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A novel high-spin tridecanuclear Ni^{II} cluster with an azido-bridged core exhibiting disk-like topology[†]

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A high-spin tridecanuclear Ni^{II} cluster, [Ni^{II}₁₃(N₃)₁₈(dpo)₄(Hdpo)₂-[Ni^{II}13(N3)18(dp0)4(Hdp0)2(H2hp0)4-(H2hpo)4(H2O)(MeOH) $(H_2O)_2$] (1) (Hdpo = 1-(dimethylamino)propan-2-one oxime and H_2 hpo = 1-(hydroxyamino)propan-2-one oxime) with a purely azido-bridged core, is reported with dominant ferromagnetic coupling between Ni^{II} ions. The latter molecule exhibits a unique planar core topology with the largest N_3^- : Ni^{II} ratio reported to date.

Organizing building blocks on a molecular scale has been a challenging task which led to the investigation of self-assembled molecular precursors.¹ In such molecules, controlling the interactions between metal ions provides a way to control the overall spin ground state of a complex. This consequently can have significant implications on its physical properties such as Single-Molecule Magnet (SMM) behaviour.² Transition metal complexes with characteristic oxido/hydroxido-bridged core structures are relatively well-known for exhibiting magnetic interactions that are ferro- or antiferromagnetic in nature without definite predictability.^{2d,3} Using chelating ligands to encapsulate a portion of metal oxido/hydroxido layers under basic solvolytic conditions has been a method of choice in nanoscale cluster chemistry where several factors can influence the nature of the interactions such as bridging ligands as well as their bridging modes, distances and angles.^{2d,3c,4} In order to exert a degree of control, oxido/hydroxido bridging moieties can be replaced by azide groups where the type of magnetic interaction promoted depends highly on the bridging mode.⁵ It has been well-documented that end-on (EO) and end-to-end (EE) bridging modes promote ferromagnetic and antiferromagnetic interactions, respectively.⁶ Therefore, azide groups provide a unique way of isolating similar structural cores with predominantly ferromagnetic coupling between metal centres.⁷ Recently, several attempts have been made towards this goal by Perlepes and co-workers^{1*f*,8} who demonstrated that replacing

 μ_4 -OH by μ_4 -N₃ in high nuclearity clusters of Co^{II}, Ni^{II} and Fe^{II} resulted in ferromagnetic coupling, however no purely azido-bridged complex has been reported. Herein, we describe a tridecanuclear Ni^{II} cluster, 1, exhibiting a heptanuclear disk-like core and the highest N_3^- : Ni^{II} ratio reported to date. To the best of our knowledge, compound 1 is an unprecedented example of a purely μ_3 -N₃ bridged planar core for a Ni^{II} cluster with an N_3^- : Ni^{II} ratio of 1.4 : 1. In addition to azide-based ligands, our synthetic strategy focuses on employing chelating ligands which arrest the formation of coordination networks/ sheets and form well-isolated complexes while maximizing intramolecular ferromagnetic interactions.

The Hdpo chelating ligand was synthesized through Cope-type hydroamination of 3-(dimethylamino)-1-propyne (dmp) with aqueous hydroxylamine in *n*-propanol (eqn (1)). Interestingly, complex 1 also shows the incorporation of a new ligand (H₃hpo) which is accessed in situ during the crystallization process and results from partial conversion of Hdpo to H₃hpo (eqn (2)). A detailed proposed mechanism of this conversion is described in Scheme S1 (ESI[†]).

The reaction of NiCl₂·6H₂O (0.059 g, 0.25 mmol) with Hdpo (0.029 g, 0.25 mmol) and sodium azide (0.033 g, 0.50 mmol) in 10 mL of MeOH resulted in a clear green solution from which dark-brown hexagonal crystals of [Ni^{II}₁₃(N₃)₁₈(dpo)₄(Hdpo)₂- $(H_2hpo)_4(H_2O)(MeOH)$] $[Ni^{II}_{13}(N_3)_{18}(dpo)_4(Hdpo)_2(H_2hpo)_4 (H_2O)_2$], **1A** and **1B**, were isolated (full experimental details are included in the ESI[†], caution should be taken during synthesis and handling as azide salts and related complexes can be potentially explosive). It is noteworthy that the singlecrystal X-ray crystallography (see Table S1 (ESI⁺) for parameters) revealed two clusters of $\{N_{i_{13}}\}$ in the same unit cell which differ only by one terminal ligand. In molecule A, terminal H₂O and MeOH are coordinated to Ni(6) and Ni(8), respectively, while

