ChemComm
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Supertetrahedral decametallic Ni(II) clusters directed by μ_6-*tris*-alkoxides†

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Received (in Cambridge, UK) 16th March 2004, Accepted 29th April 2004
First published as an Advance Article on the web 17th May 2004

We report the syntheses, structures and magnetic properties of two decametallic Ni(II) clusters with unprecedented supertetrahedral cores, stabilised by the (hitherto unobserved) μ_6-coordination modes of the tris-alkoxides $\{MeC(CH_2O)_3\}^{3-}$ and $\{C_6H_9O_3\}^{3-}$.

The disposition of the three alkoxide arms of the trianion of 1,1,1-trishydroxymethylethane (H_3thme) is known to direct the formation of triangular M_3 fragments in transition metal clusters, with each μ_2-arm bridging one edge of the triangle.[1] Thus, thme^{3-} has been used to synthesise a large array of clusters, particularly polyoxovanadates, based on triangular M_3 faces, for example Zubieta's octahedral and edge-sharing bioctahedral V(IV/V)$_{6/10}$ clusters.[2] Here we report the synthesis of two decametallic Ni(II) clusters with unprecedented supertetrahedral cores, based on expanded M_6 triangular faces exploiting the μ_6-coordination modes of thme^{3-}, and the trianion of *cis*,*cis*-1,3,5-cyclohexanetriol (chtH_3) which has potentially similar binding modes. Preliminary magnetic studies reveal intramolecular magnetic exchange interactions similar to that in bulk NiO, and intermolecular magnetic ordering below *ca.* 20 K.

Reaction of [Ni(dbm)$_2$] (0.25 g; Hdbm = dibenzoylmethane) and H_3thme (0.055 g) in EtOH (9 ml) at 150 °C in a Teflon-lined autoclave, followed by slow cooling, yields green crystals‡ of $[Ni_{10}(O)(thme)_4(dbm)_4(O_2CPh)_2(EtOH)_6]$ **1** (59%) (Fig. 1). The inorganic core of **1** is a highly regular Ni(II)$_{10}$ supertetrahedron centred on a μ_6-O^{2-} (O1); Ni(1,3,6,6A) are the vertices and the other Ni ions each bisect an edge. The molecule has C_s point symmetry with Ni(1,2,3,7) and O1 lying on the mirror plane. The triangular Ni_6 faces [Ni–Ni–Ni angles on an edge 174.4–179.5°] are near planar (mean deviation from best planes 0.017–0.030 Å), and are each held together by a fully deprotonated μ_6-thme^{3-}, each arm being μ_3 (Fig. 2). Thme^{3-} fills three of the coordination sites of each of the vertex Ni ions, and four of each of the edge Ni ions. The remaining vertex sites are filled by a chelating dbm$^-$ and either a terminal EtOH (Ni(1) and Ni(6,6A)) or a benzoate that bridges along an edge (Ni3 and Ni(6A,6)). The two μ_2-benzoates (one of which is disordered with an EtOH on the Ni(6,7,6A) edge†) presumably arise from degradation of Hdbm under the harsh reaction conditions.[3] The edge Ni ions are bound to O1, and their remaining sites are occupied by EtOH or dbm$^-$.

The most common bridging mode of thme^{3-} is μ_3, corresponding to Fig. 2 (left) with the 3 vertex metal ions removed. To the best of our knowledge, **1** presents the first example of the μ_6-bridging mode, forming expanded M_6 triangles. This inspired us to look at other ligands that could potentially bind in a similar fashion, for example chtH_3. Reaction of [Ni(dpm)$_2$] (0.25 g; Hdpm = dipivaloylmethane), $[Ni(O_2CMe)_2]$ (0.015 g) and chtH_3 (0.041 g) in MeCN (9 ml) at 150 °C yields blue/green crystals‡ of

