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Hydroxido Supported and Differently Networked Octanuclear Ni₆Ln₂ [Ln = Gd³⁺ and Dy³⁺] Complexes: Structural Variation, Magnetic Properties and Theoretical Insights

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The design and synthesis of Schiff base H₂L₄, {2-[[2-hydroxy-3-methoxybenzyl)]imino][methyl]phenol} bearing ONOO donor set has been explored for its reactivity pattern with LnCl₃·6H₂O (Ln = Gd³⁺ and Dy³⁺) and Ni(CH₃CO₂)₂·4H₂O in the presence of NEt₃ for molecular aggregation. Coordination driven spontaneous self-assembly reactions provides [Gd₆Ni₂L₄(μ-OH)L₃(H₂O)]₂[Ni₃(CH₃CO₂)₄](μ-OH)₄]·8H₂O (1), having ‘butterfly-shaped’ core and [Dy₆Ni₂L₄(μ-OH)L₂(Cl)₂(C₂H₅OH)]₂MeOH·4H₂O (2) with ‘candy-shaped’ core. Fusion of six partial cubane units led to mineral-like core in 1, developed around central Ni₃(OH)₂ moiety; whereas in case of 2, four such partial cubanes are collapsed on Dy₆(OH)₁₂. Direct-current (dc) magnetic susceptibility measurements reveal predominantly ferromagnetic interactions leading to a high-spin S = 13 ground state for 1. Complex 2 exhibits slow relaxation of magnetization in a small applied dc field with an energy barrier to reorientation of the magnetization, U₁ thaw = 19.3 K. The static and dynamic magnetic data are analysed and corroborated by density functional theory (DFT) and detailed CASSCF based calculations.

Introduction

In recent years synthetic endeavours toward the discovery of heteronuclear 3d–4f multimetallic coordination aggregates (MCAs), have attracted significant attention to rationalize the coordination behaviour of the designed ligand anions to manifest the unknown aggregation paths. Coordination networking of metal ions of two different types, having unique topology, often takes the supports of used organic ligands and account for their prospect to emerge as molecule-based magnets.1–2 These molecular magnets can exhibit slow relaxation of magnetization, can have applications in high–magnets.

Magnetic anisotropy, is often associated with structural (S) with poor zero-field splitting (D). Incorporation of selected topology, often takes the supports of used organic ligands and manifest the unknown aggregation paths. Coordination coordination behaviour of the designed ligand anions to leading to a high-spin S = 13 ground state. Coordination aggregates with multiple metal centres often possesses high-spin ground state (S) with poor zero-field splitting (D). Incorporation of selected lanthanide ions within the MCA’s with appreciable single ion magnetic anisotropy, is often associated with structural distortion and spin-orbit coupling.8–9 resulting increase of anisotropy barrier10 and suppression of ground state quantum tunneling of magnetization11 (QTM), lead to slow relaxation of magnetization.12 High spin Ni⁴⁺ ions have major contribution toward magnetic anisotropy13; moreover Ni⁴⁺ ion also possesses ferromagnetic exchange interaction with the Ln⁴⁺ ions.14–18 Widespread efforts can be exercise to synthesize new family of high nucleility MCAs having aesthetically pleasing shapes like wheels, triangle, butterfly, stars etc. Appropriate functionalization on ligand backbone can provide two adjacent but different coordination sites suitable for coordination of both 3d and 4f ions. The Lewis acidic nature of hard trivalent 4f ions are suitable to initiate hydrolysis of bound H₂O molecules.19 Exploitation of such coordination induced hydrolytic reaction conditions around 4f ions, can result large numbers of hydroxido bridges, necessary for the growth of mineral–like magnetic cores.20 Multinuclear hetero–metallic aggregates are well known during the last two decades, which includes e.g., Ni₈L₈,21 Ni₄L₄,13 Ni₁₂Gd₆,22 Co₄L₄Ni,23 and Cu₂ZnL₄. Use of semi–rigid phenol-based Schiff base ligand system bearing flexible C–N and rigid –C=C sides is presumed to control the hydrolytic aggregation reaction following 3d ion bound initially formed fragments.25

Herein, 2-[[2-hydroxy-3-methoxybenzyl)]imino][methyl]phenol (H₂L₄) (Fig. S1, ESI) was screened for preferential coordination of Ni⁴⁺ and Gd⁴⁺/Dy⁴⁺ ions. Systematic reaction protocol toward this endeavour resulted [Gd₆Ni₂L₄(μ-OH)L₃(H₂O)]₂[Ni₃(CH₃CO₂)₄](μ-OH)₄]·8H₂O (1) and [Dy₆Ni₂L₄(μ-OH)L₂(Cl)₂(C₂H₅OH)]₂MeOH·4H₂O (2) from the reactions of L²⁻, Ni(CH₃CO₂)₂·4H₂O and GdCl₃·6H₂O or DyCl₃·6H₂O, respectively. Two different 4f ions provided contrasting paths during the growth of octanuclear aggregates, is not usual in Ni–Ln family; encourage us to study the relevant functional behaviours in the solid state.

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e Electronic Supplementary Information (ESI) available: SHAPE analysis, Crystal data, PXRD curves, selected bond lengths and angles, TGA analysis, AC susceptibility and CASSCF calculations are described in Fig. S1–S14 and Tables S1–S8 in the text. CCDC 2021668 and 2021678 contain the supplementary crystallographic data for this paper. See DOI: 10.1039/x0xx00000x

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Experimental Section

Reagents and Starting Materials

All the reactions performed for this work were done at room temperature in aerobic conditions. Solvents used in this work were purified and all the starting materials used for this work were of reagent grade. 3-methoxysalicylamine was synthesized following a reported procedure. The following chemicals were used as received without further purification: Ni(CH$_3$CO$_2$)$_2$·4H$_2$O, and NEt$_3$ (S. D. Fine Chemicals, Mumbai, India), DyCl$_3$·6H$_2$O and GdCl$_3$·6H$_2$O (Alfa Aesar, India), o-vanillin (Spectrochem Pvt. Ltd. Mumbai).

Synthesis of 2-\{[(2-hydroxy-3-methoxybenzyl)imino]methyl\}phenol (H$_2$L)

The ligand H$_2$L was synthesized following our previously reported work.

