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New Structural Form of a Tetranuclear Lanthanide Hydroxo Cluster: Dy_4 Analogue Display Slow Magnetic Relaxation

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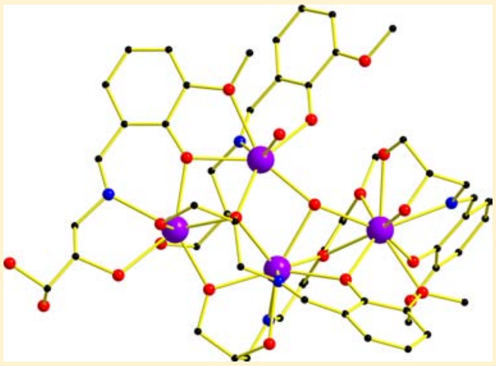
S Supporting Information

ABSTRACT: A series of tetranuclear lanthanide (Ln = Tb, Dy, Ho) hydroxo clusters has been synthesized by reaction of $LnCl_3·6H_2O$ (Ln = Tb (**1**), Dy (**2**), Ho (**3**)) with *o*-vanilin based schiff base ligand 2-(2,3 dihydroxpropyl imino methyl) 6-methoxy phenol (H_3L) in methanol and in the presence of triethylamine as base. The solid state structures of all the products were established by single crystal X-ray diffraction technique. Magnetism studies reveal that Dy_4 analogue exhibits slow magnetic relaxation at low temperatures.



INTRODUCTION

Considering the potential applications of single molecule magnets (SMMs) in information storage, processing[1] spintronics,[2] and quantum computation,[3] tremendous efforts have been made in the last two decades for synthesizing new SMMs possessing high-energy barriers (U_{eff}) and high blocking temperatures (T_B). SMMs[4] are discrete magnetic clusters which usually possess appreciable spin ground state (S) in combination with a uniaxial magnetic anisotropy (D) which leads to an energy barrier for reversal of the magnetization denoted by vector $S^2|D|$ or $(S^2 - 1/4)|D|$ for integer and half-integer spin, respectively. A large number of 3d,[5] particularly Mn based, and 3d−4f[6] based SMMs have been reported since the discovery of the first SMM Mn_{12} acetate.[5a] Though some of these SMMs exhibit a reasonably high energy barrier for reversal of magnetization with reasonable blocking temperatures still for real applications the parameters mentioned, particularly the latter, is too low. Constant efforts have been made to increase U_{eff} and T_B of the SMMs with focus more on lanthanide based SMMs owing to their high spin−orbit coupling[7] and high magneto anisotropy (D) which can potentially lead to isolation of clusters possessing high energy barriers and blocking temperatures. The observation of slow magnetic relaxation in the Dy_3 triangle[8] which possesses almost diamagnetic ground state and in mononuclear complexes Pc_2Ln (Pc = Phthalocynine, Ln = Tb, Dy, Ho)[9] stimulated further work involving synthesis of purely lanthanide-based SMMs.[10,11]

Self-assembly of lanthanide-based oxo-hydroxo clusters has been achieved by using a variety of ligands like β-diketones,[12] carboxylates,[13] aloxides,[14] aminoacids,[15] *o*-vanillin,[16] and Schiff bases[17] as ligands. Among them *o*-vanillin based Schiff base ligands[18] have been shown to be useful in the synthesis of 4f SMMs possessing high energy barriers and blocking temperatures. For example, tetranuclear dysprosium(III) clusters $[Dy_4(\mu\text{-}OH)_2(bmh)_2(msh)_4Cl_2]$[18d] and $[Dy_4(H_3L)_4(MeOH)_6]$·MeOH (H_3L = 2-hydroxy-3-methoxybenzoic acid [(2-hydroxy-3-methoxyphenyl) methylene] hydrazine)[18e] stabilized by *o*-vanillin based Schiff base ligands exhibit the energy barriers of 170 and 173 K, respectively, for reversal of magnetization. By adopting ligand controlled hydrolytic approach methodology interesting lanthanide-based SMMs have been reported with nuclearitiy ranging from Dy_2,[18b,h,19] Dy_3,[8,18c,20] Dy_4,[18a,d−f,21] Dy_5,[22] Dy_6[23] Dy_7,[24] Dy_8,[25] Dy_{10},[26] and Dy_{26}.[27] Among these a square pyramidal $[Dy_5O(OiPr)_{13}]$ molecular nanomagnet exihibits slow relaxation of magnetization with a record thermal energy barrier of 530 K and blocking temperature as high as 40 K at present.[22a]

