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# Synthesis, characterization, magnetism and theoretical analysis of hetero-metallic [Ni<sub>2</sub>Ln<sub>2</sub>] partial di-cubane assemblies<sup>+</sup>

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A family of four isostructural  $[Ln_2Ni_2(L)_2(\mu_3-OCH_3)_2(\mu_{1,3}-PhCO_2)_2(PhCO_2)_2(CH_3OH)_4]\cdot 2CH_3OH$  [where Ln = Gd (1), Tb (2), Dy (3) and Ho (4)] complexes has been synthesized using Schiff base ligand 2-[{(2-hydroxy-benzyl)imino}methyl]-6-methoxyphenol (H<sub>2</sub>L). All the complexes possess a partial di-cubane core structure where the growth of the core is contingent upon the ligand anions and solvent generated  $\mu_3$ -OCH<sub>3</sub> groups. DC magnetic analysis revealed dominating ferromagnetic interactions between the metal ions, however, we find no slow relaxation characteristics in the AC susceptibility. Further insight into the magnetic behavior of the reported complexes was achieved using DFT and CASSCF theoretical calculations, leading to the comprehension of the fast relaxation characteristics observed by magnetometry.

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# Introduction

Advances in strategies for the synthesis of oxido-hydroxido mixed transition metal-lanthanoid aggregates during the last three decades have resulted in plentiful crystalline materials that exhibit attractive structures and interesting properties. The choice, design and synthesis of new ligand systems have attracted considerable attention in the exploratory synthesis of newer 3d–4f complexes.<sup>1–5</sup> Synthesis of such multinuclear coordination clusters from newer ligand systems having predefined coordination pockets for different metal ions, unfolding the synthetic potential and versatility of the reaction conditions, has contributed to the understanding of the structure-property relationship for Single Molecule Magnets (SMMs).<sup>6,7</sup> Such newly synthesized molecular magnets have

<sup>d</sup>Institute for Quantum Materials and Technology (IQMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany expected potential for use in high-density information storage,<sup>8</sup> quantum computing,<sup>9</sup> luminescence,<sup>10</sup> and molecular spintronics.<sup>11</sup> Using lanthanoid ions within the aggregates is highly advantageous because of its large magnetic moment (J) and considerable magnetic anisotropy, though the Ln…Ln interaction often increases the rate of quantum tunneling, leading to an apparent decrease in U<sub>eff</sub> values.<sup>12</sup> The single-ion magnetic anisotropy of these metal ions is known to be modulated by changing their coordination environments and resulting ligand field.<sup>13</sup> Whereas the molecular anisotropy depends on factors like ligand field,<sup>14</sup> the relative orientation of the individual single-ion easy axes,<sup>15,16</sup> magnetic coupling,<sup>17</sup> and the structural topology of the newly found magnetic cores.18-20 New types of such magnetic cores were discovered by the incorporation of varying numbers of 3d and 4f ions bound to the multiple numbers of ligand anions and ancillary bridges.<sup>21,22</sup> Such heterometallic molecular aggregates, bearing multiple paramagnetic centers (3d and 4f ions) in close proximity, can influence the effective energy barriers<sup>23</sup>  $(U_{\rm eff})$  and magnetic blocking temperatures  $(T_{\rm B})$ .<sup>24</sup> Dy<sup>III</sup>, Tb<sup>III</sup> and Ho<sup>III</sup> ions are usually known to display a large magnetic anisotropy steaming from the unquenched spin-orbit coupling and magnetic moment. In practice, the presence of ligand anion binding 3d ions in these aggregates induces exchange interactions which can stabilize the bistable ground state and suppresses the quantum tunneling of magnetization.<sup>25</sup> The ligand design strategy for the synthesis of 3d-4f aggregates is guided by the hard-soft acid-base (HSAB) principle where imine donor atoms bind 3d ions and oxygens are utilized for coordinating/bridging 4f ions. Such a strategy is fruitful in pro-

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<sup>†</sup>Electronic supplementary information (ESI) available: SHAPE analysis, crystal data, PXRD curves, selected bond lengths and angles, and CASSCF calculations are described in Fig. S1–S11 and Tables S1–S15 in the text. CCDC 2062614–2062617. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt00510c

viding many Ni-4f complexes of different nuclearity of individual 3d and 4f ions having a unique magnetic core topology.<sup>26-29</sup>

Tetranuclear 3d-4f butterfly complexes are interesting owing to their synthetic accessibility and structural uniqueness, stimulating to the magnetochemists because of their defective partial di-cubane magnetic core and the changes in magnetic properties upon changing the metal ion position.<sup>30</sup> Within this metal-oxo core, either the 3d ions can be positioned at the tip of the core with a good range separation (inverse butterfly, type-I) or they can be located at the vertices of the body (butterfly, type-II). From the earlier reports, 3d-4f complexes with Cr(m),<sup>31</sup> Co(m)<sup>32</sup> and Mn(m)<sup>33</sup> ions provided structures with the type-I core possessing SMM properties with a high anisotropic barrier; whereas the type-II core having partial di-cubane structures are mainly found with Ni<sup>II 34</sup> ions, though reports of type-II core systems employing other 3d metal ions are also there showing fascinating SMM behavior.<sup>35,36</sup> The magnetization relaxation pathways of these "Butterfly" complexes could be well elucidated following their magnetostructural correlation data.<sup>37,38</sup> Keeping all these in mind, we have synthesized the ligand H<sub>2</sub>L, 2-[{(2-hydroxybenzyl)imino}methyl]-6-methoxyphenol, for self-aggregating reactions with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and selected Ln<sup>III</sup> metal ions. Herein we report, the synthesis and characterization of four 3d-4f isostructural aggregates,  $[Ln_2Ni_2(L)_2(\mu_3-OCH_3)_2(\mu_{1,3}-CH_3)_2($  $PhCO_2_2(PhCO_2_2(MeOH)_4) \cdot 2CH_3OH$  [where Ln = Gd(1), Tb(2), Dy(3) and Ho (4)]. To date, to the best of our knowledge, only one report of the Dy<sub>6</sub> coordination cluster is known with the present ligand system<sup>39</sup> but no 3d-4f complex has been reported.

