The self-assembly and magnetic properties of a Ni(II)$_8$(μ_4-hydroxo)$_6$ cube with μ_2-pyrazolate as an exogeneous ancillary ligand†

Jing-Yuan Xu,[a] Xin Qiao,[a] Hai-Bin Song,[b] Shi-Ping Yan,*[b] Dai-Zheng Liao,[b] Song Gao,[c]
Yves Journaux*[d] and Joan Cano[ef]

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A novel octanuclear hydroxonickel(II) complex possessing a unprecedented cube molecular structure with eight Ni(II) ions at each vertex, six μ_4-OH$^-$ groups closing each face and twelve *exo*-bidentate pyrazolate ligands (μ_2-pz) spanning each edge, has been synthesized and its magnetic properties investigated.

Molecular spin clusters have become one of the foremost topics in modern coordination chemistry. Apart from the synthetic challenge and their aesthetically pleasing structures, these polymetallic species can display unique magnetic properties, such as single molecule magnet (SMM) behavior,[1] or have potential uses in quantum computing.[2] In the past decade, considerable effort has been directed toward developing a rational approach to the generation of such fascinating clusters, containing paramagnetic ions with diverse polygonal and polyhedral structural motifs.[3] Among them, the synthesis of molecular cubes has been the focus of much excitement, most likely because the cube is the most common platonic solid encountered in the macroworld. Despite the interest in cubes, only a few examples of molecular cubes, prepared using a range of different design principles, have been reported,[4–6] and their generation presents a significant challenge.

Here, we present a new octanuclear Ni(II) cubane-type structure of formula [Ni(bma)(H$_2$O)$_3$][Ni$_8$(OH)$_6$(pz)$_{12}$]·6DMSO (**1**) (bma = bis(2-benzimidazolylmethyl)amine) containing pyrazolate (pz) as *exo*-bidentate ligands. This complex exhibits dominant antiferromagnetic exchange between the S = 1 centres of the octanuclear cluster.

The reaction of Ni(OAc)$_2$·2H$_2$O with pz and bma in MeOH gives a blue precipitate, which can be recrystallised from a DMSO solution. Blue prisms of **1** suitable for single crystal X-ray diffraction were obtained after two weeks at air.‡ Although the complex only crystallised in DMSO, further reactivity studies have shown that the μ-pz and bma ligands are NOT chemically exchangeable. The persistence of the Ni8 core in these reactions suggests that this structure is composed of a particularly stable Ni : μ-pz : bma ratio.

The structure of **1** consists of octanuclear Ni(II) anions [Ni$_8$(OH)$_6$(pz)$_{12}$]$^{2-}$, a mononuclear Ni(II) cation [Ni(bma)(H$_2$O)$_2$]$^{2+}$ and DMSO molecules of crystallization (see ESI, Fig. S1†). Fig. 1 shows the anionic structure of [Ni$_8$(OH)$_6$(pz)$_{12}$]$^{2-}$. The complex crystallized in the triclinic crystal system, and the four nickel coordination sites (Ni1, Ni2, Ni3 and Ni4) are crystallographically independent of each other. However, the cluster is highly symmetrical, a pseudo four-fold axis lies on the central μ_4-OH$^-$ group (O1) and each metal ion is in a similar coordination environment. Each anionic cube, [Ni$_8$(OH)$_6$(pz)$_{12}$]$^{2-}$, resides in position around the crystallographic center of inversion (symmetry transformation of $-x$, $-y + 1$, $-z$) and contains eight Ni(II) ions located at the vertices of the cube, six μ_4-OH$^-$ groups capping each face and twelve *exo*-bidentate pyrazolate bridging ligands (μ-pz) spanning each edge, thus affording the necessary Ni : μ_4-OH : μ_2-pz ratio of 8 : 6 : 12.

The closed cube structure is confirmed by the equally short Ni–Ni bonds of ~2.98 Å and the Ni···Ni···Ni angles at the corners of ~90° (Fig. 1 and Fig. 2). Hydroxide groups

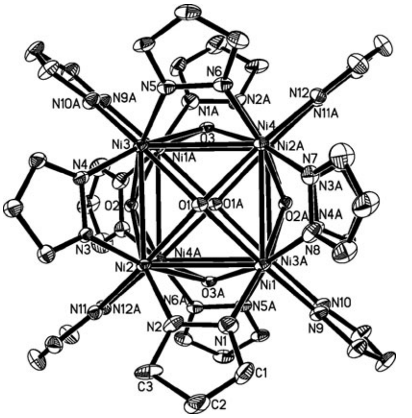

Fig. 1 ORTEP view of the octanickel anion of **1** with the atom numbering scheme for the metal coordination environments (the hydrogen atoms are omitted for clarity). Thermal ellipsoids are drawn at the 30% probability level (symmetry code: A = $-x$, $-y$ + 1, $-z$). Selected bond lengths (Å): Ni1–Ni2 2.9575(11), Ni1–Ni3A 2.9867(10), Ni1–Ni4 2.9973(10), Ni2–Ni3 2.9748(10), Ni2–Ni4A 2.9968(10), Ni3–Ni1A 2.9868(10), Ni4–Ni2A 2.9967(10).

