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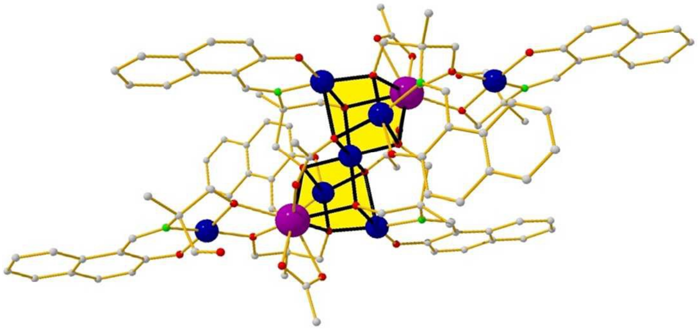
Four enneanuclear heterometallic copper-lanthanide [$\mathrm{Cu^{II}}_7\mathrm{Ln^{III}}_2$] (Ln= Gd, Tb, Dy and Y) complexes were isolated and characterized by magnetic measurements.



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Solvothermal synthesis of enneanuclear $[Cu^{II}{}_7Ln^{III}{}_2]$ clusters

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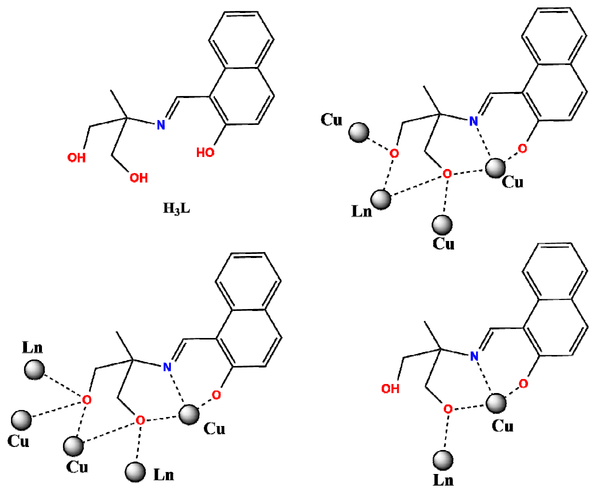
Employment of H_3L (= 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol) in mixed-metal copper-lanthanide cluster chemistry has led to the isolation of four new enneanuclear heteronuclear isostructural $[Cu^{II}{}_7Ln^{III}{}_2]$ complexes. More specifically, the solvothermal reaction of $Cu_2(OAc)_4{\cdot}2H_2O$ with LH_3 and the corresponding lanthanide nitrate salt in MeCN in the presence of base, NEt_3, yielded three complexes with the general formula $[Cu^{II}{}_7Ln^{III}{}_2(L)_4(HL)_2(OAc)_4]{\cdot}2MeCN$ (Ln: Gd, **1**·2MeCN; Tb, **2**·2MeCN; Dy, **3**·2MeCN), while in addition the Y^{III} analogue, $[Cu^{II}{}_7Y^{III}{}_2(L)_4(HL)_2(OAc)_4]{\cdot}2MeCN$ (**4**·2MeCN), was also synthesized in the same manner. The structure of the cluster describes two corner-sharing $[Cu_3Ln]$ cubane metallic units, each one further connected to one Cu^{II} ion. Dc magnetic susceptibility studies in the 5 – 300 K range for complexes **1**-**4** reveal the presence of both ferromagnetic and antiferromagnetic exchange interactions within the metallic clusters.

Introduction

The synthesis and characterization of polynuclear clusters has grown exponentially over the last two decades; complexes with various nuclearities and beautiful structures/topologies have attracted the intense interest of the scientific community due to the properties that such species often present. In the field of molecular magnetism, metallic clusters have been the pioneers opening the way toward new exciting phenomena; complexes that can retain their magnetization up to 14 K, once magnetized in the absence of an external magnetic field, have now been reported,[1] while clusters that can lower the temperature of their surroundings upon employment of a magnetic field have been termed as "molecular coolants".[2] Of great importance in molecular magnetism is the ability to control the nature and the magnitude of the magnetic exchange interaction within neighboring metallic centres, *J*, as a means of synthesizing clusters with large magnetic ground-state, *S*, as this is a main prerequisite for both phenomena mentioned. Therefore, it becomes apparent that synthesizing and studying families of related clusters is crucial, since it may provide the route for eventually controlling the magnetic behavior of the inorganic clusters.

