

Lanthanide Triangles Sandwiched by Tetranuclear Copper Complexes Afford a Family of Hendecanuclear Heterometallic Complexes $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_8]$ ($\text{Ln} = \text{La} - \text{Lu}$): Synthesis and Magnetostructural Studies

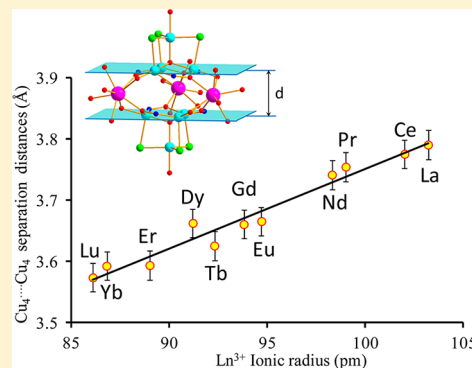
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S Supporting Information

ABSTRACT: Reaction in ethanol of 3-hydroxymethylen-5-methylsalicylaldoxime (H_3L) with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$ [$\text{Ln} = \text{La}$ (1), Ce (2), Pr (3), Nd (4), Eu (5), Gd (6), Tb (7), Dy (8), Er (9), Yb (10), Lu (11), Ho (12)] allowed the synthesis of a family of hendecanuclear heterometallic copper(II)–lanthanide(III) clusters with general formula $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_8(\text{HL})_6(\mu_4\text{-O})_2\text{Cl}_6(\text{H}_2\text{O})_8]\text{Cl}_3$ (1–12). According to the single-crystal X-ray diffraction investigation, the complexes are isomorphous and crystallize in the trigonal $R\bar{3}2$ group. The hendecanuclear cluster is formed by two tetrahedral $\mu_4\text{-oxo}$ $\{\text{Cu}_4\}$ clusters assembled by three lanthanide ions sandwiched in between. Along the family, the separation between the $\{\text{Cu}_4\}$ moieties increases linearly from Lu to La in good correlation with ionic radius of the lanthanide ions. A comparative analysis of the magnetic data for the lanthanum (1) and lutetium (11) compounds shows the presence of ferromagnetic and antiferromagnetic interactions within the $\mu_4\text{-oxo}$ $\{\text{Cu}_4\}$ moieties. For the gadolinium (6) and terbium (7) compounds, the magnetic interactions between the lanthanide and the copper ions are found to be ferromagnetic. The dysprosium (8) compound exhibits single-molecule magnet behavior.



INTRODUCTION

One major concern of coordination chemistry is currently the synthesis and investigation of polynuclear heterometallic coordination compounds possessing slow relaxation of the magnetization.^{1–7} Along this line, the use of lanthanides for the modulation and enhancement of the magnetic properties of transition metal single-molecule magnets has become common in recent years.^{8–17} This is because the magnetic anisotropy of some lanthanides can induce an increase of the blocking temperature for reversal of magnetization.^{18–20} The fundamental understanding regarding the factors that can favor a high value of the resulting ground-state spin and the associated required negative anisotropy is an important prospect of researchers working in the field. In this regards, the study of a large family of compounds, where magnetostructural correlations can be established in a systematic way, contributes to a better understanding of the relationships between the structure and the magnetic interaction or magnetic anisotropy.^{21–28} Thus, during the last two decades, several series of original heterometallic polynuclear systems have been reported particularly with respect to their single-molecule magnet properties. We can mention here the different series of heterometallic systems, Cr/Ln,^{14,29} Mn/Ln,^{8,9,19,30–35} Fe/Ln,^{36–41} Co/Ln,^{17,33,42–45} Ni/Ln,^{23,46–51} and Cu/Ln.^{15,52–67}

In this paper, we present the synthesis and magnetostructural studies of a new family of Cu/Ln heterometallic clusters that are hendecanuclear with general formula $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_8(\text{HL})_6(\mu_4\text{-O})_2\text{Cl}_6(\text{H}_2\text{O})_8]\text{Cl}_3$ (1–12) where $\text{Ln}^{\text{III}} = \text{La}$ (1), Ce (2), Pr (3), Nd (4), Eu (5), Gd (6), Tb (7), Dy (8), Er (9), Yb (10), Lu (11), and Ho (12) and $\text{H}_3\text{L} = 3\text{-hydroxymethylen-5-methylsalicylaldoxime}$. The clusters may be viewed as a triangle of lanthanide ions sandwiched between two classical tetrahedral $\mu_4\text{-oxo}$ Cu_4 clusters,^{68–75} to afford an original hendecanuclear cluster with C_3 molecular symmetry.

EXPERIMENTAL SECTION

Materials. All chemicals and solvents were purchased from Aldrich and used without further purification. Manipulations were performed under aerobic conditions using chemicals and solvents as received.

Synthesis. H_3L (3-Hydroxymethylen-5-methyl-salicylaldoxime). Hydroxylamine hydrochloride (0.84 g, 12.1 mmol) and sodium hydroxide (0.48 g, 12.1 mmol) were dissolved in 15 mL of water. The obtained solution was added to 2-(hydroxymethyl)-6-carbaldehyde-4-methylphenol⁷⁶ (2 g, 12.1 mmol) dissolved in ethanol (20 mL). The final compound was isolated by precipitation from water. Yield 70–75%. IR/cm^{−1}: ν_{max} 3384 (O–H), 2916, 2864 (C–H), 1620,

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Table 1. Crystal Data and Structure Refinement Parameters for Series of Heterometallic Clusters $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_8(\text{HL})_6(\mu_4\text{-O})_2\text{Cl}_6(\text{H}_2\text{O})_8]\text{Cl}_3$ (1–11)

