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Coordination Control of a Semicarbazide Schiff Base Ligand for Spontaneous Aggregation of a Ni₂Ln₂ Cubane Family: Influence of Ligand Arms and Carboxylate Bridges on the Organization of the **Magnetic Core**

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A family of tetranuclear Ni-4f coordination aggregates (CAs) from the support of a carbazido ligand is described. The option of altering the 4f ions during synthesis within the family, without altering the core topology gave the four members of the family. Tetranuclear (2:2) heterometallic compounds $[Ni^{1}_{2}Ln^{11}_{2}(\mu_{3}-C)_{2}(\mu_{3}-C)A_{3}(AcO)(H_{2}O)_{3}]Cl_{2}+4H_{2}O(Ln = Gd, AcO)(H_{2}O)_{3}]Cl_{2}+4H_{2}O(Ln = Gd, AcO)(H_{2}O$ 1; Tb, 2; Dy, 3; Ho, 4) have been assembled through the utilization of all the coordination sites of the anionic form of 1-(2hydroxy-3-methoxybenzylidene)semicarbazide (HL) and bridging supports from HO⁻ and AcO⁻ ions. The four metal ion centers of two different types, are held together by two μ -L⁻, two μ ₃-HO⁻ and three μ _{1,3}-AcO⁻ bridges to self-assemble into Ni₂Ln₂O₄ hetero-cubane structures. In each cube, Ln^{III} ions are linked by two hydroxido and one phenoxido bridges and each Ni^{II} ion is linked by two phenoxido and one hydroxido bridges, so that each hydroxido group in μ_3 -mode is linked to two Ln^{III} and one Ni^{II} and each phenoxido ion in μ_3 -mode linked two Ni^{II} and one Ln^{III}. Variable temperature magnetic properties have been examined to find the role of magnetic anisotropy for the single molecule magnet (SMM) behavior. All of them show large ground state magnetic moment values and absence of out-of-phase ac susceptibility signals. The absence of SMM behavior is ascribed to the lack of axial magnetic anisotropy.

Introduction

Coordination compounds of trivalent 4f ions are known to have high coordination numbers (\geq 7) and flexible coordination geometries, due to the higher positive charge, larger ionic radii and hard Lewis acid character. These features are not matching to the bivalent 3d series ions. Thus, bringing two of these types of metal ions in close proximity through the involvement and coordination control of chosen ligand anion and standardization of exact reaction condition for the accomplishment of the 3d-4f coordination aggregates (CAs) is a task to the synthetic chemists. Such CAs, assembled by organic phenol group bearing ligands incorporating appropriate number of 3d and 4f ions, represent example of multinuclear compounds having two or more types of metal ions in single molecular entity.¹⁻⁹ Single molecule magnets

(SMMs) are known to be compounds in which each molecular entity is magnetically independent and able to slow magnetic relaxation in the low temperature region.¹⁰⁻¹⁴ The long relaxation times are obtained from a large anisotropy barrier, but the process, like fast quantum tunneling of magnetization (QTM), can often cancel the anisotropy barrier. A good SMM is supposed to preserve their magnetic state for a long time even after removal of external fields, which is only possible by suppression of ground state quantum tunneling of magnetization (QTM). Presence of unquenched orbital momentum and anisotropic crystal field around the 4f ions lead to the formation of SMMs from the synthesis of coordination aggregates through utilization of spontaneous self-assembly processes. Manipulation of reaction condition and use of different combination of 3d and 4f ions lead to particular course of aggregation between initially formed fragments to provide new types of 3d-4f aggregates. Since the easy-axis magnetic anisotropy, essential for SMM behavior, can easily be produced for some lanthanide ions having large ground state magnetic moment values.^{15,16} New structures of these aggregates have shown attention for their potential in high-density information storage device, quantum computer, spintronics and magnetocaloric materials.¹⁷⁻²¹ 3d ion based molecular nanomagnets first identified in 1990s, specifically SMMs and single-chain magnets (SCMs), display magnet-type behavior without long-range magnetic ordering.²²⁻²⁴ Axially symmetric crystal-field environments around the incorporated

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⁺ Electronic supplementary information (ESI) available: Selected bond lengths and 57 angles Table S1, Shape analysis Table S2, additional structural figures Fig. S1-S6. 58 CCDC reference numbers 1941824-1941827. For ESI and crystallographic data in 59

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59 60 3d and 4f ions, and strong exchange coupling between them leads to the SMM behavior. The splitting of the degenerate 2J+1 ground state of 4f ions is highly sensitive to the coordination environment and the donor atoms bound to the metal ions, and any changes in those would be responsible to a variation in the magnetic exchange interactions. Many heterometallic 3d-4f complexes have been studied in detail and reported in recent years from the use of new types of ligand systems and utilization of room temperature solution chemistry.²⁵⁻²⁷ In polynuclear Ni^{II}-Ln^{III} complexes the ferromagnetic exchange interactions between Ni^{II} and Ln^{III} center is responsible for generating functionally interesting magnetic molecules.²⁸⁻²⁹ In particular the single-ion anisotropy of a metal ion depends primarily on its coordination environment and ligand field, while the molecular anisotropy depends on ligand field, relative orientation of the individual single-ion easy axes, magnetic coupling, and the overall structural topology of the magnetic core. Thus synthetic coordination chemists have the strong desire to design and obtain new structural motifs to manipulate these contributions.