Synthesis of 1−2

A general synthetic procedure was followed to obtain 1 and 2 in good yield. H$_2$L (0.025 g, 0.10 mmol) was dissolved in 10 mL of (2:1, v/v) MeOH−CHCl$_3$ solution. LnCl$_3$·6H$_2$O (0.05 mmol) (Ln$^{3+}$ = Gd$^{3+}$ and Dy$^{3+}$) and NEt$_3$ (0.02 g, 0.20 mmol) was added to the above solution and stirred for 2 h. Another 10 mL MeOH solution of Ni(CH$_3$CO$_2$)$_2$·4H$_2$O (0.025 g, 0.10 mmol) was then added and the green solution thus obtained was stirred for 3 h. To the filtered solution, 6 mL of CH$_2$Cl$_2$ was added and left undisturbed for slow evaporation. X-ray diffraction quality single crystals were isolated within 4−7 days and washed with cold EtOH.

$[\text{Gd}_2\text{Ni}_6\text{L}_4(\mu_3\cdot\text{OH})_2(\mu\cdot\text{OH})_2(\text{CH}_3\text{CO}_2)_2(\mu\cdot\text{H}_2\text{O}_2)(\text{MeOH})_2]\cdot 8\text{H}_2\text{O}$ (1). Yield: 0.036 g, 59% (based on Gd). Anal. Calcd for C$_{65}$H$_{95}$Gd$_2$N$_4$Ni$_6$O$_{38}$ (2207.11): C, 35.37; H, 4.34; N, 2.54. Found: C, 35.12; H, 4.37; N, 2.51. Selected FT-IR data (KBr) cm$^{-1}$: 3369 (br), 1641 (m), 1595 (m), 1576 (m), 1475 (s), 1446 (m), 1409 (m), 1341(w), 1324(m), 1280 (s), 1222 (w), 1070 (s), 1034 (m), 853 (w), 745 (s), 600 (w).

$[\text{Dy}_2\text{Ni}_6(\text{L})_4(\mu_3\cdot\text{OH})_4(\mu\cdot\text{Cl})_2\text{Cl}_2(\text{MeOH})_2]\cdot 2\text{MeOH} \cdot 4\text{H}_2\text{O}$ (2). Yield: 0.029 g, 52% (based on Dy). Anal. Calcd for C$_{64}$H$_{84}$Cl$_6$Dy$_2$N$_4$Ni$_6$O$_{26}$ (2215.24): C, 34.70; H, 3.82; N. 2.53. Found: C, 34.62; H, 3.79; N, 2.54. Selected FT-IR data (KBr) cm$^{-1}$: 1634 (m), 1550 (m), 1543 (m), 1476 (s), 1405 (m), 1287 (s), 1343 (w), 1227 (w), 851 (w), 737 (m), 602 (w).

Physical Measurements

Perkin-Elmer model RX1 FT-IR spectrometer was used to perform FT–IR spectral measurements using a KBr disk. For the Elemental analysis (C, H, N) of the complexes, a Perkin–Elmer model 240C elemental analyser was used. The purity of the bulk complexes were checked by powder XRD using a BRUKER AXS X-ray diffractometer (40 kV, 20 mA) using Cu-Kα radiation ($\lambda = 1.5418$ Å) within 5−50° ($\theta$) range and a fixed–time counting of 4 s at 25°C. Perkin Elmer Pyris Diamond TG-DTA instrument was used to perform thermogravimetric analysis.

Magnetic measurements

All magnetic measurements were carried out on powdered crystalline samples restrained in eicosane using a Quantum Design MPMS 3 SQUID magnetometer. Data were corrected for the diamagnetic contribution of the sample holder and eicosane by measurements, and for the diamagnetism of each compound.
X-ray Crystallography

Appropriate single crystals of 1 and 2 were chosen for data collection on a Bruker SMART APEX-II CCD X-ray diffractometer furnished with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation by the ω scan (width of 0.3° frame1) method at 112 K with a scan rate of 6 s per frame. SAINT and XPREP software's were used for data processing and space group determination. The crystal structures were solved by direct method technique from SHELXS-2014 and then refined by full-matrix least squares technique using SHELXL (2014/7) program package within Olex-2.32 Empirical absorption correction was applied using the SADABS.33 The locations of the heaviest atoms i.e. Ni, Gd or Dy were determined easily whereas the other non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were incorporated at calculated positions and refined using the riding model. Crystallographic diagrams were presented using DIAMOND software.34 Non-routine aspects of refinement: For both the complexes 1 and 2, modelling of all lattice solvent molecules was not possible, due to disorder. So, mask program of Olex-2 software has been performed to remove those disordered solvent molecules and from the % weight loss of thermogravimetric analysis (Fig. S2, ESI), we have assigned 8H2O for complex 1 and 2MeOH and 4H2O for complex 2, respectively. The disorder of the peripheral [NiCl2] moiety in complex 2 has been improved by changing its occupancy which has been briefly discussed in the ESI. The crystal data and the cell parameters for compounds 1–2 are summarized in Table S1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2021668 and 2021678.