	[La ₃ Cu ₈] (1)	[Ce ₃ Cu ₈] (2)	[Pr ₃ Cu ₈] (3)	[Nd ₃ Cu ₈] (4)	[Eu ₃ Cu ₈] (5)	[Gd ₃ Cu ₈] (6)
formula	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ La ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Ce ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Pr ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Nd ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Eu ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Gd ₃ N ₆ O ₂₈
fw	2495.34	2498.97	2501.34	2511.33	2534.52	2550.36
cryst syst	trigonal	trigonal	trigonal	trigonal	trigonal	trigonal
space group	R32	R32	R32	R32	R32	R32
a (Å)	22.086(2)	22.186(3)	22.132(3)	22.135(3)	22.086(2)	22.1460(10)
b (Å)	22.086(2)	22.186(3)	22.132(3)	22.135(3)	22.086(2)	22.1460(10)
c (Å)	20.661(2)	20.947(2)	20.854(3)	21.038(3)	20.661(2)	20.699(2)
α (deg)	90	90	90	90	90	90
β (deg)	90	90	90	90	90	90
γ (deg)	120	120	120	120	120	120
V (Å ³)	8728.0(14)	8929.2(19)	8846(2)	8927(2)	8728.0(14)	8791.7(10)
Z	3	3	3	3	3	3
ρ _{calcd} (g/cm ³)	1.424	1.394	1.407	1.401	1.447	1.445
μ (mm ⁻¹)	2.765	2.773	2.880	2.935	3.280	3.349
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
R ^a	0.0667	0.0748	0.0646	0.0507	0.0583	0.0565
R _w ^b	0.1235	0.1373	0.1545	0.0803	0.0998	0.0994
	[Tb ₃ Cu ₈] (7)	[Dy ₃ Cu ₈] (8)	[Er ₃ Cu ₈] (9)	[Yb ₃ Cu ₈] (10)	[Lu ₃ Cu ₈] (11)	
formula	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Tb ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Dy ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Er ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Yb ₃ N ₆ O ₂₈	C ₅₄ H ₇₀ Cl ₁₉ Cu ₈ Lu ₃ N ₆ O ₂₈	
fw	2603.52	2566.11	2580.39	2597.73	2603.52	
cryst syst	trigonal	trigonal	trigonal	trigonal	trigonal	
space group	R32	R32	R32	R32	R32	
a (Å)	22.126(2)	22.089(2)	22.291(2)	22.145(2)	22.1950(10)	
b (Å)	22.126(2)	22.089(2)	22.291(2)	22.145(2)	22.1950(10)	
c (Å)	20.559(2)	20.674(3)	20.550(2)	20.554(2)	20.4840(10)	
α (deg)	90	90	90	90	90	
β (deg)	90	90	90	90	90	
γ (deg)	120	120	120	120	120	
V (Å ³)	8716.4(14)	8735.9(17)	8843.0(14)	8729.3(14)	8738.9(7)	
Z	3	3	3	3	3	
ρ _{calcd} (g/cm ³)	1.488	1.463	1.454	1.482	1.484	
μ (mm ⁻¹)	3.491	13.993	3.777	4.074	4.203	
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	
R ^a	0.0576	0.0803	0.0421	0.0422	0.0401	
R _w ^b	0.1063	0.1866	0.0862	0.0699	0.0708	

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b R_w = \{ \sum [w(F_o^2 - F_c^2)^2] / [\sum (w(F_o^2)^2)] \}^{1/2} \text{ and } I > 2\sigma(I).$$

(C=N), 1599, (C=C), 1402, 1469, 1296 (C–H), 1236 (C–OH), 989 (CH). NMR-¹H/ppm and intensities: (DMSO-*d*₆) 11.47 (1sH), 10.10 (1sH), 8.30 (1dH), 7.16 (1dH), 7.05 (1 H), 4.50 (2 H), 2.22 (3 H).

[Ln^{III}₃Cu^{II}₈(HL)₆(μ₄-O)₂Cl₆(H₂O)₈Cl₃ (1–12). To a stirred solution of 3-hydroxymethyl-5-methylen-salicylaldehyde (1 mmol) in absolute ethanol (20 mL), the solid LnCl₃ (Ln = La (1), Ce (2), Pr (3), Nd (4), Eu (5), Gd (6), Tb (7), Dy (8), Er (9), Yb (10), Lu (11), Ho (12); 0.5 mmol) and CuCl₂·2H₂O (1.33 mmol) were added. Finally, the triethylamine (2 mmol) was added to the reaction mixture. The resulting dark green solution was stirred for 10 min and then was left undisturbed to concentrate slowly by evaporation. After 2–4 days, green cube-shaped crystals of 1–12 were collected by filtration and washed with a small amount of absolute ethanol. Specific details of each reaction are given below.

[La₃Cu₈] (1). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), LaCl₃·7H₂O (0.19 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 30% (based on Cu). Anal. Calcd (%) for C₅₄H₇₀Cl₉Cu₈La₃N₆O₂₈: C, 25.99; H, 2.83; N, 3.37. Found (%): C, 25.98; H, 2.86; N, 3.42.

[Ce₃Cu₈] (2). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), CeCl₃·7H₂O (0.19 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 29% (based on Cu). Anal. Calcd

(%) for C₅₄H₇₀Cl₉Cu₈Ce₃N₆O₂₈: C, 25.95; H, 2.82; N, 3.36. Found (%): C, 25.75; H, 2.90; N, 3.41.

[Pr₃Cu₈] (3). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), PrCl₃ (0.12 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 25% (based on Cu). Anal. Calcd (%) for C₅₄H₇₀Cl₉Cu₈Pr₃N₆O₂₈: C, 25.93; H, 2.82; N, 3.36. Found (%): C, 25.97; H, 2.88; N, 3.34.

[Nd₃Cu₈] (4). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), NdCl₃·6H₂O (0.18 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 27% (based on Cu). Anal. Calcd (%) for C₅₄H₇₀Cl₉Cu₈Nd₃N₆O₂₈: C, 25.83; H, 2.81; N, 3.35. Found (%): C, 25.76; H, 2.80; N, 3.51.

[Eu₃Cu₈] (5). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), EuCl₃·6H₂O (0.18 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 31% (based on Cu). Anal. Calcd (%) for C₅₄H₇₀Cl₉Cu₈Eu₃N₆O₂₈: C, 25.59; H, 2.78; N, 3.32. Found (%): C, 25.60; H, 2.83; N, 3.30.