Recently the *o*-vanillin based Schiff base ligand 2-(2,3-dihydroxpropyl imino methyl) 6-methoxy phenol (H_3L) have been used for isolating Mn based clusters which show catalytic biomimetic water oxidation.[28] In another report by using chiral form of the aforementioned ligand, nanoscale multiferrioc manganese clusters have been isolated.[29] Considering the versatile binding modes of the *o*-vanillin based Schiff base ligand, 2-(2,3-dihydroxpropyl imino methyl) 6-methoxy phenol has been investigated for synthesizing polynuclear lanthanide oxo-hydroxo clusters. Herein synthesis, characterization, and magnetic studies of a series of novel tetranuclear lanthanide hydroxo clusters $[Ln_4(\mu_3\text{-}OH)(HL)_3(H_2L)_2(H_2O)]·3Cl_5Py_{0.5}C_6H_6·H_2O$ are reported. Magnetic properties of all these compounds are studied.

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Scheme 1

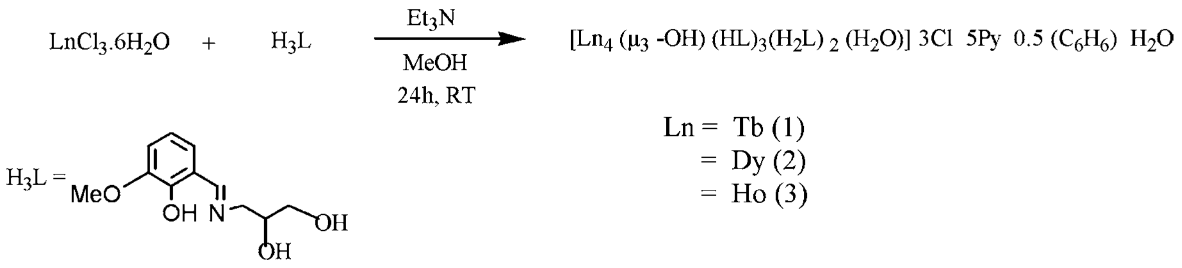


Table 1. Crystal and Refinement Data for 1−3

	1	2	3
formula	$C_{83}H_{100}O_{23}N_{10}Cl_3Tb_4$	$C_{83}H_{100}O_{23}N_{10}Cl_3Dy_4$	$C_{83}H_{100}O_{23}N_{10}Cl_3Ho_4$
fw	2347.76	2362.08	2371.80
temp (K)	100(2)	100(2)	100(2)
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
cryst size (mm)	0.24 × 0.18 × 0.12	0.26 × 0.20 × 0.16	0.20 × 0.16 × 0.10
a (Å)	13.994(11)	13.977(3)	13.972(17)
b (Å)	14.926(12)	14.953(3)	14.910(18)
c (Å)	22.252(17)	22.227(4)	22.133(3)
α (deg)	73.586(10)	73.540(3)	73.726(2)
β (deg)	76.797(10)	76.994(3)	76.970(2)
γ (deg)	85.717(10)	85.783(3)	85.834(2)
V (Å^3)	4341.9(6)	4340.5(15)	4312.2(9)
Z	2	2	2
d_{calcd} (Mg m^{-3})	1.796	1.807	1.827
μ (mm^{-1})	3.390	3.575	3.803
F(000)	2326	2334	2342
θ range for data collection (deg)	1.42 to 25.00	1.42 to 24.98	1.42 to 25.00
refln collected/unique	41835/15201	41825/15184	41366/15100
R (int)	0.0467	0.0363	0.0341
data/retraints/params	15201/0/1135	15184/1/1129	15100/0/1139
GoF on F^2	1.050	1.061	1.079
R_1/wR_2 ($I > 2\sigma(I)$)	0.0458/0.1003	0.0399/0.0958	0.0373/0.0832
R_1/wR_2 (all data)	0.0551/0.1046	0.0448/0.985	0.0416/0.0852
largest diff peak/hole, e Å^{-3}	1.417/−1.201	1.485/−1.072	1.525/−0.837

Alternating current susceptibility measurements revealed that the Dy_4 cluster exhibits slow magnetic relaxation.