Theoretical calculations

The theoretical calculations at DFT level were carried out with the ORCA 4.2 software and B3LYP hybrid functional.37–40 The DKH relativistic approximation41,42 with quadruple zeta basis SARCC-DKHK-QZVP for Dy and SARCC-DKHK-QZV for Lu,43 DKH-def2-TZVP for Ni and DKH-def2-SVP for all other atoms.44 The SARC/J Coulomb fitting basis set was utilized as an auxiliary basis set. Additionally, Gaussian finite nucleus approximation to exact exchange was applied together with chain-of-spheres (RIJCOSX) approximation to exact exchange–46,47 as implemented in ORCA. Increased integration grids (Grid7 and Grid8 in ORCA convention) and tight SCF convergence criteria were used in all calculations. Moreover, the increased radial integration accuracy for Gd and Ni atoms was also set. The state average complete active space self-consistent field (SA-CASSCF) wave functions calculations on DyIII and NiII ions were done with OpenMOLCAS 19.11.49 In the case of DyII ion, the active space was defined as 9 electrons in 7 f-orbitals, CAS(9,7). The RASSCF method was used in the CASSCF calculations with the following numbers of multiplets: 21 sextets, 224 quartets, and 490 doublets. In the case of NiII ions, CAS(8,5) active space was set resulting in 10 triplets and 15 singlets. The spin-orbit coupling based on atomic mean-field approximation (AMFI) was considered using RASSI–SO. While all multiplets of NiII were included in this procedure, due to the large number of states of DyIII, the number of states included in RASSI–SO was limited as follows: 21 sextets, 128 quartets, and 130 doublets. The relativistic effects were treated with the Douglas-Kroll Hamiltonian. The following basis sets were used: ANO–RCC–VQZP for Dy, ANO–RCC–VTZP for Ni and ANO–RCC–VDZP for coordinated oxygen/nitrogen atoms, while ANO–RCC–MB for all other atoms.50 After that SINGLE_ANISO module was applied to deduce the properties of paramagnetic ions. Subsequently, the home-made routine was used to fit experimental magnetic susceptibility in cooperation with POLY_ANISO module.54–56 All calculations were based on the experimental X-ray structures of 1 and 2, in which only hydrogen atoms positions were modified with program Mercury using normalize hydrogen function.57 The calculated spin density was visualized with VESTA 3 program.58

Results and Discussion

Design and synthesis

Schiff base H2L has been synthesized from the reaction of o-vanillin amine and salicylaldehyde. Recently we have proved that this ligand H2L having multiple numbers of donor atoms, is useful to provide NiII–LnIII and NiII–MnII–LnIII complexes while reacting with 3d metal ion salt along with LnIII nitrate or LnIII acetate salts.28 Here we further explore its coordination potency in presence of LnIII chloride and NiII metal ion salts in synergistic fashion. The stepwise reactions of H2L with GdCl3·6H2O and NET3 in MeOH–CHCl3 (2:1, v/v) solution followed by addition of Ni(CH3COO)2·4H2O in 2:2:4:2 molar ratio provided [Gd3Ni2L4(μ3-OH)4(μ-OH)2(CH3COO)2(μ-H2O)2(μ2-O2)4(μ-OH)2]·6H2O·6H2O (1) (Scheme 1). The site selective coordination of different types of metal ion, followed by hydroxide bridge driven aggregation during the formation of 1, summarized in the chemical eq. 1.

2GdCl3·6H2O + 6Ni(CH3COO)2·4H2O + 4H2L + MeOH → [Gd3Ni2L4(μ3-OH)4(μ-OH)2(CH3COO)2(μ-H2O)2(μ2-O2)4(μ-OH)2]·6H2O·6H2O + 10CH3CO2− + 6Cl− + 16H+ + 15H2O... (1)

Liberation of in situ formed acetic acid, is in the line of typical reactivity of metal ion acetate with protonated ligand molecules, could guide the course of hydrolytic aggregation behaviour. The use of DyCl3·6H2O in place of GdCl3·6H2O resulted Ni2Dy2 aggregate of same number of individual 3d and 4f ions but interestingly of different molecular architecture. Varying path of hydrolytic aggregation and coordination of chlorine ions to NiII centres resulted [Dy2Ni4L4(μ3-OH)4(μ2-Cl)2Cl6(H2O)2(μ2-OH)]·2MeOH·4H2O (2). Six available chlorido ligands from two DyCl3·6H2O are crucial in guiding a different route of aggregation for a diverse octanuclear 3d-4f complex resting on tetracubane core structure. The coordination aggregation reaction during synthesizing complex 2 is summarized in the chemical eq. 2.
Interestingly this type of reaction scheme with such lanthanide metal ion specificity is very rare in literature. The powder pattern of both the samples are matches well with simulated PXRD plot (Fig. S3 in the ESI). Initial characterization of the powder samples by FTIR spectral analysis indicated the metal ion binding through imine backbone of the ligand anion. For complex 1, the \( v_{C=O} \) stretching frequency lies at 1641 cm\(^{-1}\) whereas for complex 2 it is detected at 1634 cm\(^{-1}\). The asymmetric and symmetric stretching frequency at 1595 cm\(^{-1}\) and 1324 cm\(^{-1}\) confirms the presence of terminal acetoacetato ancillary group. The asymmetric and symmetric stretching frequency at 1634 cm\(^{-1}\) is then identified as \([\text{Gd}\text{L}^2\text{O}]^{-}\) in complex 1. The crystal parameters are unique; the \( \Delta P \) is 271 cm\(^{-1}\) in complex 1. We have tried our best, to extend our synthetic exploration for other Ln\(^{III}\) ions of similar size to explore further the role of 4f ions in variation of molecular structure, but unfortunately, we are not able to isolate any suitable single crystal from the attempted reactions using salts of other lanthanide ions.

**Crystal Structure Description for Complex 1**

Suitable single crystals of complex 1 were obtained after four days from the reaction mixture with added CH\(_2\)Cl\(_2\). The electro neutral complex crystallizes in triclinic \( \text{P} \bar{1} \text{T} \) space group. The asymmetric unit contains half of the whole molecule, where the ORTEP plots of same at 50% ellipsoid probability showed in Fig. S4 in the ESI. The molecular structure of complex 1 is then identified as \([\text{Gd}\text{Ni}_{6}\text{L}_{6}\text{S}_{2}\text{O}]^{-}\) as seen in Table S1 and the selected bond length and angles are presented in Table S5–S6 in the ESI.

Examination of the molecular structure, indicates that four L\(^2\) units are utilized for the growth of the molecular core bearing six Ni\(^{II}\) and two Gd\(^{III}\) ions. Four individual Ni\(^{II}\) ions directly bind to the imine pockets of four L\(^2\) to yield four (NiL) fragments having further coordination potential for Gd\(^{III}\) ions at the \( \text{OMe} \) donor in the di-cubane part the \( \mu\)-OH bridging. All the six Ni\(^{II}\)–O\(^{\mu}\) separations are observed within a range of 2.018(6)–2.077(6) Å. The separation involving bridging HO\(^{\cdots}\)O in comparison to HOO\(^{\cdots}\)O is longer at 2.982(5) Å at the core. The distortions in the coordination environments around Gd\(^{III}\) ions help to form this core. This core formed from six separate fused dicubane units with the participation of six \( \mu\)-OH\(^{\cdots}\)O, two \( \mu\)-OH\(^{\cdots}\)O and two \( \mu\)-OH\(^{\cdots}\)O units, which is rare in literature.