[Gd₃Cu₈] (6). 3-Hydroxymethyl-5-methyl-salicylaldehyde (0.18 g, 1 mmol), GdCl₃·H₂O (0.13 g, 0.5 mmol), CuCl₂·2H₂O (0.23 g, 1.33 mmol), and Et₃N (0.2 mL). Yield: 24% (based on Cu). Anal. Calcd (%) for C₅₄H₇₀Cl₉Cu₈Gd₃N₆O₂₈: C, 25.43; H, 2.77; N, 3.30. Found (%): C, 25.54; H, 2.80; N, 3.41.

[Tb_3Cu_8] (7). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $TbCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 29% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Tb_3N_6O_{28}$: C, 25.38; H, 2.76; N, 3.29. Found (%): C, 25.45; H, 2.71; N, 3.34.

[Dy_3Cu_8] (8). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $DyCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 32% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Dy_3N_6O_{28}$: C, 25.27; H, 2.75; N, 3.28. Found (%): C, 25.36; H, 2.72; N, 3.35.

[Er_3Cu_8] (9). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $ErCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 24% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Er_3N_6O_{28}$: C, 25.13; H, 2.73; N, 3.26. Found (%): C, 25.20; H, 2.68; N, 3.24.

[Yb_3Cu_8] (10). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $YbCl_3 \cdot 6H_2O$ (0.19 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 28% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Yb_3N_6O_{28}$: C, 24.97; H, 2.72; N, 3.24. Found (%): C, 25.01; H, 2.78; N, 3.26.

[Lu_3Cu_8] (11). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $LuCl_3$ (0.14 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 27% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Lu_3N_6O_{28}$: C, 24.91; H, 2.71; N, 3.23. Found (%): C, 24.98; H, 2.74; N, 3.31.

[Ho_3Cu_8] (12). 3-Hydroxymethylen-5-methyl-salicylaldehyde (0.18 g, 1 mmol), $HoCl_3$ (0.14 g, 0.5 mmol), $CuCl_2 \cdot 2H_2O$ (0.23 g, 1.33 mmol), and Et_3N (0.2 mL). Yield: 27% (based on Cu). Anal. Calcd (%) for $C_{54}H_{70}Cl_9Cu_8Ho_3N_6O_{28}$: C, 24.91; H, 2.71; N, 3.23. Found (%): C, 24.98; H, 2.74; N, 3.31.

Physical Measurements. NMR spectra were recorded at 300 MHz on a Bruker DRX spectrometer in $DMSO-d_6$ solution. The chemical shifts were referred to TMS using the residual signals from the solvent. IR spectra were recorded in the solid state on a NICOLET spectrophotometer in the 400–4000 cm^{-1} range. Magnetic susceptibility data (2–300 K) were collected on powdered samples using a SQUID magnetometer (Quantum Design MPMS-XL), applying magnetic field of 0.1 T. All data were corrected for the contribution of the sample holder and the diamagnetism of the samples estimated from Pascal's constants.^{77,78} Magnetic data analyses were carried out by calculations of energy levels associated with the spin Hamiltonians presented in the text and with the MAGPACK program package.⁷⁹ To take into account the intermolecular interaction, the following definition of the susceptibility has been used:^{78,80,81}

$$\chi(T) = \frac{\chi_0(T)}{1 - \frac{2zJ'\chi_0(T)}{Ng^2\beta^2}}$$

X-ray Data Collection and Structure Refinement. Diffraction data were collected at 100.0(1) K using a Gemini A Ultra diffractometer from Agilent Technologies Ltd. (Mo $K\alpha$ graphite-monochromated radiation, $\lambda = 0.71073$ Å) equipped with a CCD camera and controlled by the CrysAlisPro Software (Agilent Technologies, version 1.171.34.49). A summary of the crystallographic data and structure refinement is given in Table 1. An analytical absorption correction was applied by modeling the crystal habit.⁸² The crystals were placed in the cold stream of an Oxford Cryosystems open-flow nitrogen cryostat with a nominal stability of 0.1 K.⁸³ All the structures were solved by direct methods using the SIR97 program⁸⁴ and refined against F^2 using the CRYSTALS program.⁸⁵ All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were placed in ideal calculated positions with isotropic thermal parameters riding on their respective carbon atoms. The graphical manipulations were carried out with the DIAMOND⁸⁶ program. Selected bond distances and angles for 1–11 are listed in Table 2.

RESULTS AND DISCUSSION

The reaction of 3-hydroxymethylen-5-methylsalicylaldehyde (H_3L) with $LnCl_3 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ at room temper-

Table 2. Selected Bond Distances and Angles in [Dy_3Cu_8] (8)

N1–Cu1	1.947(11)	Cl1–Cu1–O2	94.1(4)
Cl1–Cu1	2.594(5)	Cl1–Cu1–O3	104.7(4)
O3–Cu1	1.958(11)	Cl1–Cu1–N1	97.9(4)
O5–Cu1	1.938(5)	Cl1–Cu1–O5	84.6(5)
O2–Cu1	1.978(11)	O2–Cu1–O3	81.1(4)
Cl1–Cu2	2.339(5)	O3–Cu1–O5	94.4(3)
O5–Cu2	1.931(17)	O5–Cu1–N1	93.1(4)
O6–Cu2	1.93(3)	O2–Cu1–N1	92.1(5)
O1–Dy1	2.398(13)	Cl1–Cu2–O6	87.88(15)
O2–Dy1	2.381(12)	Cl1–Cu2–O5	92.12(15)
O3–Dy1	2.347(9)	Cl1–Cu2–Cl1'	119.86(2)
O4–Dy1	2.409(14)		

ature and under aerobic conditions in 6:3:8 ratio in the presence of Et_3N leads to the formation of deep green cube-shaped crystals with formula $[Ln^{III}_3Cu^{II}_8(HL)_6(\mu_4-O)_2Cl_6(H_2O)_8]Cl_3$ where Ln = La (1), Ce (2), Pr (3), Nd (4), Eu (5), Gd (6), Tb (7), Dy (8), Er (9), Yb (10), Lu (11), and Ho (12) and H_3L = 3-hydroxymethylen-5-methylsalicylaldehyde.

Molecular Structures. The single-crystal X-ray diffraction data revealed that 1–11 are isomorphous and crystallize in the trigonal space group R32. The X-ray diffraction data was not collected for 12 due to the very small size of the single crystals. However the elementary analytical data, X-ray powder diffraction patterns, and physical measurements allow us to suggest similar structure and composition for 12 as for 1–11. Herein we will describe in detail the structure of dysprosium complex 8 as an example for the family 1–12.