We were interested to examine the heterometallic (3d-4f)influence on the aggregation process, overall structure and variable temperature magnetic behavior of the synthesized compounds. The study recommended that discrete and easy to synthesize heterometallic 2:2 cubanes serve as magnetically active and useful materials whose structures are not guided and apprehended by the ligand system and synthetic protocols. Such ligand system has appealed significant curiosity in recent past for the generation of new family of structural as well as functional heterometallic aggregates.³⁰

work, we have chosen 1-(2-hydroxy-3-In this methoxybenzylidene)semicarbazide (HL) as a ditopic ligand delivering μ_3 -phenoxido bridging mode for a family of Ni₂Ln₂ cubane-type complexes. Chosen reaction condition was appropriate to obtain solvent water derived μ_3 -hydroxido bridges and trapping of externally added carboxylate anions for incorporation into the aggregates. Both anisotropic and isotropic 4f ions, Dy^{III} and Gd^{III} were chosen to combine with the Ni^{II} to observe their coordination compatibility in adjacent pockets and the nature of magnetic exchange. Incorporation of non-Kramer 4f ion, Ho^{III} having ground-state multiplet of ⁵I₈ has also been examined. In recent time HL was used by Chen et al. to obtain [Ln^{III}₂] (Ln = Dy and Er)³¹, zigzag-shaped shaped tetranuclear $[Ni_2Dy_2]$ and $[Co_2Dy_2]$,³² and trinuclear $[Zn_2Dy]^{33}$ complexes. None of these explorations could show the unusual μ_3 -phenoxido bridge from L⁻ and development of cubic topology which is being reported in this work.

Four heterometallic $[Ni_2Ln_2L_2(\mu_3-OH)_2(O_2CCH_3)_4(H_2O)_3]Cl_2\cdot 4H_2O$ [Ln= Gd (1), Tb (2), Dy (3), Ho (4)] complexes of cubic topology have been synthesized and characterized. Detailed of the syntheses, their structures, course of aggregation and magnetic behaviors have been examined systematically.



Scheme 1 Available binding sites of HL and observed binding modes of L⁻, AcO⁻ and HO⁻ groups

Experimental Section

Materials. All the starting materials and solvents for the syntheses were analytically pure reagent grade and were used as obtained from commercial houses without further purification. The sources are: sodium acetate from SD Fine Chem Pvt. Ltd., India, semicarbazide, lanthanide chlorides from Alfa Aesar, India, triethylamine from SRL, India, nickel chloride from E. Merck, India, methanol from Finar Ltd., India. All the reactions and physical characterizations were carried out in aerobic and normal laboratory conditions.

Synthesis of HL. The Schiff base ligand was obtained from a 1:1 condensation reaction of semicarbazide and o-vanillin following a reported procedure.^{31,34} Yield: 78%. Obtained HL was characterized by FT-IR and NMR spectral measurements and used directly for reactions with metal ion salts without further purification. Selected FT-IR peaks: (KBr disc, cm⁻¹, vs = very strong, br = broad, s = strong, m = medium, w = weak): 3436 (m), 3162(m), 1664(vs), 1600(s). ¹H NMR (400 MHz, DMSO-D₆, ppm): δ 8.17 (1H, imine-H), δ 6.42 (2H, -NH₂), δ 2.49 (1H, -NH), δ 10.27 (1H, phenolic OH), δ 6.42-7.37 (3H, aromatic protons), δ 3.78 (3H, OCH₃).

Synthesis of complexes 1-4. All four complexes were obtained by following a general procedure. To a colorless solution of HL (0.1mmol) in MeOH (10 mL), a MeOH solution (2 mL) of LnCl₃·6H₂O (0.1mmol) was added under stirring condition for an initial reaction in 1:1 molar ratio and the solution color changed to light yellow. After 10 min of stirring neat Et₃N

(0.2mmol) solution was added drop by drop and the whole reaction mixture was stirred for 1h. In the next step a MeOH solution (2 mL) of NiCl₂·6H₂O (0.1mmol) was added to the previous solution drop wise followed by the addition of powder NaOAc (0.2mmol) and the entire reaction mixture was next stirred for 6h. The resulting clear green reaction mixture was then filtered and left undisturbed in a conical flask at room temperature for slow evaporation of solvent. From the reaction mixture green block shaped crystals, suitable for X-ray diffraction analysis, were obtained after 7 days.

 $\begin{bmatrix} Ni_2Gd_2(\mu_3-L)_2(\mu_3-OH)_2(\mu-OAc)_3(AcO)(H_2O)_3]Cl_2\cdot 4H_2O (1). HL \\ (0.0209 g, 0.1mmol), GdCl_3\cdot 6H_2O (0.0372 g, 0.1mmol),$ $NiCl_2\cdot 6H_2O (0.0237 g, 0.1mmol), NEt_3 (0.028 mL, 0.2mmol) and$ NaOAc (0.0164 g, 0.2mmol). Yield: 0.0478 g, 73% (based on $Gd). Anal. Calcd for C_{26}H_{48}Cl_2Gd_2N_6Ni_2O_{23} (1315.48 g mol^{-1}): C,$ 23.74; H, 3. 68; N, 6.39. Found: C, 23.64; H, 3.28; N, 6.35.Selected IR peaks (KBr cm⁻¹; s = strong, vs = very strong, m =medium, br = broad): 3370 (br), 1676(s), 1606 (m), 1560 (vs),1460(s), 1420 (vs), 1262 (m), 1226 (m), 1154 (m), 1082 (m), $1024 (m), 948 (w), 851 (w), 742 (m), 668 (w). \\ \end{bmatrix}$

