Synthesis and characterisation of a {Ni_8} single molecule magnet and another octanuclear nickel cage†

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Two new octanuclear nickel(II) cage complexes are reported; the second is a new single molecule magnet.

It is a goal of scientists pursuing the synthesis of polymetallic cage complexes to be able to control and predict the likely product of any reaction. An important recent breakthrough has been the observation by Perlepes and co-workers that bridging hydroxide ligands can be replaced by pseudo-halides such as azide.[1] From a magnetic perspective this is particularly intriguing because while hydroxide ligands normally provide anti-ferromagnetic exchange paths, bridging azides lead to ferromagnetic coupling and hence the spin ground state of a molecule can be increased dramatically.[2] This observation has inspired us to try the experiments below, with less rational results.

We have been making nickel cage complexes including pyrazolinone ligands,[3–5] and have now extended this work to include fluoride and azide bridges. When 2-methylpyrazolinone (Hmpo, 2 mmol) and *t*-butylbenzoic acid (2 mmol) in methanol (50 cm^3) are added to a solution of nickel(II) tetrafluoroborate (2 mmol) dissolved in minimal water a light green solution results. This was stirred briefly before addition of NaOMe (2 mmol) dissolved in MeOH (4 ml); the solution was then refluxed for 24 h. The solvent was removed *in vacuo* and the residue extracted with ethyl acetate (25 cm^3); crystals grew over ten days in 7% yield.‡ X-Ray diffraction studies show formation of $[Na][Ni_8Na(OH)_2F_8({}^tBuPhCO_2)_8(Hmpo)_8]$ **1**.§

The anion of **1** is a heterometallic nonanuclear complex, containing eight Ni^{II} ions and a single central Na^I ion (Fig. 1). The core is highly symmetric, crystallising in the cubic space group *I*432. There is therefore only one crystallographically unique nickel ion and the Na centre is at the origin on a 432 site. The core is arranged as a square anti-prism of nickel sites with a sodium ion at the body centre. The core is held in place by eight μ_3-fluoride ions and eight 2.11 *t*-butylbenzoates (Harris notation[8]). Each fluoride ion bridges an edge of nickel squares and bonds to the central sodium ion. The sodium is therefore eight coordinate in a perfect square anti-prism of fluoride ions. The carboxylates each bridge two nickel ions on the edge of the square faces of the square anti-prism. The bridging within the core is completed by a rather unusual μ_4-hydroxide which sits above the square faces of the anti-prism. The coordination sphere of the nickel, "F_2O_3N", is completed by binding to the α-nitrogen of a terminal pyrazolinone ligand. Hydrogen bonding from the heterocycle's β-nitrogen's hydrogen to the fluoride (N···F 2.73 Å) further stabilises the complex. The use of tetrafluoroborate as a source of fluoride has been studied previously, for example by Reedijk and co-workers.[9] The sodium cation is severely disordered through the crystal lattice and its presence is assumed for charge balance purposes and based on analytical data.

The presence of bridging hydroxides suggested that a OH/azide exchange should be possible, as shown by Perlepes.[1] Unfortunately the low solubility of **1** makes reaction with sodium azide impossible, so the original preparation was repeated but with addition of NaN_3. The preparation was identical up to the addition of NaOMe. However here we also added excess NaN_3 (10 mmol), which led to a darker green solution which was stirred for 72 h, before evaporation to dryness. Extraction with ethyl acetate (25 ml) led to crystals in one week in 6% yield.‡ X-Ray studies show formation of $[Ni_8Na_2(N_3)_{12}({}^tBuPhCO_2)_2(mpo)_4(Hmpo)_6(EtOAc)_6]$ **2**.§ $[Ni_8Na_2(N_3)_{12}(PhCO_2)_2(mpo)_4(Hmpo)_6(EtOAc)_6]$ **3**, where benzoate is the carboxylate, can be made by the same route in 13% yield. The structure of **3** was also better, and is discussed here.§

The centrosymmetric structure of **3** has a core consisting of eight nickel ions arranged as six edge-sharing azide-centred triangles in a 4 × 2 rod (Fig. 2). The nickel ions are very nearly planar with the sodiums either side of this pseudo plane. The central core is bridged by twelve azide ions, four mpo ligands and two carboxylates. Six of these azide ions bridge in a 3.30 coordination