The crystal structure of [Dy_3Cu_8] (8) consists of complex cations $[Dy^{III}_3Cu^{II}_8(HL)_6(\mu_4-O)_2Cl_6(H_2O)_8]^{3+}$ crystallizing with chloride anions for charge balance (Figure 1). The complete architecture of the cation could be described as two nearly flat $\{Cu_3\}$ fragments located in two parallel planes (crystallographic *ab*-planes) formed by coordination of three double-deprotonated ligands (HL^{2-} , Scheme 1) to three copper(II) ions in a triangular fashion. A lateral look shows that the two $\{Cu_3\}$ fragments are bridged together by three dysprosium(III) ions sandwiched between with $Cu1 \cdots Dy1$ distances of 3.4068(26) Å. The architecture is completed on the other side by two additional Cu^{II} ions $Cu(2)$ bridged to the copper(II) ions of the two $\{Cu_3\}$ fragments by chloride ions and a μ_4 -oxo oxygen atom forming two tetranuclear $\{Cu_4\}$ moieties with a classical tetrahedral arrangement of the copper(II) ions (Figure 1 and Figure S1, Supporting Information). The $Cu1 \cdots Cu1'$ and $Cu1 \cdots Cu2$ distances are 3.2269(34) and 3.0887(38) Å, respectively.

As commonly observed with such oximes,^{77–81} within the $\{Cu_3\}$ fragments, the copper(II) ions are assembled together in a triangular fashion by an oxo oxygen atom (O5) and by the bridging oximate groups that are coordinated to one copper(II) ion by the nitrogen atom and to a second copper(II) ion by the oxygen atom (Figure 1). The torsion $Cu1O3N1Cu1'$ angle is equal 13.09°. Here the oxygen of the oximate groups is also bridging the dysprosium with copper ions in a μ_3 -fashion, while the oxo oxygen atom (O5) is bridging a fourth copper ion ($Cu2$) in a μ_4 -fashion. The copper(II) ions and the dysprosium(III) ions are also bridged by the deprotonated phenoxy groups of 3-hydroxymethylen-5-methylsalicylaldehyde.

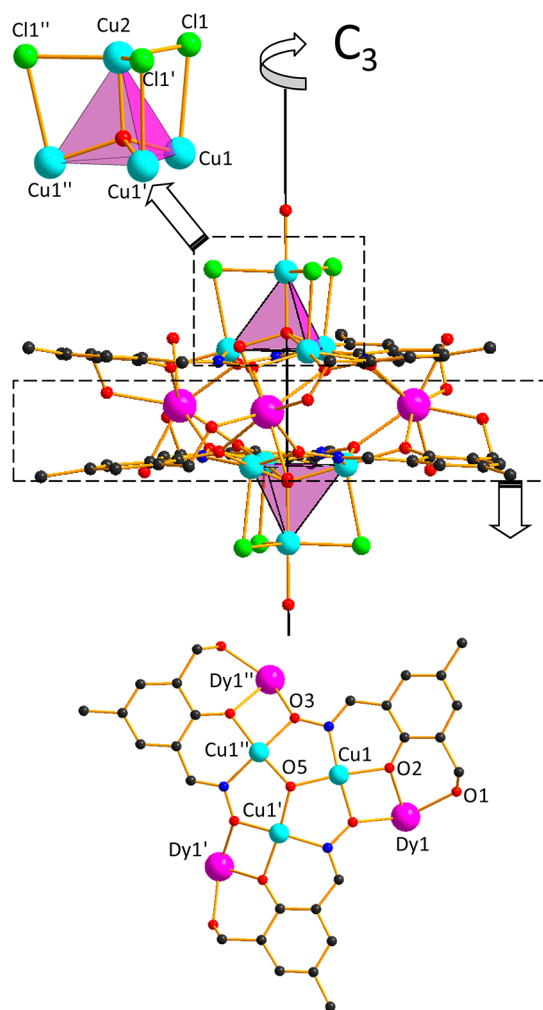
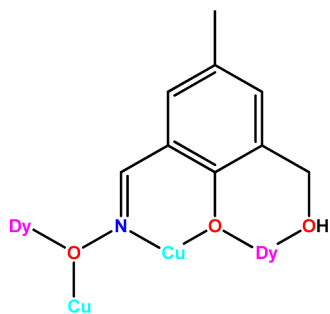


Figure 1. Molecular structure of $[\text{Dy}_3\text{Cu}_8]$ (**8**): the lateral view with tetrahedral $\{\text{Cu}_4\}$ fragment (top) and view along the 3-fold axis (bottom).

Scheme 1. Mode of Coordination ($\mu_4:\eta_2:\eta_1:\eta_2:\eta_1$) of 3-Hydroxymethylen-5-methylsalicylaldoxime (HL^{2-}) in Heterometallic Ln_3Cu_8 (1–12**) Clusters**



ime. The hydroxymethylen groups are coordinated to dysprosium(III) ions but are not deprotonated.

The three dysprosium(III) ions are eight coordinated by oxygen atoms: two come from the phenoxo groups; two from the oximate groups; two from the hydroxymethylen groups and two from water molecules.

The six copper(II) ions (Cu1) from the two $\{\text{Cu}_3\}$ fragments are in a square pyramid environment made up by one nitrogen and one oxygen atom from the oximate group, one phenoxo

oxygen and one oxygen from the oxo group. The apical position is occupied by a chloride ion. The $\text{Cu}-\text{O}$, $\text{Cu}-\text{N}$, and $\text{Cu}-\text{Cl}$ bond lengths are 1.938–1.968, 1.964, and 2.604 Å, respectively. The oxo groups (O5 , $\text{O5}'$) are located on the $R3$ -axis and serve as one of the apical positions of the trigonal bipyramid environment of the Cu2 and $\text{Cu2}'$ copper(II) ions from the additional $\{\text{Cu}-\text{Cl}_3\text{H}_2\text{O}\}$ entities. The basal plane of the bipyramid is an equilateral triangle made of the three chloride ions that bridge the copper(II) ions of the $\{\text{Cu}_3\}$ fragments, and the second apical position is a coordinated water molecule (Figure 1 and Figure S1, Supporting Information).