Within the [Ni\(_6\)Gd\(_{2}\)O\(_{12}\)]\(^{10+}\) octanuclear core of the [Ni\(_6\)HO\(_5\)]\(^{2+}\) unit was trapped by two [Ni\(_6\)Gd\(_{2}\)O\(_{12}\)] parts with the association of several other \( \text{HO}^{\cdots}\) bridges, forming the central [Ni\(_6\)Gd\(_{2}\)O\(_{12}\)]\(^{10+}\) butterfly core, where the [Ni\(_6\)HO\(_5\)]\(^{2+}\) unit has no ligand anion support.

Complex 1 has disordered six-coordinate octahedral NO\(_2\) and O\(_6\) environments around three types of Ni\(^{II}\) centres (OC–6 = 0.544 for NiI, 1.386 for Ni2 and 0.646 for Ni3; Table S2 in the ESI, Fig. 2). The imine nitrogen bond four NiO\(_2\) centres have one adjacent Ni\(^{II}\) and one Gd\(^{III}\) centres, bridged by \( \mu\)-OH and PhO\(^{\cdots}\) groups. On the contrary, two NO\(_2\) moieties are bridged by only hydroxido bridges. For the ligand coordinated Ni\(^{II}\) centres, the Ni–N distances of 1.989(7)–1.997(8) Å range and the Ni–O distances are in 1.982(6)–2.201(6) Å range showing identifiable variation due to the presence of four different types of O donors. Interestingly the Ni–O(\( \mu\)-OH) distances within 2.169(6)–2.201(6) Å range are slightly longer than the Ni–O(\( \mu\)-OH) at 2.134(6)–2.146(6) Å. Ni–O from terminal H\(_2\)O at 2.089(6)–2.111(7) Å and Ni–O(\( \mu\)-OH) at 2.018(6)–2.077(6) Å distances, respectively. Out of the five Ni–Ni distances, three are unique; the Ni3–Ni3* separation is 2.982(5) Å at the core. The Ni1–Ni3 separation involving bridging HO\(^{\cdots}\)O and H\(_2\)O groups is longer at 3.164 Å in comparison to 3.122 Å for Ni2–Ni3*. The observed difference of 0.042 Å is attributed to the weaker bridging potential of H\(_2\)O in comparison to HO\(^{\cdots}\).

The distorted nine-coordinate O\(_6\) geometry around Gd1 and Gd1* are assembled from two \( \text{OMe}_2\)O bites of L\(^2\), three HO\(^{\cdots}\) bridges, and one bidentate terminal AcO\(^{\cdots}\) group giving rise to a distorted muffin like arrangement as verified by SHAPE 2.1 calculations (MFF-9 = 2.087, Table S3 in the Electronic Supporting Information, Fig. 3a). Four different Gd–O and O–Gd distances are observed within 2.32(6)–2.69(2) Å range, following the order, Gd–O(\( \mu\)-OAcato) > Gd–O(\( \mu\)-Omethoxy) > Gd–O(hydroxido) > Gd–O(phenoxy). Within the central Ni\(_6\)Gd\(_2\)O\(_6\) dicubane part the Ni3–Gd1, Ni3–Gd1* and Gd1–Gd1* distances are longer at 3.453(5) Å, 3.471(4) Å and 6.249(7) Å respectively. Here, the Ni–O and Gd–O distances lie within 2.018(6)–2.064(5) Å and 2.382(7)–2.389(6) Å respectively. The bond angles around \( \mu\)-OH\(^{\cdots}\)O are, \( \angle \text{Ni3}–\text{O9}–\text{Gd1} = 101.9(19)° \) and \( \angle \text{Ni3}–\text{O9}–\text{Gd1*} = 102.1(19)° \) and for \( \angle \text{Ni3}–\text{O9}–\text{Ni3*} = 92.8(2)° \) showing the flattened cube vertex at the bigger Gd\(^{III}\) ions (Fig. 3b). The other Ni–O–Gd angles are also wider, \( \angle \text{Ni3}–\text{O8}–\text{Gd1}; 103.1(2)° \) and \( \angle \text{Ni3*}–\text{O11}–\text{Gd1}; 103.5(2)° \). The Ni–O–Ni angle is slightly narrow for aqua bridged structure \( \angle \text{Ni1}–\text{O7}–\text{Ni3}; 92.8(2)° \) compared to \( \angle \text{Ni2}–\text{O10}–\text{Ni3} = 93.7(2)° \) for hydroxido bridging. All the six Ni\(^{II}\) centres remain within the plane and the Gd1 and Gd1* atoms show deviation by 0.253 Å from the
plane. No characteristic non-covalent and intermolecular interactions are observed, except two weak hydrogen bonding interactions between the coordinated H$_2$O and dangling O atoms of adjacent acetate groups.

**Crystal Structure Description for Complex 2**

Needle-shaped single crystals of 2 were obtained after one week from the reaction mixture following solvent evaporation. The neutral complex [Dy$_2$Ni$_6$L$_4$(μ-OH)$_4$(μ-Cl)$_2$Cl$_4$(H$_2$O)$_2$(MeOH)$_2$]·2MeOH·4H$_2$O crystallizes in monoclinic space group C2/c (Fig. 4). The ORTEP plots of asymmetric unit viz., [Ni$_3$Dy$_2$(μ-OH)$_2$(μ-Cl)$_2$Cl$_4$(H$_2$O)(MeOH)] with 50% ellipsoid probability showed in Fig. S5 of ESI. The crystal parameters of 2 are given in Table S1 and the selected bond length and angles are in Table S7–S8 in the ESI.