 $\begin{bmatrix} Ni_2Tb_2(\mu_3-CH)_2(\mu_3-CH)_2(\mu-OAc)_3(AcO)(H_2O)_3]Cl_2-4H_2O & (2). HL \\ (0.0209 g, 0.1mmol), TbCl_3-6H_2O & (0.0373 g, 0.1mmol), \\ NiCl_2-6H_2O & (0.0237 g, 0.1mmol), NEt_3 & (0.028 mL, 0.2mmol) and \\ NaOAc & (0.0164 g, 0.2mmol). Yield: 0.0492 g, 75% & (based on Tb). Anal. Calcd for C_{26}H_{48}Cl_2Tb_2N_6Ni_2O_{23} & (1318.83 g mol^{-1}): C, \\ 23.68; H, 3. 67; N, 6.37. Found: C, 24.01; H, 3.70; N, 6.59. \\ Selected IR peaks & (KBr cm-1; s = strong, vs = very strong, m = medium, br = broad): 3370 & (br), 1674 & (s), 1605 & (m), 1551 & (vs), \\ 1460 & (s), 1412 & (vs), 1260 & (m), 1225 & (m), 1151 & (m), 1080 & (m), \\ 1022 & (m), 948 & (w), 847 & (w), 737 & (m), 663 & (w). \\ \end{bmatrix}$

 $[Ni_2Dy_2(\mu_3-L)_2(\mu_3-OH)_2(\mu-OAc)_3(AcO)(H_2O)_3]Cl_2·4H_2O (3). HL (0.0209 g, 0.1mmol), DyCl_3·6H_2O (0.0377 g, 0.1mmol), NiCl_2·6H_2O (0.0237 g, 0.1mmol), NEt_3 (0.028 mL, 0.2mmol) and NaOAc (0.0164 g, 0.2mmol). Yield: 0.0512 g, 77% (based on Dy). Anal. Calcd for C_{26}H_{48}Cl_2Dy_2N_6Ni_2O_{23} (1325.98 g mol⁻¹): C, 23.55; H, 3.65; N, 6.34. Found: C, 23.77; H, 3.44; N; 6.18. Selected IR peaks (KBr cm⁻¹; s = strong, vs = very strong, m = medium, br = broad): 3366 (br), 1678(s), 1606 (m),1560 (vs), 1461 (m), 1420 (vs), 1262 (m), 1226 (m), 1152 (m), 1082 (m), 1024 (m), 948 (w), 848 (w), 740 (m), 666 (w).$

 $[Ni_2Ho_2(\mu_3-L)_2(\mu_3-OH)_2(\mu-OAc)_3(AcO)(H_2O)_3]Cl_2\cdot 4H_2O$ (4). HL 43 (0.0209 g, 0.1mmol), HoCl₃·6H₂O (0.0379 g, 0.1mmol), 44 NiCl₂·6H₂O (0.0237 g, 0.1mmol), NEt₃ (0.028mL, 0.2mmol) and 45 NaOAc (0.0164 g, 0.2mmol). Yield: 0.0500 g, 75% (based on 46 Ho). Anal. Calcd for C₂₆H₄₈Cl₂Ho₂N₆Ni₂O₂₃ (1330.84 g mol⁻¹): C, 23.47; H, 3.64; N, 6.31. Found: C, 23.15; H, 3.51; N, 6.47. 48 Selected IR peaks (KBr cm⁻¹; s = strong, vs = very strong, m = 49 medium, br = broad): 3368 (br), 1678 (s), 1606 (m), 1560 (vs), 50 1462 (m), 1414 (vs), 1262 (m), 1226 (m), 1152 (m), 1082 (m), 51 1024 (m), 948 (w), 848 (w), 740 (m), 668 (w). 52

Physical Measurements. Elemental analyses (C, H, N) for 1-4
were performed on a Perkin-Elmer (model 240C) elemental
analyzer. FT-IR spectra were recorded on a Perkin-Elmer RX1
spectrometer and solution electronic spectra were measured
using Shimadzu UV 3100 UV–Vis–NIR spectrophotometer. The
diffuse reflectance spectra (DRS) were measured using a CARY5000 UV-vis-NIR spectrophotometer. Powder X-ray diffraction

patterns were measured on Bruker AXS X-ray difficaction terms using Cu K α radiation ($\lambda = 1.5418$ Å) within the /525005(20) range. Magnetic measurements were carried out in the Unitat de Mesures Magnètiques (Universitat de Barcelona) on polycrystalline samples with a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections were calculated using Pascal's constants and an experimental correction for the sample holder was applied. Thermogravimetric analysis of the complexes was carried out using Netzsch STA 409 PC Luxx thermal analyzer within a temperature range of 30–700 °C and heating rate of 10 °C min⁻¹.

Single Crystal X-ray Diffraction Analysis. Suitable single crystals of complexes 1-4 were selected for data collection on Bruker SMART APEX-II CCD X-ray diffractometer equipped with a graphite-monochromated Mo-K α (λ = 0.710 73 Å) source with a counting time of 6s per frame. Space group determination was performed by using XPREP and integration of intensity for 25 reflections and reduction was performed using SAINT software. The structures were solved by direct methods SHELXS-2014³⁵, followed by refinement with fullmatrix least squares on F² using SHELXL-(2014/7)³⁶ software available with WINGX system Version 2014.137 and Olex-2 software³⁸ to mask the disordered solvent molecules. Multiscan absorption correction was performed using SADABS³⁹ program. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and refined with fixed geometry and riding thermal parameters on their carrier atoms. The locations of heaviest atoms (Ni, Ln) were determined easily and positions of O, N, C were determined from difference Fourier maps. The crystallographic figures were generated using Mercury, DIAMOND⁴⁰ and POV-ray⁴¹ software. Crystallographic data refinements details are summarized in Table 1, and selected bond distances and angles are given in Table S1. CCDC 1941824-1941827 contain the supplementary crystallographic data for complexes 1-4. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures."