The study of the magnetic exchange interactions between 3*d* and 4*f* metal centers is not a new trend in magnetism.[3] Yet, it is now more topical than ever, since the use of 4*f* centers for constructing large 4*f* and 3*d*-4*f* "magnetic" clusters has witnessed a major impetus recently,[4] due to the intrinsic properties of the lanthanide centers: i) their large magnetic moments, and ii) their spin-orbit coupling based magnetic anisotropy (with the exceptions of La^{III}, Gd^{III} and Lu^{III}).

We recently reported the use of the naphthalene-based triol ligand 2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol, H_3L (Scheme 1),[5] in Co(II/III), Ni(II) and Cu(II) chemistry,[6] while very recently we expanded our studies in mixed-metal Mn/Ln and Ni/Ln chemistry reporting on a family of octanuclear $[Mn^{III}{}_6Ln^{III}{}_2]$ complexes[7], dodecanuclear $[Mn^{III}{}_6Ln^{III}{}_6]$ clusters[8] and enneanuclear $[Ni^{II}{}_6Ln^{III}{}_3]$ species[9]. We herein continue our efforts and present the synthesis,



Scheme 1 The structure of LH_3 and its coordination modes in **1-4**.

structures and magnetic properties of four mixed-metal enneanuclear [$Cu^{II}_7Ln^{III}_2$] complexes (Ln= Gd, Dy, Tb and Y).

Experimental Section

Materials and physical measurements

All manipulations were performed under aerobic conditions, using materials as received. Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service. Variable-temperature, solid-state direct current (dc) magnetic susceptibility data down to 2.0 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T DC magnet at the University of Edinburgh. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal's constants. Powder XRD measurements were collected on freshly prepared samples of **2**, **3** and **4** on a PANalytical X'Pert Pro MPD diffractometer at the University of Crete.

Syntheses

General synthetic strategy applicable to **1**-**4***:*

All four complexes were obtained from the same general procedure. An acetonitrile solution of $Cu_2(OAc)_4\cdot 2H_2O$ (68 mg, 0.15 mmol), the corresponding $Ln(NO_3)_3\cdot 6H_2O$ salt (0.1 mmol) and the H_3L (78 mg, 0.3 mmol) ligand in the presence of excess base, NEt_3, was transferred into a 25 ml Teflon-lined stainless-steel autoclave and heated at 95 °C for 24 hours. After slow cooling to room temperature, dark green crystals of the general formulae $[Cu_7Ln_2(HL)_2(L)_4(OAc)_4]\cdot 2MeCN$ were isolated in ~ 25-30% yields (Ln= Gd, **1**$\cdot$ 2MeCN; Tb, **2**$\cdot$2MeCN; Dy **3**$\cdot$2MeCN; Y, **4**$\cdot$2MeCN).

Elemental Anal. calcd (found) for **1**$\cdot$ 2MeCN: C 46.80 (46.93), H 4.00 (3.77), N 4.28 (4.18); **2**$\cdot$2MeCN: C 46.75 (46.87), H 4.00 (3.83), N 4.28 (4.15); **3**$\cdot$2MeCN: C 46.62 (46.49), H 3.98 (4.22), N 4.26 (4.16); **4**$\cdot$2MeCN: C 49.39 (49.52), H 4.23 (4.42), N 4.52 (4.39)%.

X-Ray Crystallography

Diffraction data for **1**$\cdot$2MeCN were collected at 170 K on a Kuma diffractometer with CCD camera. The structure was solved by direct methods and refined by full-matrix least-squares technique on F^2 with SHELXL.[10] The non-hydrogen atoms, except disordered atoms of solvent, were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model, except for hydrogen atoms of disordered CH_2–OH group. The acetonitrile molecule is disordered over two positions with occupation of 0.72 and 0.28. The CH_2–OH group from one of the L^{3-} ligand shows disorder with occupation 0.7/0.3.

Data collection parameters and structures solution and refinement details are listed in Table S1. Full details can be found in the CIF file: CCDC 1423483.

