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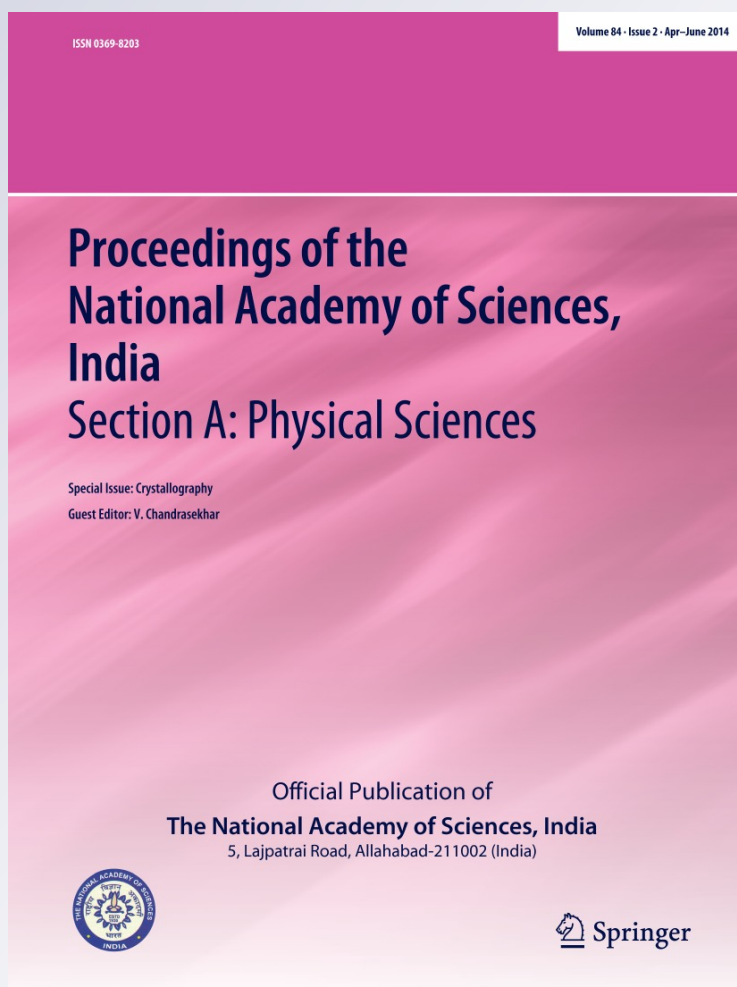
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Slow Magnetic Relaxation in an Asymmetrically Coupled Heptanuclear Dysprosium(III)–Nickel(II) Architecture

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Abstract A new dysprosium(III)–nickel(II) heterometallic cluster, namely, $[\text{Dy}_3^{\text{III}}\text{Ni}_4^{\text{II}}(\text{L})_6(\text{OH})_4(\text{CH}_3\text{OH})_3(\text{CH}_3\text{CN})(\text{NO}_3)(\text{OH}_2)] \cdot (\text{CH}_3\text{CN})_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2$ (**1**), has been synthesized from the schiff-base ligand H_2L ($\text{L} = o$ -phenol-salicylimine), dysprosium nitrate and nickel nitrate. A single-crystal X-ray diffraction study reveals that the highly asymmetric core of **1** consists of an unprecedented edge-sharing arrangement of three dissimilar Dy_2Ni triangles, along with one Dy_2Ni_2 rectangle, connected to one side of the central metallic core. Both static (dc) and dynamic (ac) magnetic properties of **1** have been studied. The results reveal that compound **1** exhibits slow relaxation of the magnetization, making **1** a remarkable new addition to the family of Ln–Ni single molecule magnets, having a new asymmetric Ni_4Dy_3 -architecture.