## **Experimental section**

#### Reagents and starting materials

All solvents were purified according to the literature procedures,<sup>40</sup> while the remaining starting materials were used as obtained without further purification. 2-(Aminomethyl)phenol was synthesized following a reported procedure.<sup>41</sup> The following chemicals were used as received: Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NEt<sub>3</sub> (S. D. Fine Chemicals, Mumbai, India);  $Gd(NO_3)_3 \cdot 6H_2O$ , Tb  $(NO_3)_3 \cdot 5H_2O$ , Dy $(NO_3)_3 \cdot 5H_2O$  and Ho $(NO_3)_3 \cdot 5H_2O$  (Alfa Aesar, India); and *o*-vanillin (Spectrochem Pvt. Ltd Mumbai).

# Synthesis of 2-[{(2-hydroxybenzyl)imino}methyl]-6-methoxyphenol $(H_2L)$

The Schiff base ligand was synthesized by following a modified reported procedure.  $^{\rm 42}$ 

#### General protocol for synthesizing complexes 1-4

All the complexes reported in this work were synthesized following a similar reaction protocol.  $H_2L$  (0.1 mmol, 0.025 g) was dissolved in 10 mL of MeOH–DCM (2 : 1) solution. 5 mL methanolic solution of  $Ln(NO_3)_3 \cdot nH_2O$  (0.10 mmol) [n = 6 for  $Ln^{3+} = Gd$  (1) and n = 5 for  $Ln^{3+} = Tb$  (2), Dy (3) and Ho (4), Scheme 1] was dissolved into the ligand solution, followed by stirring for 1 h. Solid Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.10 mmol, 0.03 g), sodium benzoate (0.20 mmol, 0.029 g) and NEt<sub>3</sub> (0.20 mmol, 0.02 g) were further added to the preceding pale yellow solution and the reaction mixture was stirred for a further 7 h at room temperature. The clear bright green solution was then filtered and left undisturbed for slow evaporation. Green block shaped air stable crystals were acquired after a week, suitable for single crystal analysis. The characterization data of the complexes are given below.

[Gd<sub>2</sub>Ni<sub>2</sub>(L)<sub>2</sub>(µ<sub>3</sub>-OCH<sub>3</sub>)<sub>2</sub>(µ<sub>1,3</sub>-

H<sub>3</sub>C

Ln(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O/Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O/Na-Benzoate MeOH:DCM (2:1), 8hr

Ln = Gd (1), Tb (2), Dy (3) and Ho (4)

**PhCO**<sub>2</sub>)<sub>2</sub>(**PhCO**<sub>2</sub>)<sub>2</sub>(**MeOH**)<sub>4</sub>]-**2CH**<sub>3</sub>**OH** (1). Yield: 0.035 g, 42% (based on Gd). Anal. Calcd for  $C_{66}H_{76}Gd_2N_2Ni_2O_{22}$  (1681.19): C, 47.19; H, 4.56; N, 1.67. Found: C, 47.33; H, 4.57; N, 1.61. Selected FT-IR data (KBr) cm<sup>-1</sup>: 1636 (w), 1593 (m), 1556 (m), 1474 (s), 1454 (m) 1397 (s), 1307 (m), 1276 (s), 1220 (s), 1169 (s), 1077 (s), 1025 (s), 848 (m), 718 (s), 589 (w), 471 (m), 419 (s). [Tb<sub>2</sub>Ni<sub>2</sub>(L)<sub>2</sub>( $\mu_3$ -OCH<sub>3</sub>)<sub>2</sub>( $\mu_{1,3}$ -

**PhCO**<sub>2</sub>)<sub>2</sub>(**PhCO**<sub>2</sub>)<sub>2</sub>(**MeOH**)<sub>4</sub>]·2CH<sub>3</sub>OH (2). Yield: 0.031 g, 37% (based on Tb). Anal. Calcd for  $C_{66}H_{76}Tb_2N_2Ni_2O_{22}$  (1684.54): C, 47.06; H, 4.55; N, 1.66. Found: C, 47.27; H, 4.59; N, 1.59. Selected FT-IR data (KBr) cm<sup>-1</sup>: 1637 (w), 1592 (m), 1556 (m), 1472 (s), 1454 (m), 1397 (s), 1305 (m), 1275 (s), 1219 (s), 1170 (s), 1074 (s), 1020 (s), 853 (m), 718 (s), 590 (w), 467 (m), 416 (s). **[Dy**<sub>2</sub>Ni<sub>2</sub>(L)<sub>2</sub>( $\mu$ <sub>3</sub>-OCH<sub>3</sub>)<sub>2</sub>( $\mu$ <sub>1.3</sub>-

PhCO<sub>2</sub>)<sub>2</sub>(PhCO<sub>2</sub>)<sub>2</sub>(MeOH)<sub>4</sub>]·2CH<sub>3</sub>OH (3). Yield: 0.037 g, 44%



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(based on Dy). Anal. Calcd for  $C_{66}H_{76}Dy_2N_2Ni_2O_{22}$  (1691.69): C, 46.86; H, 4.53; N, 1.66. Found: C, 46.73; H, 4.51; N, 1.63. Selected FT-IR data (KBr) cm<sup>-1</sup>: 1634 (w), 1593 (m), 1560 (m), 1475 (s), 1454 (m), 1394 (s), 1309 (m), 1275 (s), 1220 (s), 1173 (s), 1075 (s), 1019 (s), 851 (m), 720 (s), 592 (w), 468 (m), 419 (s). **[Ho\_2Ni\_2(L)\_2(\mu\_3-OCH\_3)\_2(\mu\_{1.3}-**

**PhCO**<sub>2</sub>)<sub>2</sub>(**PhCO**<sub>2</sub>)<sub>2</sub>(**MeOH**)<sub>4</sub>]·2CH<sub>3</sub>OH (4). Yield: 0.033 g, 39% (based on Ho). Anal. Calcd for  $C_{66}H_{76}HO_2N_2Ni_2O_{22}$  (1696.55): C, 46.72; H, 4.52; N, 1.65. Found: C, 46.53; H, 4.50; N, 1.61. Selected FT-IR data (KBr) cm<sup>-1</sup>: 1632 (w), 1594 (m), 1561 (m), 1475 (s), 1456 (m), 1394 (s), 1309 (m), 1275 (s), 1219 (s), 1173 (s), 1073 (s), 1020 (s), 852 (m), 719 (s), 592 (w), 469 (m), 415 (s).