Results and Discussion

Syntheses

The reaction between $Cu_2(OAc)_4\cdot 2H_2O$, $Ln(NO_3)_3\cdot 6H_2O$ (Ln = Gd, Tb, Dy, Y) and H_3L in CH_3CN under solvothermal conditions in the presence of excess base, NEt_3, afforded four new enneanuclear clusters of the general formulae $[Cu_7Ln_2(HL)_2(L)_4(OAc)_4]\cdot 2CH_3CN$ (Gd, **1**$\cdot$2CH_3CN; Tb, **2**$\cdot$2CH_3CN; Dy **3**$\cdot$2CH_3CN; Y, **4**$\cdot$2CH_3CN) according to eq (1).

$$7/2Cu_2(OAc)_4\cdot 2H_2O + 2Ln(NO_3)_3\cdot 6H_2O + 6H_3L \xrightarrow{MeCN}$$

$$[Cu_7Ln_2(HL)_2(L)_4(OAc)_4] + 10OAc^- + 6NO_3^- + 16H^+ + 19H_2O \quad (1)$$

The reaction was performed by adopting a 3:1:3 Cu:Ln:ligand ratio, in agreement with the 3.5:1:3 Cu:Ln:ligand ratio found in complexes **1**-**4**. In order to investigate the parameters that affect the products identity we repeated the reaction that forms complex **1** for 12 h (instead of 24 h), and we obtained the same product as verified by means of pXRD measurements, *albeit* in lower yields. In addition, switching to 1:1:1 and 1:2:2 Cu:Gd:ligand ratios did not lead to different products. Furthermore, repeating the reaction in the absence of base produces the same [Cu_7Ln_2] enneanuclear clusters; a quite surprising feature since there are six ligands present in the structure, four fully deprotonated, L^{3-}, and two in their doubly deprotonated form, HL^{2-}. Finally, upon changing the solvent to MeOH, we managed to obtain a highly distorted tetranuclear ring-like [Cu_4] cluster, previously reported by us.[6]

We were able to obtain large single crystals suitable for X-ray single-crystal crystallography for all **1-4** complexes. Yet, since all complexes displayed similar pXRD diagrams (Fig. S1, top) and IR spectra (Fig. S1, bottom), we chose to solve only the crystal structure of the Gd analogue, **1**$\cdot$2MeCN.

In addition, we performed Energy Dispersive X-ray Spectroscopy measurements, EDS, in order to further check the homogeneity of our crystals and to investigate the purity of the bulk crystalline material (Fig. S2); all Cu:Ln ratios were found ~ 78:22, in excellent agreement with the theoretical value of 77.77:22.22 established by single crystal X-ray crystallography.

Description of structures

The molecular structure of complex **1** is shown in Fig. 1, while all interatomic distances and angles for **1** are listed in Table S2. All four clusters are isostructural, and therefore, we will only discuss the structure of complex **1**; compound **1** crystallizes in the triclinic P-1 space group and possesses an inversion center. Its metallic core consists of two distorted corner sharing $[Cu_3Gd(OR)_4]^{+5}$ cubanes, with each one carrying a square-planar Cu^{II} "antenna", held by two ligands; one fully deprotonated 5.3311 ligand, L^{3-}, and one doubly deprotonated 2.2101 ligand, HL^{2-} (Harris notation).[18]

