ChemComm

COMMUNICATION

View Article Online
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Cite this: *Chem. Commun.*, 2017, 53, 8660

Received 12th June 2017,
Accepted 7th July 2017

DOI: 10.1039/c7cc04554a

rsc.li/chemcomm

Strong ferromagnetic exchange coupling in a $\{Ni^{II}_4\}$ cluster mediated through an air-stable tetrazine-based radical anion†

Maykon A. Lemes,[a] Gabriel Brunet,[a] Amélie Pialat,[a] Liviu Ungur,[b] Ilia Korobkov[a] and Muralee Murugesu *[a]

A planar tetradentate 3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine (BpymTz) templating chelate affords the formation of an unprecedented $BpymTz^{\bullet-}$ radical anion bridged $\{Ni^{II}_4\}$ complex. Detailed magnetic measurements performed on the isolated air stable $[Ni^{II}_4(BpymTz^{\bullet-})Cl_6(DMF)_8]Cl\cdot0.5(H_2O)$ compound reveal strong ferromagnetic Ni^{II}–$BpymTz^{\bullet-}$ interactions with a coupling constant of $J = 98.84$ cm^{-1}.

Chelating ligands play a vital role in coordination chemistry; they provide ideal environments for metals to bind and form stable compounds. Since the development of coordination complexes, chemists have designed and synthesized chelates with various donor atoms in order to isolate discrete metal complexes. Through careful design strategies, it is possible to target and isolate mono-,[1] di-,[2] and trinuclear metal complexes.[3] However, discrete polymetallic complexes with one single templating ligand remain extremely rare. Chelates with multiple coordination pockets still require more than one ligand to isolate cluster aggregates.[4] This is mainly due to the difficulty in the synthesis and stabilization of the resulting metal complexes.

Polymetallic complexes are highly sought after owing to their catalytic,[5] bio-mimicking[6] and magnetic properties,[7] to name a few. In molecular magnetism, investigation of polymetallic transition metal complexes is an active area of research since the discovery of a $\{Mn_{12}\}$ complex that exhibits magnet-like behaviour of slow relaxation of the magnetisation.[8] Such discrete molecules are termed Single-Molecule Magnets (SMMs). Several thousands of polymetallic complexes have been reported since then, in an attempt to obtain SMM behaviour at high temperatures. The vast majority of these complexes are frequently synthesized *via* a directed yet serendipitous approach.[9] One common goal in the isolation of these magnetic cluster aggregates is the promotion of ferromagnetic interactions, *i.e.* parallel alignment of the spins, to achieve high-spin molecules. Often, carefully selected ligands such as N_3^- led to the formation of self-assembled clusters with large spin ground states.[10] However, in these molecules, the magnetic exchange between the metal ions occurs *via* superexchange pathways. These interactions tend to be weak and difficult to control or predict. Thus, recent focus has shifted towards radical-bridged systems where strong exchange coupling can be expected. For instance, quinones and verdazyl radical bridging ligands can afford considerable coupling constants with magnitudes greater than 200 cm^{-1}, thanks to the presence of an unpaired electron on the bridging moiety.[3]

With these goals in mind, we have focused our attention on synthesizing a rigid ligand framework that offers a unique template in which coordination pockets are centered around a central tetrazine bridging motif (Fig. 1). Tetrazines are strong π-acceptors due to the presence of a low-lying π^* LUMO arising from the four nitrogen atoms in the cycle leading to the electrophilic nature. As a result of this unique characteristic, it can be easily reduced and act as an electron reservoir.[11] Interestingly, the BpymTz ligand may be isolated in metal complexes as both a neutral species and a radical anion. In fact, our recent work with Ag^+ ions and BpymTz yielded 1- and 2-dimensional anion templated networks, while the BpymTz ligand remained neutral.[12] Moreover, attempts to isolate paramagnetic species with Fe^{III} centres led to the cleavage of the central tetrazine moiety.[13] Also notable is the work by Kaim, Dunbar and co-workers, who reported six examples of BpymTz-based complexes, however, none of these molecules exhibit full occupancy of BpymTz's coordination pockets.[14] Herein, we present the first example of a strategically designed tetrametallic Ni^{II} complex templated around the BpymTz radical, notable for being synthesized and isolated under aerobic condition.