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[a] *College of Pharmacy, Tianjin Medical University, Tianjin 300070, P. R. China*
[b] *Department of Chemistry, Nankai University, Tianjin 300071, P. R. China. E-mail: yansp@nankai.edu.cn; Tel: +86 22 23505063*
[c] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China*
[d] *Laboratoire de Chimie Inorganique et Matériaux Moléculaires, UPMC Univ Paris 06, CNRS UMR 7071, Paris, France. E-mail: yves.journaux@upmc.fr; Fax: +33 144273841; Tel: +33 144275562*
[e] *Departament de Química Inorgànica and Institut de Química Teòrica i Computacional (IQTC), Universitat de Barcelona, Barcelona, Spain*
[f] *Institució Catalana de Recerca i Estudis Avançats (ICREA), Barcelona, Spain*

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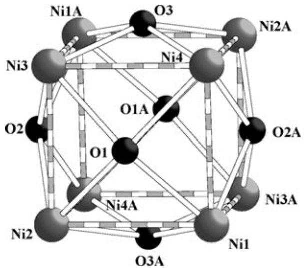

Fig. 2 Schematic view of the $Ni_8(\mu_4\text{-}O)_6$ cubic core in **1**.

bridging in an μ_4 manner is rather rare, and few complexes involving first row transition metal ions are known.[8] Complex **1** is, in fact, the second example of a cube with a face-capping μ_4-OH^- group.[6f] Furthermore, to the best of our knowledge, only one tetranuclear pz-bridging Ni(II) cluster complex has been described in the literature.[9] The $[Ni(bma)(H_2O)_3]^{2+}$ cations of **1** consist of mononuclear octahedral Ni(II) complexes, in which each Ni(II) ion is coordinated to one alkylamino- and two imidazolyl-N atoms from a tridentate bma ligand, and three O atoms from H_2O molecules. Each $[Ni(bma)(H_2O)_3]^{2+}$ cation is disordered over two positions above an inversion center (symmetry transformation of $-x + 1, -y + 2, -z + 1$) (see ESI, Fig. S2†).The preference of all the pyrazole groups in the Ni_8 cluster to lie as far apart as possible supports a very open structure, whereby the neighboring Ni_8 anions and Ni cations are well isolated from each other, with closest distances of 3.729 Å (C11···C11AA, AA = $-x, -y + 1, -z + 1$) and 4.263 Å (C30···C1), respectively, between their outermost carbon atoms (see ESI, Fig. S3†).

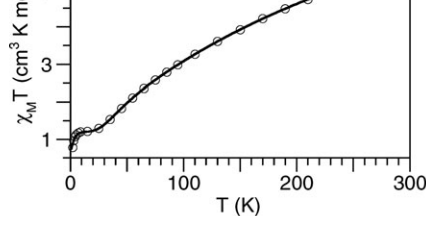

Fig. 3 A plot of $\chi_M T$ *vs.* T (○) in the range 2.0–300 K at 2000 Oe for **1**.

Fig. 3 shows the temperature dependence of the $\chi_M T$ product for **1**, where χ_M is the magnetic susceptibility per nine Ni(II) ions. The value of $\chi_M T$ for **1** at room temperature was *ca.* 5.66 cm^3 mol^{-1} K. This value is lower than that expected for nine isolated $S = 1$ centers (9.0 cm^3 mol^{-1} K for $g = 2.0$). This is indicative of the presence of antiferromagnetic exchange couplings. Upon cooling, the $\chi_M T$ for **1** decreases, reaching at plateau at 20 K. At this temperature, the $\chi_M T$ value (1.20 cm^3 mol^{-1} K) is equivalent to that expected for an isolated $S = 1$ Ni(II) ion ($g = 2.195$). These features confirm the presence of antiferromagnetic exchange couplings in the Ni_8 cube complex, leading to a singlet ($S = 0$) spin ground state. At temperatures lower than 10 K, decreasing of the $\chi_M T$ product, associated with the axial magnetic anisotropy of the Ni(II) mononuclear counterion $[Ni(bma)(H_2O)_3]^{2+}$, is observed. In fact, attending to the geometric considerations, two different exchange couplings (J_a and J_b) must be considered. One of them, corresponding to the edge of a cube (J_a), involves a pyrazole and two hydroxo (μ_4-OH) groups as bridging ligands. On the other hand, in the coupling related to the diagonal of the cube face (J_b), only a μ_4-OH group mediates between the Ni(II) ions. The existence of more than one exchange coupling prevents a unique set of J values from being obtained. This is the reason why density functional (DF) calculations have been carried out using the NWCHEM package, in order to evaluate the magnitude of the J couplings.[10,11] The methodology used here has been described in previous work.[12] More details about these calculations can be found in the ESI.† The values obtained by this procedure are $J_a = -6$ cm^{-1} and $J_b = -58$ cm^{-1}. Starting from these values, the magnetic data have modelled using the following Hamiltonian:

$$\begin{aligned} H = {} & -J_a[\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_4 + \hat{S}_2\cdot\hat{S}_3 + \hat{S}_3\cdot\hat{S}_4 + \hat{S}_{1A}\cdot\hat{S}_{2A} \\ & + \hat{S}_{1A}\cdot\hat{S}_{4A} + \hat{S}_{2A}\cdot\hat{S}_{3A} + \hat{S}_{3A}\cdot\hat{S}_{4A} + \hat{S}_1\cdot\hat{S}_{3A} + \hat{S}_2\cdot\hat{S}_{4A} \\ & + \hat{S}_3\cdot\hat{S}_{1A} + \hat{S}_4\cdot\hat{S}_{2A}] - J_b[\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4 + \hat{S}_{1A}\cdot\hat{S}_{3A} \\ & + \hat{S}_{2A}\cdot\hat{S}_{4A} + \hat{S}_1\cdot\hat{S}_{4A} + \hat{S}_2\cdot\hat{S}_{3A} + \hat{S}_1\cdot\hat{S}_{2A} + \hat{S}_4\cdot\hat{S}_{3A} \\ & + \hat{S}_3\cdot\hat{S}_{2A} + \hat{S}_4\cdot\hat{S}_{1A} + \hat{S}_2\cdot\hat{S}_{1A} + \hat{S}_3\cdot\hat{S}_{4A}] \\ & + D[\hat{S}_{5z}{}^2 - \tfrac{1}{3}S_5(S_5 + 1)] \end{aligned}$$

where the notation is that employed in Fig. 2 and D is the axial magnetic anisotropy for the mononuclear $[Ni(bma)(H_2O)_3]^{2+}$ species. The least-squares fit of the experimental data by full-matrix diagonalization gives exchange coupling constant values of -2.6 and -87.9 cm^{-1} for J_a and J_b, respectively. The axial magnetic anisotropy of the $[Ni(bma)(H_2O)_3]^{2+}$ complex is then equal to -5.7 cm^{-1}. The g-factor values found for the Ni(II) ions in Ni_8 and the counterion mononuclear complexes are 2.159 and 2.195, respectively. The agreement factor, defined as $R = \Sigma[(\chi_M T)_{exp} - (\chi_M T)_{calc}]^2/\Sigma[(\chi_M T)_{exp}]^2$ is then equal to 6×10^{-7}.

Among Ni(II) complexes, those containing pz as an *exo*-bidentate bridging ligand mainly focus on dinuclear systems[13] and, to the best of our knowledge, only one tetranuclear pz-bridged Ni(II) complex has been reported in the literature.[9] In contrast, complex **1** seems to be a unique example of compact "cubane-like" systems resulting from the self-assembly of binary *exo*-bidentate pz ligands, hydroxo ligands and Ni(II) metal ions. Our strategy has been revealed as a successful one to assemble transition metals owing to their matching small-sized coordination geometry. As the modelling of the magnetic properties of a large molecular spin cluster like **1** is difficult because of competitive interactions, we have shown that DF calculations can allow a robust and meaningful determination of the exchange coupling parameters within the cluster to be obtained.

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Notes and references

‡ Crystal data for **1**: $C_{64}H_{99}N_{29}Ni_9O_{15}S_6$, M_w = 2235.47, triclinic, $P\bar{1}$, a = 13.118(2), b = 13.782(2), c = 15.595(3) Å, α = 81.716(9), β = 79.430(8), γ = 77.472(10)°, V = 2689.6(8) Å^3, Z = 1, $D_{calc.}$ = 1.380 g cm^{-3}, μ(Mo-K$_\alpha$) = 1.717 mm^{-1}, T = 113 K, GOF = 1.134. Using Mo-K$_\alpha$ radiation (0.71070 Å), a total of 22 203 reflections were collected, of which 10 475 were independent (R_{int} = 0.0270). The refinement converged to R_1 = 0.0656, wR_2 = 0.1808 [$I > 2\sigma(I)$]. Data collection, structure solution and refinement used the programs SMART, SHELXS-97[7a] and SHELXL-97,[7b] respectively.† Anal. calc. for $[Ni_8(C_3H_3N_2)_{12}(OH)_6][Ni(bma)(H_2O)_3](DMSO)_6$: C, 34.38; H, 4.39; N, 18.17. Found C, 34.27; H, 4.46; N, 18.09%. IR (KBr)/cm^{-1}: 3000–3500br s, 1600 m, 1480m, 1440m, 1430s, 1410s, 1375s, 1305w, 1270m, 1160m, 1054s, 1010s, 945m and 750s. UV-vis (DMSO)/nm (ε/L mol^{-1} cm^{-1}): 258 (4.55 × 10^4), 274 (4.91 × 10^4), 282 (4.35 × 10^4), 380 (151), 624 (85) and 983 (46).

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