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Continuous Shape Measures. The Continuous Shape Measures (CShM) have been performed using the SHAPE 2.1 software.⁴²⁻⁴⁴ To retrieve the coordination sphere of the lanthanide ion, a search for all bonded atoms was done using the criteria that the atom-atom bond length has to be below the sum of the atoms covalent radii.⁴⁵ This procedure recovers a total of eight oxygen atoms around each lanthanide ion. As reference shapes, a total of thirteen ideal polyhedral structures having eight vertices have been used.

Results and discussion

Synthesis, Isolation and Crystallization from Reaction Medium. Ligand HL used in this work has adjacent tridentate (ONO) and bidentate (OO) coordination pockets appropriate





Scheme 2 One pot synthesis of HL

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for the binding of *3d* and *4f* ions. HL was synthesized from Schiff base condensation reaction between *o*-vanillin and semicarbazide at room temperature in MeOH medium. (Scheme 2) The ligand is chosen to use the (ONO) pocket to bind a smaller and 'border line' Ni^{II} ion and the adjacent (OO) site was made available to trap a bigger and 'hard' Ln^{III} (Gd, Tb, Dy and Ho) ions. Hard O-donors are known to favor the coordination of Ln^{III} ions whereas border-line N-donors have higher affinity to bind the *3d* M^{II} ions. Use of LnCl₃ salts in 1:1 molar ratio with HL in the chosen reaction medium inhibit the formation of any kind of [Ln₂] type complex as obtained by others.²⁷ *In situ* generation of hydroxide ions in the presence of available acetate ions drove the reaction in solution followed by crystallization to the Ni₂Ln₂ aggregate formation.

The reactions of HL from sequential addition of LnCl₃·6H₂O and NiCl₂·6H₂O in MeOH in the presence of NEt₃ and NaOAc has been explored for the generation of solid crystalline coordination aggregates [Ni₂Ln₂(μ_{3} -L)₂(μ_{3} -OH)₂(O₂CCH₃)₄(H₂O)₃]Cl₂·nH₂O (Ln = Gd, **1**; Tb, **2**; Dy, **3**; Ho,**4**). All the four complexes (**1-4**) were isolated as single-crystalline materials, and good quality single crystals were selected for X-ray structure determinations. The chemical reaction involved during the generation of the complexes is summarized in eq **1**.

 $\begin{array}{l} \underset{MeOH}{\overset{MeOH}{\longrightarrow}} 2\text{HL} + 2\text{Ln}Cl_3 \cdot 6H_2O + 2NiCl_2 \cdot 6H_2O + 4NEt_3 + 4CH_3COONa} \\ \xrightarrow{MeOH} [Ni_2Ln_2(\mu_3 - L)_2(\mu_3 - OH)_2(OOCCH_3)_4(H_2O)_3]Cl_2 \cdot nH_2O + \\ 4(NEt_3H)Cl + 4NaCl + (19 - n)H_2O \dots \dots \dots (1) \end{array}$

In solution L⁻ anion initially binds Ln^{III} and Ni^{II} to generate reactive {NiLn(μ -L)} fragments, having hydroxide and acetato links gave [NiLn(μ -L)(μ -OH)(OOCCH₃)₂(H₂O)_n]¹⁺. Spontaneous dimerization of two such units resulted **1-4** (Scheme S1).

Addition of bidentate ligands such as bpy, o-phen, acacH (acetylacetone) and oxine (8-hydroxy quinoline) in the reaction medium immediately after the complete addition of metal ions



Scheme 3 Synthesis of compounds 1-4

did not provide the hitherto unknown dinuclear Acomplex [NiLn(μ -L)(μ -OH)(OOCCH₃)₂(H₂O)_n]Cl or and above/methodiated ligand anion bound species.⁴⁶

Green block-shaped crystals of **1-4** in 73-78% yield were isolated from the reaction mixture after different time intervals of 7 to 10 days. X-ray structure analysis of the single

crystals confirm the final product as $[Ni_2Ln_2(\mu_3-L)_2(\mu_3-OH)_2(O_2CCH_3)_4(H_2O)_3]Cl_2\cdot nH_2O$. (Scheme 3) Elemental analysis and physical characterizations of the products confirmed the formation of the tetranuclear cationic aggregates as chloride salts.

Solid State Characterizations

FT-IR Spectra. For all the four complexes 1-4, a broad band of medium intensity within 3660-3370 cm⁻¹ range is attributed to the $\tilde{v}_{\text{O-H}}$ and $\tilde{v}_{\text{N-H}}$ stretches. In case of free HL, two characteristic medium intensity peaks were found at 3434 and 3278 cm⁻¹ due to the $\tilde{v}_{\text{O-H}}$ and $\tilde{v}_{\text{N-H}}$ stretches. The characteristic $\tilde{v}_{C=N}$ stretching frequency from the Ni^{II} bound L⁻ is observed at 1605 cm^{-I}, confirming a small shift from the corresponding value at 1598 cm^{-I} for HL. The Ln^{III} bound $\tilde{\nu}_{C=O}$ stretching frequencies on the other hand for the entire family of complexes appear within 1674-1678 cm^{-I}, compared to the free ligand value of 1669 cm^{-1.47} For the whole family, the asymmetric ($\tilde{v}_{as(COO)}$) and symmetric ($\tilde{v}_{s(COO)}$) stretching vibrations of three bridging acetato groups are detected at 1560, 1551, 1560 and 1560 cm⁻¹, and 1420, 1412, 1420, 1414 cm⁻¹, respectively for 1-4. The differences in respective cases $(\Delta \tilde{v} = \tilde{v}_{as(COO)} - \tilde{v}_{s(COO)})$ are within 139-146 cm⁻¹, which is in agreement with the presence of $\mu_{1,3}$ -carboxylato bridges between Ni^{II} and Ln^{III} centers. The symmetric ($\tilde{v}_{s(COO)}$) stretching vibrations for terminal AcO⁻ groups in 1-4 appear at 1228, 1224, 1228 and 1228 cm⁻¹. As a result the higher magnitude of $\Delta \tilde{v}$ values of 327-332 cm⁻¹ confirm the terminal carboxylate binding to the Ln^{III} centers.⁴⁸