Each cubane unit is assembled by three fully deprotonated, L^{3-}, ligands and one 4.31 acetate group. The three trianionic ligands adopt two different coordination modes, with two in a 5.3311 and one in a 4.3211 coordination mode. The $[Cu_3Gd(OR)_4]^{+5}$ cubane sub-unit contains two five-coordinate and one six-coordinate Cu(II) ions, while the Ln(III) center is eight-coordinate, exclusively ligated by oxygen atoms. The five coordinate Cu(II) centers adopt distorted square pyramidal environment, while the six-coordinate center adopts a *Jahn-Teller* distorted octahedral geometry. Finally, a SHAPE[11] analysis for the lanthanide centers revealed a triangular dodecahedral geometry (Fig.2). An inspection of the crystal lattice of **1** reveals that there are no intermolecular H-bonds interactions between the clusters, while the molecules of **1** form sheets along the *ab* plane (Fig. 3). A detailed CCDC search revealed that there are only four examples of previously reported enneanuclear [Cu_xLn_y] ($x + y = 9$) clusters: (i) complexes [$Cu^{II}_5Ln^{III}_4teaH_4$](Ln=Gd, Tb, Dy, Ho) ($H_3$tea= triethanolamine), with the Cu^{II} ions forming a "bow-tie" arrangement and the four Ln^{III} ions forming a rectangle that lies above and below the plane of the Cu^{II} ions,[12] (ii) cluster [$Cu_7Gd_2(L^2)_2$ $(L^3)_2$] (H_2L^2=gem-diol of picolinaldehyde, H_2L^3= hemiacetal of picolinaldehyde) with two butterfly-like [$Dy^{III}Cu^{II}_4$] units,[13] (iii) complex [$Gd^{III}_6Cu^{II}_3(pdm)_3$] ($H_2$pdm= pyridine-2,6-dimethanol) with an icosahedral structure,[14] and (iv) clusters [$Ln^{III}_3Cu^{II}_6L_6$] (Ln=Y, Gd, Dy) (H_2L = 1,1,1-trifluoro-7-hydroxy-4-methyl-5-azahept-3-en-2-one) with a trigonal prismatic structure.[15]

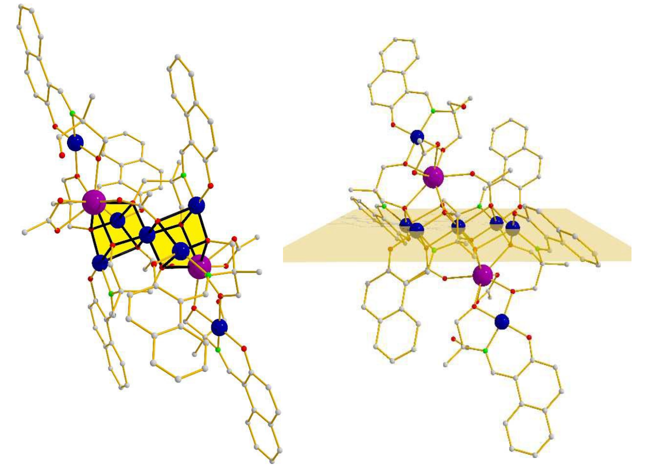


Fig. 1 Molecular structure of complex **1**. Solvent molecules and H atoms are omitted for clarity. Color code: Cu= blue, Gd= purple, O= red, N= green and C= grey.

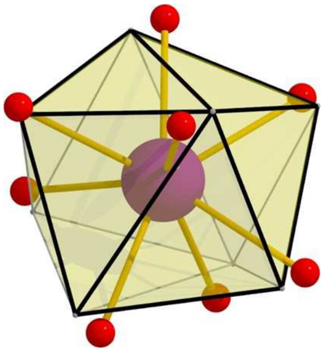


Fig. 2 Triangular dodecahedral coordination sphere for the lanthanide ions in complexes **1**-**4**, as calculated by the program SHAPE.

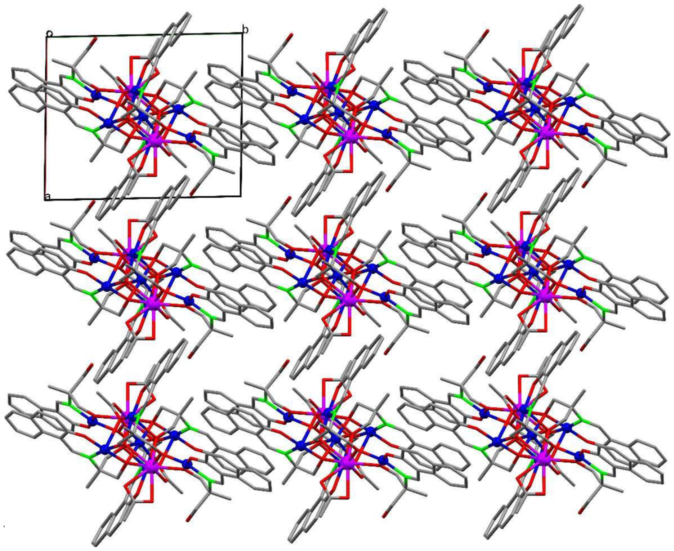


Fig. 3 Crystal packing of complex **1** along the *ab* plane. Color code: same as in Figure 3.