The analysis of molecular structure revealed that each L$^{2-}$ unit binds single Ni$^{ii}$ centre through its imine N and adjacent O donors to yield (NiL) fragments suitable to trap oxophillic Dy$^{iii}$ ions through free –OMe donor and bridging action of O donor of already bound phenolate group. Two such (NiL) fragments in opposite directions bind a single Dy$^{iii}$ ion to afford (Ni$_2$Dy$L_2$) units susceptible for aggregation. Fusion of four partial open cubes via four solvent derived μ$_3$-OH and six μ-OPh bridges from L$^{2-}$ finally results the Ni$_6$Dy$_2$ complex 2. The six-coordinated Ni$^{ii}$ centres are of two types in distorted octahedral NO$_5$ or NO$_4$Cl environments (OC−6 = 0.937 for Ni1 and 1.386 for Ni2, Table S2 in the ESI) and the tetrahedral four coordinated sites are completed within Cl$_3$O milieu (Fig. 5). The τ$_4$ index$^{60}$ for slight D$_{2d}$ distortion around the Ni3/Ni3* centres is found to be 0.997 (τ$_4$ is 0 and 1 for perfect square planar and tetrahedral geometries, respectively). The in-situ generated NiCl$_2$ parts link terminal chlorido and bridging phenoxido groups with Ni2 and Ni2* to stabilize the tetrahedral sites. Longer N1–Ni1, 2.011(7) Å and O7–Ni1, 2.132(5) Å bonds...
result longest N1−Ni1−O7 axis around Ni1(Ni1*). Similarly, for Ni2/Ni2* the longest alignment is C1−Ni2−O3 from longer C1−Ni2, 2.658(3) Å and O3−Ni2, 2.078(6) Å bonds. Around tetrahedral NiII centres (Ni3/Ni3*), the C1−Ni3 bond distances vary within 2.188(3)−2.320(3) Å range. Presence of three different types of O donors lead to appreciable modulation in the Ni−O bond distances from 1.971(6) Å to 2.132(5) Å. Three diverse types of NiII centres are responsible for registering Ni1···Ni2 and Ni2···Ni3 separations of 3.079(12) Å and 3.110(12) Å, respectively. The Ni−O−Ni angles at the phenoxido and hydroxido heads are different at 97.4(2)° (∠Ni1−O3−Ni2), 102.2(2)° (Ni2−O6−Ni3) and 96.3(19)° (∠Ni1−O8−Ni2). The Ni2−Cl1−Ni3 angle is acute enough at 77.1(18)° due to the presence of longer Ni2−Cl1 bond at 2.658(3) Å.

Bigger Dy1 and Dy1* centres in O8 coordination environment is accomplished by bidentate −OMe,O parts of L2−, three HO− bridges, and one terminal H2O donor. Placement of eight oxygen donors around Dy1 and Dy1* centres reveal distorted trigonal dodecahedron environments supported by SHAPE 2.1 (TDD-8 = 0.835 in Table S4 in the ESI, Fig. 6a). Unlike complex 1, here Dy1 and Dy1* are bridged by two μ3-HO− groups to form a Dy2O2 rhombus having ∠Dy1−O7−Dy1* and ∠O7−Dy1−O7* angles of 106.4(19)° and 73.6(18)° respectively providing the Dy1···Dy1* separation of 3.743(14) Å (Fig. 6b).

Four different types of oxygen donors, around the each DyIII centre resulted variation in Dy−O bond distances from 2.263(5) Å to 2.532(6) Å, where the longest one is registered for −OMe function as Dy1−O4. The Ni−O−Dy angles at different bridges register angles from 100.5(2)° to 107.2(2)° and the Ni−Dy remain within 3.408(13)−3.463(13) Å range. The μ-phenoxido bridges are wider at 105.2(2)°−107.3(2)° compared to μ3-hydroxido bridges within 101.0(2)°−102.1(2)°. All the metal ion centres in the central Ni4Dy2 unit are mostly coplanar, and the Ni3 and Ni3* centres are 3.185 Å away from the best plane.

**Magnetic Studies**

The temperature dependent magnetic susceptibility values of complexes 1 and 2 were measured from 2−290 K in a field of 0.1 T and the χT versus T data are shown in Fig. 7. At 290 K, χT = 23.6 cm^3 mol^−1 K for complex 1, and 35.3 cm^3 mol^−1 K for complex 2, which are consistent with the expected values for these complexes at room temperature (χTcalc = 22.7 cm^3 mol^−1 K for 1 {gNi = 2.15 and gGd = 2.0} and 35.3 cm^3 mol^−1 K for 2 {gNi = 2.15 and gDy = 4/3}). As the temperature decreases, the χT value for complex 1 increases to 74.2 cm^3 mol^−1 K at 3 K, before decreasing slightly to 73.0 cm^3 mol^−1 K at 2 K. The χT vs. T data for complex 1 is consistent with a large spin ground state resulting from predominantly ferromagnetic intra-molecular exchange interactions and the presence of zero-field
splitting (ZFS) from Ni\textsuperscript{II} and/or antiferromagnetic intermolecular interactions. For complex 2, predominant ferromagnetic exchange interactions are also evident as $\chi T$ increases to 89.0 cm\textsuperscript{3} mol\textsuperscript{-1} K at 4 K, before decreasing to 79.7 cm\textsuperscript{3} mol\textsuperscript{-1} K. For complex 1 $M/N\beta$ at 2 K and 7 Tesla = 26.2 (see Fig. 7 inset), consistent with a high-spin ground state $S$ = 13. The magnetization vs. field plots for complex 2 are shown in Fig. S6a in the electronic supporting information where $M/N\beta$ = 20.9 at 2 K and 7 Tesla.