Electronic Spectra. Solid state DRS for 1-4 were recorded in 1200-200 nm range. (Figure S2) The presence of distorted octahedral Ni^{II} centers, bridged to the Ln^{III} centers, showed characteristic peaks for the characteristic ligand field transitions. Broad absorption bands with maxima at 987, 982, 987 and 989 nm can be assigned to the spin allowed ${}^{3}A_{2g}(F) \rightarrow$ ³T_{1g} (F) transitions of the complexes **1-4**, respectively. The next high energy bands with maxima at 617, 617, 613 and 624 nm, respectively can be assigned to the ${}^{3}A_{2g}$ (F) $\rightarrow {}^{3}T_{1g}$ (P) transitions. Unfortunately, the lowest energy ${}^{3}\text{A}_{2g}\left(F\right) \rightarrow {}^{3}\text{T}_{2g}\left(F\right)$ transition was missing for all the complexes at the used thickness of solid state sample materials. Very weak transitions at 766, 767, 759 and 766 nm for 1-4 were appeared as a shoulder for the spin forbidden ${}^{3}A_{2g}$ (F) $\rightarrow {}^{1}E_{g}$ (D) transitions. Highly intense $PhO^- \rightarrow Ni^{II}$ LMCT transitions were observed at 369, 365, 365 and 369 nm for 1-4, respectively. The intraligand π \rightarrow π^{*} transitions centered on C=C, C=O and C=N functions within the Ni^{II}-bound ligand anion back bone were found at 277, 281, 275 and 274 nm, respectively for 1-4.

Powder X-ray Diffraction and thermogravimetric analysis. The identical nature and composition of the as synthesized solid state polycrystalline samples and those obtained from single-crystal X-ray structure determination within the same family of

compounds have been compared from the powder X-ray diffraction (PXRD) analysis and TGA analysis. The PXRD patterns have been analyzed to identify and characterize the individual phases of solid crystalline compounds of **1-4**. The patterns for **1-4** are shown in Figure S3 in SI. These patterns are matching nicely with the simulated ones obtained from the single-crystal X-ray diffraction data. The obtained 20 values corresponding to the lattice spacing and the relative intensity of the diffraction lines found are revealing the particular phase of the compounds **1-4**. The position of a characteristic

diffraction peak is exclusively determined by the Asize and shape of the unit cell of the DOcrAstallMeON phase. Thermogravimetric analysis (TGA) showed a similar decomposition pattern for the complexes **1-4** towards heating of the samples for weight loss. A weight loss in 40–125 °C range was observed uniformly for all the complexes due to the removal of solvents of crystallization. The next higher temperature loss is attributed to the removal of water molecules coordinated to the lanthanide ions. (Figure S4 in SI)

Complex	1 (Ln=Gd)	2 (Ln=Tb)	3 (Ln=Dy)	4 (Ln=Ho)
Empirical formula ^a	C ₂₆ H ₄₂ Cl ₂ Gd ₂ N ₆ Ni ₂ O ₂₀	C ₂₆ H ₄₂ Cl ₂ Tb ₂ N ₆ Ni ₂ O ₂₀	C ₂₆ H ₄₂ Cl ₂ Dy ₂ N ₆ Ni ₂ O ₂₀	C ₂₆ H ₄₂ Cl ₂ Ho ₂ N ₆ Ni ₂ O
Formula weight ^a	1261.46	1264.81	1271.96	1276.83
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n	<i>P</i> 2 ₁ /n
a (Å)	13.8573(8)	13.757(5)	13.419(17)	13.421(3)
b (Å)	23.9482(14)	24.089(14)	23.74(3)	23.686(5)
c (Å)	14.3941(8)	14.377(5)	14.18(3)	14.348(3)
β (°)	105.322(2)	104.228(10)	103.61(3)	100.79(3)
Volume (Å ³)	4607.0(5)	4618(3)	4392(12)	4480.4(17)
Z	4	4	4	4
D _{calcd} (g cm ⁻³)	1.816	1.819	1.921	1.893
Absorption coefficient (mm ⁻¹)	3.837	4.018	4.407	4.516
F (000)	2464	2480	2480	2496
Temperature/K	293(2)	298(2)	293(2)	296(2)
Reflections collected/unique	55213 / 9023	59727 / 10195	44294 / 9236	38048 / 9920
Parameters	533	528	526	537
Goodness-of-fit (F ²)	1.026	1.022	1.122	1.063
R _{int}	0.0713	0.0658	0.0802	0.0646
R1; wR2 [I >2σ(I)]	0.0687, 0.2064	0.0607, 0.1787	0.0779, 0.2168	0.0391, 0.0949
CCDC No.	1941824	1941825	1941826	1941827

Table 1 Crystal data and structure refinement summary of complexes 1-4

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58 59 60 **Descriptions for the Crystal Structures.** Single crystals suitable for X-ray analysis were directly obtained from the mother liquor after 7 to 10 days in the four cases through evaporation of the solvent mixtures.