#### **Physical measurements**

For the elemental analysis (C, H, N) of the powder samples, a PerkinElmer model 240C elemental analyzer was used. A PerkinElmer model RX1 FT-IR spectrometer fitted with KBr disks is used for FT-IR spectral measurements. Powder X-ray diffraction was carried out using a BRUKER D2 PHASER diffractometer (30 kV/10 mA) using Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) within the 5–50° (2 $\theta$ ) range.

#### Magnetic measurements

The magnetic susceptibility data for all complexes were collected using a Quantum Design MPMS®3 magnetometer on a polycrystalline material in the temperature range 2–300 K under an applied DC magnetic field (*H*). The magnetization data were collected between 2 and 5 K and fields ranging from 0 to 7 T. The data were corrected for diamagnetic contributions from the eicosane and core diamagnetism employing Pascal's constants.<sup>43</sup>

#### X-ray crystallography

Single crystal X-ray structural studies of complexes 1-4 were performed in a Bruker SMART APEX-II CCD X-ray diffractometer equipped with a graphite-monochromated Mo-K $\alpha$  ( $\lambda$  = 0.71073 Å) radiation source using the  $\omega$  scan (width of 0.3° per frame) at 293 K with a scan rate of 5 s per frame. For indexing, integration and space group determination, SAINT, SMART and XPREP software programs have been used. Direct methods using SHELXS-2014 were used to solve crystal structures and refined by the full-matrix least squares technique using SHELXL (2014/7) programs. The empirical absorption corrections were done by the Multi-scan method of the SADABS program and the H atoms were incorporated using the riding model. The DIAMOND software was used for presenting molecular structures. The cell parameters for complexes 1-4 are summarized in Table S1 in the ESI.† Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 2062614-2062617 (1-4).†

#### Theoretical calculations

First, the ORCA 4.2 software<sup>44–46</sup> was used for the theoretical calculations. All calculations were based on the experimental X-ray structures of  $Ni_2Ln_2$  complexes of **1–4**, in which only

hydrogen atom positions were optimized using the B97M-D3BJ functional and DKH-def2-TZVP for Ni, N, and O atoms; SARC2-DKH-QZV for Ln atoms; and DKH-def2-SVP for C and H atoms.<sup>47,48</sup> The Douglas-Kroll-Hess Hamiltonian was used to treat relativistic effects<sup>49,50</sup> together with the Gaussian finite nucleus model<sup>51</sup> and the increased radial integration accuracy for metal atoms was also set. The auxiliary basis sets were generated using the AutoAux<sup>52</sup> and the chain-of-spheres (RIJCOSX) approximation to the exact exchange was also used.53,54 The isotropic exchange parameters were calculated using the B3LYP hybrid functional.<sup>55</sup> The state average complete active space self-consistent field (SA-CASSCF) wave function calculations were done for NiZnLu<sub>2</sub> or Zn<sub>2</sub>LnLu complexes 1-4, in which only one paramagnetic metal ion was preserved. The active space is defined by five d-orbitals/seven f-orbitals and the respective number of electrons for nickel/lanthanide ions. The number of the involved multiplets was as follows: Ni<sup>II</sup> – 10 triplets and 15 singlets; Tb<sup>III</sup> – 7 septets, 140 quintets, 588 triplets, and 490 singlets; Dy<sup>III</sup> - 21 sextets, 224 quartets, and 490 doublets; and HoIII - 35 quintets, 210 triplets, and 196 singlets. These calculations employed slightly different basis sets: SARC2-DKH-QZVP for paramagnetic Ln or DKHdef2-TZVP for Ni, DKH-def2-TZVP for all donor atoms attached to paramagnetic metal, and DKH-def2-SVP for all other atoms, except for Lu for which SARC-DKH-TZVP was used. In the case of complexes 2-4, analogous CASSCF calculations were done using OpenMOLCAS 19.11.56 The RASSCF method was used in the CASSCF calculations with the following numbers of multiplets: 7 septets, 140 quintets, 113 triplets, and 123 singlets for Tb<sup>III</sup>; 21 sextets, 224 quartets, and 490 doublets for Dy<sup>III</sup>; 35 quintets, 210 triplets, and 196 singlets for Ho<sup>III</sup>; and 10 triplets and 15 singlets for Ni<sup>II</sup>. While all multiplets of Tb<sup>III</sup>, Ho<sup>III</sup> and Ni<sup>II</sup> were included in the spin-orbit RASSI-SO procedure, the number of states for Dy<sup>III</sup> was limited as follows: 21 sextets, 128 quartets, and 130 doublets. The following basis sets were used: Tb, ANO-RCC-VQZP; Dy, ANO-RCC-VQZP; Ho, ANO-RCC-VQZP; Lu, ANO-RCC-VDZP; Zn, ANO-RCC-VDZP; O, ANO-RCC-VDZP; N, ANO-RCC-VDZP; C, ANO-RCC-VDZ; and H, ANO-RCC-VDZ.<sup>57</sup> The calculated spin density and tensor axis were visualized using the VESTA 3 program.58