To determine the magnitude of the exchange interactions between metal ions in complex 1, the susceptibility and magnetisation data were fitted simultaneously using the program PHI 2.0.\textsuperscript{61} The obtained $J$ values are reported according to the form of the Hamiltonian shown below (eq. 3), to enable comparison to those obtained from the theoretical studies:

$$\hat{H} = -J_1 (S_1 S_7 + S_2 S_8 + S_3 S_9 + S_4 S_5 + S_5 S_6 + S_6 S_7 + S_7 S_8 + S_8 S_9) - J_2 (S_1 S_3 + S_2 S_6 + S_3 S_5 + S_4 S_8) - J_3 (S_5 S_3 + S_6 S_4) + g_{Ni} \mu_B B \sum_{i=1}^6 S_i + g_{Gd} \mu_B B \sum_{j=7}^8 S_j$$

Note that the large magnetic anisotropy of Dy\textsuperscript{III} precludes a similar fit of the data for 2. In light of the different bridging angles between the Ni\textsuperscript{II} and Gd\textsuperscript{III} centres in 1, three different exchange pathways were used in the fit, as shown in Fig. 7. In addition, $g$-values were fixed to 2.15 for Ni\textsuperscript{II}, 2.0 for Gd\textsuperscript{III} and ZFS was not included, in order to reduce the size and complexity of the computation. The exclusion of ZFS has a more noticeable effect on the fit of the magnetization vs. field data (Fig. 7 inset), as expected for a complex containing Ni\textsuperscript{II}

where ZFS is expected. However, the fit to the $\chi T$ versus $T$ data is excellent apart from at the very lowest temperatures. The exchange interactions between neighbouring Ni\textsuperscript{II} ions ($J_2$ and $J_3$) were found to be +14.8 (±1.2) cm\textsuperscript{-1} and +32.2 (±10.0) cm\textsuperscript{-1}, respectively and the exchange interactions between Ni\textsuperscript{II} and Gd\textsuperscript{III} were found to be +0.33 (±0.02) cm\textsuperscript{-1}. Weak exchange interactions are commonly observed in large Ni\textsuperscript{II}-Gd\textsuperscript{III} complexes and the magnitude of the Ni\textsuperscript{II}-Gd\textsuperscript{III} exchange interactions in 1 agree with those found previously in the literature.\textsuperscript{62-65}
Complex 1 displays no slow magnetic relaxation with, or without, an applied dc field. Complex 2 requires an applied dc field to observe any significant slow magnetic relaxation, consistent with the presence of transverse magnetic anisotropy, which given the structure of 2 could arise from the Ni\textsuperscript{iii} and/or Dy\textsuperscript{iii} centres. The ac magnetic susceptibility measurements of complex 2 were measured from 1-941 Hz with an optimum applied dc field of 600 Oe (see Fig. S6b). The ac data were then fitted using the program CCFit, in order to derive the relaxation times $\tau$. The in-phase ($\chi'$) and out-of-phase ($\chi''$) ac susceptibility vs. temperature data are shown in Fig. 8 and indicate slow relaxation of the magnetization typical of a single-molecule magnet. The Arrenhius plot derived from the data for 2 at 600 Oe is shown in Fig. S7, yielding the energy barrier $U_{\text{eff}} = 19.3$ (0.1) K and the pre-exponential factor $\tau_0 = 1.22 (0.07) \times 10^{-7}$ s.

**Theoretical Studies**

The interpretation of the magnetic properties of 1 and 2 was also supported by theoretical calculations. First, the DFT calculations were used for the estimation of the magnetic exchange coupling within the formalism of the spin Hamiltonian. We used two hybrid functionals B3LYP and PBE0, which recently showed good results for polynuclear systems.\textsuperscript{66-67} In order to facilitate such calculations in complex systems like herein presented complexes 1 and 2, the broken-symmetry approach was applied in such way that only two paramagnetic ions were preserved in the respective molecular structures extracted from X-ray data, while all other metal atoms were replaced by their diamagnetic analogues (Dy→Lu, Gd→Lu, Ni→Zn). Then, the energy of the broken-symmetry spin state (BS) was compared to the energy of high-spin state (HS), $\Delta = E_{\text{BS}} - E_{\text{HS}}$, leading to the isotropic exchange parameter $J$ computed according to the Yamaguchi method\textsuperscript{68-69} as

$$J = 2\Delta/[(S^2_{\text{HS}} - (S^2_{\text{BS}})]... (4)$$

for spin Hamiltonian of the form

$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2) ... (5)$$

The respective results together with selected structural parameters are listed in Table 1 and the calculated spin density plots for selected cases are shown in Fig. S8 in the electronic supporting information. As there are various types and combinations of the bridging ligands (OH, H\textsubscript{2}O, OPh, CI) it is hard to deduce magneto-structural correlation (Fig. 9). However, it is evident that at least for Ni–(µ-OH)–Ni bridge, the decreasing the Ni–Ni distance and/or average Ni–O–Ni angle led to switching of antiferromagnetic to ferromagnetic exchange interaction as expected from the other studies of similar systems.\textsuperscript{70-72} The validity of these calculations was assessed by the comparison of calculated magnetic properties using DFT-derived $J$-values with the experimental data (Fig. 10). Evidently, both functionals correctly predict the increase of $\chi T$ product due to prevailing ferromagnetic exchange interactions, however, only PBE0 functional correctly predicted $S = 13$ ground state as visualized in plots of the spin energy levels in Fig. S10 in the ESI, and therefore excellent agreement with the experimental magnetic data was achieved. Moreover, the magnetic anisotropy of Ni\textsuperscript{ii} was also evaluated by CASSCF method (Table 2, vide infra), but the large dimension of interaction matrices, $3^{82} = 46656$, makes the direct computation of magnetic properties of 1 with ZFS impossible. In the case of compound 2, both DFT functional supported large ferromagnetic Ni–Ni exchange coupling in accordance with the experimental data showing an increase of $\chi T$ on cooling. However, the ground state $^6H_{15/2}$ of Dy\textsuperscript{iii} ion cannot be described by the spin Hamilton formalism, and therefore the computation of Ni–Dy magnetic interactions is precluded by DFT. However, the post–Hartree–Fock CASSCF calculations were utilized in order to better understand the magnetic properties of these compounds. Thus, the CASSCF calculations were performed with OpenMOLCAS program for Ni\textsuperscript{ii} ions of 1 and 2 and also for Dy\textsuperscript{iii} ion for 2 by leaving only one Ni or Dy atom in molecular structures and replacing all other paramagnetic ions by Zn or Lu atoms. The spin-orbit coupling affecting ligand field multiplets of $^6H_{15/2}$ atomic term were subsequently analysed with the SINGLE_ANISO module of OpenMOLCAS and the relevant parameters of all eight Kramers doublets are listed in Table 3. Ground states of Dy\textsuperscript{iii} ion in 2 has a very large axial magnetic anisotropy, $g_x = g_y = 0$