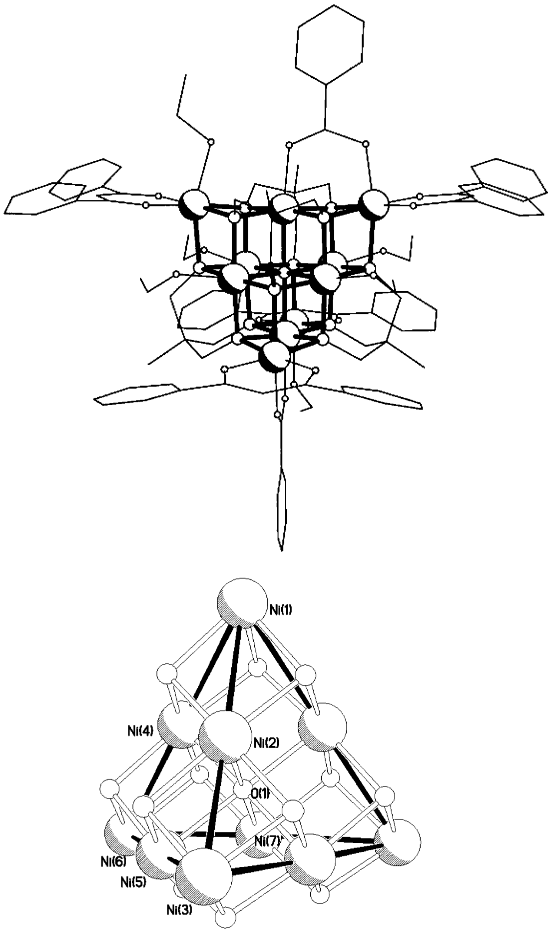

Fig. 1 Views of **1** (top, major occupancy disordered sites shown), and (bottom) the Ni_{10} core of **1** highlighting the supertetrahedron [Ni large shaded, O open, C connectivity only, H omitted]. Structural parameter ranges: distances (Å) Ni–Ni 2.929(1)–2.999(1), Ni–O1 2.101(2)–2.126(3), Ni–O(thme^{3-}) 1.993(3)–2.164(8); angles (°) Ni–O1–Ni 89.6(1)–90.4(1) and 179.3(2)–179.6(2), Ni–O(thme^{3-})–Ni 91.9(1)–99.4(1).

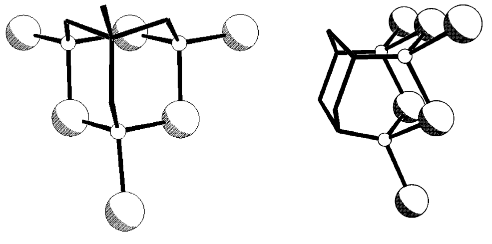

Fig. 2 Views of the Ni_6 faces of the supertetrahedra, and the μ_6-binding of the tris-alkoxide ligands thme^{3-} in **1** (left) and cht^{3-} in **2** (right).

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† Electronic supplementary information (ESI) available: disordered ethanol and benzoate on the Ni6, Ni7, Ni6A edge. See http://www.rsc.org/suppdata/cc/b4/b403876b/

DOI: 10.1039/b403876b

$[Ni_{10}(O)(cht)_4(dpm)_4(O_2CMe)_2(H_2O)_2]$ **2** (50%). **2** is structurally very similar to **1**, but with the Ni_6 faces now bound by μ_6-cht^{3-} with the three deprotonated alcohols locked in the axial positions of the cyclohexane ring (Fig. 2). Again, this coordination mode has not been observed previously.

An alternative view of the Ni_{10} cores is as four $\{Ni_4O_4\}$ heterocubanes, each sharing one edge with each of the other three, and all sharing a common vertex (O1). In isolated cubanes the arrangement with respect to metal ions is tetrahedral. Fused cubanes give higher-nuclearity clusters, exemplified by Hendrickson's Mn_{13} supercubane.[4] M_6 octahedra,[2,5] the supercubane, and **1** and **2** are all related. Capping a M_6 octahedron on alternate faces gives a supertetrahedron, capping the remaining four faces gives a supercubane (Fig. 3). Such materials can be considered as trapped fragments of a parent mineral lattice (rock salt structure). For example, each face of the supertetrahedron in **1** corresponds to a {111} plane of bulk NiO (bunsenite). NiO is an antiferromagnet, dominated by the strong interactions across linear Ni–O–Ni bridges, while simple $\{Ni_4O_4\}$ cubanes are weakly ferromagnetically coupled ($S = 4$ ground states) *via* the approximately right angled Ni–O–Ni interactions.[6] Therefore, we were intrigued as to how the magnetic properties of **1** would relate to these two materials.

χT for **1** at 300 K is significantly less than that expected for ten uncoupled Ni(II) ions (12.1 cm^3 K mol^{-1} with $g = 2.2$), and decreases down to *ca.* 40 K, consistent with dominant antiferromagnetic intramolecular exchange (Fig. 4).§ The data in this range are independent of field strength. However, below 40 K χT increases to a maximum value at 10 K, χT(max) having an inverse field dependence—this is indicative of a magnetic ordering effect. Zero-field-cooled, field-cooled and remanent magnetization data are consistent with this, revealing a non-vanishing net magnetization below 20 K (Fig. 4 inset). In this temperature range we also observe an AC susceptibility signal with a very small frequency dependence, and hysteresis in magnetisation *vs.* field. The mechanism of this ordering is unclear since there is no obvious intermolecular exchange pathway in the crystal structure of **1** (the shortest intermolecular Ni–Ni distances are 9.93 Å). Very similar behaviour, interpreted as ferromagnetic ordering, has been observed for a Fe_3Ni_2 cluster with similar intermolecular distances.[7]

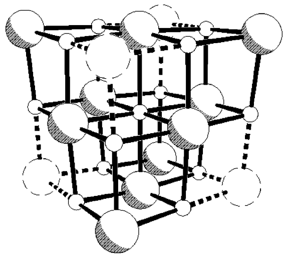

Fig. 3 Relationship between the supertetrahedral core of **1**, and a supercubane.

