LETTER

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Ferromagnetic coupling in a heptanuclear nickel cluster with a vertex-shared dicubane structure

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Hydrothermal synthesis under basic conditions has given a new cluster compound, $Ni_7(OH)_8(ox)_3(pip)_3$ (ox = oxalate; pip = piperazine). This hybrid material comprises inorganic $Ni_7(OH)_8$ clusters, which have a vertex-shared dicubane structure. These units are held together in a 3-dimensional coordination network by organic bridging ligands. Magnetic susceptibility studies suggest a ferromagnetic coupling within the cluster and an antiferromagnetic interaction between neighbouring Ni_7 units. At low temperatures the material appears to undergo a magnetic phase transition to an ordered antiferromagnetic state with $T_N = 17$ K.

Recent years have seen growing interest in polynuclear transition metal clusters.[1] In such compounds, in which a finite number of paramagnetic centres are coupled together, unusual quantum behaviour can be observed. In particular, the discovery of 'single-molecule magnets' and resonant quantum tunnelling of magnetisation in large high-spin clusters[2] has reshaped the field of magnetochemistry. The quest by synthetic chemists for new materials displaying this phenomena has been successful.[3] In addition, many other exotic high nuclearity cluster compounds have been serendipitously discovered.[4] Much more recently Rüegg *et al.*[5] have demonstrated the formation of a Bose–Einstein quantum condensate in a material composed of antiferromagnetically coupled copper dimers. At this stage it is difficult to know what technological impact this discovery might have, or how it may shape future research in cluster chemistry.

We have previously reported[6] on the hydrothermal reaction of $Ni(OH)_2$ and $(pipH_2)(ox)(H_2O)$, which yields Ni(ox)(pip), an exchange-coupled coordination network. The addition of base to these reaction mixtures results in the formation of $Ni_7(OH)_8(ox)_3(pip)_3$ (**1**), obtained as a green microcrystalline solid, in good yield. X-Ray structure analysis of **1** shows it to be isostructural with $Co_7(OH)_8(ox)_3(pip)_3$ (**2**),[7] crystallising in the trigonal space group $R\bar{3}$ with $a = 14.6951(12)$, $c = 12.813(21)$ Å. The compound consists of heptanuclear $Ni_7(OH)_8$ clusters, which have the vertex-shared heteronuclear dicubane structure, where Ni ions are connected by μ^3-bridging hydroxide ions (Fig. 1). This unit occurs in the crystals with its maximum possible symmetry. There are two unique Ni atoms in the asymmetric unit. Ni1 lies on the $\bar{3}$ centre (3b Wyckoff site in hexagonal setting) at the shared vertex, while Ni2 lies on a general position. The Ni2 ion is also coordinated by a chelating oxalate ion that symmetrically bridges to a Ni ion in a neighbouring cluster; thus, each cluster is linked by six oxalate ions to six neighbouring heptanuclear clusters. The Ni2 atom is also coordinated by a piperazine molecule. This links each cluster to an additional six neighbouring clusters. Interestingly, the network formed by the Ni2 atoms bridged by the hydroxide and oxalate ions is a rare example of the 2-dimensional 3-connected 3.12.12 Archimedean net (Fig. 2). The Ni1 ions link these sheets into a 3-dimensional exchange-coupled network.

The Ni–O bond lengths all fall between 2.040 and 2.101 Å, typical for octahedral Ni(II), and as expected all bonds are slightly shorter than the corresponding Co–O distances reported for **2**. The Ni_4O_4 cubane unit is distorted with internal O–Ni–O angles in the range 80.32° to 85.02° and Ni–O–Ni angles between 94.43° and 100.62 °. We note a very close correspondence to the angles in the cobalt derivative **2**.

Despite the tendency of Ni(II) containing clusters to couple ferromagneically, comparatively few heptanuclear structures are known. Of the previously reported heptanuclear clusters one adopts a vertex -shared diadamantane structure,[8] another forms a linear array,[9] while all of the others[10] are less symmetric, showing a variety of vertex- and edge-sharing of the

