Dalton
Transactions

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 3044

Received 15th October 2013,
Accepted 30th October 2013

DOI: 10.1039/c3dt52903g

www.rsc.org/dalton

A semi-flexible aminotriazine-based bis-methylpyridine ligand for the design of nickel(II) spin clusters†

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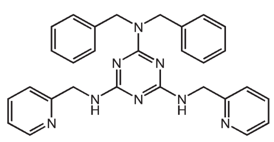
The self-assembly of a semi-flexible aminotriazine-based bis-methylpyridine ligand, *N*^{2},*N*^{2}-dibenzyl-*N*^{4},*N*^{6}-di(pyridylmethyl)-1,3,5-triazine-2,4,6-triamine (H_2L), with $NiCl_2$ and $NiBr_2$ afforded two new nickel(II) clusters, $(H_2NMe_2)_2[Ni_5(OH)_2(H_2L)_2Cl_{10}]$ (1) and $[Ni_6(OH)_2(H_2L)_2Br_{10}(THF)_2]$ (2) showing a high spin ground state of *S* = 3.



Scheme 1 Schematic representation of H_2L ligand.

The development of new molecule-based magnets is an important research topic in the fields of chemistry and physics, due to their impressive structural diversity and intriguing physical properties as well as complicated magneto-structural correlations.[1] One of the major challenges in the area of molecular magnetism is the construction of a polynuclear metal cluster that exhibits interesting magnetic properties, such as the high-spin ground state and/or single-molecule magnet (SMM) behavior.[2–5] For the preparation of such metal clusters, using a polychelating ligand with an unused arm or a donor site has been recognized.[6,7] An alternative preparation method is to utilize the flexidentate behavior of a multidentate ligand and judicial choice of bridging ligands, such as carboxylate and azide.[8,9] Among the bridging ligands, halide ions have been known for their versatile bridging coordination modes that generate polymeric compounds.[10]

Poly-pyridyl ligands had a major impact in the field of supramolecular chemistry for decades, which have led to a variety of metal/ligand supramolecular ensembles to be obtained such as double and triple helices, grids, ladders, and so forth.[11] However, the flexible poly-pyridyl ligands are rarely exploited in the formation of polynuclear metal clusters; especially the resulting structures may potentially exhibit interesting magnetic properties.

We herein report the self-assembly of two Ni(II) clusters, $(H_2NMe_2)_2[Ni_5(OH)_2(H_2L)_2Cl_{10}]$ (**1**) and $[Ni_6(OH)_2(H_2L)_2Br_{10}(THF)_2]$ (**2**), using a semi-flexible aminotriazine-based bis-methylpyridine ligand, *N*^{2},*N*^{2}-dibenzyl-*N*^{4},*N*^{6}-di(pyridylmethyl)-1,3,5-triazine-2,4,6-triamine (H_2L). The designed ligand, H_2L (Scheme 1), contains an aminotriazine ring and two flexible methylpyridine arms, which could chelate metal ions into clusters **1** and **2**, exhibiting an $S = 3$ spin ground state arising from the uncanceled spin arrangement of the antiferro- and ferromagnetic interactions in **1** and ferromagnetic interaction in **2**, respectively.

X-ray crystal structure analysis showed that **1** and **2**‡ crystallize in the monoclinic space groups $P2_1/n$ and in the triclinic space groups $P\bar{1}$, respectively. In complex **1**, the geometry of the centrosymmetric Ni^{II}_5 cluster can be described as two corner-sharing μ_3-OH-centred Ni^{II}_3 triangles with bowtie topology (Fig. 1). Two H_2L groups connect the central Ni^{II} atom (Ni1) and two peripheral metal ions in the two sides of a bow tie (Ni2 and Ni3) in a $\mu_3\text{-H}_2\text{L-}\kappa^5\text{-}N,N':N'':N''',N''''$ coordination mode, in which two methylpyridine groups exhibit in a *trans*-conformation. The base (Ni2⋯Ni3) of each triangle is bridged by two μ_2-Cl^- anions. The μ_3-OH^- group links the central Ni1 to the two peripheral metal ions on either side of the molecule and the O atom of OH^- lie out of the plane of the Ni_3 triangle about 0.402 Å. Peripheral ligations around each Ni centers are completed by terminal Cl^- anions.