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[a] *Department of Chemistry and Biomolecular Sciences, University of Ottawa, ON K1N 6N5, Canada. E-mail: m.murugesu@uottawa.ca; Fax: +1 (613) 562 5170; Tel: +1 (613) 562 5800, ext. 2733*

[b] *Theory of Nanomaterials Group and INPC – Institute for Nanoscale Physics and Chemistry, Katholieke Universitiet Leuven, Celestijnenlaan, 200F, 3001 Leuven, Belgium*

† Electronic supplementary information (ESI) available: Experimental details, crystallography information, spectroscopy plots and magnetic results. CCDC 1553992. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7cc04554a

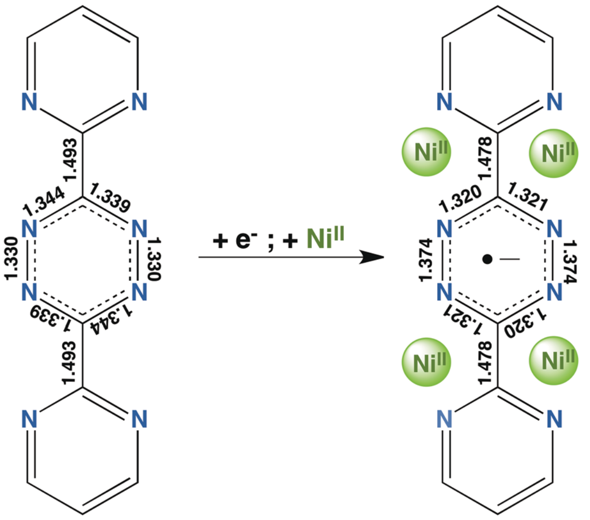

Fig. 1 Selected bond distances (Å) for the neutral BpymTz (left) and the radical anion $\text{BpymTz}^{\bullet-}$ (right) highlighting the structural changes of the ligand upon metal ion coordination.

The reaction of $\text{NiCl}_2\cdot6\text{H}_2\text{O}$ (4 equiv.) with BpymTz (1 equiv.) in *N*,*N*-dimethylformamide (DMF) gave a dark green solution. After one month, pale orange rectangular block-shaped crystals of $[\text{Ni}^{\text{II}}_4(\text{BpymTz}^{\bullet-})\text{Cl}_6(\text{DMF})_8]\text{Cl}\cdot0.5(\text{H}_2\text{O})$ (**1**) were isolated in 30% yield. Complex **1** crystallizes in the monoclinic space group *C*2/*c* (Fig. 2). Crystallographic data and selected bond lengths and angles are summarized in Tables S1–S3 (ESI†). The structure of the centrosymmetric complex **1** consists of a central $\text{BpymTz}^{\bullet-}$ radical acting as a template for four Ni^{II} ions to bind to all four bpym-like coordination pockets (bpym = 2,2′-bipyrimidine). Two Cl atoms (Cl1, Cl1′) act as bridges between Ni1 and Ni2, as well as their symmetrically equivalents Ni1′ and Ni2′ atoms. Two axially coordinating DMF molecules fill the remainder of the octahedral environment of each Ni^{II} ions. The side view of the molecular unit shown in Fig. 2b and Fig. S1 (ESI†) highlights that all four Ni^{II} ions lie perfectly in the plane formed by the $\text{BpymTz}^{\bullet-}$ radical. The overall charge of the complex is balanced by one Cl^- anion located in the crystal lattice. Close inspection of the packing arrangement reveals that the closest Ni···Ni separation occurs at a distance of 7.28 Å, which likely precludes any significant intermolecular magnetic interactions (*vide infra* Fig. S2, ESI†). Although initially predicted by Kaim and co-workers,[11] this is the first time four metal ions occupancy is reported on the $\text{BpymTz}^{\bullet-}$ radical.

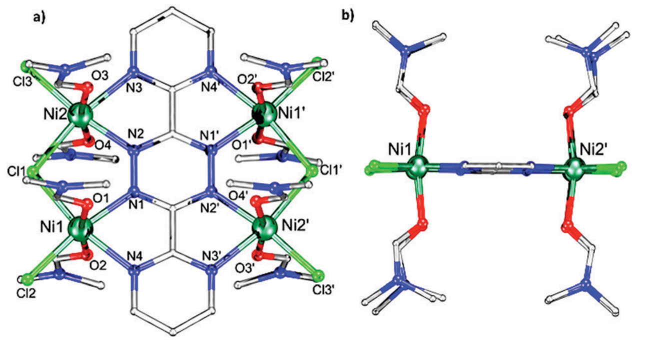

Fig. 2 (a) Ball-and-stick representation of the molecular structure of **1** with (b) side view of the molecule. Colour code: Ni (green), N (blue), O (red), Cl (light green) and C (grey). Hydrogen atoms, counter anions and lattice water molecules are omitted for clarity.

FT-IR spectroscopy studies (Fig. S3, ESI†) reveal an asymmetric doublet that are at 1590 and 1567 cm^{-1} almost suppressed by the strong absorption peak at 1643 cm^{-1}, assigned to coordinated DMF molecules. These quasi-symmetrical peaks are assigned to the ring-stretching of the bpym-type coordination mode. For non-coordinated BpymTz, bpym ring-stretching is observed at lower wavenumbers of 1566 and 1557 cm^{-1}. Nevertheless, the doublet observed at relatively higher wavenumbers in the spectra of **1** is indicative of chelating bpym ligand.[15] A strong absorption band centered at 3400 cm^{-1} can also be observed due to the presence of lattice water molecules.