Keywords Dysprosium · Nickel · Cluster compounds · Asymmetry · Slow magnetic relaxation

Introduction

The field of a group of paramagnetic metal-ion aggregates, specifically termed as single molecule magnets (SMM) [1–12], continue to receive a great deal of attention due to the potential applications of such compounds in high-density information storage and information-processing technologies at the molecular level. SMMs are molecular species that are characterized by the slow relaxation of magnetization originating from the combination of a high-spin ground state and easy-axis magnetic anisotropy [13]. The discovery of SMM behaviour in dodecanuclear Mn_{12} acetate family in 1993 [14–16], where slow relaxation [17–21] and quantum tunnelling [22–24] of the magnetization is purely of molecular origin, triggered a lot of ground-breaking advances in this field over the last decade. Significantly, the inherent molecular spin-inversion barrier and blocking temperature (T_B) in these materials have a direct command [25, 26] over the fascinating success of such applications.

These SMMs can have potential applications in high-density information storage, quantum computing and molecular spintronics, owing to the fact that these molecules can retain spin information over long periods of time at low temperature [27, 28]. In the initial years of discovery, studies had largely been focused on polynuclear 3d metal aggregates and large manganese complexes [29]. But, recent years have seen quite a huge development in this field, the attention being clearly shifted to 4f-shell lanthanide ion based materials and 3d–4f mixed metal clusters, due to the significant magnetic anisotropy arising from the large unquenched orbital angular momentum of 4f metal ions, which increases the D value for the complex, resulting in higher energy barriers. An enhanced concern over SMMs based on 3d–4f mixed metal ions has grown dramatically after quite a large number of reports came

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over the last decade, on magnetic materials based on only 4f-metal ions [30–37]. To achieve better efficiency of these kind of magnetic materials, attainment of a deeper insight into the structure–property correlation of these kind of Ln–Ni complexes with varying nuclearity, is an extremely important issue to be addressed. Keeping in mind, that Dy^{III} shows remarkable magnetic behavior [38–41] and taking benefit of the Ni^{II} ion's significant single-ion anisotropy [42–49], we aimed to explore the possibility of obtaining a $\text{Ni}^{\text{II}}/\text{Dy}^{\text{III}}$ heterometallic cluster assembled from the schiff-base ligand H_2L ($\text{L} = o\text{-phenolsalicylimine}$, Fig. 1) having ditopic binding sites, as the bifunctional ligand to combine the 3d and 4f centers. The organic ligand H_2L has an inflexible molecular structure, capable of both coordinating and linking the two different types of metal ion centers. Recent years have seen only eight kinds of $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ cluster complexes to get reported till now, exhibiting interesting magnetic properties, with different heterometallic cores like, Ni_2Ln_2 , NiLn , $\text{Ni}_6\text{Gd}_6\text{P}_6$, Ni_3Gd , Ni_8Dy_8 , Ni_3Dy and Ni_2Ln [42–49]. Therefore, enough scope is still left to understand the fascinating $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ core's magnetism. In the present work, we report the use of H_2L for exploring new avenues for the much less-studied $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ cluster chemistry by describing an unprecedented heptanuclear Ni_4Dy_3 cluster, which presents novel structural features and interesting slow relaxation of magnetization.

Results and Discussion

Herein we report the preparation, structural description, and magnetic properties of a heptanuclear $\text{Ni}^{\text{II}}/\text{Dy}^{\text{III}}$ cluster, $[\text{Dy}_3^{\text{III}}\text{Ni}_4^{\text{II}}(\text{L})_6(\text{OH})_4(\text{CH}_3\text{OH})_3(\text{CH}_3\text{CN})(\text{NO}_3)(\text{OH}_2)](\text{CH}_3\text{CN})_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2$ (**1**), with a unique structural motif, incorporating the π -conjugated Schiff base ligand

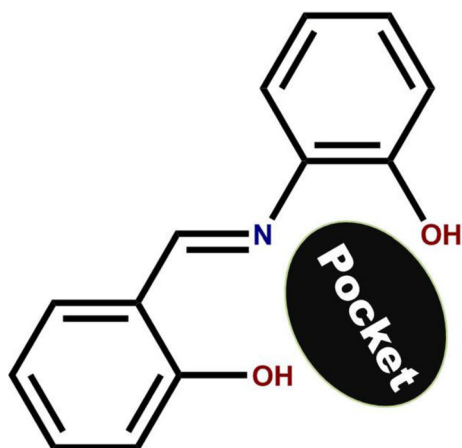


Fig. 1 Structure of the ligand H_2L with a potential pocket to fit in the metal ion (s) M [$\text{M} = \text{Dysprosium(III)/Nickel(II)}$]