The structure of complex **2** reveals a dimer of $[Ni^{II}_3(\mu_3\text{-OH})(\mu_3\text{-Br})(\mu_2\text{-Br})_3]^+$ core which is connected by two bis-chelating H_2L ligands (Fig. 2). The structure $[Ni^{II}_3(\mu_3\text{-OH})(\mu_3\text{-Br})(\mu_2\text{-Br})_3]^+$ adopts a near-equilateral Ni^{II}_3 triangle core, which is bonded

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† Electronic supplementary information (ESI) available: Detailed experimental procedures, additional crystallographic diagrams and magnetic diagram. CCDC 947250 and 947251. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt52903g

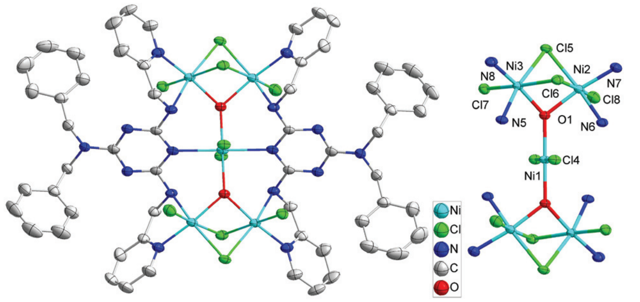

Fig. 1 Crystal structure of the anion complex **1** (left) and its Ni^{II}_5 core structure (right). The Me_2NH_2 cations and H atoms were omitted for clarity.

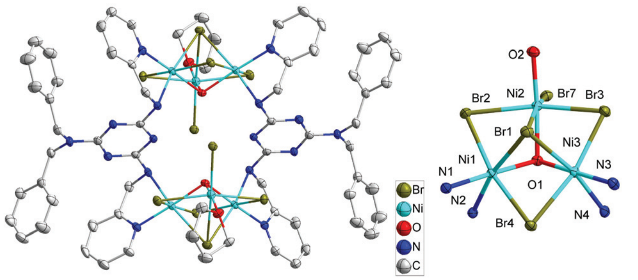

Fig. 2 Crystal structure of the complex **2** (left) and its Ni^{II}_3 core structure (right). The H atoms were omitted for clarity.

by a μ_3-oxide (O1) and a μ_3-Br^- (Br1) on both sides of the central planar where the central OH^- and Br^- bridges are located 0.902 and 2.056 Å above the Ni_3 plane. Each base of the Ni^{II}_3 triangle is connected by μ_2-Br^- anions (Br2–Br4). Two H_2L ligands in complex **2** exhibit a μ_2-H_2L-κ^4-*N*,*N*′:*N*″,*N*‴ coordination mode with *trans*-conformation of their two methylpyridine groups and connects the two Ni_3 triangles into a hexanuclear dimer of Ni_3 structure. Peripheral ligations around each Ni2 centers are ended by one terminal Br^- anion and one THF molecule.

The solid-state, variable-temperature magnetic susceptibility measurements were performed on microcrystalline samples of complexes **1** and **2** in the 2–300 K range in a 1 kOe magnetic field, which was suspended in eicosane to prevent torquing.

For complex **1**, the $\chi_M T$ value of 6.01 cm^3 K mol^{-1} at 300 K decreases gradually with decreasing temperature in the range of 300 to 70 K, then abruptly increases, reaching a maximum of 7.05 cm^3 K mol^{-1} at 10 K, and decreases to 4.38 cm^3 K mol^{-1} at 2 K (Fig. 3). The change in $\chi_M T$ value indicates that antiferromagnetic dominated in the Ni_5 unit with a non-canceled spin ground state and the $\chi_M T$ value at 10 K is consistent with $S = 3$ ($g = 2.2$). Below 10 K, the $\chi_M T$ values slowly decrease, probably due to weak intermolecular antiferromagnetic interactions, zero field splitting and/or small anisotropy.