 $[Ni^{II}_{2}Tb^{III}_{2}(\mu_{3}-L)_{2}(\mu_{3}-OH)_{2}(\mu-OAc)_{3}(AcO)(H_{2}O)_{3}]CI_{2}\cdot4H_{2}O$ (2). In this section detail discussion on the X-ray structure is made for 2 as a representative case. All the tetranuclear [Ni₂Ln₂] compounds (1-4) crystallize in monoclinic P21/n space group with Z = 4. Crystal data and the important refinement parameters are presented in Table 1. The perspective view of 2 is shown in Figure 1a. Selected bond distances and angles are presented in Table S1. All the CShM values for the Ln ions are provided in Table S2. The analysis of the X-ray structure for 2 revealed that each L⁻ unit, delivering NO₃ donor set, binds one Tb^{III} and one Ni^{II} center in two adjacent pockets around the bridging phenoxido group giving a {Ni^{II}Tb^{III}L} fragment. To the Ni^{II} center the ONO pocket of L⁻ showed meridional coordination. The adjacent bidentate OO pocket on the other hand is used to bind the bigger and oxophilic Tb^{III} ion. In situ generation of HO⁻ ion from the solvent medium then holds the previous entity as {Ni^{II}Tb^{III}L(OH)}. Water molecules from the reaction medium and available AcO⁻ ions occupy the vacant coordination sites around Ni^{II} and Tb^{III} to provide {Ni^{II}Tb^{III}L(OH)(AcO)_m(H₂O)_n}. Self-aggregation of two such units provide the cubane core of 2 (Figure 1b).

The tetranuclear [Ni₂Tb₂] core thus assembled around two μ_3 -PhO⁻ (O1 and O2) parts of L⁻ and two water derived μ_3 -HO⁻ (O3 and O4) groups at the four alternate corners of the cube. The aggregation is supported by the μ -O,O'-acetato bridges in three (one Tb···Tb and two Ni···Tb) faces of the cube. Higher (eight) coordination number around the Tb^{III} centers are fulfilled by the monodentate coordination from H₂O and AcO⁻. Within the cube structure, the Ni–O distances vary within 2.011(6)-2.230(5) Å, due to presence of three types of O donor atoms and Ni–N bond lengths remain within 2.017(7)-2.024(7) Å, which are in normal range for distorted octahedral coordination environment around any Ni^{II} center (Figure 2, left). Each Ni^{II} center in NO₅ coordination environment bound



Fig. 1 (a) Perspective view of **2.** Hydrogen atoms and solvent molecules are omitted for clarity; (b) core view of **2** with partial atom numbering scheme. Color scheme: cyan, Tb; green, Ni; red, O; blue, N; gray, C



Fig. 2 Highlighted cube core of **2** (middle) and the bridged coordination environments around two Ni^{II} (left) and two Tb^{III} (right) centers. Color code as above

to one imine N (Ni1–N1, 2.017(7) Å), two bridging phenoxido O (Ni1–O1, 2.059(6) Å; Ni1–O2, 2.230(5) Å), one hydroxido O (Ni1–O3, 2.012(6) Å), one acetato O (Ni1–O10, 2.050(6) Å) and one semicarbazide O (Ni1–O15, 2.072(7) Å). The hydroxido donor showed shortest Ni–O distance and one of the phenoxido donors the longest.

The eight-coordinate (O₈) environment around Tb1 (distorted triangular dodecahedron, S(TDD-8)= 0.65) and Tb2 (distorted square antiprism, S(SAPR-8)= 0.76) are accomplished by one bidentate OO donor part from L⁻, two hydroxido bridges, two acetato bridges (Tb…Tb and Tb…Ni) and two terminal monodentate water to Tb2 center and one terminal monodentate water and an acetate anion to Tb1 center. The CShM analysis revealed that the structures cannot be described as intermediate one following any interconversion path. In **2** the phenoxido O donors (O1 and O2) provide shorter distances (Tb1–O2, 2.474(5) Å; Tb2–O1, 2.486(6) Å), in comparison to the separations from –OMe (O5 and O6) groups (Tb1–O5, 2.556(7) Å; Tb2–O6, 2.620(9) Å). The Tb–O distances for hydroxido bridges are in 2.341(6)-2.411(7) Å range. Unlike the known 3d ion based cube structures, the structure of 2 has the shortest Ni…Ni separation of 3.225 Å. Presence of bigger Tb^{III} ions increases the Tb···Tb separation to 3.779 Å. On the four other faces, the Ni…Tb separations are slightly longer than the Ni…Ni separation (3.225 Å) and ranging from 3.396 to 3.598 Å. The three acetato-bridged faces show shorter separation (Figure 4). The μ_3 -PhO⁻ (O1 and O2) part of L⁻ toward Ni^{II} ions record two shorter in plane and two longer out of plane Ni-O bonds in 2.050(6), 2.059(6) Å and 2.227(6), 2.230(5) Å range. Two μ_3 -HO⁻ bridges provide shorter Ni–O bonds at 2.011(6), 2.012(6) Å and longer Tb-O bonds at 2.341(6)-2.411(7) Å. The presence of three AcO⁻ bridges on three faces of the cube register Ni-O and Tb-O bonds in 2.050(6)-2.059(6) Å and 2.320(8)-2.367(7) Å range. The μ_{3} -PhO⁻ and μ_3 -HO⁻ bridges register different magnitudes of Ni-O-Ni 97.50(2)° and 97.70(2)°, Ni-O_{Ph}-Tb 96.20(2)°-99.30(2)° and Tb–O–Tb 104.00(2)° and 106.80(2)° angles.