H_2L , namely, $o\text{-phenolsalicylimine}$ [50] (Schiff base resulting from the condensation of salicaldehyde and 2-aminophenol) (“Experimental Section”). This cluster complex contains three non-equivalent fused triangles coupled on one side by a Ni_2Dy_2 rectangle, in an asymmetric fashion to give rise to a new Ni_4Dy_3 central core, which is unprecedented in $\text{Ni}^{\text{II}}/\text{Ln}^{\text{III}}$ coordination chemistry. Such an irregular arrangement of dysprosium and nickel atoms in the central core of this kind of heterometallic cluster, can give rise to interesting magnetic properties; since the asymmetric structural motif, comprised of the exclusive blend of three Dy^{III} triangles and a Ni_2Dy_2 rectangle, assembled by an unparalleled combination of two different joining modes, should have a direct influence over the magnetism properties of the complex. Notably, the “edge-to-edge” arrangement between the three Ln_2Ni triangles was similar to the one first reported between two Dy_3 triangles to constitute a Dy_6 Cluster [41]. The reaction of $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with H_2L (1:1:2 mol ratio, respectively) (ligand synthesized according to reported literature [50]) in MeOH/MeCN (2:1, v/v) in the presence of Et_3N (see “Experimental Section” for detailed synthesis procedure) produces greenish-brown crystals of $\text{Dy}_3^{\text{III}}\text{Ni}_4^{\text{II}}(\text{L})_6(\text{OH})_4(\text{CH}_3\text{OH})_3(\text{CH}_3\text{CN})(\text{NO}_3)(\text{OH}_2)] \cdot (\text{CH}_3\text{CN})_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2$ (**1**), after one week of slow evaporation.

A perspective view of the heptanuclear $\text{Ni}_4\text{Dy}_3^{\text{III}}$ motif is represented in Fig. 2. Overall arrangement of these two metals in the central core depicts one with considerably high asymmetry. All the six ligands present in the molecule are completely deprotonated. The ligands coordinated by each of their two oxygen donor sites and central nitrogen site are making one five membered and one six membered chelating ring with each of the Dy and Ni centers. L is coordinated in bridging, as well as chelating mode where none of the metal centers are bridged by central nitrogen, but linked by their terminals containing phenoxo group (Figure S2). First triangle A (Fig. 3) comprised of Dy2, Dy3 and Ni4 centres connected through η^2 chelating mode of phenoxo side of the L and the central $\mu_3\text{-OH}$ bridge (O12, O17, O18), gives indirect Dy–Dy and Dy–Ni distances as follows: 3.743 Å (Dy2–Dy3), 3.939 Å (Dy2–Ni4), 3.509 Å (Dy3–Ni4), respectively. Second triangle B is constituted of Dy1, Dy2 and Ni4 centres in a similar fashion to give intermetallic distances as Dy1–Dy2 = 3.559 Å, Dy1–Ni4 = 3.452 Å, Dy2–Ni4 = 3.939 Å respectively, whereas the other triangle C is comprised of Dy1, Dy2, Ni1 centres, having Dy1–Dy2 = 3.559 Å, Dy1–Ni1 = 3.400 Å, Dy2–Ni1 = 3.881 Å respectively. The Dy_2Ni triangle is a bit different from the perspective of coordination modes as compared to the analogous triangles B and C, since it is the only distinct heterometallic triangle in this core devoid of any $\mu_3\text{-oxo}$ bridge.

