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Synthesis, structure and magnetism of a new dicubane-like ferromagnetic tetranuclear nickel cluster containing versatile azido-only bridges and a bis(bidentate) Schiff base blocker†

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A new tetranuclear double-open dicubane complex [Ni$_4$(μ$_2$-N$_3$)$_4$(μ$_3$-N$_3$)$_2$(N$_3$)$_2$(enbzpy)$_2$]·2H$_2$O (enbzpy = [*N*,*N*-bis(pyridin-2-yl)benzylidene]ethane-1,2-diamine) has been characterised structurally and magnetostructurally.

Polynuclear 3d metal ion complexes have spawned great interest in the search for new magnetic materials, especially molecule-based magnets or nanomagnets in which each microcrystal behaves as a single domain.[1] The essential prerequisite of such work is to prepare molecular species with high spin ground states[2] and the strategy is to generate ferromagnetic interactions between unpaired spin centres. An efficient way to propagate such exchange involves the use of a versatile azido bridging unit, since it induces ferromagnetic coupling while bridging end-on.[3] The few reported tetranuclear Ni(II) complexes contain dicubane-like,[4] butterfly,[5] cubane[6] or rhomb-like[7] architectures and exhibit ferromagnetic coupling mostly through oxo bridges or oxo-azido bridging matrices except with only one rare case having triply bridging azido-only connectors in a cubane core.[6b] Here we first report on a new ferromagnetic tetranuclear double-open dicubane complex [Ni$_4$(μ$_2$-N$_3$)$_4$(μ$_3$-N$_3$)$_2$(N$_3$)$_2$(enbzpy)$_2$]·2H$_2$O, **1** to contain end-on coordinated doubly and triply bridging azides and terminal attachment as well, which is novel in contrast to reported dicubane-like clusters that have oxo intermediaries[4] along with azido connectors.

Complex **1** initially formed in an MeOH solution containing a 1:1:2 mixture of Ni(NO$_3$)$_2$·6H$_2$O, enbzpy and NaN$_3$, a reactant ratio expected to yield a mononuclear species of the composition [Ni(enbzpy)(N$_3$)$_2$]. However, microanalyses showed a 2:1:4 ratio of metal, blocking ligand and the pseudohalide. Reactant ratios corresponding to the product stoichiometry afforded better yields of **1**.‡ Tetrameric units of **1** contain two types of environmentally different Ni(II) centres connected by two Schiff bases acting as bis(bidentate) ligand, four 1,1- and two 1,1,1-azido intermediaries, and two pseudohalide terminals (Fig. 1).§ Additionally, there are two crystallisation molecules of water per tetrameric unit. This is the first report of an azido containing tetranuclear 'double-open' dicubane complex for any metal ion, where the versatility of the azide is revealed through coordination as terminal, μ$_2$- and μ$_3$-bridging motifs. Each metal centre has a distorted octahedral NiN$_6$ coordination environment. Ni1 is attached with two N atoms of a Schiff base, and two 1,1-, one 1,1,1- and one terminal azido N atoms, whereas neighbouring Ni2 is ligated to the other two N donor set of the same Schiff base completing its bis(bidentate) mode, and two 1,1- and two 1,1,1-azido N atoms.

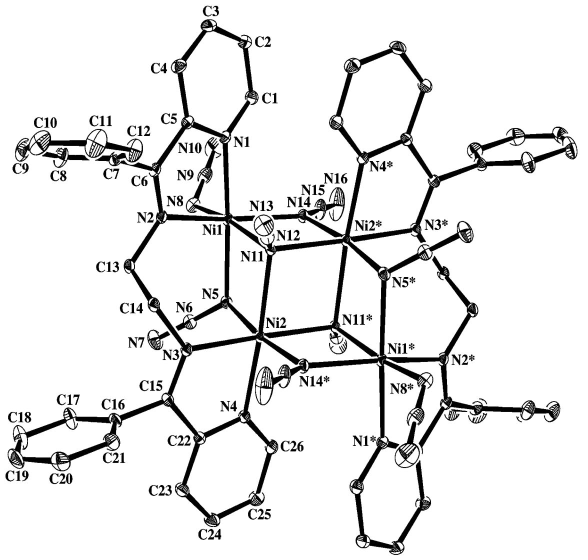

Fig. 1 Perspective view (30% probability ellipsoids) of **1** (H atoms and H$_2$O molecules are omitted).