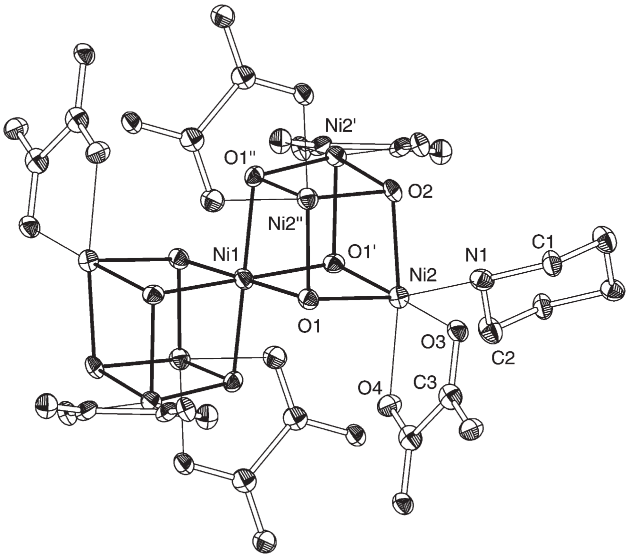

Fig. 1 The asymmetric unit of **1** and selected symmetry equivalent atoms. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Metal–metal separations: Ni1···Ni2 3.012(1), Ni2···Ni2′ 3.159(1) Å. Selected bond lengths: Ni1–O1 2.040(5), Ni2–O1 2.064(3), Ni2–O1′ 2.042(3), Ni2–O2 2.101(3), Ni2–O3 2.071(3), Ni2–O4 2.085(4), Ni2–N1 2.074(6) Å. Selected bond angles: O1–Ni1–O1′ 85.02(10), O1–Ni2–O1′ 84.40(16), O1–Ni2–O2 80.32(9), O1′–Ni2–O2 80.81(11), Ni1–O1–Ni2 94.43(16), Ni1–O1′–Ni2 95.09(16), Ni2–O1′–Ni2′ 100.62(17), Ni2–O2–Ni2′ 97.52(3) °.

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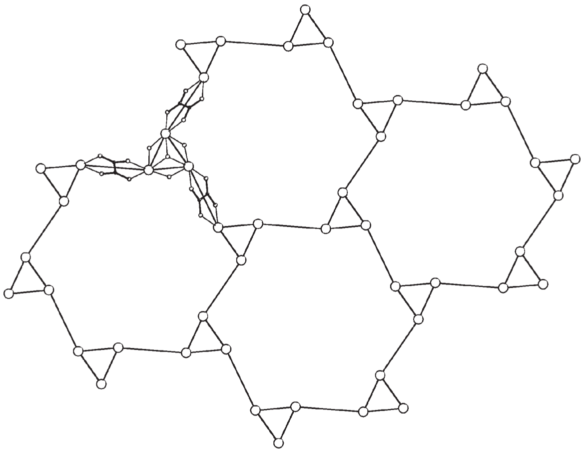

Fig. 2 The semi-regular 3.12.12 network formed by Ni2 cations bridged by hydroxyl and oxalate anions. The coordination geometry of the bridging groups is shown on a portion of the network.

NiX_6 coordination polyhedra. The heterocubane structure seen in **1** can be thought of as a portion of the NaCl or NiO structures. While the dicubane structure is previously unknown in Ni(II) chemistry, there are examples of isolated clusters containing this M_7O_8 dicubane motif for a variety of other divalent metal ions, such as Ca,[11] Co,[7] Cu,[12] Zn[13] and Cd.[14]

The magnetic behaviour of **1** is in many ways similar to that reported for **2**. On cooling the susceptibility increases, reaching a maximum at 27(1) K of 0.0288(2) $cm^3\ mol^{-1}$, before rapidly decreasing (maximum in $d\chi T/dT$ at 17 K) and then levelling off to a constant value of 0.0182(1) $cm^3\ mol^{-1}$ as $T \rightarrow 0$ K [Fig. 3(a)]. A plot of the reciprocal susceptibility shows the data to significantly deviate from the Curie–Weiss law below 50 K; however, a good fit to Curie–Weiss behaviour was obtained for high temperature data between 150 and 320 K giving $C = 1.25(1)$ cm^3 K mol^{-1} and $\theta = +12(2)$ K [Fig. 3(a)]. It is useful to convert the susceptibility to an average effective moment. This gives a high temperature value of 3.24 μ_B. On cooling μ_{eff} increases slightly, reaching a maximum of 3.33 μ_B at about 110 K, after which it decreases rapidly, reaching 0.53 μ_B by 1.9 K [Fig. 3(b)]. The gradient of the curve at the lowest experimental temperature suggest that we might expect μ_{eff} to continue to decrease on further cooling.

The observation of Curie–Weiss behaviour at high temperature implies a paramagnetic state. The high temperature moment and the Curie constant are consistent with non-interacting $S = 1$ moments with an average g value of 2.24. This is typical of the values commonly reported in octahedrally coordinated Ni(II) ions with a $^3A_{2g}$ ground state.[15] The positive Weiss constant suggests a dominant ferromagnetic interaction, as observed in **2**. In contrast, the behaviour at lower temperatures (*i.e.*, the decrease in χ and μ_{eff} on further cooling) suggests a significant antiferromagnetic interaction. In fact, the relative values of χ at $T(\chi_{max})$ and 0 K, in addition to the apparently temperature-independent behaviour of χ at the lowest thermal energies (a crucial observation), suggest a long-range antiferromagnetically ordered state. A plot of the derivative $d\chi T/dT$ shows quite a sharp maximum, consistent with a magnetic phase transition to an antiferromagnetic state at the Néel temperature of 17 K [Fig. 3(b)].