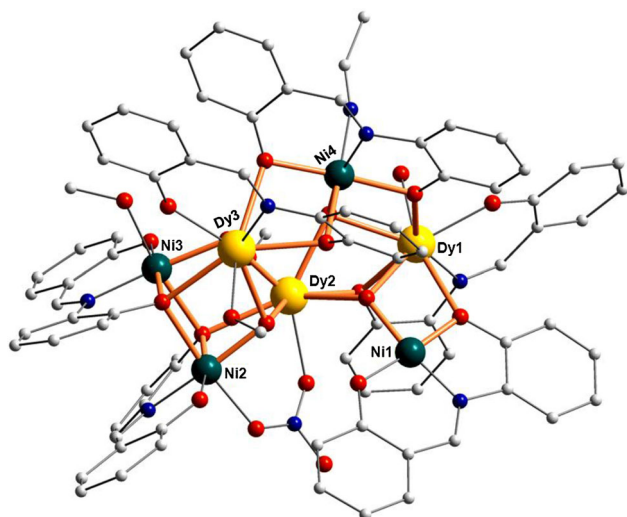


Fig. 2 Heptanuclear unit of **1** with the central core highlighted by bold bonds. H atoms are omitted for clarity. Color scheme: yellow Dy; red O; blue N. (Color figure online)

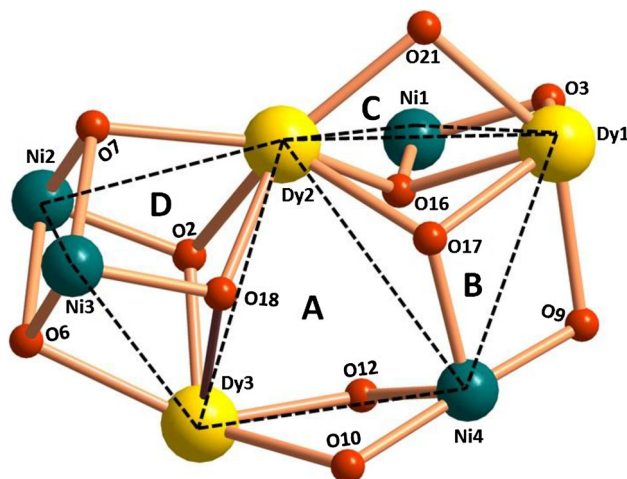


Fig. 3 The central heterometallic core of **1**; similar Dy₂Ni triangular subunits A, B and C being distinctly different from the rectangular Dy₂Ni₂ subunit (D)

Importantly, any two of these three triangles have one side common to them, making the motif of three triangles a typical edge-sharing one. Asymmetry aspect of the central heterometallic core gets further enhanced due to the presence of Ni₂Dy₂ rectangle composed of Dy₂, Dy₃, Ni₃ and Ni₂ centers, which shares one edge with the Ni₂Dy₂ triangular subunits A. The indirect inter-metal distances in this rectangle are: Dy₂–Dy₃ = 3.743 Å, Dy₃–Ni₂ = 3.564 Å, Ni₃–Ni₂ = 3.145 Å, Ni₃–Dy₂ = 3.554 Å (Figure S3). Except six chelated ligands and four μ_3 -OH bridges, there are also water, acetonitrile and methanol molecules to fulfil the coordination sphere of the metallic centers. Noteworthy is that the nitrate bridges the Dy₂ and Ni₂ centres in μ_2 -nitrate-O,O' fashion. All the three dysprosium centres are

eight-coordinated whereas, three of the four nickel centres are octahedral i.e., Ni₂, Ni₃ and Ni₄ being hexacoordinated and the other Ni-centre Ni₁, is present in square-planar arrangement. The entire asymmetric arrangement of the central metallic core is depicted in Fig. 3 and also in the coordination polyhedra shown in Figure S1. Intramolecular π – π interactions are present between two pairs of ligands among the total three pairs present in the heptanuclear complex (Figure S4).