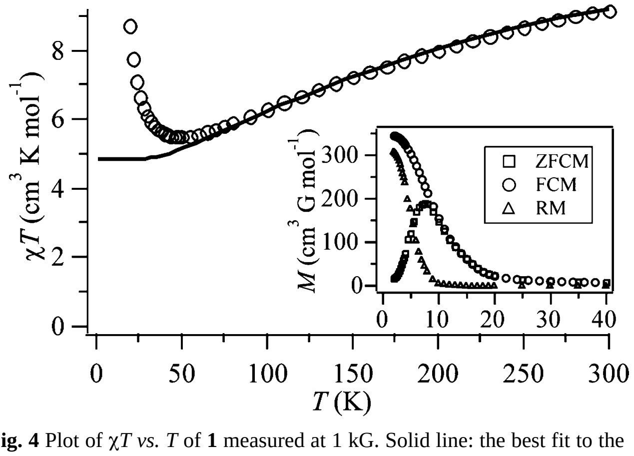

Fig. 4 Plot of χT *vs.* T of **1** measured at 1 kG. Solid line: the best fit to the data above 50 K with one floating parameter: $2J_1 = -123.0$ cm^{-1} ($2J_2 = 0$, $g = 2.2$ fixed). Inset: zero-field-cooled (ZFCM), field-cooled (FCM) and remanent magnetization (RM) *vs.* T below 40 K. Applied field 50 G.

The ordering below 20 K precludes fitting the low-T behaviour. Therefore, we have restricted ourselves to fitting the data between 50 and 300 K with a single antiferromagnetic coupling J_1 across the three linear Ni–O–Ni connections *via* O1. The fits are insensitive to the weak ferromagnetic couplings (J_2) expected[6] to arise from the right angled Ni–O–Ni connections (89.6°–90.4°). Fixing $J_2 = 0$ and $g = 2.2$, we get an excellent fit with $2J_1 = -123$ cm^{-1} (Fig. 4). This is slightly smaller than $2J = -140$ cm^{-1} in NiO and much less than $2J = -224$ cm^{-1} in Y_2BaNiO_5 (which also has linear Ni–O–Ni), in excellent correlation with the Ni–O distances: 2.10 to 2.12 Å in **1**, 2.09 Å in NiO, and 1.88 Å in Y_2BaNiO_5.[8]

Thus, the high-T susceptibility data of **1** is dominated by the antiferromagnetic linear Ni–O–Ni exchange *via* the μ_6-O^{2-}, analogous to the behaviour of bulk NiO. This results in a total spin within the Ni_6 core of $S_{core} = 0$. In the absence of intermolecular effects the low-T magnetism would be dominated by the coupling of the vertex Ni(II) ions. Although these are expected to be weakly ferromagnetically coupled, the supertetrahedral topology would lead to spin frustration, with the cluster having near degenerate states with $S = 0$ to 4. The magnetic ordering implies that non-zero spin states must be populated at low temperature. We are now attempting to isolate analogues of **1** where the ordering is absent in order to probe these phenomena.

Although supertetrahedral metal topologies have been observed in zero-valent metal carbonyl clusters,[9] it is unprecedented in coordination chemistry. It is likely that the supertetrahedral structures are stabilized by the binding of each Ni_6 face by a single ligand, and this principle could be used to stabilize other M_x architectures in a predictable fashion with suitably designed ligands. These will be important molecules in the study of the transition between molecular and bulk materials in, for example, magnetic properties.

This work was supported by the Leverhulme Trust, the EPSRC, the Swiss National Science Foundation and the European Community (contract HPRN-CT-1999-00012/TMR network "MolNanoMag"). We are grateful to Dr S. Teat (Daresbury) for helpful discussions regarding the X-ray crystallography.

Notes and references

‡ Crystal details for **1**: $Ni_{10}O_{31}C_{106}H_{126}$, orthorhombic, *Pnma*, green block, $a = 24.723(2)$, $b = 24.201(2)$, $c = 17.6490(15)$ Å, $V = 10559.6(15)$ Å^3, 100 K, $Z = 4$, $R = 0.0504$. Crystal details for **2**: $Ni_{10}O_{27}C_{72}H_{122}$, tetragonal, $I4_1/amd$, light blue/green block, $a = b = 23.881(3)$, $c = 16.096(3)$ Å, $V = 9179(2)$ Å^3, 100 K, $Z = 4$, $R = 0.0814$. Compound **2** has crystallographically imposed S_4 point symmetry. CCDC 234406–234407. See http://www.rsc.org/suppdata/cc/b4/b403876b/ for crystallographic data in .cif or other electronic format. **1** and **2** give excellent C:H:Ni microanalyses.

§ Magnetic measurements were performed on a Quantum Design SQUID magnetometer on polycrystalline samples restrained in eicosane. Data were corrected for diamagnetism of the sample and holder.

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