The tetramer is centrosymmetric with a central core (Fig. 2) that can be described as a 'double-open' face-shared dicubane with two missing vertices. One of the two cubanes may be outlined by three four-membered rings: the essentially planar (i) Ni2–N11–Ni2*–N11* (* = −*x* + 1, −*y*, −*z* + 2) and the non-planar (ii) Ni1–N11–Ni2–N5 and (iii) Ni1–N11–Ni2*–N14. The two open cubanes are related by a crystallographic centre of

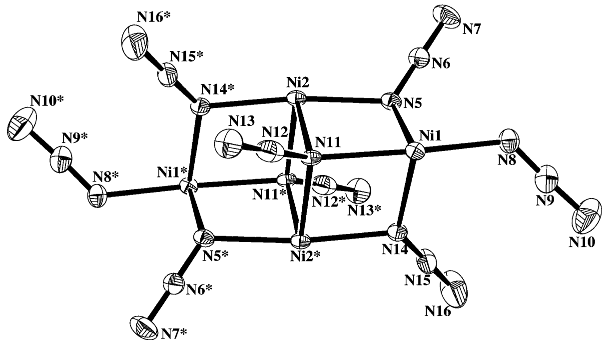

Fig. 2 Highlights of tetrameric Ni(II) core. Selected bond lengths (Å) and angles (°): Ni1–N5 2.088(3), Ni1–N11 2.191(3), Ni1–N14 2.118(3), Ni2–N5 2.074(3), Ni2–N11 2.163(3), Ni2–N11* 2.101(3), Ni2–N14* 2.102(3), Ni1*–Ni2 3.215(1), Ni1–Ni2* 3.263(1), Ni2–Ni2* 3.219(1), Ni1–Ni1* 5.622(1), Ni1–N5–Ni2 101.18(12), Ni1–N11–Ni2 95.21(11), Ni2–N11–Ni2* 98.05(11), Ni1–N11–Ni2* 98.97(11), Ni1–Ni14–Ni2* 101.30(12). Symmetry code: (*) *x* + 1, −*y*, −*z* + 2.

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† Electronic supplementary information (ESI) available: a plot of the reduced magnetisation (*M*/*Nβ*) *vs.* H for **1** at 2 K. See http://www.rsc.org/suppdata/cc/b2/b205375f/

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symmetry located at the centroid of the face (i). The Ni–(μ_2-N) and Ni–(μ_3-N) distances are in the ranges 2.074(3)–2.118(3) Å and 2.101(3)–2.191(3) Å, respectively. The ranges of angles at Ni centres and at bridging N atoms are respectively 78.60(10)–93.59(10)° and 95.21(11)–101.30(12)°. The bis(bidentate) organic blocker, of course has a major role for such distortion. The Ni···Ni distances are in the range 3.215(1)–3.263(1) Å. The diagonal Ni1–Ni1* distance is 5.622(1) Å.

The magnetic behaviour [Fig. 3(a)] of **1** was investigated in the 2–300 K temperature range. From room temperature down to 15 K the χ_MT product increases continuously to 11.5 cm^3 mol^{-1} K (that clearly corresponds to a $S = 4$ ground state with $g > 2.0$) and then decreases to 11.0 cm^{3}mol^{-1}K at 2 K. This shows an overall ferromagnetic coupling with the presence of zero field splitting (ZFS) for Ni(II) and/or antiferromagnetic intermolecular interactions prevailing at low temperature. Considering cluster topology and connectivity, the exchange pathway in **1** is shown in Fig. 3(b). J_1 and J_2 may be treated equal with the close similarity (Fig. 2) in Ni–N$_3$–Ni angles. The magnetic data are analysed with the following spin Hamiltonian [the spin numbering follows the nickel atoms in Fig. 3(b)]:

$$H = -J_1(S_1S_2 + S_2S_{1'} + S_{1'}S_{2'} + S_{2'}S_1) - J_3(S_2S_{2'})$$

To consider the decrease in the χ_MT value at the low temperature region, a new J' parameter (antiferromagnetic intermolecular interactions) has been introduced according to the molecular-field approximation. The best parameters obtained with this computing model are: $J_1 = J_2 = 15.20$ cm^{-1}, $J_3 = 15.46$ cm^{-1}, $J' = -0.012$ cm^{-1}; $g = 2.15$ and $R = 1.1 \times 10^{-5}$. TIP was assumed as 400×10^{-6} cm^3 mol^{-1}. However, this does not take into account the single-ion anisotropy (ZFS) of Ni(II). More exact calculations including D have been performed with the magnetic package MAGPACK.[8] The best fit is: $J_1 = J_2 = 15.8$ cm^{-1}, $J_3 = 14.6$ cm^{-1}, $D = 3.5$ cm^{-1}, $g = 2.15$ and $R = 1.2 \times 10^{-5}$. These agree with the above results. The positive J values for all magnetic pathways agree well with reported ones (11 to 18 cm^{-1})[3,6] of related complexes with similar structural parameters. The D value is also consistent with those reported for other Ni$_4$ complexes.[9] The reduced molar magnetization (*M/Nβ*) in the range 0–5 T at 2 K tends to 8.2, which corresponds to an $S = 4$ ground state, in agreement with the ferromagnetic coupling.

In summary, complex **1** constitutes a new example of tetranuclear dicubane-type molecular framework with azido(1,1/1,1,1)-only connector that provides global ferromagnetic exchange. We are currently investigating the ability of such a tetranuclear ferromagnetic synthon to bind other paramagnetic species through the two terminal pseudohalides to produce extended networks resulting in new supramolecular magnetic materials, which can show ferromagnetic coupling.[10] With free-radicals, for example, the final species could be ferrimagnets. The end-on azido bridges may also give end-to-end connectivity to other ions and extend the solid.[11,12]

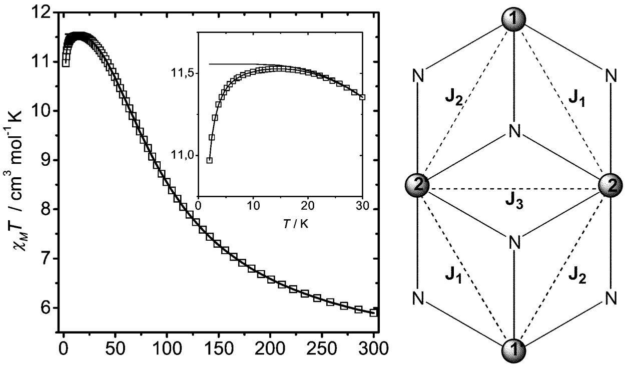

Fig. 3 (a) A plot of χ_MT *vs.* T for **1**. The line represents the best fit and the points the experimental data. The theoretical behavior of a fully isotropic ferromagnetic Ni4 cluster is included as a dotted line in the inset; (b) spin topology for 1 assuming different J values.

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Notes and references

‡ *Experimental details.* Azido compounds of metal ions are potentially explosive. Only a small amount of material should be prepared and handled with caution. The Schiff base was prepared from the condensation of 2-benzoylpyridine (2 mmol) and ethylenediamine (1 mmol) under reflux in dehydrated alcohol. Crystalline **1** was obtained from slow evaporation of an MeOH solution (50 mL) of Ni(NO$_3$)$_2$·6H$_2$O (580 mg, 2 mmol), enbzpy (390 mg, 1 mmol) and NaN$_3$ (260 mg, 4 mmol). Yield: 485 mg (70% based on nickel); elemental analyses calcd (%): C 45.00, H 3.49, N 32.29; found: C 44.68, H 3.43, N 31.92%; IR (KBr): $\nu = 2063$ (N–N–N), 1590 cm^{-1} (C–N).

§ *Crystal data* for **1**: $C_{52}H_{44}N_{32}Ni_4 \cdot 2H_2O$, $M = 1388.06$, monoclinic, space group $P2_1/n$, $a = 12.9364(9)$, $b = 17.7700(13)$, $c = 14.4261(10)$ Å, $\beta = 106.690(2)°$, $V = 3176.6(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.451$ g cm^{-3}, Siemens SMART CCD, λ(Mo-Kα) = 0.71073, $\mu = 1.234$ mm^{-1}, $T = 295$ K, Final $R = 0.0457$, Rw = 0.1445 for 7116 unique reflections ($R_{int} = 0.036$). CCDC 178948. See http://www.rsc.org/suppdata/cc/b2/b205375f/ for crystallographic data in .cif or other electronic format.

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