<table>
<thead>
<tr>
<th>M-M' pairs</th>
<th>d(M-M') (Å)</th>
<th>$\theta$(°)</th>
<th>$J$ (cm$^{-1}$) fitted</th>
<th>$J$ (cm$^{-1}$) fitted</th>
<th>Bridging ligands</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd1Ni1</td>
<td>3.476</td>
<td>104.145</td>
<td>1.38</td>
<td>1.43</td>
<td>+0.33(±0.02)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Gd1Ni2</td>
<td>3.470</td>
<td>103.61</td>
<td>1.15</td>
<td>1.24</td>
<td>+0.33(±0.02)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Gd1Ni3</td>
<td>3.453</td>
<td>102.47</td>
<td>0.92</td>
<td>0.91</td>
<td>+0.33(±0.02)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Gd1Ni'1</td>
<td>3.471</td>
<td>102.79</td>
<td>0.44</td>
<td>0.52</td>
<td>+0.33(±0.02)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Ni1Ni1</td>
<td>3.164</td>
<td>97.305</td>
<td>9.70</td>
<td>9.03</td>
<td>+14.8 (±1.2)</td>
<td>H\textsubscript{2}O, OH</td>
</tr>
<tr>
<td>Ni1Ni2</td>
<td>3.122</td>
<td>96.3</td>
<td>-4.86</td>
<td>-0.78</td>
<td>+14.8 (±1.2)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Ni1Ni'1</td>
<td>2.982</td>
<td>92.87</td>
<td>21.2</td>
<td>17.3</td>
<td>32.2(±10.0)</td>
<td>OH, OPh</td>
</tr>
<tr>
<td>Ni2Ni1</td>
<td>3.079</td>
<td>97.025</td>
<td>30.4</td>
<td>26.1</td>
<td>OH, OPh</td>
<td>Cl, OPh</td>
</tr>
<tr>
<td>Ni2Ni'1</td>
<td>3.110</td>
<td>89.63</td>
<td>22.7</td>
<td>19.4</td>
<td>Cl, OPh</td>
<td>Cl, OPh</td>
</tr>
</tbody>
</table>
and $g_z = 19.1$, and first and second excited states separated by 131 and 205 cm$^{-1}$ also possess large axial magnetic anisotropy (Table 3). The orientation of $g_z$-axes of these three states is visualized in Fig. 11 and they are oriented almost in the same direction, which may generally improve the SMM properties. Next, the plot of the magnetization blocking barrier was constructed (Fig. 11), where the values of the transition magnetic moments between Kramers levels are shown and this plot suggests that there is a very low probability of the quantum tunneling of the ground state, but temperature-assisted quantum tunneling is possible through the first and second excited states and there is very high probability of magnetization reversal through the third excited state. Similarly, SINGLE_ANISO module applied to CASSCF calculation of Ni atoms resulted in single-ion zero-field splitting parameters $D$ and $E$, and $g$-factors listed in Table 2. The calculated $D$-values are in the range $-19$ cm$^{-1}$ $< D < 20$ cm$^{-1}$, thus rather large values were achieved for octahedrally coordinated Ni$^{II}$ ions in 1 and 2, because ideal $O_h$ symmetry of the ligand field would result in zero value of $D$.\(^73\) This can be explained by deviation from $O_h$ symmetry (Table S2) and also by heteroleptic coordination sphere. However, the extremely large value of $D = -194$ cm$^{-1}$ was found for tetra-coordinate Ni$^3$ atom of 2, which may significantly contribute to the overall magnetic anisotropy of 2. The ideal $T_d$ symmetry of the ligand field would result in $T_{2g}$ ground state, however, the man-in-Teller effect induced deformation of (NiCl$_2$O) chromophore, but the contribution of the low-lying excited states to ZFS parameters is still enormous. The respective energies of ligand field terms and multiplets are showed in Fig. S11. Usually, NEVPT2 or CASPT2 additional correction are needed to better predict ZFS parameters of 3d-metals, which is prohibited here by large number of atoms in 2. Nevertheless, the small molecular fragment was extracted for which we were able to perform CASSCF/CASPT2 calculations clearly confirming very large $D$ parameter of Ni$^3$ atom in 2 (Fig. S12, ESI).

Fig. 9 The variation of $j$-parameters calculated by PBE0 functional for compounds 1 and 2 for various bridging modes.

Fig. 10 The calculation of magnetic properties of 1 based on $j$-parameters in Table 1 and average $g$-value equal 2.07. Experimental data are plotted as empty circles and the calculated data are showed as blue line for B3LYP’s derived $j$-parameters and as orange line for PBE0’s derived $j$-parameters.

So far, such large $D$-parameters were usually reported for penta-coordinate Ni$^{II}$ complexes approaching $D_{5h}$ symmetry with $D = -400$ to -535 cm$^{-1}$,\(^74\) $D = -185$ cm$^{-1}$,\(^75\) while quite large $D = 45.4$ cm$^{-1}$ was found for tetrahedral complex with (NiSe$_4$) chromophore.\(^76\) Next the POLY_ANISO module was applied to analyse the dipole-dipole interaction of the ground states magnetic moments of two Dy$^{III}$ ions of 2, which are connected by the inversion operation of the symmetry. The orientation of the magnetic moment with respect to Dy···Dy linking line (angle $\theta$) in such centro-symmetric compounds is the crucial factor for the nature of the dipole-dipole interaction, either antiferromagnetic or ferromagnetic, due to the following relationship for the energy of the dipole-dipole interaction.\(^77\)

$$E_{dip} = -\frac{\mu_i \mu_j}{4\pi} \frac{1}{r^3} (3\cos^2 \theta - 1)$$

Therefore, the ferromagnetic interaction is expected for $\theta < 54.7^\circ$, whereas for $\theta > 54.7^\circ$ the antiferromagnetic interaction is predicted. In the case of compound 2, the angle $\theta$ equals $84^\circ$ and therefore the antiferromagnetic dipolar interaction is expected. Indeed, POLY_ANISO calculations between two ground state Kramers doublets of both Dy atoms confirmed such expectation as is depicted in Fig. S11 in the ESI. Thus, this interaction may be responsible for speeding up the relaxation of the magnetization. However, we are aware that the exchange coupling of the types Dy···Dy and Dy···Ni may also contribute to the whole picture of the magnetization blocking barrier significantly leading to further modification of dynamic magnetic properties of 2. Therefore, the experimental magnetic susceptibility of 2 was fitted with a home-made
routine in cooperation with POLY_ANISO module. According to the molecular structure of 2, six different magnetic exchange coupling can be expected between nearest-neighbour paramagnetic Dy or Ni atoms. Such a large number of free parameters would lead to over-parameterization of the model, thus J-values of Ni···Ni interactions were set to values calculated by DFT calculation with PBE0 functional. Moreover, Dy1···Ni1, Dy1···Ni2 and Dy1···Ni1* were expected to be equal having similar Dy···Ni distances. Therefore, we are left with just two free parameters, namely $J_{\text{Dy-Dy}}$ and $J_{\text{Dy-Ni}}$ interactions.