## Results and discussion

#### General synthetic procedures

In our previous work, we have shown that the presence of a flexible amine arm in the ligand backbone does facilitate the coordination driven aggregation during the synthesis of a new family of Ni–Ln complexes.<sup>59</sup> Earlier, while using 2-{[(2-hydroxy-3-methoxybenzyl)imino]methyl}phenol (H<sub>2</sub>L') as a ligand, we have seen that the flexible –CH<sub>2</sub> moiety plays an important role in trapping Ln<sup>III</sup> metal ions within the hexanuclear cluster.<sup>60</sup> In continuation of our previous study, herein we have synthesized H<sub>2</sub>L by reacting *o*-vanillin and 2-(aminomethyl)phenol (Scheme 2). The overall molecular structure of H<sub>2</sub>L' and H<sub>2</sub>L are the same, while the flexibility around the



imine nitrogen donor has transferred from *o*-vanillin to the salicylaldehyde part. The used ligand skeleton, 2-[{(2-hydroxybenzyl)imino}methyl]-6-methoxyphenol, has shown to be an excellent coordination support for synthesizing high nuclearity 4f-complexes by Zhang *et al.*,<sup>39</sup> but never explored for synthesizing 3d–4f complexes. Thus, we have explored the efficacy of H<sub>2</sub>L for the coordination induced self-assembly reactions with Ln<sup>III</sup> nitrate salts in the presence of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, PhCO<sub>2</sub>Na and NEt<sub>3</sub> at a ratio of 1:1:1:2:2 in MeOH–DCM (2:1) solvent medium. The reaction resulted in the formation of  $[Ln_2Ni_2(L)_2(\mu_3-OCH_3)_2(\mu_{1,3}-PhCO_2)_2(PhCO_2)_2(MeOH)_4]\cdot 2CH_3OH$  (where Ln = Gd (1), Tb (2), Dy(3) and Ho (4)). These electroneutral complexes 1–4 were synthesized as per eqn (1).

$$\begin{aligned} & 2H_{2}L + 2Ln(NO_{3})_{3} \cdot 6H_{2}O + 2Ni(NO_{3})_{2} \cdot 6H_{2}O \\ & + 4PhCO_{2}Na + 8CH_{3}OH \rightarrow [Ln_{2}Ni_{2}(L)_{2}(\mu_{3} - OCH_{3})_{2} \\ & (\mu_{1,3} - PhCO_{2})_{2}(PhCO_{2})_{2}(CH_{3}OH)_{4}] \cdot 2CH_{3}OH \\ & + 10NO_{3}^{-} + 6H^{+} + 4Na^{+} + 24H_{2}O \end{aligned}$$
(1)

The initial characterization of all the obtained complexes was done from FTIR spectroscopic and PXRD analyses. Complex 1 has been taken as a representative for the series for the discussion. The imine nitrogen bound to the Ni<sup>II</sup> center recorded the characteristic stretching frequency for the Ni<sup>II</sup> bound C=N bond at 1636 cm<sup>-1</sup> for 1 in comparison to the free ligand value of 1648 cm<sup>-1</sup>. The two types of benzoato group are recorded as sharp asymmetric stretches at 1593 and 1556 cm<sup>-1</sup> and the symmetric stretches appear at 1454 and 1397 cm<sup>-1</sup> (Fig. S2 in the ESI†). The differences of ( $\bar{\nu}_{asymm}$  –  $\bar{\nu}_{\text{symm}}$ ) 102 cm<sup>-1</sup> and 196 cm<sup>-1</sup> in stretching frequency values unequivocally confirm the presence of both the  $\mu_{1,3}$ -bridged and terminal benzoato groups, respectively, within the molecular aggregates. Experimental PXRD data of the synthesized complexes are in good agreement with the simulated ones derived from the single crystal X-ray diffraction data for all the complexes (Fig. S3 in the ESI<sup>†</sup>).

Several other Ni<sub>2</sub>Ln<sub>2</sub> complexes capped by several classes of ligand anions are reported earlier showing interesting magnetic behavior. In 2014, Shanmugam *et al.* reported a series of bent Ni<sub>2</sub>Ln<sub>2</sub> complexes showing zero field SMM properties.<sup>61</sup> Zhao *et al.* reported a linear Ni<sub>2</sub>Dy<sub>2</sub> complex showing slow relaxation of magnetization with an appreciable anisotropic barrier.<sup>62</sup> The Ni<sub>2</sub>Ln<sub>2</sub> complexes with an Ni<sub>2</sub>Ln<sub>2</sub>O<sub>6</sub> butterfly core topology have also been proved as excellent candidates for single molecule magnets (Fig. 1). In 2011, Powell *et al.* reported two types of Ni<sub>2</sub>Dy<sub>2</sub> and Ni<sub>2</sub>Tb<sub>2</sub> butterfly complexes<sup>34</sup> using an ((*E*)-2-(2-hydroxy-3-methoxybenzylideneamino)phenol ligand and in 2015 Winpenny *et al.* reported a systematic study



Fig. 1 Earlier reported Ni<sub>2</sub>Dy<sub>2</sub> complexes with a butterfly topology: (a), (b),  $^{34}$  (c), (d),  $^{62}$  (e)  $^{61}$  and (f).  $^{63}$ 

on several  $M_2Ln_2$  complexes using  $HO_2C^tBu$  as a ligand backbone where  $Ni_2Dy_2$  and  $Ni_2Er_2$  complexes show slow relaxation of magnetization.<sup>63</sup> Zhang *et al.* have synthesized an  $Ni_2Dy_2$ complex using a 2-(((2-hydroxy-3-methoxyphenyl)methylene) amino)-2-(hydroxymethyl)-1,3-propanediol ligand and  $Ni_2Dy_2$ and  $Ni_2Tb_2$  butterfly complexes with a 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol ligand.<sup>64</sup> Later on in 2018, Mohanta *et al.* also reported a series of  $Ni_2Ln_2$  complexes using an ((*E*)-2-(2-hydroxy-3-ethoxybenzylideneamino)phenol ligand.<sup>65</sup> In all these butterfly shaped  $Ni_2Ln_2$  complexes, either the carboxylato backbone or Schiff base ligand anion frame is exploited to get the coordination aggregates bearing 3d and 4f ions. In the present case, we have been successful in incorporating both Schiff base ligand anions and benzoato groups for the growth of the new family.