■ EXPERIMENTAL SECTION

General Information. The lanthanide starting materials were synthesized from corresponding oxides by neutralizing with concentrated HCl, followed by evaporation to dryness. Ligand 2-(2,3-dihydroxpropyl imino methyl) 6-methoxy phenol (H_3L) was prepared based on reported procedures.[29] Common organic solvents and triethylamine were purchased from commercial sources and used as such without further purification. Infrared spectra were recorded on a JASCO-5300 FT-IR spectrometer as KBr pellets. Elemental analysis was performed on Flash EA Series 1112 CHNS analyzer. Powder X-ray diffraction patterns were recorded on a Bruker D8-Advance diffractometer using graphite monochromated Cu Kα_1 (1.5406 Å) radiation, Serial number 204795. Thermogravimetric analyses were carried out an SDT-Q600 supplied by Ta instruments. Magnetic measurements were carried out in the Unitat de Mesures Magnètiques (Universitat de Barcelona) on polycrystalline samples (ca. 30 mg) 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.

Synthetic Methodology. Lanthanide trichloride hydrate $LnCl_3·6H_2O$ (Ln = Tb, Dy, Ho) and the ligand were taken into 30 mL of methanol and stirred at room temperature for 10 min during which time a clear solution was obtained. To this clear solution triethylamine was added dropwise, and the stirring was continued for a period of 24 h at room temperature. Then the solution was filtered off and evaporated under vacuum yielding a solid yellow residue. X-ray quality crystals were grown from the mixture of pyridine and benzene in a 5:1 ratio with hexane as the diffusing solvent at room temperature in two weeks time. All the crystals were characterized using standard analytical and spectroscopic techniques.

The stoichiometry and amounts of the reagents used are as follows.

1: $TbCl_3·6H_2O$ (0.20g, 0.535 mmol), H_3L (0.240g, 1.07 mmol), Et_3N (0.216g, 2.14 mmol). Yield: 0.18 g, 57.32%. Anal. Calcd for $C_{83}H_{100}O_{23}N_{10}Cl_3Tb_4$: C, 42.46%; H, 4.29%; N, 5.96%. Found: C, 42.51%; H, 4.36%; N, 6.07%. IR (KBr, cm^{-1}): 3413 (b), 2936 (w), 1632 (s),1462(s), 1445(w), 1303(m), 1243(m), 1226(m), 1084(m), 1056(w), 974(w), 859(w), 744(s), 618(m).

2: $DyCl_3·6H_2O$ (0.20g, 0.836 mmol), H_3L (0.238g, 1.06 mmol), Et_3N (0.214g, 2.12 mmol). Yield: 0.16 g, 51.11%. Anal. Calcd for $C_{83}H_{100}O_{23}N_{10}Cl_3Dy_4$: C, 42.20%; H, 4.27%; N, 5.93%. Found: C, 42.35%; H, 4.16%; N, 5.85%. IR(KBr, cm^{-1}): 3407(b), 2931 (w), 1637 (s),1462(s), 1435(w), 1303(m), 1243(m), 1221(m), 1045(m), 974(w), 859(w), 749(s).

3: $HoCl_3·6H_2O$ (0.20 g, 0.527 mmol), H_3L (0.237g, 1.05 mmol), Et_3N (0.213g, 2.10 mmol). Yield: 0.19 g, 60.89%. Anal. Calcd for $C_{83}H_{100}O_{23}N_{10}Cl_3Ho_4$: C, 42.03%; H, 4.24%; N, 5.90%. Found: C, 42.15%; H, 4.32%; N, 5.81%. IR (KBr, cm^{-1}): 3402(b), 2936 (w),