Furthermore, the calculations were limited to the inclusion of two lowest Kramers doublets resulting in already 38%|±11/2> + 8%|±15/2> of two lowest Kramers doublets resulting in already 38%|±11/2> + 8%|±15/2> of the ground state. The second excited state is dominated by 49%|±7/2> + 13%|±11/2>, while the first excited state is dominated by 54%|±13/2> + 38%|±11/2> + 8%|±15/2>.

Table 2. CASSCF/DKH2/SINGLE_ANISO calculated parameters for Ni atoms in 1 and 2

<table>
<thead>
<tr>
<th></th>
<th>$D$ (cm$^{-1}$)</th>
<th>$E$ (cm$^{-1}$)</th>
<th>$E/D$</th>
<th>$g$-factors ($g_x$, $g_y$, $g_z$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni1 of 1</td>
<td>-18.7</td>
<td>5.35</td>
<td>-0.287</td>
<td>2.239, 2.323, 2.411</td>
</tr>
<tr>
<td>Ni2 of 1</td>
<td>10.4</td>
<td>-2.87</td>
<td>0.275</td>
<td>2.340, 2.303, 2.245</td>
</tr>
<tr>
<td>Ni3 of 1</td>
<td>-8.44</td>
<td>2.31</td>
<td>-0.274</td>
<td>2.295, 2.331, 2.374</td>
</tr>
<tr>
<td>Ni1 of 2</td>
<td>-9.39</td>
<td>1.97</td>
<td>-0.210</td>
<td>2.256, 2.288, 2.342</td>
</tr>
<tr>
<td>Ni2 of 2</td>
<td>19.9</td>
<td>-5.37</td>
<td>0.271</td>
<td>2.415, 2.346, 2.235</td>
</tr>
<tr>
<td>Ni3 of 2</td>
<td>-194</td>
<td>21.0</td>
<td>-0.108</td>
<td>2.310, 2.401, 3.558</td>
</tr>
</tbody>
</table>

Table 3. CASSCF/DKH2/SINGLE_ANISO calculated energy levels for the complex [Zn$_2$DyLu] of 2 with the respective g-factors for each Kramers doublet with effective spin ½.

<table>
<thead>
<tr>
<th>$E$ (cm$^{-1}$)</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.002</td>
<td>0.005</td>
<td>19.116</td>
</tr>
<tr>
<td>130.6</td>
<td>0.149</td>
<td>0.273</td>
<td>14.537</td>
</tr>
<tr>
<td>205.1</td>
<td>0.045</td>
<td>0.347</td>
<td>12.277</td>
</tr>
<tr>
<td>324.0</td>
<td>2.646</td>
<td>3.563</td>
<td>9.452</td>
</tr>
<tr>
<td>423.8</td>
<td>3.080</td>
<td>5.187</td>
<td>8.534</td>
</tr>
<tr>
<td>508.7</td>
<td>1.781</td>
<td>3.620</td>
<td>11.682</td>
</tr>
<tr>
<td>561.6</td>
<td>2.138</td>
<td>3.607</td>
<td>14.214</td>
</tr>
<tr>
<td>651.5</td>
<td>0.234</td>
<td>0.616</td>
<td>17.849</td>
</tr>
</tbody>
</table>

The wave-function for the ground state is dominated by 86%|±15/2> + 13%|±11/2>, while the first excited state is dominated by 54%|±13/2> + 42%|±9/2> and the second excited state is dominated by 49%|±7/2> + 38%|±11/2> + 8%|±15/2>.

Conclusions

Coordination driven hydrolysis reaction triggered the heterometallic aggregation potency of L$^2$- for cooperative binding of Ni$^\text{II}$ and Gd$^\text{III}$/Dy$^\text{III}$ metal ions. Selective coordination of Ni$^\text{II}$ and 4f ions by multiple number of ligand anions have established hydroxido, chlorido and aqua bridge–driven aggregation reactions for the generation of two different types of 3d–4f coordination aggregates. During the formation of complex 1, entrapment of in-situ formed Ni$_2$(OH)$_2$ unit and for 2, the terminal NiCl$_2$ unit, supports the formation of both the molecular architecture. The solution chemistry of Gd$^\text{III}$ and Dy$^\text{III}$ ions in the MeOH-CHCl$_3$ medium are different in terms of liquid-liquid equilibrium, in situ formed reactive species and Lewis acidity of the 4f metal ions. Thus, the interchange of the 4f ions (Gd$^\text{III}$ vs. Dy$^\text{III}$) has substantial consequences in the
serendipitous yet standardized new synthesis and structural aspects, discovering mineralization like coordination aggregation pathways. The resulting 3d-4f metal ion-based core structure and the topology of 1 and 2, led to predominantly ferromagnetic exchange coupling interactions with large magnetic ground states as proofed by DC magnetic data as well as by DFT calculations. The antiferromagnetic exchange and dipolar interaction between DyIII ions were established by analysis of the respective CASSCF calculations with SINGLE_ANISO and POLY_ANISO modules in respect to the experimental data, revealing ferromagnetic exchange between NiII and DyIII ions. The scheme of the magnetic moment reversal barrier was provided for 2 helping us to rationalize the experimentally found Ueff value 19.3 K, while the necessity to apply small static magnetic field to suppress the quantum tunneling of the magnetization was ascribed to the intermolecular interactions in solid state.

Conflicts of interest

The authors declare no conflict of interest.

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