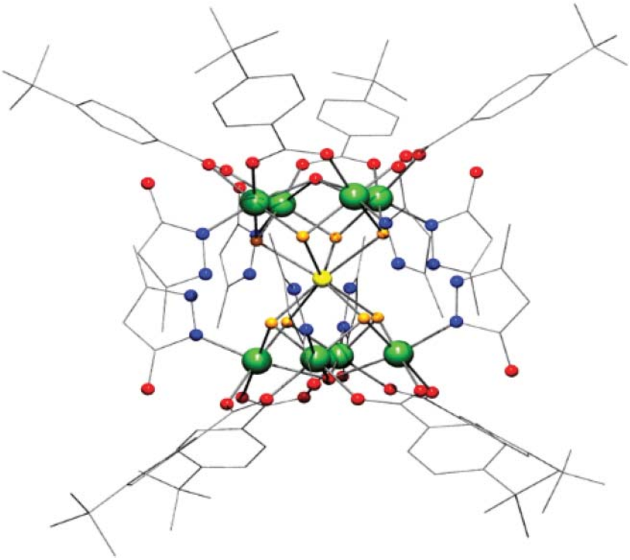

Fig. 1 The structure of **1** in the crystal. Ni, green; Na, yellow; F, orange; N, blue; O, red; C, grey lines.

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† Electronic supplementary information (ESI) available: full synthetic procedures. See http://www.rsc.org/suppdata/cc/b5/b500581g/

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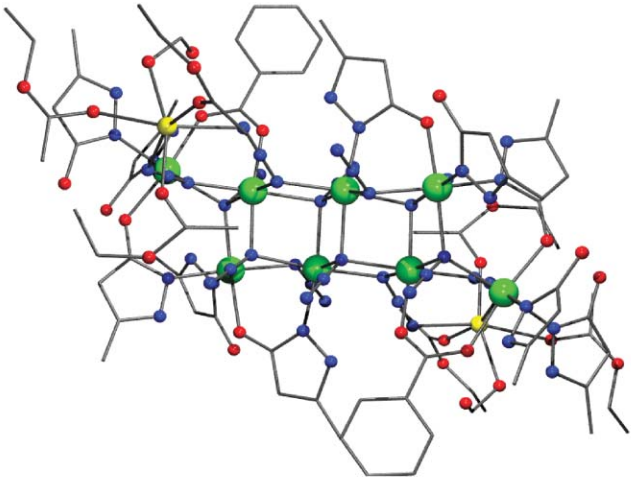

Fig. 2 The structure of **3**. Colours as in Fig. 1.

mode, acting as the centre point of each of the edge-sharing triangles. The other six azides bridge the long edges of the rod, four are in a 3.21 coordination mode and two in 2.20 bridging modes; for the former the azide is also bound to a sodium ion. The mpo ligands show 2.110 coordination mode, and the benzoates are found in the typical 2.11 mode. Three terminal Hmpo ligands are also bound to Ni sites. The Na site is bound to the core through the tail of two azides mentioned earlier, and has its coordination sphere completed by heavily disordered ethyl acetates of crystallisation. The Ni–N–Ni angles at the bridging azides range from 90.42(19) to 124.1(2)°.

Bulk magnetization data¶ from complex **3** were collected under constant magnetic field (300 G) in the 2–300 K temperature range (Fig. 3). At room temperature, the value of $\chi_m T$ equals 9.7 cm^3 K mol^{-1}, very close to that expected for eight magnetically uncoupled Ni^{II} centres and $g = 2.2$ (9.7 cm^3 K mol^{-1}). This value increases, giving a maximum of 44 cm^3 K mol^{-1} at 10 K, demonstrating that ferromagnetic exchange is present through the 3.30 azide groups. Isofield magnetization measurements are consistent with a spin ground state of $S = 8$ and can be fitted with a small D-value of -0.066 cm^{-1} and $g = 2.35$. The fit is not perfect, and may reflect occupation of other spin states even at this low temperature.