#### Structural description of complexes 1-4

Diffraction quality single crystals of complexes 1–4 were obtained from the MeOH–CHCl<sub>3</sub> solution mixture. All the four crystals are isostructural and found to crystalize in the triclinic  $P\overline{1}$  space group with Z = 1. To describe the structural features, complex 1 has been taken as a representative of the whole series with identical atom numbering schemes for all structures for easy comparison of the structural parameters. In all the four cases an asymmetric unit contains half of the whole molecule, *viz.*, [NiLn(L)( $\mu_3$ -OCH<sub>3</sub>)( $\mu_{1,3}$ -PhCO<sub>2</sub>)(PhCO<sub>2</sub>)(MeOH)<sub>2</sub>] (where Ln = Gd (1), Tb (2), Dy (3) and Ho (4), Fig. S4 in the ESI†). The crystal refinement parameters are presented in Table S1† whereas the bond distances and bond angles are presented in Tables S4–S11 in the ESI.†



Fig. 2 (a) Molecular structure of complex 1. H atoms and solvent molecules are removed for clarity. Colour code: C, grey; O, red; N, blue; Ni, green and Gd, yellow. (b) Distorted partial dicubane core of complex 1.

The X-ray structure analysis revealed that the metal ion centers of the tetranuclear core are well supported by two L<sup>2-</sup> ligand anions and two  $\mu_3$ -OCH<sub>3</sub> groups, derived from solvent MeOH used in the reaction medium. A detailed insight into the structure revealed that each imine N atom of the ligand anion specifically binds Ni<sup>II</sup> centers with chelating support of two adjacent phenolato O donors (Fig. 2a). Both the phenolate oxygen atoms are used for bridging Ni<sup>II</sup> and its adjacent Gd<sup>III</sup> metal centers. The bidentate O,OMe donor of each ligand preferentially traps the oxophillic Gd<sup>III</sup> ions, making each ligand susceptible to coordinate two Gd<sup>III</sup> and one Ni<sup>II</sup> through its OONO donor atoms. The Ni1 and Gd1 bound to pocket I and pocket II of  $L^{2-}$  and further bridged by the  $\mu_{1,3}$ -PhCO<sub>2</sub> moiety, making a shorter intrametallic distance of 3.397(3) Å, whereas the other part bound to Gd1\* possesses no bridging benzoate group and records a distance of 3.485(3) Å from Ni1. This Ni<sub>2</sub>Gd<sub>2</sub>O<sub>6</sub> butterfly-shaped partial di-cubane core is mainly built over two µ3-methoxo groups, providing a Ni1…Ni1\* separation of 3.142(3) Å where both the  $Ni^{II}$  metal ions present at the vertices of the body position and two Gd<sup>III</sup> metal centers are at the tip of the wing position of the butterfly core. The Ni<sup>II</sup> metal centers are in a distorted octahedral environment (OC-6



Fig. 3 Distorted octahedral geometry of Ni<sup>II</sup> metal ions (left) and distorted trigonal dodecahedral geometry of  $Gd^{III}$  ions (right).

= 0.751, Table S2 in the ESI<sup>†</sup>) and the coordination sites are occupied by ligand L<sup>2-</sup>, two  $\mu_3$ -OCH<sub>3</sub> groups and one benzoate group (Fig. 3). Around Ni1, the N1–Ni1–O4 axis is the longest one at 4.181 Å with bond distances N1–Ni1, 2.064(6) Å and O4–Ni1, 2.124(5) Å. The remaining Ni–O distances lie within the range 2.009(5)–2.070(5) Å. Both the Ni<sup>II</sup> centers along with two  $\mu_3$ -methoxo groups formed a rhombus where the Ni1–O4–Ni1\* angle is 97.4(2)° and the O4–Ni1–O4\* angle is 82.6(2)°. The formation of this Ni<sub>2</sub>O<sub>2</sub> rhombus is important for the formation of the self-assembled Ni<sub>2</sub>Gd<sub>2</sub> butterfly core.

The eight coordinated environments around the Gd1/Gd1\* centers are occupied by the eight O atoms of four different types: three O atoms from two L<sup>2–</sup> ligands, two O from MeOH, two O from the -PhCO<sub>2</sub> moiety and one O from the  $\mu_3$ -OCH<sub>3</sub> group. SHAPE 2.1 analysis confirmed the distorted trigonal dodecahedral environment around the Gd<sup>III</sup> center (Fig. 3, TDD-8 = 1.193, Table S3 in the ESI<sup>†</sup>). The Gd–O bond distances lie within the range 2.297(5)-2.646(6) Å, where the longest bond corresponds to Gd1-O1. Within the partial di-cubane core a total of four different Ni-O-Gd angles is present in the range of 98.15(19)°-105.2(2)° due to the presence of two different types of O donors; where the smallest angle encompassed over the participation of the  $\mu_3$ -methoxido oxygen atom and the largest one for the µ-phenoxido oxygen atom. The mean plane analysis suggests all four metal centers are coplanar and the µ3-methoxo oxygen atoms are displaced by 1.020 Å from the plane. The search for a hydrogen bonding network showed that the molecule has no intramolecular H-bonding interaction present but a 1D intermolecular weak H-bonding connection propagates through the lattice MeOH (Fig. S2, ESI<sup>†</sup>).

#### Magnetic studies

Several 3d–4f butterfly complexes have been shown to behave as SMMs, a characteristic mainly arising from the lanthanide complex.<sup>33,36,64</sup> Interestingly, it has been shown that the relaxation characteristics are contingent upon the neighboring 3d metal, which could in principle be a consequence of the interaction between the 3d–4f pairs and the relative orientation of the easy axes between the ions. To investigate the magnetic characteristics of the complexes herein studied, DC SQUID measurements were carried out for all systems. The room temperature  $\chi_{\rm M}T$  value for all complexes is very close to that expected for the non-interacting systems, *i.e.*, 17.8, 27.1, 29.9 and 30.3 cm<sup>3</sup> K mol<sup>-1</sup> for Ni<sub>2</sub>Gd<sub>2</sub>, Ni<sub>2</sub>Tb<sub>2</sub>, Ni<sub>2</sub>Dy<sub>2</sub> and Ni<sub>2</sub>Ho<sub>2</sub>, respectively.