Magnetochemistry

Dc Magnetic Susceptibility Studies

Direct current magnetic susceptibility studies were performed on polycrystalline samples of **1**-**4** in the 5 – 300 K range under an applied field of 0.1 T, and the results are plotted as the $\chi_M T$ product *vs*. *T* in Figure 4. From a quick glance at Figure 6, we can clearly see that the complexes display different behavior; for **1** the $\chi_M T$ product increases upon cooling, for **2** and **4** it decreases upon cooling and then increases at low temperatures, while for **3** it decreases upon cooling. More specifically, for **1** the room temperature $\chi_M T$ value of 18.49 cm^3 mol^{-1} K, slightly smaller than the theoretical value of 18.64 cm^3 mol^{-1} K for seven non-interacting Cu^{II} ions (g = 2.1) and two Gd^{III} ions (g =2.00), remains practically unchanged until ~ 50 K, below which it increases to reach the maximum value of 22.27 cm^3 mol^{-1} K at 5 K. For **2**, the room temperature $\chi_M T$ value of 30.56 cm^3 mol^{-1} K is very close to the theoretical value of 31.22 cm^3 mol^{-1} K for seven non-interacting Cu^{II} ions (g = 2.1) and two non-interacting Dy^{III} ions (S = 5/2, L = 5, J = 15/2, g_j = 4/3). Upon cooling, the $\chi_M T$ product decreases to reach the minimum value of 27.12 cm^3 mol^{-1} K at 26 K, before it increases to 27.69 cm^3 mol^{-1} K at 5 K. For **3**, the room temperature $\chi_M T$ value of 26.62 cm^3 mol^{-1} K, very close to the theoretical value of 26.51 cm^3 mol^{-1} K for seven non-interacting Cu^{II} ions (g = 2.1) and two Tb^{III} ions (S =3, L = 3, J = 6, g_j = 1.5), slightly increases to 27.51 cm^3 mol^{-1} K at ~60 K, below which it decreases to reach the minimum value of 25.90 cm^3 mol^{-1} K at 5 K. Finally, for **4**, the room temperature $\chi_M T$ value of 2.86 cm^3 mol^{-1} K is very close to the theoretical value of 2.89 cm^3 mol^{-1} K for seven non-interacting Cu^{II} ions (g = 2.1). Upon cooling, the $\chi_M T$ product slightly increases upon cooling at 2.93 cm^3 mol^{-1} K until ~ 110 K, below which it decrease to reach the minimum value of 2.56 cm^3 mol^{-1} K at 20 K, before it increases to 2.65 cm^3 mol^{-1} K at 6.6 K. Finally, below ~6.6 K a drop of the $\chi_M T$ product is observed.

We were able to successfully fit the magnetic susceptibility data for complex **4**, adopting a 2-J model (Fig. 5, top) and the Hamiltonian eqn (1) assuming the following interactions: one J_1 interaction between Cu2-Cu3 (and Cu2'-Cu3') mediated by two μ_3-OR alkoxide bridges with Cu2-O_R-Cu3 angles of ~103.5° and ~86.0°, and Cu2¨Cu3 distance of ~3.1 Å, and one J_2 interaction between (i) Cu1-Cu2 (and Cu1-Cu2'), mediated by two μ_3-OR alkoxide groups with Cu1-O_R-Cu2 angles of ~106.4° and 80.8°, and Cu1¨Cu2 distance of ~3.2 Å, (ii) Cu1-Cu3 (and Cu1-Cu3') mediated by two μ_3-OR alkoxide groups with the corresponding angles Cu1-O_R-Cu3 being ~105.0° and ~98.8°, and Cu1···Cu3 distance of ~3.5 Å. Using the program PHI[16] and employing the Hamiltonian in eq (1):

$$\hat{H} = -2J_1 (\hat{S}_2\cdot\hat{S}_3+\hat{S}_{2'}\cdot\hat{S}_{3'}) -2J_2 (\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_{2'}+ \hat{S}_1\cdot\hat{S}_{3'}) \qquad (1)$$

afforded J_1 = +4.82 cm^{-1}, J_2 = -6.53 cm^{-1}, and g = 2.13. These parameters lead to S states of value S = 1/2, S = 3/2 and S = 5/2, all being populated even at 2 K. The nature and magnitude of J_1 and J_2 are in good agreement with previously reported interactions in Cu clusters with similar geometric parameters.[6, 17]