The magnetic analysis is simplified by the high symmetry of the clusters. We need only consider three significant superexchange pathways. In the first, Ni1 is connected to six neighbouring Ni2 atoms through six μ^3-bridging hydroxide ions with a coupling constant J_1. The second interaction, J_2, is between symmetry equivalent Ni2 atoms, again through the μ^3-bridging hydroxide ions. Thus, J_2 links three Ni2 ions in an equilateral triangle. These two coupling pathways describe the magnetic states of the isolated Ni_7 clusters (Fig. 4). The third coupling, J_3, an intercluster interaction, links nickel ions bridged by the oxalate dianions. Together J_1 and J_3 form a 3-dimensional bipartite network. If the coupling J_2 is antiferromagnetic it may act as a source of spin frustration.

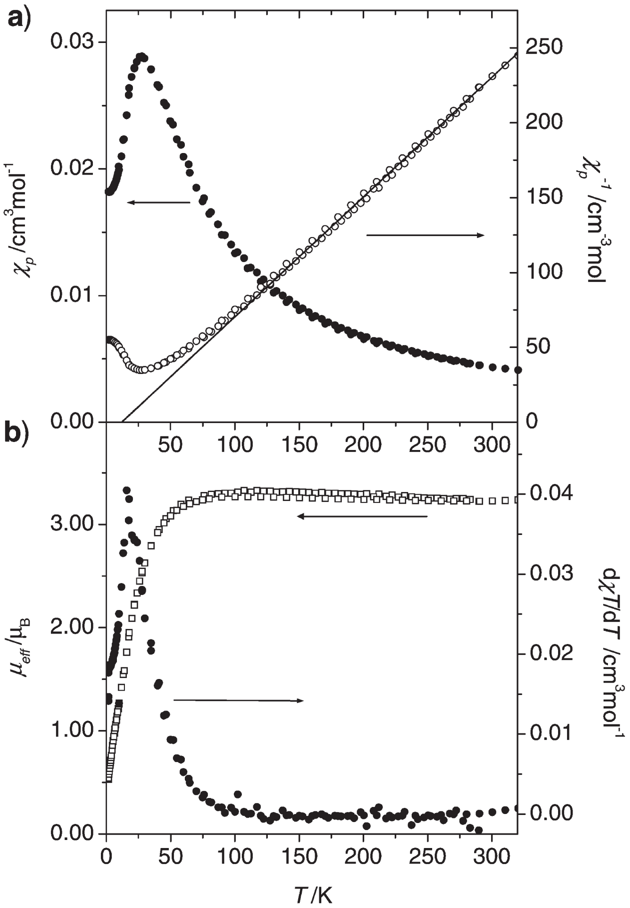

Fig. 3 (a) A plot of the magnetic susceptibility, $\chi(T)$, and its reciprocal $\chi^{-1}(T)$ for **1**, showing also the best fit to Curie–Weiss behaviour at high temperature. (b) The thermal variation of the effective moment, μ_{eff}, and the related derivative $d\chi T/dT$. Data is shown for both heating and cooling cycles.

Magnetostructural studies on Ni(II) in cubane-like structures[16] has shown that the exchange interaction depends crucially on the M–O–M angle, with a ferromagnetic interaction being observed for angles close to 90° and antiferromagnetic coupling when the angle is much greater. It appears that the threshold between these regimes is ~99°. Using these studies we can reliably estimate the coupling constants[17] in the Ni_7 clusters: $J_1/k_B \sim +40$ K (average Ni1–O–Ni2 angle: 94.8°); $J_2/k_B \sim 0$ K (average Ni2–O–Ni2′ angle: 99.1°). Thus, we expect ferromagnetically coupled clusters and the potentially spin frustrating interaction J_2 to be negligible. The interaction J_3 through the symmetric bis-chelating oxalate bridge has been well studied in many nickel(II) compounds.[18] It is

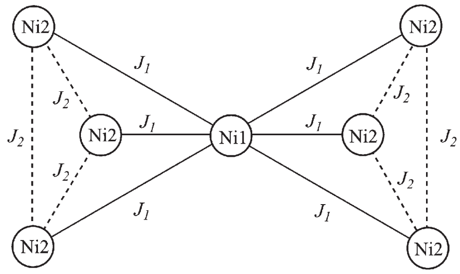

Fig. 4 The coupling scheme in the heptanuclear nickel clusters.

partially dependent upon the coordination environment of the ion, but is of the order $\sim\!-30$ K. These coupling constants qualitatively fit the observed data well with the larger ferromagnetic interaction being observed at the highest thermal energies and the antiferromagnetic coupling being more evident at low energy.