Close inspection of the tetrazine motif indicates the reduction of tetrazine upon chelation. Elongation between the azo N═N bond length by 0.04 Å (Fig. 1) suggest reduction. This type of elongation is commonly observed in several tetrazine-based ligand radical anions.[14*b*,*e*,16] In addition, Bond Valence Sum (BVS) calculations on nickel ions (Ni1/Ni1′ = 2.06; Ni2/N2′ = 2.04) along with charge balance consideration corroborates well with the presence of central radical anion. DFT calculations confirms the reduced nature of the BpymTz in **1** (*vide infra*). The presence of such bridging radical units in molecular frameworks is anticipated to lead to strong magnetic exchange.[17]

Therefore, to probe the magnetic interactions between the various spin carrying units, we have measured the direct current (dc) magnetic susceptibility of **1** over the temperature range of 1.8–300 K and under an applied field of 1000 Oe. The corresponding χT *vs.* T curve is presented in Fig. 3. The room temperature χT value of 6.98 cm^3 K mol^{-1} is significantly higher than the expected value of 4.94 cm^3 K mol^{-1} for four $S = 1$ and one $S = 1/2$ independent spins, corresponding to four Ni^{II} ions with $g = 2.14$ and the central tetrazine-based radical, respectively. Such behaviour is consistent with nickel complexes magnetically coupled to radical ligands even at room temperature suggesting strong interaction.[3*d*,18] Upon decreasing temperature, the χT product increases monotonically up to a maximum value of 13.80 cm^3 K mol^{-1} at 9.0 K, where further cooling results in a drop to 12.20 cm^3 K mol^{-1} at 1.8 K. The drastic increase of the χT product with decreasing temperatures is indicative of strong ferromagnetic coupling between the spin carriers.[19] Indeed, the strength of the ferromagnetic interactions is clearly evident even at room temperature, where the χT product is appreciably higher than the aforementioned theoretical value. In addition to the structural parameters which suggest that the tetrazine ring in BpymTz is in fact a radical anion (*vide infra*), another viable method to confirm the presence of an additional spin carrier consists of evaluating the χT value at key points of interest. The maximum value of χT (13.80 cm^3 K mol^{-1}) is in strong agreement with a large spin ground state of $S = 9/2$, where the expected χT value is 14.17 K cm^3 mol^{-1} with $g = 2.14$. A scenario involving the absence of a radical species ($S = 4$), would yield an approximate χT value of 11.39 K cm^3 mol^{-1}, which has been observed in a number of previously described ferromagnetic tetranuclear Ni^{II} complexes.[20] The final decrease of the χT curve below 9 K can be explained by zero-field splitting effects since intermolecular antiferromagnetic interactions can be precluded due to the large Ni–Ni separations (>7.28 Å). Alternating current (ac) measurements were also performed, however no out-of-phase (χ'') signal was observed at zero or 1000 Oe applied static field thus precluding any Single-Molecule Magnet behaviour.

Initial attempts to fit the magnetic susceptibility data was carried out assuming an equivalent exchange interaction between all four Ni^{II} ions, however no appropriate fit could be obtained. Thus, to more accurately quantify the intramolecular magnetic exchange interactions, the magnetic data (susceptibility and magnetization) were fitted using the program PHI,[21] according to the Hamiltonian: $H = -2J_1(S_1{\cdot}S_2 + S_3{\cdot}S_4) - 2J_2(S_1{\cdot}S_4 + S_3{\cdot}S_4) - 2J_3(S_1{\cdot}S_5 + S_2{\cdot}S_5 + S_3{\cdot}S_5 + S_4{\cdot}S_5)$ as shown in the inset of Fig. 3. It is important to note that the isotropic g-factors were allowed to vary, while single ion anisotropy due to the ligand field was also taken into account. The best fit obtained led to the following parameters: $J_1 = -13.28$ cm^{-1}, $J_2 = -0.55$ cm^{-1}, $J_3 = 98.84$ cm^{-1}, $g = 2.14$, and $D = 2.81$ cm^{-1}. From these values, we can conclude that the interaction between the Ni^{II} ions and radical ligand spins is ferromagnetic (J_3), corroborating the $S = 9/2$ spin ground state. Field-dependent magnetic properties were also investigated between 1.9 and 7 K, and up to fields of 7 T (Fig. S4, ESI†). The magnetization (M) *vs.* field (H) data could be fit simultaneously with the magnetic susceptibility, and supports the aforementioned parameters. The value of M at 1.9 K and 7 T of 9.44 μ_B is in strong agreement with the expected value of 9.63 μ_B using $g = 2.14$ and $S_T = 9/2$. The M *vs.* H/T plot shows non-saturation and non-superposition of the magnization curves indicating the presence of low-lying excited states even at the low temperature region.

