A novel large Ni-azido circle with tridentate (*NNO*) Schiff base co-ligands: hexagonal structure and ferromagnetic properties†

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The reaction of nickel acetate tetrahydrate with Schiff base 2-[(pyridin-2-ylmethylimino)methyl] phenol (HL) in a methanol–water solution, adding NaN_3 as a bridging ligand, yielded the complex $[Ni(L)(\mu_{1,1}\text{-}N_3)H_2O]_6{\cdot}H_2O$. An X-ray structure determination showed that the complex is nearly a perfect hexagonal structure, and temperature (2–300 K) dependent magnetic susceptibility measurements indicated that it possesses ferromagnetic behavior.

It has been reported that azido bridging ligands are efficient transmitters for propagating magnetic interactions between paramagnetic divalent metal centers (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}).[1–4] Generally, there are two different coordination modes in azido bridging systems: end-to-end (EE) coordination and end-on (EO) coordination. According to the study of a number of polynuclear and polymeric magnetic complexes with azido bridging ligands,[5] it can be clearly seen that EE coordination usually exhibits antiferromagnetic coupling, while EO-azido bridges normally lead to ferromagnetic exchange paths, bringing about a dramatic increase in the spin ground state of the molecule.[6] This phenomenon has inspired great interest in constructing and studying complexes with EO-azido bridges. Meanwhile, several groups have been involved in researching the relationship between the structural parameters and magnetic coupling in these complexes. To date, Ni(II) complexes containing three or two EO-azido bridging ligands have been summarized in detail in Thompson's review.[7] According to this report, the Ni–N–Ni angles commonly show a narrow range of θ values ($83.2° \leq \theta \leq 86.9°$ for complexes with three EO-azido bridging ligands and $94.8° \leq \theta \leq 104.9°$ for complexes with two EO-azido bridging ligands). Nevertheless, it is still worth assembling large metal circles bridged by ferromagnetically-coupled EO-azido ligands, not only as the structures are novel and rare, but also since such systems might be possible candidates for single-molecule magnets (SMMs).[8–10] In order to establish such complexes, we have tried to apply many different kinds of co-ligand to accompany azido, one class of which is Schiff bases. Schiff bases play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architecture.[11,12] Here, we have successfully furnished just such an interesting magnetic cluster system, $[Ni(\text{Schiff base})(N_3)H_2O]_6{\cdot}H_2O$, in which the nickel ions and azido bridging N atom are on the edge of a hexagon, and each nickel ion is coordinated with one Schiff base molecule and one water molecule (Fig. s1).†

The Schiff base with tridentate *NNO* donors, HL, was prepared by the condensation of salicylaldehyde with 2-aminomethylpyridine in methanol at room temperature.[13] HL was then dissolved in methanol and an aqueous solution of $Ni(CH_3COO)_2{\cdot}4H_2O$ added. After 10 min of stirring, an aqueous solution of NaN_3 was added dropwise. Yellow-green crystals of complex **1** suitable for X-ray analysis were obtained by slow evaporation of the solution at room temperature over 7 d.

Single-crystal X-ray analysis revealed that **1** crystallizes in the orthorhombic space group *Pbac*.‡ In the complex molecule, the crystallographically-independent unit cell (Fig. 1) contains three Ni(II) atoms, three L ligands and three azido bridges. Each Ni(II) ion has a slightly distorted octahedral geometry coordinated by four N atoms (two from *trans*-azides with Ni–N = 2.182(4) to 2.272(4) Å and two from L ligands with Ni–N = 1.998(4) to 2.077(4) Å), two O atoms from separate L ligands (Ni–O = 2.008(3) to 2.019(3) Å) and one water molecule (Ni–O = 2.000(3) to 2.038(3) Å). Two N atoms and one O atom from the L ligand, as well as one

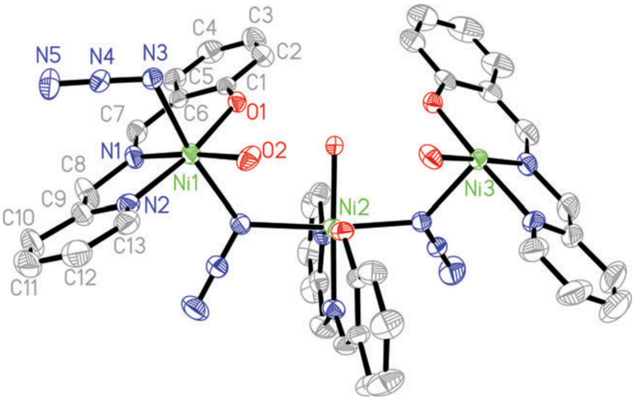

Fig. 1 The asymmetric unit structure representation of complex **1** with atom numbering displacement ellipsoids drawn at 30% probability. All hydrogen atoms and solvent water molecules are omitted for clarity.