Our discovery of **1** has revealed the first example of Ni(II) in a high symmetry dicubane motif. Magnetically it appears to behave as expected with a ferromagnetic interaction within the clusters, probably yielding an $S = 7$ ground state. These units are coupled antiferromagnetically in a 3-dimensional oxalate bridged network and it appears that long-range ordering is seen below 17 K. While there are many similarities between **1** and the isostructural cobalt material **2**, the differences in the magnetic behaviour are wholly attributable to the addition of a single electron to the metal d orbitals.

Experimental

General methods

Diffuse reflectance spectra were obtained in the infrared region on a Perkin Elmer Spectrum One FTIR and across the UV/VIS/NIR region with a Perkin Elmer Lambda 19 spectrometer. C, H and N analysis was performed commercially by Medac, Ltd (Surrey, UK). Thermogravimetric analysis was performed on a Mettler Toledo TGA/SDTA851e equipped with a T50800GCI gas control system and a T50801RD sample robot, in an atmosphere of approximately 60% O_2 and 40% N_2 and heating at a rate of 10 °C min^{-1} up to a maximum temperature of 800 °C. Magnetisation measurements were performed between 1.8 and 320 K in an applied field of 200 G on a Quantum Design MPMS SQUID magnetometer. The sample was embedded in an eicosane matrix to prevent reorientation effects and a diamagnetic correction was determined from Pascal's constants.[19] All magnetic quantities are given per Ni ion and not per unit formula.

Synthesis of $Ni_7(OH)_8(ox)_3(pip)_3$ (1)

$Ni(OH)_2$ (93 mg, 1.00 mmol), $[C_4H_{12}N_2][C_2O_4]\cdot H_2O$ (520 mg, 5.35 mmol), LiOH (90 mg, 2.00 mmol) and distilled water (10 ml) were heated in a 23 ml capacity Teflon-lined autoclave to 180 °C under autogeneous pressure for 72 h. Upon cooling a green microcrystalline product was obtained. Yield: 90 mg, 97%. Anal. found: C, 19.81; H, 3.50; N, 7.60; $Ni_7C_{18}H_{38}N_6O_{20}$ requires: C, 20.22; H, 3.58, N, 7.86%. IR (KBr, cm^{-1}): 3647 w, 3590 s, 3528 m, 3444 m, 3223 s, 3070 w, 2963 m, 2923 m, 2868 m, 2346 w, 2138 w, 1630 s, 1590 m, 1451 m, 1439 m, 1360 m, 1311 s, 1079 m, 1022 s, 1002 m, 886 s, 798 s, 773 s, 705 s, 610 s, 492 s, 434 s, 420 s. UV/VIS/NIR [$BaSO_4$, cm^{-1}, (rel. absorption)]: 9500 (0.90) $^3A_{2g} \rightarrow {}^3T_{2g}$, 15 700 (1.00) $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, 25 800 (0.79) $^3A_{2g} \rightarrow {}^3T_{1g}(P)$, 34 600 (0.84) oxalate. TGA shows a single-step decomposition with an onset at 360 °C and a mass loss of 61% (expected mass loss for the formation of Ni: 61.5%).

X-Ray crystallography

Data was collected at 150 K with Mo-Kα radiation (0. 71073 Å) on an Enraf Nonius Kappa CCD area detector as ϕ and ω scans to fill the Ewald sphere. Data collection and cell refinement were managed by DENZO,[20] absorption corrections were applied using SORTAV,[21] structure solution and refinement were performed with SHELXS97[22] and SHELXL97[23] in the WinGX environment.[24] Crystal data for **1**: $Ni_7C_{18}H_{38}N_6O_{20}$, $M = 1069.37$, trigonal, $R\bar{3}$ (no. 148), hexagonal axis setting, $a = 14.6951(12)$, $c = 12.813(2)$ Å, $U = 2396.22(50)$ Å^3, μ(Mo-Kα) = 4.130 mm^{-1}, $Z = 3$, $T = 120$ K.; 7605 reflections collected, 1225 unique ($R_{\text{int}} = 0.1981$), $R_1 = 0.0575$ for 826 reflections with $I(\sigma) > 2\sigma$ and 78 parameters; wR_2 on all data was 0.1318.‡

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