The isostructurality of the $[\text{Ln}_3\text{Cu}_8]$ family gives an opportunity to track the impact of variation of ionic radius of lanthanides on structural parameters of clusters. As may be expected, we found that the distance between the two $\{\text{Cu}_3\}$ fragments that lie in parallel planes increases with the ionic radii of lanthanides. More remarkably this increases in a linear fashion as shown in Figure 2. A linear dependence on the ionic

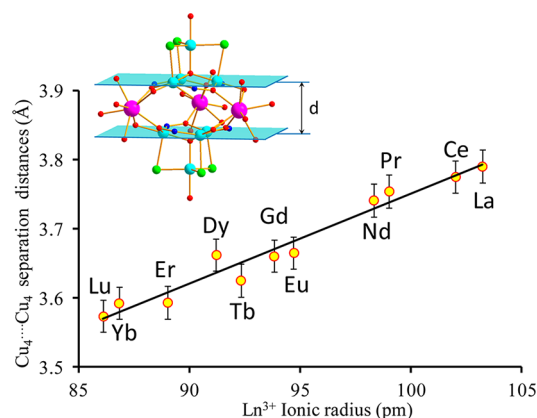


Figure 2. $\{\text{Cu}_4\}\cdots\{\text{Cu}_4\}$ separation distances, d (Å), as a function of ionic radius of lanthanides in the family of heterometallic clusters $[\text{Ln}_3\text{Cu}_8]$ (**1–11**). Solid line is a linear correlation ($R^2 = 0.959$).

radii of lanthanides was also found for CuONCu dihedral angle (β) (Figure S3, Supporting Information). In contrast, the angle between OCuO and OLnO planes (α), which is known to strongly affect magnetic interactions, especially for Cu/Gd heterometallic systems,^{24–26} has small variation along the series of complexes **1–11**. Its variation is limited by crystallographic errors in structural determination (Figure S4, Supporting Information). No strong variation was found in IR spectra ($4000\text{--}400\text{ cm}^{-1}$) of $[\text{Ln}_3\text{Cu}_8]$ series, excepted for the $\nu(\text{CH}_2\text{--O})$ stretching vibration, which shows strong correlation with the ionic radius of lanthanides taking values from 1039.4 cm^{-1} for La to 1052.2 cm^{-1} in the case of Lu clusters (Figure S5, Supporting Information).

Magnetic Properties. The magnetic susceptibility data for all $[\text{Ln}_3\text{Cu}_8]$ series are shown in Figure 3 and Table S2, Supporting Information.

The temperature dependence of the χT product for $[\text{La}_3\text{Cu}_8]$ (**1**) and $[\text{Lu}_3\text{Cu}_8]$ (**11**) under an applied magnetic field of 0.1 T is shown in Figure 4. Both compounds give similar evolution of magnetic susceptibility as a function of temperature. At 300 K, the χT product is 2.24 and $2.03\text{ cm}^3\text{ K mol}^{-1}$ for **1** and **11**, respectively, which is lower than the expected value of $3.00\text{ cm}^3\text{ K mol}^{-1}$ for eight noninteracting Cu^{II} ions ($S = 1/2$) with $g = 2$. Upon cooling, the χT product continuously decreases down to 90 K ($\chi T = 1.69$ for **1** and $1.66\text{ cm}^3\text{ K mol}^{-1}$ for **11**) then it

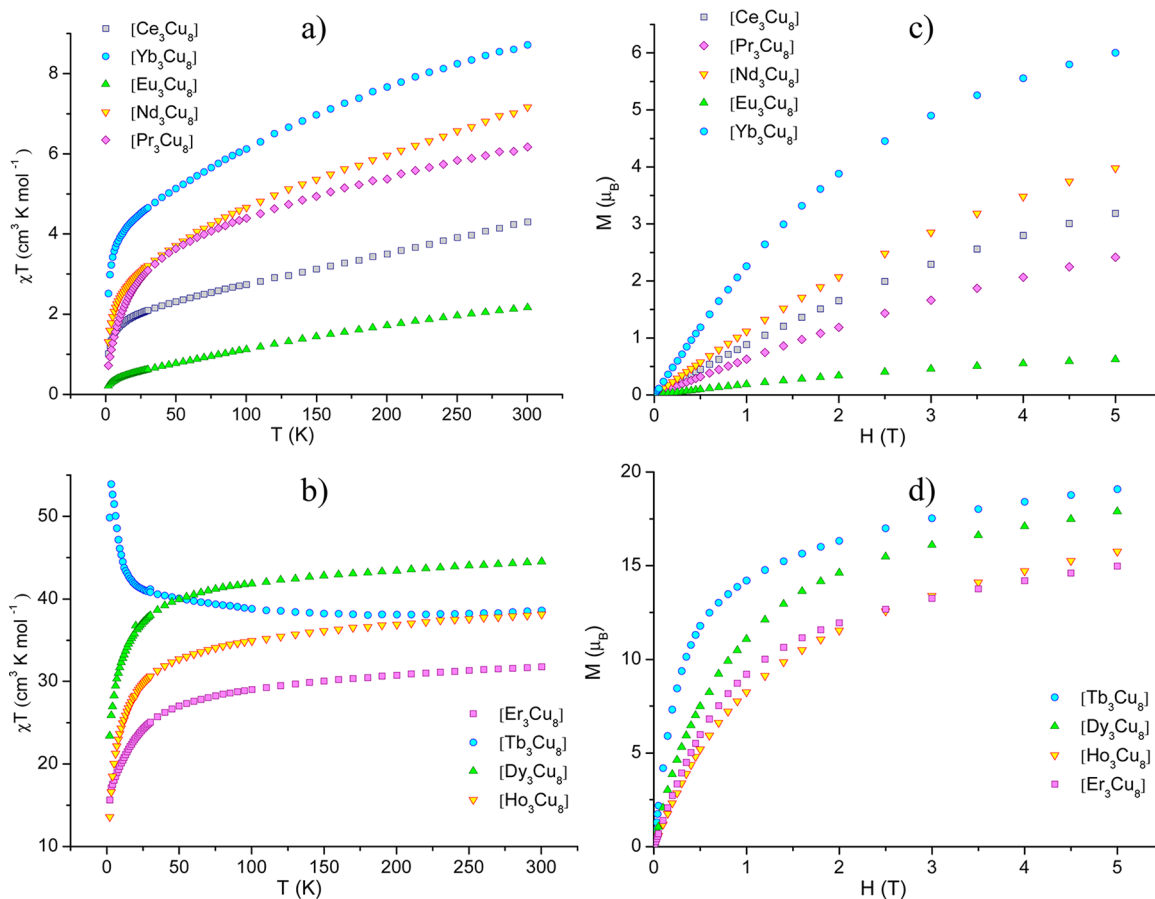


Figure 3. χT versus T plots data (a,b) and magnetization curves (c,d) for 2–5, 7–10, and 12.