For the distorted square anti-prism coordination geometry around Tb2, α is considered as the angle between the S_8 axis of the square anti-prism and the central atom-ligand bond (Figure S6).^{49,50} The same can be considered through $\gamma = 2\alpha$, where γ is the angle between the opposite bonds within one hemisphere. For Tb2, the magnitude of α varies from 50.4 to 64.28°, with the smallest one as $\alpha_{(O4, O6)}$ and largest one as $\alpha_{(O3, O18)}$. Page 7 of 11

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Fig. 3 (a) Distorted octahedral coordination environment of adjacent Ni^{II} centers; (b) distorted triangular dodecahedron and distorted square antiprism coordination geometry around Tb1 and Tb2, respectively

In case of Tb1 the two square planes of any square antiprism like structure deviate from planarity to provide two triangular parts instead and resulting in a distorted trigonal dodecahedral structure. The situation is clueless with regard to the binding of L^- and ancillary bridges for different amounts of distortion around the two Tb^{III} centers. The different magnitude of distortion around the Ni^{II} centers is less pronounced.

Along the series, the shortest Ni1…Ni2 and longest Ln1…Ln2 separations are in the ranges of 3.181-3.255 Å and 3.737-3.786 Å, respectively. For the entire family of Ni₂Ln₂ complexes the variety of Ni^{II}…Ln^{III} separations fall in 3.355-3.598 Å range along the *4f* series.

Magnetic Properties

Susceptibility data for **1-4** were collected at 2 to 300 K (applied field: 0.5 T for **1**, **3** and 0.3 T for **2**, **4**). Below 30 K an additional data set were collected with applied field values of 295 Oe (**1**, **3**) and 275 Oe (**2**, **4**). As can be seen in Figure 5, both the data sets overlap. The χ T products at 300 K have values as shown in Table 2 and are in agreement with the expected values for two Ni^{II} centers in octahedral environment with S = 1 and g = 2.0 and two Ln^{III} ions.



Fig. 4 Three acetato bridged structure of **2** with different M– O–M angles within the cube

As the temperature decreases, the χT product increases for 1 and 2, indicating the onset of overalpingerformagnetic interactions between the Ni^{II} and Ln^{III} centers. For 3 and 4 the shape of the χT product curve is typical of the lanthanide ions having strong spin orbit coupling and it shows the thermal depopulation of the Mj states. This is consistent with weak ferromagnetic coupling, however, the possibility that one of the exchange pathways is antiferromagnetic cannot be ruled out. The three exchange pathways J₁(Ni–Ni), J₂(Ln–Ln) and J_3 (Ln–Ni) were considered within the [Ni₂Ln₂O₄] core, as shown in Scheme 5. For the series 1-4 the Ln-OH-Ln angles are between 104–108° and the Ln–OH–Ln–OH diamond is not flat. with an average Ln–OH–OH–Ln torsion angle of 153°. The Ln– O–Ni angles are on average 98°, while the Ln–OH–Ni angles are between 101° and 110°. With these structural parameters in hand, a weak ferromagnetic coupling should have been expected for adjacent Ln...Ni centers. The syn, syn-AcObridges between Ln...Ni and Ln...Ln parts are known to mediate antiferromagnetic coupling. Thus for Ln…Ln and Ni…Ln both the feasible pathways, ferromagnetic via the OHor O bridge, and antiferromagnetic via the syn, syn-AcO⁻ bridge will finally result in only very weak exchange coupling values. The Ni–O–Ni angles, in the 97° to 98° range, and the Ni…Ni distance of 3.2 Å are in good agreement for reported values of Ni₄O₄ cube structures. In the 97-99° range the coupling can be either ferromagnetic or antiferromagnetic for this angular range, and in all cases the values are close to zero.^{51,52} For the Gd^{III} complex 1, the magnetic data has been fitted using the software PHI.53 The program uses the Hamiltonian of Eq. 2 and 3.

$$\widehat{H}_{EX} = -2\sum_{i < j}^{\iota, j \in N} \vec{\hat{S}}_i \cdot \overline{\overline{J}_{\iota j}} \cdot \vec{\hat{S}}_j = \widehat{H}_{(an)iso} + \widehat{H}_{anti}$$

To avoid overparametrization, the susceptibility data for complex 1 was fitted using only the exchange Hamiltonian with fixed g values for Ni^{II} and Gd^{III} at the default software values. The three fitting parameters used were $J_1(Ni-Ni) = -0.91 \text{ cm}^{-1}$, $J_2(Gd-Gd) = 0.14 \text{ cm}^{-1} \text{ and } J_3(Ni-Gd) = 0.02 \text{ cm}^{-1}$, as shown in Scheme 5. According to the fitting, the weakest exchange is that between Ni-Gd. The exchange values obtained are in agreement with the expected values discussed previously. Bear in mind that even the two Gd ions are not crystallographically equivalent, they are considered equivalent in this simplified model. The fitting is shown in Figure 5 as a solid line. The same values were used to calculate the magnetization as a function of field for the complex 1, and the calculated magnetization is shown in Figure 6 as a solid line. There is good agreement between calculated and experimental data. The coupling model results in a spin ground state for **1** of S_T = 7 that is not well isolated in energy due to the very small values of the exchange constants. Similar situations can be expected for the complexes 1-4.

Eq(3)

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coordination environment, as shown in Figure 3rti(b) for

complex 2. Since Gd is isotropic, such considerations do not

apply and the anisotropy of complex 1 arises from the Ni₂ unit.