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in molecule B (Fig. S2, ESI^{\dagger}), terminal H₂O molecules are coordinated to the corresponding Ni^{II} centres, Ni(19) and Ni(21).

Complex 1 consists of both units A and B differing by one terminal solvent molecule which are arranged in layers that correspond to an ABA ordering. Although the packing arrangement along the *c*-axis shows overlapping A and B units within the layer, they are in fact positioned one in front of the other. This can be seen clearly in the packing diagram along the *b*-axis (Fig. S5, ESI[†]) with the shortest intra-layer Ni^{II}–Ni^{II} distance of 8.71 Å between Ni(6) and Ni(20). Moreover, the layers are arranged in an anti-parallel fashion permitting the closest packing possible with the shortest inter-layer distance of 8.88 Å between Ni(5) and Ni(21). Overall complex 1 consists of 1.4:1 N₃⁻: Ni^{II} ratio which makes this system potentially attractive for high-energy materials study. The initial "shock test" reveals that the latter complex is rather stable. Further studies are currently underway to examine the energetic content and methods of release for this complex. The structure of 1A consists of thirteen octahedral Ni^{II} ions arranged in a disk-like fashion (Fig. 1, top, with a fully labelled core structure in Fig. S3, ESI[†]). The coordination environment of the central Ni(7) atom consists of six N atoms exclusively from μ_3 -N₃ groups while the remaining Ni^{II} ions coordinate to both N- and O-based ligands. Complex 1A is rich in azide groups which display electronic versatility by bridging in two different modes: EO and EE. The planar



Fig. 1 Top: partially labelled tridecanuclear structure of complex **1A**. Hdpo and dpo⁻ ligands are shown in orange while H₂hpo⁻ ligands are shown in black. Colour code: green (Ni^{II}), blue (N), red (O). Bottom: side view of **1A** with the mean plane shown in dark green.



Fig. 2 Packing of **1** along the *c*-axis in an ABA arrangement in both *a*- and *b*-directions. Complex **1** consists of both units A and B which differ by one terminal coordinated solvent molecule.

central core consists of seven Ni^{II} ions bridged solely via six μ_3 -N₃ moieties which alternate above and below the mean plane (Fig. 1, bottom). The outer shell consisting of six Ni^{II} centres is linked to the planar core through μ_3 -N₃, μ -N₃ as well as oxime-based ligands which are highlighted in Fig. 1 in orange and black. Ni(6) and Ni(8) are connected to the central core exclusively through N_3^- moieties resulting in their orientation within the plane. The remaining four Ni^{II} centres are slightly out of the mean plane as illustrated in Fig. 2 due to twisting of the oxime bridges. Both Ni(12) and Ni(1) are above the plane by 0.43 and 0.42 Å, respectively, while Ni(13) and Ni(2) are below the plane by 0.44 and 0.42 Å, respectively. Selected bond distances, angles and torsion angles are listed in Table S2 (ESI[†]). Within the outer shell, Ni(1) and Ni(2) as well as Ni(12) and Ni(13) are bridged by N_3^- in an EE fashion. Bidentate Hdpo as well as tridentate dpo⁻ and H₂hpo⁻ oximebased ligands serve as capping agents in 1A forming fivemembered rings with peripheral Ni atoms resulting in isolated molecular entities. Additionally, compound 1A exhibits near C_2 symmetry through the central Ni^{II} ion as well as the mean plane of the core. Packing arrangements along the a-, b- and c-axes are shown in Fig. S4 and S5 (ESI⁺), and Fig. 2, respectively.