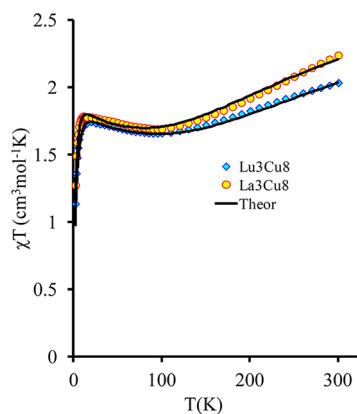


Figure 4. χT versus T plots data for $[\text{La}_3\text{Cu}_8]$ (1) and $[\text{Lu}_3\text{Cu}_8]$ (11). The black solid lines correspond to the simulation according to the Hamiltonian (eq 1) with parameters described in the text.

increases to reach the maximal value of 1.79 and 1.73 $\text{cm}^3 \text{K mol}^{-1}$ at 20 K for 1 and 11, respectively. Below 20 K, the χT sharply decreases with temperature and reaches the values of 1.27 and 1.14 $\text{cm}^3 \text{K mol}^{-1}$ for 1 and 11, respectively, at 2 K. (Figure 4). This behavior suggests the presence of both ferromagnetic and antiferromagnetic interactions in 1 and 11.

To understand the magnetic interactions in 1 and 11, we simulated the temperature dependence of the magnetic susceptibility. Taking into account the structural parameters and that 1 and 11 are isostructural, the general spin-

Hamiltonian describing the isotropic exchange interactions (Figure 5) can be written as

$$H = -2J_a(S_1S_2 + S_1S_3 + S_1S_4) - 2J_b(S_2S_3 + S_3S_4 + S_2S_4) - 2J_a(S_5S_6 + S_5S_7 + S_5S_8) - 2J_b(S_6S_7 + S_7S_8 + S_6S_8) \quad (1)$$

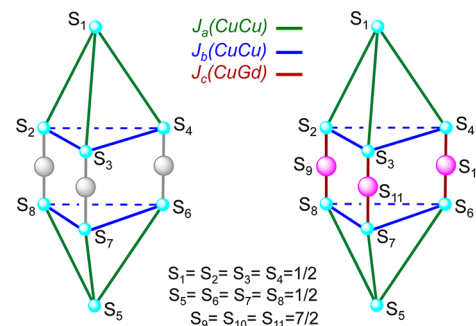


Figure 5. Spin topology for clusters $[\text{La}_3\text{Cu}_8]$ (1) and $[\text{Lu}_3\text{Cu}_8]$ (11) (left) and $[\text{Gd}_3\text{Cu}_8]$ (6) (right).

J_a corresponds to the magnetic interaction between the apical copper(II) ion ($\text{Cu}2$) and each of the three copper(II) ions ($\text{Cu}1$, $\text{Cu}1'$, $\text{Cu}1''$) of the $\{\text{Cu}_3\}$ fragment (Figures 1 and 5). J_b holds for the magnetic interaction among the three $\text{Cu}(\text{II})$ within the $\{\text{Cu}_3\}$ fragments and should be related to the CuONCu dihedral angle (β) (Figure S3, Supporting Information). In order to minimize over parametrization and

considering the 3-fold axis and the symmetry plane on which lie the molecule, we use only these two constants (J_a and J_b) to describe the magnetic interactions. We are aware of frustration phenomena in trinuclear $\{\text{Cu}_3\}$ fragments,^{87,88} as well as in the tetranuclear^{68,73,74} units, and our model is oversimplified. The constants given below are intended to have an estimation of the strength of interactions between the copper(II) ions within the $\{\text{Cu}_3\}$ trinuclear fragments (J_b) and with apical copper(II) (J_a). Similar simplifications were previously used.^{89–92} The best agreement between the experimental and theoretical data⁷⁹ was obtained with parameters $J_a(\text{CuCu}) = +7.0 \text{ cm}^{-1}$, $J_b(\text{CuCu}) = -111.0 \text{ cm}^{-1}$, $zJ' = -0.34 \text{ cm}^{-1}$, and $g = 2.08$ for $[\text{La}_3\text{Cu}_8]$ (**1**) and $J_a(\text{CuCu}) = +9.0 \text{ cm}^{-1}$, $J_b(\text{CuCu}) = -130.0 \text{ cm}^{-1}$, $zJ' = -0.38 \text{ cm}^{-1}$, and $g = 2.05$ for $[\text{Lu}_3\text{Cu}_8]$ (**11**). The relatively high values of intermolecular terms (zJ') are well evidenced in the low temperature range 2–10 K. These can be ascribed to magnetic interactions between the two tetrahedral Cu_4 clusters occurring through the noninnocent diamagnetic ions as has been suggested elsewhere^{11,93–96} or to interactions operating via the π – π stacking^{89,92,97} that is evidenced in the structures of **1** and **11**. The strong antiferromagnetic interaction (J_b) within the $\{\text{Cu}_3\}$ fragments found for **1** and **11**, which may operate through the oximate groups and oxo oxygen atom, is consistent with previously reported examples of clusters with similar bridging mode.⁷ The ferromagnetic interaction (J_a) between apical Cu^{2+} ion and $\{\text{Cu}_3\}$ oxime fragment is also consistent with previous findings in $[\text{Cu}_4\text{OCl}_6\text{L}]$ complexes.^{68,74,98} It has been shown that magnetic interaction in such complexes is sensitive to small modifications of geometrical parameters in μ_4 -O and μ_2 -Cl bridging ligands^{68,74,98} and affected by strong Jahn–Teller effect⁷⁵ characteristic for Cu^{II} ions (d^9).