In order to understand the magnetic coupling of complex **1**, the magnetic susceptibility data were fitted using a Ni^{II}_5 Heisenberg–van Vleck model. Based on the structure analysis, the number of magnetic interactions can be reduced significantly: J_1 for $Ni^{II}\cdots Ni^{II}$ through one μ_3-OH and one H_2L bridgings and J_2 for $Ni^{II}\cdots Ni^{II}$ through one μ_3-OH^- and two μ_2-Cl^- bridges (see Fig. S5 in the ESI†), hence the Hamiltonian can be written as:

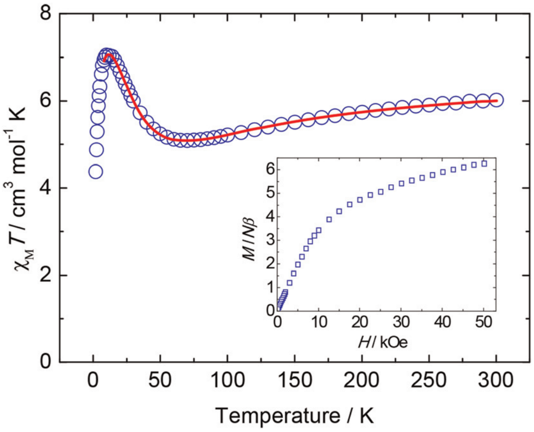

Fig. 3 Plots of $\chi_M T$ *versus* *T* for **1** in an applied field of 1 kOe from 2.0 to 300 K. The solid line represents a least-squares fit of the data (see text). The inset shows a 2 K magnetization isotherm collected between 0 and 50 kOe.

$$H = -2J_1(S_1S_2 + S_1S_3 + S_1S_4 + S_1S_5) - 2J_2(S_2S_3 + S_4S_5)$$

The $\chi_M T$ data could be well fitted by this Heisenberg–van Vleck model with the addition of an intermolecular interaction by the mean-field approximation (zJ'). The results from fitting the experimental data are shown as solid lines in Fig. 3, with final parameters being $g = 2.30$, $J_1 = -11.7\ cm^{-1}$, $J_2 = 3.5\ cm^{-1}$ and $zJ' = -0.10\ cm^{-1}$. This set of parameters leads to the conclusion that the ground state is $S_T = 3$ and the first excited state is $S = 2$ at 24 cm^{-1} above the ground state (Fig. S6†). The estimated values, for the intracluster magnetic exchange interactions, indicate that the antiferro- and ferromagnetic interactions are provided within the Ni^{II}_5 cluster in **1**, and are associated with an $S = 3$ spin ground state. Both interactions (J_1 and J_2) are close to the reported exchange interactions of $Ni^{II}\cdots Ni^{II}$ through the similar pathways.[12] The magnetization curve recorded at 2 K of complex **1** shows a continuous increase up to the saturation value of 6.3$N\beta$ (Fig. 3 inset), which corresponds well to a ground-state spin $S = 3$, in agreement with the $\chi_M T$ data. However, this magnetization curve cannot be nicely fitted by the Brillouin equation for $S = 3$, probably due to the presence of intermolecular interaction, zero field splitting and/or anisotropy.

For complex **2**, the value of $\chi_M T$ increases steadily from 4.24 cm^3 mol^{-1} K at 300 K as the temperature decreases to reach a maximum of 6.03 cm^3 mol^{-1} K at 18 K, and then decreases to 1.00 cm^3 mol^{-1} K at 2.0 K (Fig. 4). The $\chi_M T$ value at 300 K is slightly larger than 4.00 cm^3 mol^{-1} K, the expected value for a Ni^{II}_3 complex with noninteracting metal centers with $g = 2.3$. This behavior clearly indicates the ferromagnetic coupling within complex **2** and the decrease in $\chi_M T$ at low temperature (<28 K) is likely due to the intermolecular ($Ni_3\cdots Ni_3$) interaction, the Zeeman effect or zero-field splitting

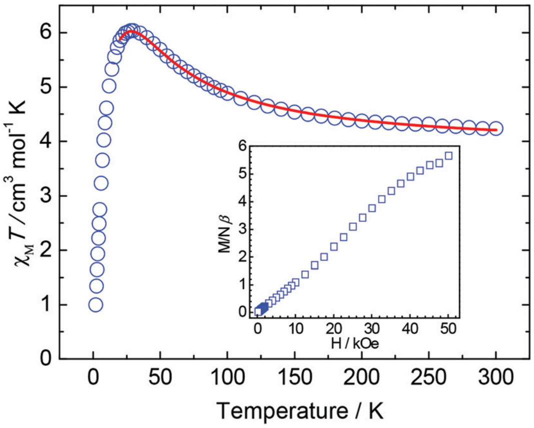

Fig. 4 Plots of $\chi_M T$ *versus* *T* for **2** in an applied field of 1 kOe from 2.0 to 300 K. The solid line represents a least-squares fit of the data (see text). The inset shows a 2 K magnetization isotherm collected between 0 and 50 kOe.