Table 2. Bond Length and Bond Angle Parameters for Compounds 1−3

	1 (Ln = Tb)	2 (Ln = Dy)	3 (Ln = Ho)
Ln1−O1	2.304(4)	2.304(4)	2.285(3)
Ln1−O2	2.271(4)	2.251(4)	2.246(4)
Ln1−O3	2.376(4)	2.377(4)	2.364(4)
Ln1−O14	2.404(5)	2.398(4)	2.377(4)
Ln1−N1	2.466(5)	2.458(5)	2.441(4)
Ln1−O16	2.509(5)	2.493(4)	2.488(4)
Ln1−O22	2.372(5)	2.364(4)	2.343(4)
Ln2−O3	2.402(4)	2.394(4)	2.381(4)
Ln2−O7	2.330(4)	2.324(4)	2.304(4)
Ln2−O8	2.406(5)	2.400(5)	2.391(4)
Ln2−O12	2.243(5)	2.224(4)	2.223(4)
Ln2−O15	2.403(6)	2.400(5)	2.381(5)
Ln2−N2	2.486(6)	2.474(5)	2.471(5)
Ln3−O1	2.451(4)	2.440(4)	2.423(3)
Ln3−O3	2.478(4)	2.454(4)	2.438(3)
Ln3−O6	2.347(4)	2.341(3)	2.328(3)
Ln3−O7	2.510(4)	2.501(4)	2.499(4)
Ln3−O10	2.330(4)	2.322(4)	2.310(4)
Ln3−O12	2.306(4)	2.294(4)	2.283(4)
Ln3−N3	2.503(5)	2.495(5)	2.482(4)
Ln4−O1	2.463(4)	2.444(4)	2.449(3)
Ln4−O9	2.617(4)	2.623(4)	2.613(3)
Ln4−O10	2.332(4)	2.317(4)	2.306(4)
Ln4−O20	2.468(4)	2.456(4)	2.442(4)
Ln4−N5	2.475(5)	2.471(5)	2.447(5)
Ln1−O1−Ln3	98.51(15)	98.17(13)	98.64(13)
Ln1−O14−Ln2	97.59(15)	97.67(14)	97.70(13)
Ln1−O7−Ln2	97.81(15)	98.03(13)	97.99(13)
Ln1−O3−Ln3	95.85(15)	95.85(13)	96.06(12)
Ln2−O12−Ln3	103.08(18)	103.35(16)	102.99(15)
Ln3−O1−Ln4	94.95(14)	95.21(12)	94.73(12)
Ln3− O10−Ln4	101.93(16)	102.07(14)	101.88(13)
Ln3−O6−Ln4	100.90(15)	100.69(13)	100.68(13)
O1−Ln1−O3	80.45(15)	80.21(13)	80.06(12)
O1−Ln3−O3	75.64(14)	76.08(12)	75.94(12)
O1−Ln3−O10	67.93(14)	67.57(12)	67.89(12)
O3−Ln1−O14	73.11(15)	73.12(12)	73.29(13)
O7−Ln2−O12	74.82(16)	74.70(14)	74.80(14)
O10−Ln4−O6	69.42(14)	69.35(12)	69.50(12)
Ln1···Ln2	3.578	3.564	3.543
Ln2···Ln3	3.562	3.545	3.526
Ln3···Ln4	3.621	3.607	3.584
Ln3···Ln1	3.603	3.586	3.571

1632 (s),1473(s), 1391(w), 1298(m), 1221(m), 1079(m), 1046(w), 969(w), 849(w), 734(s), 701(m).

X-ray Structure Determination. Single-crystal X-ray data collection for compounds **1**−**3** were carried out at 100(2) K on Bruker Smart Apex CCD area detector system (λ(Mo Kα) = 0.71073 Å) equipped with Oxford Cryo stream low temperature device and graphite monochromator. The data were reduced using SAINTPLUS, and the structures were solved using SHELXS-97 and refined using SHELXL-97.[30] The structures were solved by direct methods and refined by full-martix least-squares cycles on F^2. All non-hydrogen atoms were refined anisotropically.

■ RESULT AND DISCUSSION

Synthesis. The ligand controlled hydrolytic approach was employed for synthesis of **1**−**3**. Hydrated lanthanide salts were treated with a base in the presence of the liagnd to generate