Upon lowering the temperature,  $\chi_M T$  remains practically constant until about 20 K where it sharply increases to  $\chi_M T$ values of 34.6 cm<sup>3</sup> K mol<sup>-1</sup> for Ni<sub>2</sub>Gd<sub>2</sub>. For Ni<sub>2</sub>Tb<sub>2</sub>, Ni<sub>2</sub>Dy<sub>2</sub> and Ni<sub>2</sub>Ho<sub>2</sub> the  $\chi_M T$  also increases below 20 K reaching maximum  $\chi_M T$  values of 55.3 (at 3 K), 47.7 (at 2.5 K) and 40.8 cm<sup>3</sup> K mol<sup>-1</sup> (at 2.5 K) before decreasing to 53.7, 46.8 and 40.0 cm<sup>3</sup> K mol<sup>-1</sup>, respectively (Fig. 4). The upsurge observed in the  $\chi_M T$ data indicates the existence of ferromagnetic interaction occurring between the 3d–4f pairs. Further magnetization investigations at variable fields and temperatures result in a saturation value of 18.0  $\mu_B$  for Ni<sub>2</sub>Gd<sub>2</sub> at 7 T and 2 K, while for Ni<sub>2</sub>Tb<sub>2</sub>, Ni<sub>2</sub>Dy<sub>2</sub> and Ni<sub>2</sub>Ho<sub>2</sub> the magnetization values at the lowest temperature (2 K) and the highest field (7 T) are 14.5, 15.4, and 16.4  $\mu_B$ , respectively, without reaching saturation. The lack of saturation in these systems indicates strong anisotropy in the systems. We also explore the dynamic characteristics of the complexes *via* AC magnetic susceptibility; however, slow relaxation characteristics were not found for any of the butterfly complexes without and with an applied  $H_{\rm DC}$ field, and thus none of them shows SMM properties.

In the case of compound **1** containing Gd<sup>III</sup>, the spin Hamiltonian formalism is adequate for describing the magnetic properties. Based on the molecular structure of **1**, the following spin Hamiltonian was employed:

$$\begin{aligned} \hat{H} &= -J_{\rm Gd-Ni}(\vec{S}_{\rm Gd} \cdot \vec{S}_{\rm Ni} + \vec{S}_{\rm Gd} \cdot \vec{S}_{\rm Ni^*} + \vec{S}_{\rm Gd^*} \cdot \vec{S}_{\rm Ni} + \vec{S}_{\rm Gd^*} \cdot \vec{S}_{\rm Ni^*}) \\ &- J_{\rm Ni-Ni}(\vec{S}_{\rm Ni} \cdot \vec{S}_{\rm Ni^*}) + \sum_{k=1}^{4} D_k(\hat{S}_{z,k}{}^2 - \hat{S}_k{}^2/3) + \mu_{\rm B}B \sum_{k=1}^{4} g_k \hat{S}_{a,k} \end{aligned}$$

$$(2)$$

where the first two terms describe the isotropic exchange among Gd–Ni and Ni–Ni ions, then the single-ion zero-field splitting term is added and finally there is a Zeeman term defined for the *a*-direction of the magnetic field as  $B_a = B(\sin (\theta)\cos(\varphi), \sin(\theta)\sin(\varphi), \cos(\theta))$ .<sup>66</sup> Usually, it holds that  $D(Gd^{III})$ is very small, and therefore we assumed  $D(Gd^{III}) = E(Gd^{III}) = 0$ . With the aim to minimize the number of free parameters, ZFS parameters of Ni<sup>II</sup> were fixed to values calculated using the



**Fig. 4** Temperature dependence of the  $\chi T$  product and the isothermal magnetizations measured at T = 2, 3, 4, and 5 K for (a) Ni<sub>2</sub>Gd<sub>2</sub> (1). The empty circles represent the experimental data points while the full lines in panel (a) represent the best fits calculated using eqn (2) and  $J_{Gd-Ni} = 0.715$  cm<sup>-1</sup>,  $J_{Ni-Ni} = 6.49$  cm<sup>-1</sup>,  $D_{Ni} = 4.35$  cm<sup>-1</sup>, g = 1.98 and zj = -0.469 cm<sup>-1</sup>; (b) Ni<sub>2</sub>Tb<sub>2</sub>; (c) Ni<sub>2</sub>Dy<sub>2</sub>; and (d) Ni<sub>2</sub>Ho<sub>2</sub>.

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Table 1 The CASSCF calculated *D*-tensor and *g*-tensor values of Ni<sup>II</sup> in 1–4 performed using ORCA

Compound	D(Ni)	E/D(Ni)	g-factors
1	5.43	0.173	2.274, 2.304, 2.316
2	4.69	0.147	2.273, 2.299, 2.309
3	4.56	0.165	2.259, 2.284, 2.295
4	4.52	0.133	2.261, 2.287, 2.295

CASSCF method (Table 1) and we also assumed  $g_{\text{Ni}} = g_{\text{Gd}} = g$ , and thus, we are left with three parameters ( $J_{\text{Gd-Ni}}$ ,  $J_{\text{Ni-Ni}}$ , and g). Here, all experimental magnetic data were treated simultaneously using the POLYMAGNET program<sup>67</sup> and the bestfitted parameters were found as  $J_{\text{Gd-Ni}} = 0.685 \text{ cm}^{-1}$ ,  $J_{\text{Ni-Ni}} =$ 7.16 cm<sup>-1</sup>, and g = 1.98 providing good agreement with the experiment – Fig. 4a. Obviously, both exchange interactions are ferromagnetic in nature. The obtained ferromagnetic  $J_{\text{Ni-Ni}}$ interaction also bodes well with the small Ni1–O4–Ni1\* angle in the complex, *i.e.*, 97.4(2) Å, which has been found to induce ferromagnetic interactions when the angle is small (<98°) and antiferromagnetic interaction can likewise be related to the small



Fig. 5 The magnetostructural correlation of  $J_{Ni-Ni^{\star}}$  calculated using the B3LYP functional in a series of 1–4 compounds.