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water O-coordinated with the Ni, are almost on the same equatorial plane, while the two N atoms from two bridging azido atoms are in axial positions (with N–Ni–N angles of about 170°). All of the L ligands are not actually in perfect planes; the dihedral angles between the pyridyl and phenyl rings are 8.16(33), 8.42(17) and 10.51(26)° for each L coordinated to Ni1, Ni2 and Ni3, respectively. With the symmetry operations, the structure of the complex forms a centrosymmetric hexanuclear $[Ni(L)(\mu_{1,1}\text{-}N_3)H_2O]_6$ molecule (Fig. s1).† The six Ni atoms are bridged by six $\mu_{1,1}$-N_3 groups (three up and three down the circle plane) to form an $[Ni(N_3)]_6$ circle. Each Ni(II) ion is enwrapped by a combination of L ligands from outside the $[Ni(N_3)]_6$ circle and water molecules from inside the circle. It is noteworthy that the $[Ni_6]$ wheel[14,15] is nearly planar and is perhaps best described as a hexagon with side (N–Ni–N) lengths from 4.352(1) to 4.374(3) Å and six angles ($\angle_{\text{Ni–N–Ni}}$) from 125.9 to 130.2°. The X-ray structure also showed water molecules outside the hexanuclear $[Ni_6]$ ring.

Additionally, each coordinated water molecule in the $[Ni_6]$ cavity forms two intramolecular hydrogen bonds as a H-donor with neighboring O atoms of L ligands. This establishes an interesting structure where the O–H···O hydrogen bonds form two cycle rings up and down the $[Ni_6]$ circle, which makes the $[Ni_6]$ structure more stable, as shown in Fig. s1 with dashed bonds.† All hydrogen bond parameters are listed in Table s1.†

Variable-temperature, solid state magnetic susceptibility measurements were performed on powdered crystalline samples of complex **1** in a 1 KG (0.1 T) field in the 2.0–300 K range. The obtained data are shown as $\chi_M{}^{-1} - T$ and $\chi_M T - T$ plots in Fig. 2. According to the $\chi_M{}^{-1} - T$ line, the magnetic behavior of **1** follows the Curie–Weiss law, $\chi_M = C/(T - \theta)$, with a Curie constant, C, value of 8.79 cm^3 K mol^{-1} and a Weiss temperature, θ, of 14.02 K. Turning to the $\chi_M T - T$ curve, $\chi_M T$ has a practically constant value of 9.0 cm^3 K mol^{-1} in the 300–100 K range, which significantly increases to a maximum of 20.3 cm^3 K mol^{-1} at 5.96 K before decreasing slightly. The 300 K $\chi_M T$ value is significantly larger than the expected value of 6.0 cm^3 K mol^{-1} for $g = 2$ if the constituent Ni(II)$_6$ atoms are non-interacting. This behavior is characteristic of a system with predominant ferromagnetic interactions. The maximum $\chi_M T$ value of 20.3 cm^3 K mol^{-1} indicates a large ground state spin $S = 6$ (20.5 for $g = 2$). Additionally, the field magnetization data were checked at 1.9 K with an external magnetic field ranging from 0 to 5 T (Fig. s2†). At 5 T, the value of the magnetization was 13.2 $N\beta$, which is a little larger than that expected for an $S = 6$ state (12 for $g = 2$). The in-phase (χ'_M) and out-of-phase (χ''_M) magnetic ac susceptibility signals are shown in Fig. s3.† The $\chi'_M T$ *vs.* T plot in Fig. s3, with a maximum 19.06 cm^3 K mol^{-1}, is nearly equal to the highest value of $\chi_M T$, which is further evidence suggesting an $S = 6$ ground state. Meanwhile, it can be clearly seen that there is no out-of-phase ac signal and hysteresis loop, which allows the deduction that **1** is not characteristic of a SMM.

As an appropriate analytical expression of an anisotropic model for this complicated system is lacking, we attempted to approximate statistically the magnetic susceptibility of **1** by an S_6 symmetric hexanuclear model with an isotropic g factor and an identical isotropic coupling constant, J (Scheme 1).

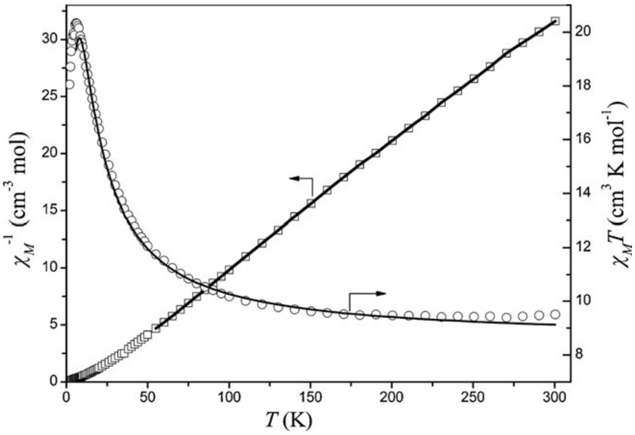
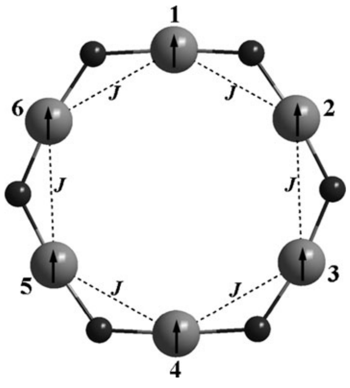


Fig. 2 The temperature dependence of the $\chi_M T$ and $\chi_M{}^{-1}$ of **1** at an applied field (H) of 10 kOe. The solid lines represent the best fit to the Curie–Weiss law and the calculated magnetic susceptibility by MAGPACK.