The temperature dependence of the χT product for the $[\text{Gd}_3\text{Cu}_8]$ compound **6** decreases upon cooling from $26.07 \text{ cm}^3 \text{ K mol}^{-1}$ at 300 K down to $25.36 \text{ cm}^3 \text{ K mol}^{-1}$ at 65 K. Then it increases up to the maximum value $26.21 \text{ cm}^3 \text{ K mol}^{-1}$ at 13 K (Figure 6) and finally sharply falls to reach the value of $13.52 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K. The value at 300 K is slightly lower than the expected value for eight noninteracting Cu^{II} ($S = 1/2$) and three Gd^{III} ($S = 7/2$) ions ($3.0 + 23.625 = 26.625 \text{ cm}^3 \text{ K mol}^{-1}$) with $g = 2$. The decrease of the χT product in the temperature

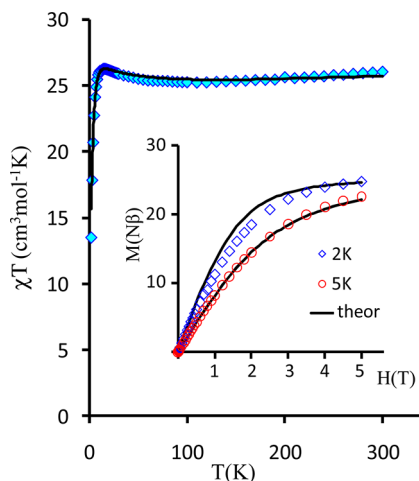


Figure 6. χT versus T plots data for $[\text{Gd}_3\text{Cu}_8]$ (**6**). Insert shows magnetization curves for $[\text{Gd}_3\text{Cu}_8]$ (**6**) at 2 and 5 K. The black solid lines correspond to the simulation according the Hamiltonian (eq 2) with parameters described in the text.

range 300–70 K suggests the presence of antiferromagnetic interactions within the $[\text{Gd}_3\text{Cu}_8]$ core, while the increase below 60 K suggests the presence of a ferromagnetic exchange interaction.

The magnetic interaction in $[\text{Gd}_3\text{Cu}_8]$ (**6**) can be described by Hamiltonian (see Figure 5 for spin topology):

$$\begin{aligned}
 H = & -2J_a(S_1S_2 + S_1S_3 + S_1S_4) - 2J_b(S_2S_3 + S_3S_4 + S_2S_4) \\
 & - 2J_a(S_5S_6 + S_5S_7 + S_5S_8) - 2J_b(S_6S_7 + S_7S_8 + S_6S_8) \\
 & - 2J_c(S_2S_9 + S_8S_9 + S_4S_{10} + S_6S_{10} + S_3S_{11} + S_7S_{11})
 \end{aligned}
 \quad (2)$$

In comparison with compounds **1** and **11**, the J_c exchange parameter was added to take into account the magnetic interaction between the gadolinium(III) ions and the copper(II) ions within the $\{\text{Cu}_3\}$ fragment of the $[\text{Gd}_3\text{Cu}_8]$ (**6**) cluster. As evident from the crystal structure, the molecular structure of **6** is similar to all other $[\text{Ln}_3\text{Cu}_8]$ clusters investigated in this work. According to structural data, the bond lengths and angles for $[\text{Gd}_3\text{Cu}_8]$ are close and between those found for the lanthanum (**1**) and lutetium (**11**) analogue compounds. To simulate the magnetic susceptibility for **6**, we took the values J_a and J_b obtained from the magnetic analysis of **1** and **11** as limits for those in **6** ($+7.0 \leq J_a \leq +9.0 \text{ cm}^{-1}$; $-130.0 \leq J_b \leq -110.0 \text{ cm}^{-1}$).

Assuming that magnetic interaction between 3d and 4f metal centers are approximately 1 order of magnitude lower than 3d–3d interactions and using medium values of magnetic interactions for J_a and J_b obtained from $[\text{La}_3\text{Cu}_8]$ (**1**) and $[\text{Lu}_3\text{Cu}_8]$ (**11**), the best agreement between experimental and theoretical values of magnetic susceptibility (Figure 6) was obtained considering a ferromagnetic interaction between gadolinium(III) ions and the copper(II) ions $J_c(\text{CuGd}) = +1.4 \text{ cm}^{-1}$ with $J_a(\text{CuCu}) = +9.0 \text{ cm}^{-1}$ and $J_b(\text{CuCu}) = -130.0 \text{ cm}^{-1}$ with $g = 2.0$. The value J_c found for the CuGd interaction is lower than the one that may be calculated via two phenoxo bridges as a function of angle between planes OCuO and OLnO (α) (Figure S4, Supporting Information) from reported magnetostructural correlations.^{24–26,66,67} One explanation is that in compound **6** one phenoxo bridge is replaced by an oximate bridge, which could give an antiferromagnetic contribution to the overall interaction. The values obtained for the exchange parameters from the simulation of the temperature dependence of magnetic susceptibility (0.1 T) for **6** were used to simulate the magnetization curves (0–5.0 T; $g = 2.0$) using the same Hamiltonian (eq 2) (Figure 5). This gave a good agreement between experimental and theoretical data, which suggests the reliability of J_a , J_b , and J_c values estimated from our magnetic analysis of **1**, **6**, and **11**. For **6**, a very small constant $zJ' = -0.003 \text{ cm}^{-1}$ was found for intermolecular interaction. This small value is consistent with the crystal packing of compounds **1–12** that results in well isolated $[\text{Ln}_3\text{Cu}_8]$ molecules. This has not to be compared with those found for **1** and **11** where the intermolecular term in our model takes also into account the “intramolecular” interaction between the two $\{\text{Cu}_4\}$ moieties via three diamagnetic lanthanides La and Lu (vide infra).