interaction between the inner 4f orbitals and the 3d orbitals of nickel, which often induces ferromagnetic interaction between 3d–4f metal pairs.<sup>63,70</sup> Moreover, the ferromagnetic interaction is in line with the magnetostructural correlation of Ni–Gd exchange and the respective Ni–O–Gd angle.<sup>71</sup>

#### Theoretical studies

The magnetic interactions and magnetic anisotropy are key points in understanding the magnetic behavior of polynuclear metal complexes. The complexity of such interactions is usually hard to grasp from the experimental data alone, and Density Functional Theory (DFT) and multireference calculations such as Complete Active Space Self-Consistent Field (CASSCF) Methods are essential for better understanding the behavior of this class of compounds. First, magnetic interactions were investigated using DFT calculations with the B3LYP hybrid functional using the ORCA 4.2 software.<sup>45</sup> Here, the broken-symmetry approach was applied to evaluate  $J_{Ni-Ni}$ and  $J_{Gd-Ni}$  in the whole series 1–4, for which the respective molecular structures were extracted from X-ray experimental data. For complex 1, the following spin Hamiltonian was considered:

$$\hat{H} = -J_{\rm Gd-Ni}(\vec{S}_{\rm Gd} \cdot \vec{S}_{\rm Ni} + \vec{S}_{\rm Gd^*} \cdot \vec{S}_{\rm Ni^*}) - J_{\rm Gd^*-Ni}(\vec{S}_{\rm Gd} \cdot \vec{S}_{\rm Ni^*} + \vec{S}_{\rm Gd^*} \cdot \vec{S}_{\rm Ni}) - J_{\rm Ni-Ni}(\vec{S}_{\rm Ni} \cdot \vec{S}_{\rm Ni^*}).$$
(3)

The comparison of energies of the high-spin state (HS) and several broken–symmetry spin states (BS\_NiNi\*, BS\_NiGd, BS\_NiGd\*) was utilized for the calculations of the isotropic exchange parameter *J* by Ruiz's approach<sup>72</sup>

$$\varepsilon_{\text{BS_NiNi}^*} - \varepsilon_{\text{HS}} = 16J_{\text{Gd}-\text{Ni}} + 16J_{\text{Gd}^*-\text{Ni}}$$

$$\varepsilon_{\text{BS_NiGd}} - \varepsilon_{\text{HS}} = \frac{37}{2}J_{\text{Gd}^*-\text{Ni}} + 3J_{\text{Ni}-\text{Ni}}$$

$$\varepsilon_{\text{BS_NiGd}^*} - \varepsilon_{\text{HS}} = \frac{37}{2}J_{\text{Gd}-\text{Ni}} + 3J_{\text{Ni}-\text{Ni}}$$
(4)



Fig. 6 The output of the ORCA CASSCF calculations with CAS(8,5) for Ni ions in complexes 1–4. The plot of the d-orbital splitting calculated using *ab initio* ligand field theory (AILFT) (left), low-lying ligand-field terms (middle), and ligand-field multiplets showing splitting of the ground triplet state (right).

which resulted in  $J_{\text{Ni-Ni}*} = 5.89 \text{ cm}^{-1}$ ,  $J_{\text{Gd-Ni}} = 0.968 \text{ cm}^{-1}$  and  $J_{\text{Gd}*-\text{Ni}} = 0.948 \text{ cm}^{-1}$ . Thus, both types of isotropic exchange are ferromagnetic, which is in accordance with fitted values from the magnetic data. The respective plots of the calculated spin densities of **1** are shown in Fig. S9.† For the rest of compounds **2–4**, two paramagnetic lanthanide ions were replaced by the diamagnetic Lu analogue and calculations of BS\_Ni were used to evaluate  $J_{\text{Ni-Ni}*}$  in these complexes as presented in Table S12.† Generally, it holds that the value of  $J_{\text{Ni-Ni}*}$  correlates with the Ni–Ni\* distance as well as with the average <Ni–O–Ni\* angle – Fig. 5. Next, we were interested in the zero-field splitting of Ni and Ln ions (Tb, Dy, Ho) in **1–4** induced by the



**Fig. 7** The output of the ORCA CASSCF calculations with CAS(8,7) for Tb in 2, with CAS(9,7) for Dy in 3 and with CAS(10,7) for Ho in 4. The plot of the f-orbital splitting calculated using *ab initio* ligand field theory (AILFT) (left), and ligand-field multiplets showing splitting of ground states ( $^{7}F_{6}$ ,  $^{6}H_{15/2}$  and  $^{5}I_{8}$ ) (right).

spin-orbit coupling and the ligand-field. Therefore, CASSCF calculations were performed using ORCA, which enabled us to evaluate the energies of d- or f-orbitals with ab initio ligand field theory (AILFT)<sup>73,74</sup> and respective ligand-field terms and ligand-field multiplets. The details of these calculations are stated in the Experimental section. The splitting of d-orbitals shows a typical pattern for pseudooctahedral complexes and 10Dq is reaching values of  $\approx 8000 \text{ cm}^{-1}$  (Fig. 6). The lowest triplet ligand field term is well separated from the excited terms, and therefore, relatively small zero-field splitting of the (2S + 1) ground state is expected and found as plotted in Fig. 6 (right), reaching  $D \approx 5.4-4.5 \text{ cm}^{-1}$  with E/D values close to 0.13–0.17 (Table 1), where the values of  $D_{Ni}$  are in the expected range for the hexacoordinate Ni<sup>II</sup> ion.<sup>75,76</sup> Interestingly, D is constantly decreasing in 1-4 with an increase in the atomic number of Ln and mostly correlates with a decrease in the SHAPE index of OC-6 geometry (Table S2<sup>†</sup>). Similar CASSCF calculations for Tb, Dy, and Ho in compounds 2-4 are shown in Fig. 7.