With these hypotheses, the experimental magnetic data for **1** were analyzed by means of the full-matrix diagonalization program MAGPACK[16,17] based on the Hamiltonian $H = -\Sigma J_{i,j} S_i S_j + \Sigma D_i S_i^2$. The satisfactory fit parameters obtained from this computing model were $J = 0.75$ cm^{-1}, $D = 1.85$ cm^{-1} and $g = 2.39$. The solid line in Fig. 2 represents the best-fit result. Meanwhile, this result has further verified the ferromagnetic interaction between EO-azido bridged Ni(II) ions (the arrowhead in Scheme 1).

Compared with the previously reported Ni(II) ions bridged by EO-azido,[18–21] the decrease of the coupling interaction in complex **1** through the EO-azido bridges presumably originates from the dramatically larger Ni–N–Ni angle, with an average θ value of 127(1)°. To date, there has been only one other $[Ni_6N_6]$ circle system, reported by Tong *et al.*,[22] in which the MAGPACK program was also employed to analyze the $\chi_M T$ experimental data. As the Ni(II) ions in that system were bridged by other ligands (O atom and carboxyl) together with azido groups, the exchange pathways connecting the Ni(II) ions were schematized in two J-schemes according to their bridging environmental differences. In addition, its Ni–N–Ni angles are within the common range (about 91° on average). As a result, its best-fit parameters ($J_1 = 2.88$ cm^{-1}, $J_2 = 25.4$ cm^{-1}, $g = 2.28$, $D = 10.3$ cm^{-1}) are different from those in this



Scheme 1

article. Although the exchange coupling constant here is small, with a value of 0.75 cm^{-1}, it is still coincident with the DFT B3LYP calculations of Ruiz *et al.*[5], who proposed that, even at high θ angles, Ni(II) dimers could be ferromagnetically coupled. The sign of the D parameter in the best fit is positive and it failed to fit the susceptibility data with negative values of D. Meanwhile, a value of $D > 0$ is in agreement with the absence of SMM properties.

In conclusion, a novel [Ni$_6$N$_6$] wheel, $[Ni(L)(\mu_{1,1}\text{-}N_3)H_2O]_6\cdot H_2O$, has been prepared with azido bridging and co-ligand Schiff base (L) ligands that exhibits a nearly hexagonal structure and has significantly large Ni–N–Ni angles (127(1)°). Despite the value of its exchange coupling constant, J, being much smaller than that of complexes with Ni–N–Ni angles between 90 to 110°, it is positive and coincident with the proposition of DFT calculations.

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Experimental section

All chemicals used (reagent grade) were commercially available. Salicylaldehyde (12.2 mg, 0.1 mmol) was dissolved in methanol (5 mL) and 2-aminomethylpyridine (10.8 mg, 0.1 mmol) in a methanol (5 mL) solution was added slowly with stirring. The resulting yellow solution was continuously stirred for 30 min at room temperature and then concentrated, yielding Schiff base (HL). This was washed with diethyl ether and dried *in vacuo* (yield 68%). The HL was then dissolved in methanol (10 mL) and a $Ni(CH_3COO)_2\cdot 4H_2O$ (24.9 mg, 0.1 mmol) aqueous solution (5 mL) added with stirring over 10 min. An aqueous solution of NaN_3 (13.0 mg, 0.2 mmol) was then added dropwise with stirring over 30 min and the reaction vessel placed to one side. 7 d later, yellow-green crystals were obtained. Anal. calc. for $[Ni(L)(\mu_{1,1}\text{-}N_3)H_2O]_6\cdot H_2O$: C, 46.89; H, 4.04; N, 20.91. Found: C, 47.35; H, 4.36; N, 21.03%. IR (KBr/cm^{-1}): 3500–3700, 2054, 1643, 1603, 1543, 1479, 1446, 1149, 1047 and 860.

In order to obtain more information about the thermal stability of the complex, TG-DSC was performed. The results can be found in the ESI.†

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‡ X-Ray data for **1**·H$_2$O: orthorhombic system, space group *Pbac*, a = 16.860(3), b = 22.734(5), c = 23.243(5) Å, $\alpha = \beta = \gamma = 90°$, V = 8909(3) Å^3, Z = 4, D_c = 1.490 g cm^{-3}, $F(000)$ = 4120, μ = 1.319 mm^{-1}, 70 062 reflections measured, 7825 were unique (R_{int} = 0.961) and 7825 were observed for $I > 2(\sigma)$, R_1 = 0.0558 and wR_2 = 0.1217, final GOF = 1.099, 587 parameters.†

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