From the standpoint of the magnetic property, ignoring the diamagnetic Ni^{II} ions, which has O₃N coordination sphere, thus the metallic core of Dy₃Ni₄ can be regarded as Dy₃Ni₃. Direct-current (dc) magnetic susceptibility studies (Figs. 4, 5) reveal a room-temperature $\chi_M T$ value of 50.61 cm³Kmol^{−1}, higher than the expected values of 45.51 cm³Kmol^{−1} for three isolated non-interacting Dy³⁺ ions

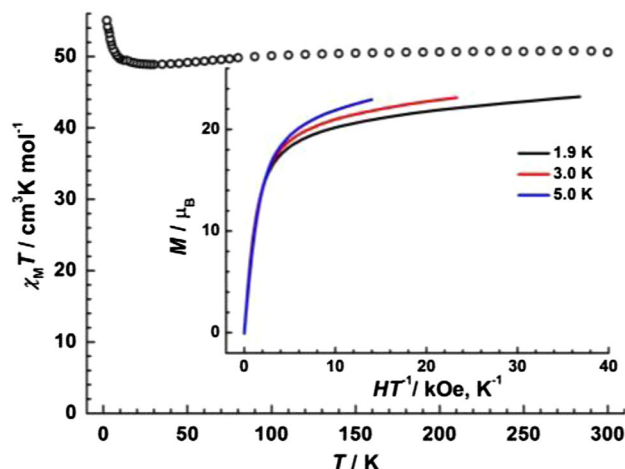


Fig. 4 Temperature dependence of $\chi_M T$ at 1 kOe for **1** (with $\chi = M/H$ normalized per mol). Inset M versus HT plot at various temperatures between 1.9 and 5 K

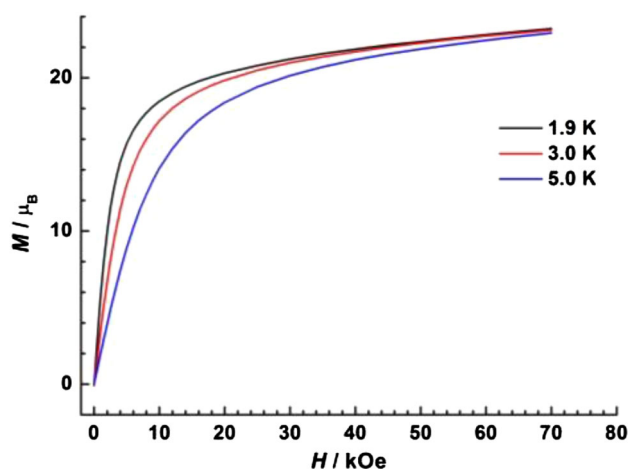


Fig. 5 Field dependence of the magnetization for **1** at various temperatures between 1.9 and 5 K

($S = 5/2$, $L = 5$, ${}^6\text{H}_{15/2}$, $g = 4/3$) and three Ni^{2+} ($S = 1$, $g = 2$). Upon lowering the temperature, $\chi_{\text{M}}T$ stays fairly constant down to 20 K and then increases markedly to $55.04 \text{ cm}^3 \text{ K mol}^{-1}$ at 2.0 K. This increase of $\chi_{\text{M}}T$ at low temperature may suggest the presence of intramolecular ferromagnetic interactions within the metallic Dy_3Ni_3 core as observed in other $\text{Ni}^{\text{II}}\text{-Ln}^{\text{III}}$ systems [51–58].

The field dependence of magnetization of **1** is not all superimposed on a single master curve, implying the presence of significant magnetic anisotropy and/or low-lying excited states. The magnetization eventually reaches the value of $23.21 \mu_{\text{B}}$ for **1** at 1.9 K and 70 kOe without clear saturation.

AC magnetic susceptibility studies were performed on **1** in a zero applied dc field and a 3 Oe ac-field oscillating at frequencies in the 3–1,200 Hz range (Fig. 6). Compound **1** exhibited a frequency-dependent out-of-phase (χ'') signal below 25 K, indicative of the onset of slow relaxation. However, no maxima has been observed in the temperature dependence of χ'' above 2 K at frequencies reaching 1,200 Hz, due to the existence of fast quantum tunnelling relaxation of the magnetization. Thus a combined input of the experimental efforts like this one, coupled with field-dependent measurements, theoretical calculations, and simulations and doping studies, is extremely crucial in

future to realize the underlying fundamental mechanism in polynuclear lanthanide-nickel complexes and their structure–property relationships, which will eventually help to open up new avenues for investigating the relaxation dynamics of the interesting Ln/Ni aggregates.