As expected, the impact of the ligand-field on f-orbitals is much smaller, f-orbitals are split in the range up to 800 cm<sup>-1</sup> and the splitting of the respective  ${}^{7}F_{6}$ ,  ${}^{6}H_{15/2}$  and  ${}^{5}I_{8}$  states are shown in Fig. 7 (right) and the respective energy levels are presented in Table S13.† In the case of Dy<sup>III</sup>, the ground state Kramers doublet has large axial magnetic anisotropy (calculated *g*-factors: 0.061, 0.135, 19.342) and the axes of this *g*-tensor are shown in Fig. S10.† The first excited state is located at 108 cm<sup>-1</sup>, which makes a good predisposition for SMM properties. Moreover, these calculations also suggest an antiferromagnetic dipole–dipole interaction between two Dy atoms, because the angle between the orientation of the magnetic moment of the ground Kramers doublet with respect to



**Fig. 8** Magnetization blocking barrier of  $Dy^{II}$  in 3 calculated using SINGLE\_ANISO (left) and the magnetization blocking barrier of  $Ni_2Dy_2$  in 3 calculated using POLY\_ANISO with  $J_{Dy-Ni} = 0.873 \text{ cm}^{-1}$  and  $J_{Ni-Ni} = 7.96 \text{ cm}^{-1}$  (right), zoomed to the lowest energy levels. The numbers presented in the plot represent the corresponding matrix element of the transversal magnetic moment (for values larger than 0.1 an efficient relaxation mechanism is expected), and  $\Delta_{tun}$  shows the tunnelling gap of the indicated pseudo-doublets. Dashed lines refer to (temperature assisted) quantum tunnelling (blue), Orbach/Raman mechanisms (red) and direct/Raman mechanisms (green).<sup>81</sup>

the Dy…Dy connecting line is 87°, which is more than the border value of 54.7°.<sup>77</sup> However, the relatively large distance between two ions means that this contribution to the whole magnetic behavior will be minimal.

To better understand the magnetic behavior of 2-4, the magnetic exchange interactions need to be determined. Therefore, the OpenMOLCAS program was employed, because with SINGLE ANISO and POLY ANISO modules we are able to calculate the dipolar and exchange magnetic interactions and on top of that also the magnetization reversal barrier for whole complexes. Thus, analogous CASSCF calculations were performed for Ni<sup>II</sup> and Ln<sup>III</sup> ions in 2-4 using OpenMOLCAS with the SINGLE ANISO module resulting in similar parameters of the zero-field splitting of these ions - Tables S14 and S15.† Evidently, the tunneling should be very fast in Tb<sup>III</sup> of 2 and Ho<sup>III</sup> of 4, because there is a large energy gap of the first pseudo-doublet,  $\Delta_{tun} = 2.09 \text{ cm}^{-1}$  for Tb<sup>III</sup> and  $\Delta_{tun} = 4.14 \text{ cm}^{-1}$ for Ho<sup>III</sup>, which clarify why compounds 2 and 4 lack slow relaxation of the magnetization. In contrast, the Dy<sup>III</sup> ion possesses large axial anisotropy of the first Kramers doublet, and the tunneling probability is small as shown in the magnetization blocking diagram in Fig. 8.

Subsequently, a homemade routine was used to fit experimental dc magnetic data of 2-4, both temperature and field dependent in cooperation with the POLY\_ANISO module.78-80 Within these calculations, the six lowest states for each Ln<sup>III</sup> ions and triplet ground states for Ni<sup>II</sup> ions were included in the exchange interaction. During fitting, J<sub>Ni-Ni</sub> was fixed to a value found using DFT (Table S12<sup>+</sup>), and therefore we were left with fitting just the J<sub>Dy-Ni</sub> parameter and scaling coefficient. The best agreement was obtained with  $J_{\text{Tb-Ni}} = 1.25 \text{ cm}^{-1}$  for 2,  $J_{\rm Dy-Ni}$  = 0.873 cm<sup>-1</sup> for 3 and  $J_{\rm Ho-Ni}$  = 1.42 cm<sup>-1</sup> for 4 -Fig. S11.<sup>†</sup> Interestingly, all magnetic exchanges in 1-4 are ferromagnetic in nature. To understand also the dynamic magnetic properties of 3, the magnetization reversal barrier for  $Ni_2Dy_2$  of 3 is plotted in Fig. 8 (right) showing dense splitting of low energy levels, and a low-lying first pseudo-doublet at  $\sim 2.5 \text{ cm}^{-1}$  with zero magnetic moment, which most likely precludes slow relaxation of the magnetization in this compound.

# Conclusions

Four isostructural and new 3d–4f aggregates have been synthesized from the coordinating support of the anionic form of 2-[{(2-hydroxybenzyl)imino}methyl]-6-methoxyphenol reacting with Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ln(NO<sub>3</sub>)<sub>3</sub>·nH<sub>2</sub>O salts. The synergistic and preferential coordination of 3d and 4f ions results in the formation of a batch of partial di-cubane Ni<sub>2</sub>Ln<sub>2</sub> compounds. Typical involvement of benzoato anions from the externally added sodium salt shapes the network within the aggregate without giving any scope for further extended solvent water derived hydroxido/oxido bridges. The detailed quantitative analysis of the magnetic data supported by DFT and CASSCF calculations revealed a ferromagnetic exchange between Ni<sup>II</sup> ions and also between 3d–4f ions ( $J_{Gd-Ni} = 0.715 \text{ cm}^{-1}$ ,  $J_{Tb-Ni} =$  1.25 cm<sup>-1</sup>,  $J_{\text{Dy-Ni}} = 0.873$  cm<sup>-1</sup> and  $J_{\text{Ho-Ni}} = 1.42$  cm<sup>-1</sup>) and the respective magnetic anisotropy of the axial symmetry for Dy<sup>III</sup> ions in **3**. The ferromagnetic interaction between the Ni…Ni couple can be understood by the relatively narrow Ni–O–Ni angle. Furthermore, the lack of SMM characteristics can be explained by a complex interplay of magnetic interactions in the compounds leading to low lying energy levels with zero magnetic moments and thus diminishing the effective energy barrier for the Orbach relaxation mechanism.

# Conflicts of interest

The authors declare no conflict of interest.

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