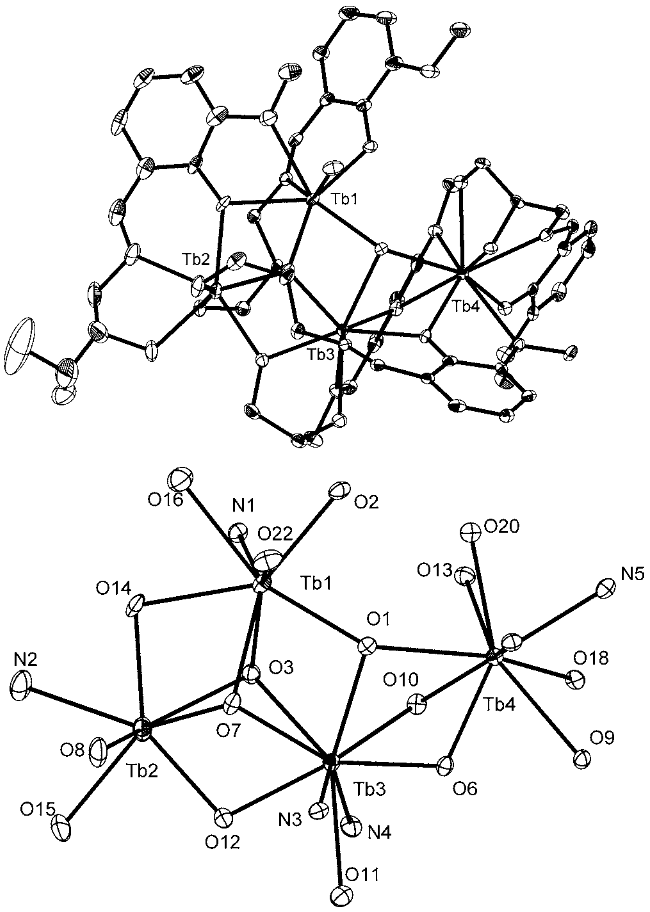


Figure 1. (a) Solid state structure of **1**; hydrogen atoms and solvents of crystallization are omitted for clarity. (b) Terbium oxo core of the cluster **1** omitting carbon and hydrogen atoms.

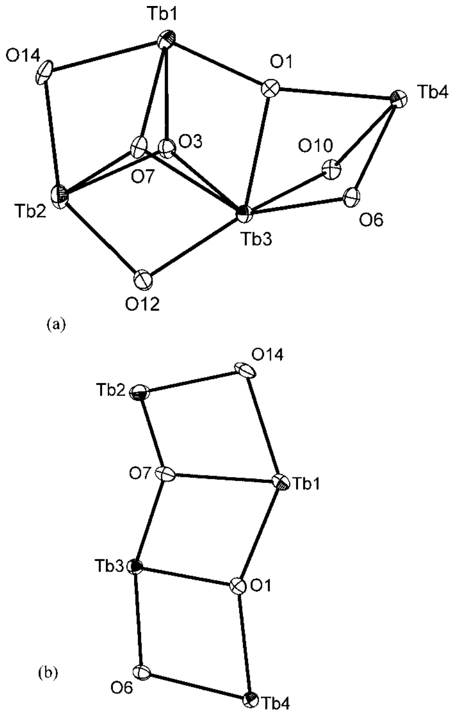
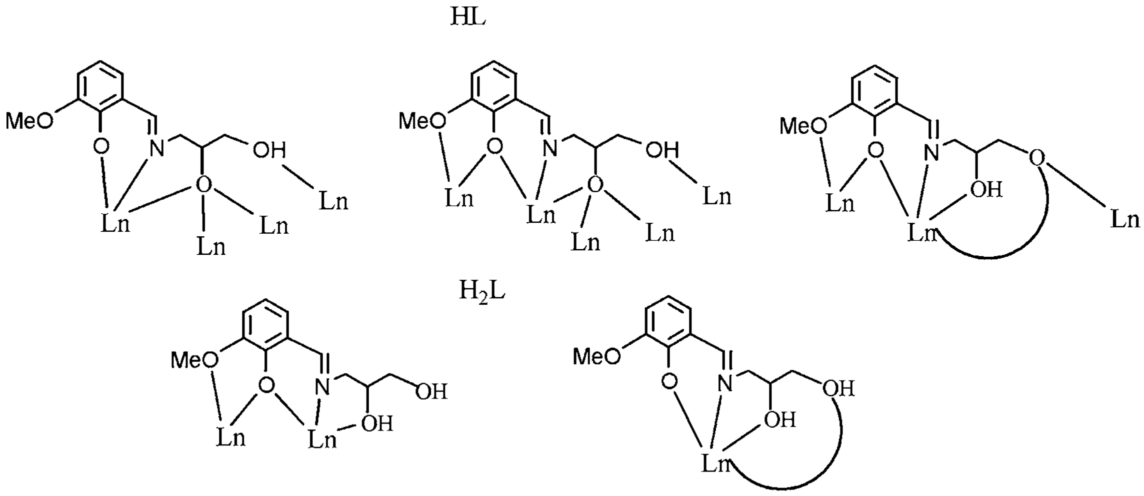


Figure 2. (a) Terbium oxo core of the cluster **1** omitting carbon and hydrogen atoms. (b) Ladder view of terbium oxo core of **1**.