Conclusions

In summary, a tridentate Schiff-base ligand *o*-phenolsalicylimine has been effectively employed to bring together Ni^{II} ions along with Dy^{III} ions, affording a new heptanuclear $\text{Ni}_4^{\text{II}}\text{Dy}_3^{\text{III}}$ complex with a distinctive asymmetric motif, constructed by an unmatched combination of three edge-sharing NiDy_2 triangle units and one Ni_2Dy_2 rectangular unit. This compound is an important addition to the family of Ln–Ni single molecule magnets having a unique asymmetric Ni_4Dy_3 -architecture exhibiting slow relaxation of the magnetization.

Experimental Section

Synthesis of compound 1: The compound $[\text{Dy}_3^{\text{III}}\text{Ni}_4^{\text{II}}(\text{L})_6(\text{OH})_4(\text{CH}_3\text{OH})_3(\text{CH}_3\text{CN})(\text{NO}_3)(\text{OH}_2)] \cdot (\text{CH}_3\text{CN})_3(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2$ (**1**) was synthesized as following: triethylamine (0.056 mL, 0.4 mmol) was added to the ligand H_2L (0.2 mmol, 42.6 mg) dissolved in methanol/acetonitrile (10 mL/5 mL). The reaction mixture was sonicated for 1 h. Solid dysprosium nitrate hexahydrate (0.1 mmol, 45.6 mg) was added along with solid nickel nitrate hexahydrate (0.1 mmol, 29 mg), and the resulting yellow solution was stirred for 1 h. The reaction mixture was left unperturbed to allow slow evaporation of the solvent. Rod-shaped dark greenish-brown single crystals were obtained after one week. Yield: 46 mg, (53 %, based on the metal). Anal. calcd. (found) for $\text{C}_{91} \text{H}_{89} \text{N}_{11} \text{O}_{27} \text{Dy}_3 \text{Ni}_4$: C, 49.08 (49.06); H, 4.68 (4.59); N, 2.58 (2.61).

CCDC-941834 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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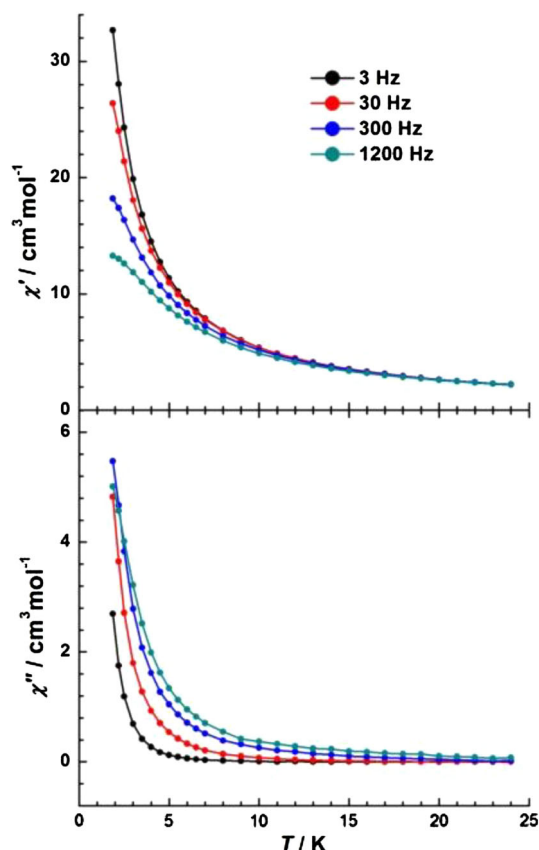


Fig. 6 Temperature-dependence ac susceptibility data for **1** collected under zero dc field at the indicated frequencies

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