in the ground state. In order to describe the coupling within the cluster, the magnetic susceptibility data were fitted using a Ni^{II}_3 Heisenberg–van Vleck model: $H = -2J(S_1S_2 + S_2S_3 + S_1S_3)$ with an interunit interaction by the mean-field approximation (zJ') (Fig. S7†). The data below 20 K were omitted in the fitting, because zero-field splitting and Zeeman effect likely dominate in this temperature range. The fitting result of dc data in 1 kOe gave the best fit parameters of $g = 2.26$, $J = 8.10$ cm^{-1} and $zJ' = -0.50$ cm^{-1}. This set of parameters gives the ground state of $S_T = 3$ and the first excited state $S = 2$ at -48 cm^{-1} above the ground state (Fig. S8†). Although the magnetic interaction between Ni^{II} ions through such bridges (one μ_3-OH, one μ_3-Br and one μ_2-Br) has not been reported in the literature, it is believed that the ferromagnetic interactions ensue from 6-coordinate geometry and the Ni–X–Ni bridging angles close to 90°.[13] The magnetization curve recorded at 2 K of **2** is shown in Fig. 4 inset, in which the magnetization slowly increases with the increase of field and becomes saturated around 50 kOe with a value of 5.65$N\beta$. The less rapid saturation of magnetization at low field may result from the antiferromagnetic interaction of $Ni_3 \cdots Ni_3$ interunit and the saturation magnetization value corresponds well to a ground-state spin $S = 3$, in agreement with the $\chi_M T$ data. Again, this magnetization curve cannot be well fitted by the Brillouin equation for $S = 3$, due to the presence of intermolecular interaction and/or zero field splitting.

To investigate whether **1** and **2** might be a SMM, ac susceptibility measurements were performed with a zero applied dc field. Representative results for **1** and **2** are shown in Fig. S9 and S10.† At lower temperatures, the in-phase signal ($\chi_M'T$) increases to ~6.8 and 6.5 cm^3 K mol^{-1} for **1** and **2**, respectively, confirming the spin ground state of $S = 3$ for both complexes. For complex **1**, a weak χ_M'' signal appears below 5 K, which is indicative of a slow magnetic relaxation within **1**. However, the peak maxima clearly lie in the temperatures below 1.8 K, the operating limit of our instrument. These data thus suggest that compound **1** indeed exhibits a slow magnetic relaxation or long-range magnetic ordering at temperatures below 1.8 K. In contrast, the complex **2** shows no SMM behavior from the absence of χ_M'' signal.

In conclusion, the use of semi-flexible aminotriazine-based bis-methylpyridine ligands (H_2L) has allowed the access of two novel Ni clusters with interesting magnetic properties. The H_2L ligand represents a 'proof of feasibility' for the belief that such ligands may provide a rich source of new transition-metal clusters. Further studies are in progress.

Notes and references

‡ The complexes analyzed as (C, H, N) **1**, calcd (found): C, 42.52 (42.17); H, 4.26 (4.79); N, 14.40 (14.35)% and **2**, calcd (found): C, 34.37 (34.03); H, 3.23 (3.34); N, 9.72 (9.72)%. Crystal-structure data for **1**, $C_{62}H_{70}Cl_{10}N_{18}Ni_5O_2$, $M = 1747.31$, monoclinic, $P2_1/n$, $a = 15.7038(12)$ Å, $b = 9.9564(7)$ Å, $c = 23.8274(18)$ Å, $\beta = 93.4680(10)°$, $V = 3718.7(5)$ Å^3, $T = 150(2)$ K, $Z = 2$. ($R_{int} = 0.0426$), 8215 parameters, $R(R_w) = 0.0382(0.0865)$ with $[I > 2\sigma(I)]$ and for **2**, $C_{66}H_{74}Br_{10}N_{16}Ni_6O_4$, $M = 2306.56$, triclinic, $P\bar{1}$, $a = 11.9623(7)$ Å, $b = 13.3874(8)$ Å, $c = 14.2964(9)$ Å, $\alpha = 65.3520(10)°$, $\beta = 72.9400(10)°$, $\gamma = 75.1400(10)°$, $V = 1965.5(2)$ Å^3, $T = 150(2)$ K, $Z = 1$. ($R_{int} = 0.0291$), 9051 parameters, $R(R_w) = 0.0256(0.0481)$ with $[I > 2\sigma(I)]$.

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