.1$, $Z = 4$ (the molecule lies on a twofold axis), $\mu = 0.764$ mm^{-1}, $T = 150.0(2)$ K, $R1 = 0.1344$.

For $C_{112}H_{80}Cr_8O_{36}\cdot 5\ CH_2Cl_2$ **3**: monoclinic, space group $P2_1/c$, $a = 16.165(8)$, $b = 45.24(3)$, $c = 17.638(10)$ Å, $\beta = 110.52(5)°$, $V = 12079(12)$ Å^3, $M = 2842.4$, $Z = 4$, $\mu = 0.993$ mm^{-1}, $T = 150.0(2)$ K, $R1 = 0.1025$.

Data collection, structure solution and refinement were performed using programs SIR92,[5] DIRDIF[6] and SHELXL-97.[7] All crystals of **2** were badly twinned leading to the poor refinement which is sufficient to unambiguously derive connectivity. Diffuse lattice solvent (1.5 CH_2Cl_2 per formula unit) was treated by the van der Sluis-Spek method.[8] Only Cr and O atoms were refined anisotropically. Full details have been deposited and will be published later. CCDC 182/1128. See http://www.rsc.org/suppdata/cc/1999/285/ for crystallographic files in .cif format.

¶ Variable-temperature magnetic measurements on **2** and **3** 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. The data were fitted with Hamiltonians: for **2,** $H = JS_xS_{x+1} + JS_8S_1$ $(1 \leqslant x \leqslant 7)$; and for **3**, $H = J_1(S_1S_2 + S_1S_3 + S_1S_4 + S_2S_3 + S_2S_4 + S_3S_4) + J_2\{S_5(S_1 + S_2 + S_4) + S_6(S_2 + S_3 + S_4) + S_7(S_1 + S_2 + S_3) + S_8(S_1 + S_3 + S_4)\}$.

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