The large spin of Gd has been shown to be the key to good

SMM properties if combined with a highly anisotropic

transition metal unit, as in a Co-Gd complex reported by

Sañudo et al, the analogous Ni complex lacked sufficient

anisotropy and was not an SMM.55 Since in the complexes

reported here the Ni-Ni coupling is antiferromagnetic, complex

1 is not an SMM. The software MAGELLAN⁵⁶ can be used to

compute the anisotropy axes on Dy^{III} ions. Thus we used

MAGELLAN for complex 3 in order to confirm the lack of

anisotropy of the Ni₂Ln₂ core. The software uses a purely

electrostatic model and the results are shown in Figure 7. The

solid red lines indicate the anisotropy axes on the two Dy^{III} ions

in the complex. Clearly these axes are not aligned. This fact

combined with the two different ligand environments for Ln1

and Ln2 result in a lack of SMM properties for these

The Ni₂Ln₂ cube complexes synthesized by Liu et al. showed Ni…Ni

antiferromagnetic interactions with J(Ni–Ni) value of -3.91 cm⁻

¹ within <Ni-O-Ni angle of 98.44 and 99.72°.⁵² Other reported

Ni₂Ln₂ cube structures showed ferromagnetic interactions

between Ni···Ni with J(Ni-Ni) values of +3.28, +3.30 and +5.20

cm⁻¹ within comparable <Ni-O-Ni angle of 99° and <Gd-O-Gd

angle of 109° and weak Ni…Gd ferromagnetic interactions,

where none of the complexes showed SMM behavior.57-59

Hence, from these reports of Ni₂Ln₂ cubanes it is clearly seen

that only weak exchange couplings are operative which clearly

suggest a strong dependence on the geometrical parameters

distorting the cubane structure Table S3.



Scheme 5 Coupling interactions within the magnetic $[Ni_2Ln_2O_4]$ core. The three exchange pathways $J_1(Ni-Ni)$ (red), $J_2(Ln-Ln)$ (blue) and J_3 (Ln-Ni) (green)

Heterometallic 3d-4f SMMs are relatively common, in particular when the ground state magnetic moment is large as for the Ni-Gd complex reported here.²⁵ The other complexes in the series should also display ground states with large magnetic moments given the magnetization vs. field behaviour at 2 K. Thus, the relaxation dynamics for the complexes 1-4 were studied in a commercial SQUID. Out-of-phase ac susceptibility signals were not observed for any of the complexes. Since the complexes reported here have significant (if not well isolated) spin ground states, the lack of SMM behavior must be attributed to the lack of axial magnetic anisotropy in these species. Following the crystal structure description, it is clear that only one Ln^{III} ion in the complex shows the appropriate ligand field to present SMM properties. For Tb, Dy and Ho, Rinehart and Long predicted strong anisotropy with an axial distribution of ligands due to the oblate distribution of electron density.54 According to the crystal structure of these complexes, only one of the lanthanide(III) ions presents such a strong axial ligand arrangement in a square antiprism coordination sphere while the other lanthanide in the complex is in a less axial

Table 2 Comparison of calculated and experimental χT data

Complex	Calculated χT at 300 K (cm ³ K mol ⁻¹)	Experimental χT at 300 K (cm ³ K mol ⁻¹)	Ni(II) (S = 1, g = 2.0)
1	17.8	17.41	Gd(III) ion (⁸ S _{7/2} , S = 7/2, L = 0, g = 2.0)
2	25.26	25.31	Tb(III) ion (${}^{7}F_{6}$, S = 3, L = 3, J = 6 and g _J = 3/2)
3	30.32	29.38	Dy(III) ion (${}^{6}H_{15/2}$, S = 5/2, L = 5, J = 15/2 and
			g _J = 4/3)
4	30.0	29.17	Ho(III) ion (${}^{5}I_{8}$, S = 2, L = 6, J = 8 and g _J = 10/8)

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Fig. 5 Plot of χ T products vs. T for the complexes 1-4. The solid line is the best fitting to the experimental data for complex 1 using PHI software



Fig. 6 Magnetization vs. field plots for complexes **1-4**. The solid line is the calculated magnetization data for complex **1** using PHI software



Fig. 7 Illustration of the structure of **3** with the anisotropy axes (shown in red) calculated using the MAGELLAN software. Hydrogen atoms are omitted for clarity. Dy^{III} shown as light green (large spheres), Ni^{II} as dark green (smaller spheres)

Conclusions

Using the semicarbazide tail bearing Schiff base ligand system for the first time we were able to synthesize a family of Ni-4*f* aggregates having cube topology. This is the first report of such cubic aggregate from the use of semicarbazide containing ligand system. Standardization of the reaction condition provided the option for systematic Peplacemennet of the lanthanide ions within the family, without altering the paramagnetic core structure. We were successful in exploiting all the coordination sites of the used ligand system while trapping two 3d and two 4f ions. The magnetic properties of 1-4 indicated a combination of weak exchange couplings, and comparison with other Ni₂Ln₂ cubanes known in the literature, suggest a strong dependence of the coupling behavior on the structural distortions. Out-of-phase ac susceptibility signals were not observed for any of the complexes in the family, not even for the Dy complex 3. Out-of-phase ac susceptibility signals were also not observed for any of the complexes in the family. For **3**, the anisotropy axes on the two Dy^{III} ions are not aligned and the anisotropy of the complex is not large. The entire family of the complexes lacked axial anisotropy and SMM behavior even though the ground state magnetic moment values are quite large.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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Table of Content

A new family of tetranuclear $[Ni_2Ln_2O_4]$ cubane complexes has been assembled from the coordinating support of a carbazido ligand. The opportunity of altering the 4f ions during synthesis within the family, without changing the core topology provided the family to show weak ferromagnetic and antiferromagnetic interactions.