To corroborate the experimental magnetic behaviour of **1**, we have performed Broken-Symmetry DFT calculations, which confirm the strong ferromagnetic interaction between all Ni^{II} sites and the BpymTz$^{\bullet-}$ radical anion (>200 cm^{-1}, for BP and B3LYP functionals). The large calculated coupling constant is not surprising give the significant amount of the equally distributed spin density on the nitrogen atoms of the tetrazine core (Fig. 4). For the sake of comparison a TD-DFT calculations was also performed for the neutral and the anionic ligand. The results show the BpymTz$^{\bullet-}$ specie would promote a more effective exchange coupling within metal ions in virtue of the much lower excited states compared with its neutral version (Table S4, ESI†). The strong ferromagnetic exchange between Ni^{II} ions and the tetrazine radical is probably due to the orthogonality of the magnetic orbitals in the system, preventing antiferromagnetic exchange mechanisms from being operational in this system. Such remarkable observation of ferromagnetic interactions is exceptional and uncommon. To the best of our knowledge, this is the first example of a ferromagnetic interaction involving a tetrazine radical. The presence of radicals in molecular frameworks that have led to ferromagnetic exchange interactions have been previously observed in verdazyl-based complexes,[3c,d] however it is unprecedented in tetrazinyl-based systems. Future work will be devoted towards a deeper understanding of the origin and mechanism of the magnetic exchange in this compound.

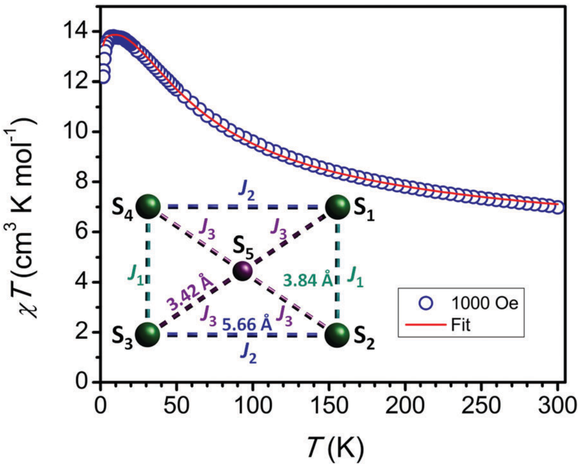

Fig. 3 Temperature dependence of the χT product at 1000 Oe for **1**. The solid red line corresponds to the best fit using the magnetic model described in the text. Inset: Schematic representation of the exchange coupling in the Ni$_4$ core of **1** with principal exchange pathways J_1, J_2 and J_3.

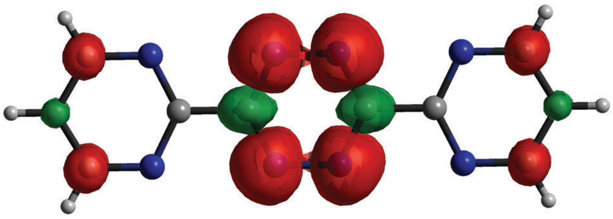

Fig. 4 Distribution of the spin density of the BpymTz$^{\bullet-}$ radical anion in **1**. Colour code: N (blue), C (grey). Note the antiferromagnetic coupling of the spin densities on N and C of the central C$_2$N$_4$ unit of the tetrazine.

The use of BpymTz as a template for four Ni^{II} metal ions has yielded the first example of a fully coordinated tetrazine-based ligand. The crystallographic and the magnetic investigations reveal evident ligand reduction upon coordination. Moreover, the magnetic properties unequivocally demonstrate strong intramolecular ferromagnetic interactions between the Ni^{II} ions and the tetrazine radical anion, with a large coupling constant of $J = 98.84$ cm^{-1}. DFT calculations confirm the dc measurements and the strength of the Ni^{II}–BpymTz$^{\bullet-}$ interactions in the system through which multinuclear metal complexes can be obtained with strong ferromagnetic interactions. Overall, this work demonstrates the spontaneous reduction of a tetrazine-based ligand in the presence of metal ions, leading to an air-stable tetrametallic complex which eliminates the need of exhaustive air-free conditions or reducing agents. Such unexpected ligand reduction of tetrazine-based ligands has been previously observed and are closely associated with the reaction conditions, where even diamagnetic starting metal salts we seen to be oxidized.[14c,e,16b] Thus, the results reported herein open a new avenue for designing and synthesizing air-stable radical-based complexes in the field of molecular magnetism.

We thank the University of Ottawa, the CFI and NSERC for their financial support. M. A. L. thanks Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ; 201395/2014-6) for a PhD scholarship. The authors also thank Dr N. F. Chilton for assistance with PHI.

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