$[\text{Gd}_3\text{Cu}_8]$ (**6**) and $[\text{Tb}_3\text{Cu}_8]$ (**7**) show the signature (Figure 3) of Cu/Ln ferromagnetic interaction that is not observed with the other lanthanides (**2–5**, **8–10**, **12**). All compounds are strongly affected by dominant antiferromagnetic exchange

interactions in the Cu_4OCl_3 core and spin orbital components of anisotropic lanthanides.

The ac susceptibility has been measured at zero and 0.1 T dc fields for all compounds, and only in the case of $[\text{Dy}_3\text{Cu}_8]$ complex, the frequency dependence of slow magnetic relaxation was detected (Figure 7). In the case of the strongly anisotropic $[\text{Tb}_3\text{Cu}_8]$ (7) compound with an evident ferromagnetic interaction at low temperature, we did not detect any ac signal.

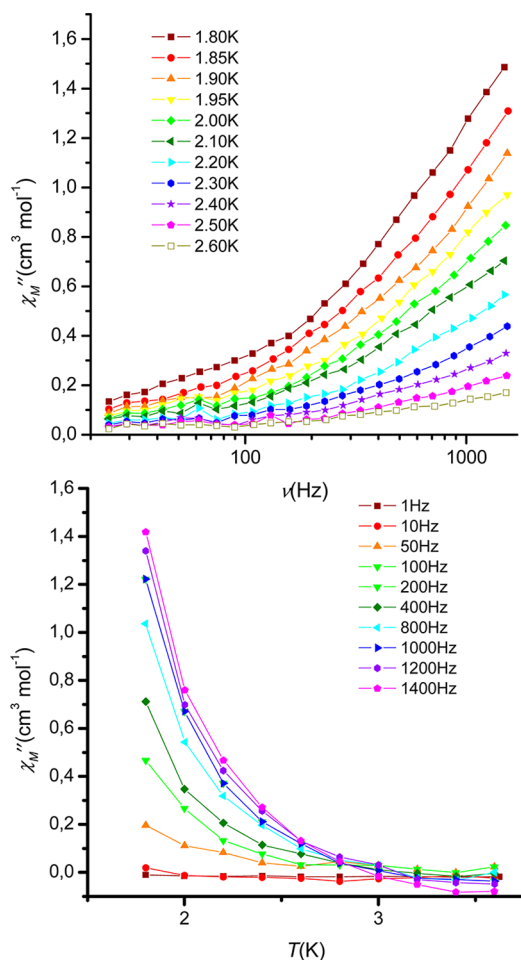


Figure 7. Frequency dependence (top) and temperature dependence (bottom) of the out-of-phase (χ'') ac susceptibility component for $[\text{Dy}_3\text{Cu}_8]$ (8).

The $[\text{Dy}_3\text{Cu}_8]$ (8) compound shows slow magnetic relaxation (Figure 7) and merits to be additionally mentioned. The product of χT for compound $[\text{Dy}_3\text{Cu}_8]$ (8) at $H = 0.1$ T decreases from $44.51 \text{ cm}^3 \text{K mol}^{-1}$ at room temperature to $23.39 \text{ cm}^3 \text{K mol}^{-1}$ at 2.0 K (Figure S6, Supporting Information). The value at room temperature is close to the expected value of $45.51 \text{ cm}^3 \text{K mol}^{-1}$ for three Dy^{III} ($^6\text{H}_{15/2}$, $L = 5$, $g = 4/3$) and eight Cu^{II} ($S = 1/2$, $g = 2.0$) ions.^{99,100} The experimental value for the field dependence of magnetization at 2 K for 8 is typical and indicates the presence of anisotropy in compound 8 (Figure 3). The ac magnetic susceptibility measurements for compound 8 were performed in a 1.8–4 K range using a 2.7 G ac field oscillation in a 1–1400 Hz frequency range (Figure 7). The temperature dependence and frequency sweeping of out of phase susceptibility shows strong frequency dependence without maxima as a result of either a low energy barrier of magnetic relaxation or tunnelling. The

application of a small dc field in the range 0.01–0.2 T does not change the ac signal profile, suggesting that the slow magnetic relaxation (at 2 K) is not influenced by tunnelling effects. The presence of a slow magnetic relaxation in the $[\text{Dy}_3\text{Cu}_8]$ (8) compound suggests a single-molecule magnet (SMM) behavior.^{8,10,32,45–57,92–97}

CONCLUSION

An original series of hendecanuclear heterometallic clusters based on the 3-hydroxymethylen-5-methylsalicylaldehyde (H_3L) with general formula $[\text{Ln}^{\text{III}}_3\text{Cu}^{\text{II}}_8(\text{HL})_6(\mu_4\text{-O})_2\text{Cl}_6(\text{H}_2\text{O})_8]\text{Cl}_3$ (1–12) where $\text{Ln} = \text{La}$ (1), Ce (2), Pr (3), Nd (4), Eu (5), Gd (6), Tb (7), Dy (8), Er (9), Yb (10), Lu (11), and Ho (12) have been synthesized. According to single-crystal X-ray investigations, the complexes are isomorphous and crystallize in the trigonal $R\bar{3}2$ group. The hendecanuclear cluster is formed by two tetrahedral μ_4 -oxo Cu_4 clusters connected by three lanthanide ions. Along the family, the separation between the $\{\text{Cu}_4\}$ moieties increases linearly from Lu to La. Comparative analysis of magnetic data shows the presence of ferromagnetic (J_a) and antiferromagnetic (J_b) interactions within the μ_4 -oxo Cu_4 clusters (Figure 4). In the case of diamagnetic ions, La (1) and Lu (11), our analysis suggested long-distance antiferromagnetic intramolecular interactions. For the isotropic gadolinium and anisotropic terbium compounds, $[\text{Gd}_3\text{Cu}_8]$ (6) and $[\text{Tb}_3\text{Cu}_8]$ (7), the magnetic studies evidence ferromagnetic interactions (J_c) between the lanthanide ions and the copper ions. Only the $[\text{Dy}_3\text{Cu}_8]$ (8) compound exhibits SMM behavior as suggested from the temperature dependence and frequency sweeping of out of phase susceptibility that shows strong frequency dependence.

ASSOCIATED CONTENT

Supporting Information

Crystallographic refinement details and magnetic results for 1–12. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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