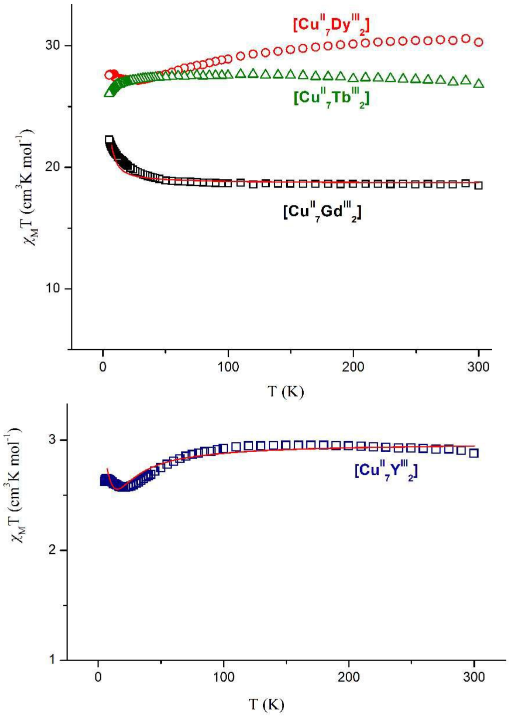


Fig. 4 $\chi_M T$ *vs.* T plot for complexes **1**([Cu_7Gd_2]), **2**([Cu_7Tb_2]), **3** ([Cu_7Dy_2]), (top) and **4**([Cu_6Y_2]) (bottom) under an applied *dc* field of 1000 G. The solid lines represent fit of the data in the 5 – 300 K (see text for details).

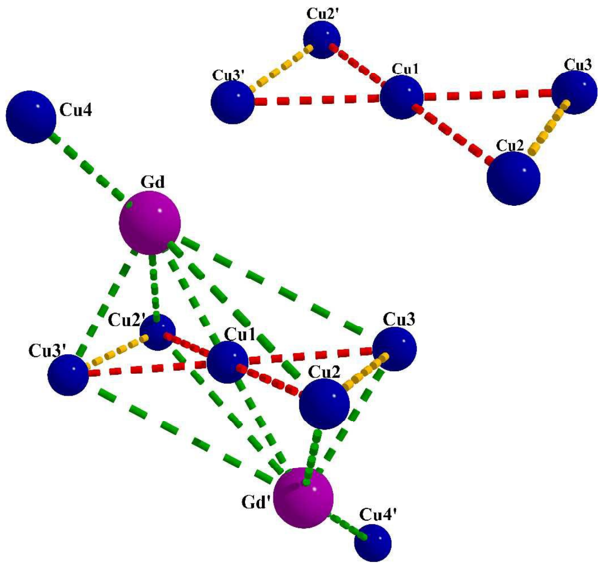


Fig. 5 Exchange interaction scheme for complexes **1** (bottom) and **4** (top). Color code: orange line=J_1, red line= J_2, green line= J_3.

We were able to successfully fit the the $\chi_M T$ data for the [Cu_7Gd_2] cluster (**1**) by "locking" J_1 and J_2 exchange interactions as were found in complex **4**, and by simply adding the exchange interaction J_3 between the Cu^{II}-Gd^{III} ions. Therefore, adopting the 3-*J* model (Fig. 5, bottom) and the Hamiltonian in eqn (2):

$$\hat{H} = -2J_1 (\hat{S}_2\cdot\hat{S}_3+\hat{S}_{2'}\cdot\hat{S}_{3'}) -2J_2 (\hat{S}_1\cdot\hat{S}_2 + \hat{S}_1\cdot\hat{S}_3 + \hat{S}_1\cdot\hat{S}_{2'} + \hat{S}_1\cdot\hat{S}_{3'}) -2J_3 (\hat{S}_1\cdot\hat{S}_{Gd} + \hat{S}_1\cdot\hat{S}_{Gd'} + \hat{S}_2\cdot\hat{S}_{Gd} + \hat{S}_2\cdot\hat{S}_{Gd'} + \hat{S}_3\cdot\hat{S}_{Gd} + \hat{S}_3\cdot\hat{S}_{Gd'} + \hat{S}_{2'}\cdot\hat{S}_{Gd} + \hat{S}_{2'}\cdot\hat{S}_{Gd'} + \hat{S}_{3'}\cdot\hat{S}_{Gd} + \hat{S}_{3'}\cdot\hat{S}_{Gd'} + \hat{S}_4\cdot\hat{S}_{Gd} + \hat{S}_{4'}\cdot\hat{S}_{Gd'}) \qquad (2)$$