Magnetic studies were performed on a polycrystalline sample of 1. The direct current (dc) magnetic susceptibility under an applied dc field of 1000 Oe is plotted as $\chi T vs. T$ and shown in Fig. 3. The room temperature χT value of 18.86 cm³ K mol⁻¹ is slightly higher than the expected value of 13.00 cm³ K mol⁻¹ for thirteen non-interacting Ni^{II} ions with g = 2.0. As the temperature decreases, the χT value continuously increases reaching a maximum of 58.27 cm³ K mol⁻¹ at 5.5 K then drops to 56.36 cm³ K mol⁻¹ at 2.5 K. The increase of χT with decreasing temperatures is indicative of strong ferromagnetic coupling between the metal centres which is evident even at room temperature since the χT value is slightly higher than the aforementioned theoretical value. The observed ferromagnetic coupling is induced by the EO-N₃ bridges which tend to



Fig. 3 Temperature dependence of the magnetic susceptibility for 1 under an applied dc field of 1000 Oe. Inset: M vs. H/T plot showing non-saturation and non-superposition of the magnetization curves at different temperatures.

promote magnetic-orbital orthogonality due to sharp bridging angles.^{5b,c,6b} The maximum value of χT indicates a large spin ground state of 9 \leq S_T \leq 10 for g = 2. The *M* vs. *H*/*T* plot (Fig. 3, inset) shows non-saturation as well as non-superposition of the magnetization curves at low temperatures (2.5 K) and high applied magnetic fields (up to 7 T). This indicates the presence of low-lying excited states which significantly complicate the calculations of the spin ground state for 1. Additionally, in order to obtain a reasonable fit of the magnetic susceptibility, all six different magnetic exchange pathways (Fig. S6, ESI⁺) must be taken into consideration rendering the Hamiltonian equation quite complicated. The value of M at 2.5 K and 7 T of 17.76 $\mu_{\rm B}$ is in good agreement with $g \approx 2$ and $9 \leq S_{\rm T} \leq 10$. Moreover, the presence of two types of $\{Ni_{13}\}$ complexes (1A and 1B) further complicates the detailed analysis of the exact spin ground state. Alternating current (ac) magnetic measurements were performed on 1 in order to probe other potential properties such as slow magnetic relaxation characteristic of SMM behaviour. However, no out-of-phase, frequencydependent signal was detected even at low temperatures (down to 2.5 K) indicating the absence of such SMM behaviour.

In conclusion, an in-depth study of a novel, high-spin {Ni^{II}}₁₃ cluster has been reported focusing on its unique architectural features as well as magnetic properties. In recent vears, complexes with planar oxido/hvdroxido-bridged core structures have been investigated where the prediction of ferromagnetic interactions in such systems was not possible. We were able to alleviate this problem by promoting predominantly EO azido bridges between metal centres thus leading to dominant ferromagnetic interactions. To our knowledge, this is the first transition metal complex containing a single bridging mode, μ_3 -N₃, within the core as well as μ -N₃ and μ_3 -N₃ in the outer shell resulting in the highest N₃⁻ : Ni^{II} ratio reported to date of 1.4 : 1. Complexes with such a high N_3^- to metal ratio provide a route to novel high-energy materials, where energy storage and release could potentially be controlled by molecular architectures. Extension of this synthetic methodology may provide new avenues for molecular nanoscale materials with multiple applications. One of which could be the release of energy triggered *via* an applied magnetic field. To achieve such goals we are currently pursuing the isolation of high-energy materials with controllable magnetic properties.

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Notes and References

‡ Crystal data for 1: C₈₅H₁₉₀N₁₄₈Ni₂₆O₃₄, M = 5356.31, green block, monoclinic, $P2_1$, a = 19.046(3), b = 29.147(6), c = 23.518(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 100.48(1)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 12838(4) Å³, Z = 2, T = 200(2) K, $\lambda = 0.71073$ Å, $\theta_{\text{max}} = 21.97^{\circ}$, 78 643 reflections collected of which 9914 were independent, $R_1 = 0.0763$ [based on $I > 2\sigma(I)$], w $R_2 = 0.2366$ (based on F^2 and all data), GOF on $F^2 = 1.041$. CCDC 847307.

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