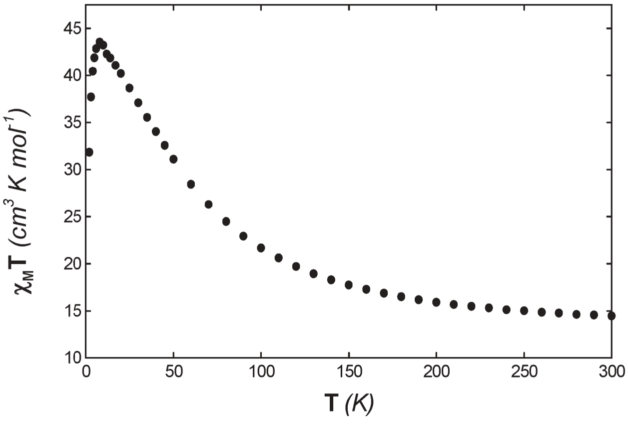

Fig. 3 $\chi_m T$ against T for **3**.

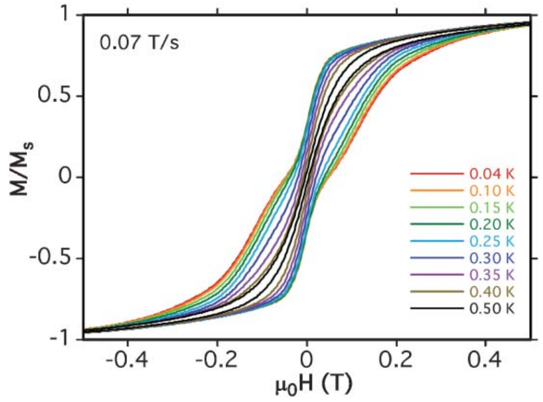

Fig. 4 Magnetisation against field for **3** measured at nine temperatures.

The small negative D-value suggests **3** is a single molecule magnet[10] (SMM) with a very small energy barrier to reorientation of magnetisation. Single crystal measurements on a micro-SQUID array confirms this with hysteresis seen below 0.4 K (Fig. 4). Compound **3** therefore joins the very small number of SMMs known which contain Ni(II) ions.[11] As with all nickel SMMs, the energy barrier for reorientation of magnetisation, given by DS^2, is very low; in this case *ca.* 4 K.

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Notes and references

‡ Anal. calcd (found): for **1** for $C_{120}H_{155}F_8N_{12}Na_2Ni_8O_{26.5}$: C 49.6 (48.8); H 5.3 (5.3); N 7.1 (7.1); F 5.2 (6.2), Na 1.6 (1.6); Ni 16.2 (15.8); for **2** for $C_{62}H_{94}N_{56}Na_2Ni_8O_{20}$: C 30.2 (31.5); H 3.8 (3.9); N 31.9 (30.0); for **3** for $C_{54}H_{78}N_{56}Na_2Ni_8O_{20}$: C 27.6 (26.7); H 3.3 (3.4); N 33.4 (33.0). For **2** and **3** the calculated analysis assumes replacement of six EtOAc molecules by six H_2O molecules. Supplementary data includes full synthetic procedures.†

§ Crystal data for $C_{120}H_{155}F_8N_{12}Na_2Ni_8O_{26.5}$, **1**: cubic, $I432$, $a = 29.5764(13)$ Å, $V = 25872(2)$ Å^3, $M = 2913.3$, $Z = 6$, $T = 150(2)$ K, $R1 = 0.0459$, CCDC 260899. Crystal data for $C_{77.3}H_{115}N_{56}Na_2Ni_8O_{29.3}$ **3**: monoclinic, $P2_1/c$, $a = 16.055(6)$, $b = 16.408(6)$, $c = 23.826(9)$ Å, $\beta = 103.176(7)°$, $V = 6111(4)$ Å^3, $M = 2790.5$, $Z = 2$, $T = 100(2)$ K, $R1 = 0.0573$, CCDC 260900. Unit cell parameters for $C_{62}H_{106}N_{56}O_{14}Ni_8Na_2$ **2**: triclinic, $P\bar{1}$, $a = 15.799(3)$, $b = 17.182(3)$, $c = 24.358(4)$ Å, $\alpha = 95.873(3)$, $\beta = 105.679(3)$, $\gamma = 98.143(3)°$. Data collection, structure solution and refinement used programs SHELXL.[6,7] Full details have been deposited and will be published later. See http://www.rsc.org/suppdata/cc/b5/b500581g/ for crystallographic data in .cif or other electronic format.

¶ Variable temperature magnetic measurements on **3** (8.6 mg) in the region 2–300 K were made using a MPMS-XL SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules in a 300 G field. The data have been adjusted for the diamagnetism of the sample using Pascal's constants.

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