yielded J_3 = +0.17 cm^{-1}, g_{Gd} = 2.00 and g_{Cu} = 2.03, with J_1 = +4.82 cm^{-1} and J_2 = -6.53 cm^{-1}, as found in complex **4**, leading to a band of degenerate states ranging from S = 19/2 to S = 9/2, all located within 2 cm^{-1}. Alternatively, if we let all three *J*'s "free" in our calculation, we obtain J_1= +10.4 cm^{-1} (*vs.* +4.82 cm^{-1} in **4**), J_2= -1.26 cm^{-1} (*vs.* -6.53 cm^{-1} in **4**) and J_3= +0.14 cm^{-1}, while the quality of the fit remains practically unchanged. Therefore, we prefer keeping the former set of parameters, since the two clusters, **1** and **4**, are isostructural, and as such the differences in bond distances and angles are very small, if any. Finally, neglecting the presence of the J_3 interaction given its small value, led to very poor fit of the magnetic susceptibility data, thus rendering its presence crucial.

In addition, magnetization data were collected for all complexes in the magnetic field and temperature ranges of 1 – 5 T and 2.0 – 7.0 K, but a good fit for the reduced magnetization data of **1** and **4** was not possible assuming that only the ground state is populated, as was already evidenced by the dc magnetic susceptibility fit. Yet, we managed to successfully simulate the *M* vs. *H* data for **4**, by using with the parameters obtained from the *dc* susceptibility fit (Fig. 6).

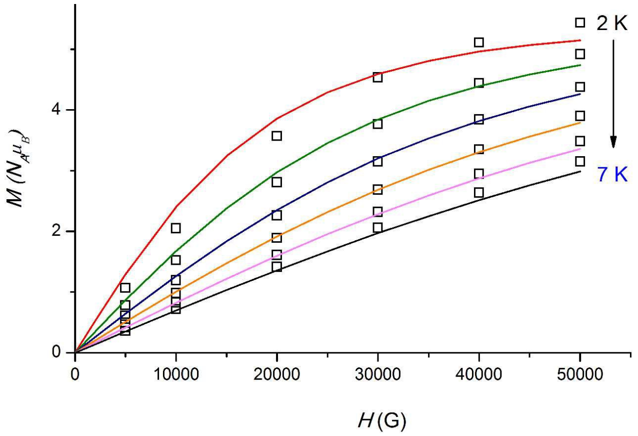


Fig. 6 M vs. H for **4** in the 1 – 5 T and 2.0 – 7.0 K field and temperature range. The solid lines represent simulation of the magnetization isotherms in the 1-5 T field range and 2-7 K temperature range (top-to-bottom), assuming the parameters obtained from the dc susceptibility simulation (see text for details).

Finally, complexes **1**, **2**, **3** and **4** were also studied by alternating current *ac* magnetic susceptibility studies as a means of investigating potential single molecule magnetism behavior, but no out-of-phase signals were observed, thus ruling out this possibility

Conclusions

In conclusion, in this work we presented the syntheses, structures, and magnetism of four heterometallic enneanuclear $[Cu^{II}_7Ln_2]$ clusters, upon using the (2-(β-naphthalideneamino)-2-hydroxymethyl-1-propanol) ligand, LH_3. Following our results upon employment of LH_3 in Co(II/III), Ni(II) and Cu(II) chemistry,[6] and in Mn/Ln,[7, 8] and Ni/Ln[9] 3d-4f chemistry, we have now expanded our work in order to include Cu/Ln clusters in our studies. Once again, the H_3L ligand proved a versatile ligand, capable of producing beautiful molecules with new structures/topologies and metallic cores.

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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