Chart 1



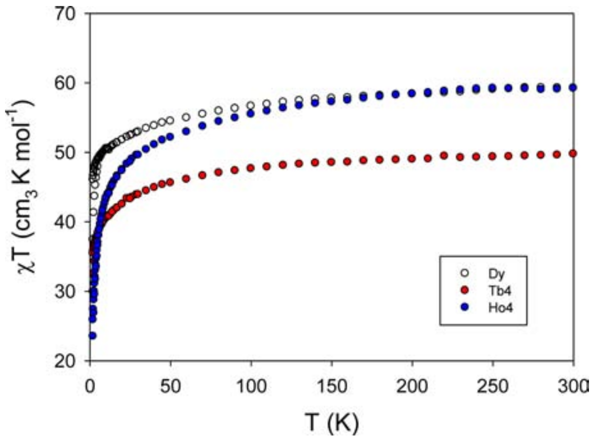


Figure 3. χT vs T plot for Ln_4 (Ln = Dy, Tb, and Ho) at 0.02 and 0.3 T.

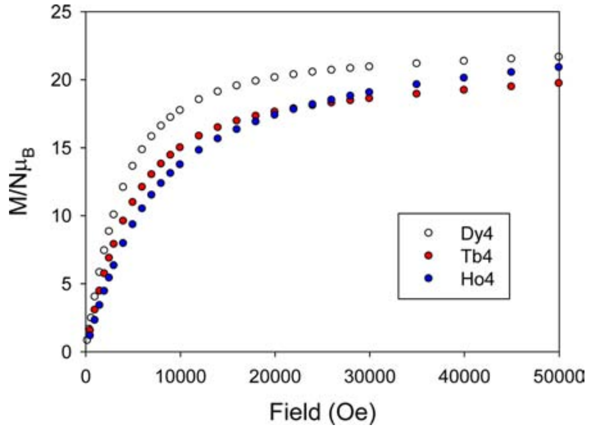


Figure 4. Magnetization vs field plot for Ln_4 (Ln = Dy, Tb, and Ho) at 2 K.

soluble and finite sized lanthanide oxo-hydroxo clusters. The lanthanide hydroxo clusters (Scheme 1) were synthesized by using a mixture of one equivalent lanthanide trichloride·hexahydrate ($LnCl_3 \cdot 6H_2O$, Ln = Tb (**1**), Dy (**2**), Ho (**3**)) and two equivalents of the ligand H_3L, followed by dropwise addition of four equivalents triethylamine (Et_3N) base in methanol as solvent. The triethylamine base abstracted the proton from ligand H_3L to form $[HEt_3N]Cl$, and as a result the deprotanated ligands of HL/H_2L readily chelate or bridge to the lanthanide ions. Further, the excess triethylamine base removes protons from coordinated water molecules of lanthanide chloride salt to form hydroxo bridges, which could bridge the lanthanide ions and make up the cluster core, while organic ligand groups HL/H_2L took up position the peripheral part of the resultant clusters.

X-ray quality yellow block-like crystals were grown from the solvent mixture of pyridine and benzene in 5:1 ratio with hexane or cyclochexane as diffusing solvent in 1−2 weeks at room temperature. **1**−**3** were characterized by standard analytical and spectroscopic techniques.

Description of the Crystal Structure. The solid state structures of compounds **1**−**3** were established by single crystal X-ray diffraction. X-ray data parameters for **1**−**3** are given in Table 1. Selected metric parameters of **1**−**3** are in Table 2. Structural elucidation revealed the formation of a new series of tetranuclear hydroxo clusters $[Ln_4(\mu_3\text{-}OH)(HL)_3(H_2L)_2(H_2O)]^{3+}$ where Ln = Tb (**1**), Dy (**2**), Ho(**3**). The clusters crystallize as a trication along with three chloride anions, five pyridines, 0.5 benzenes, and one water molecule in asymmetric unit. **1**−**3** crystallized in the triclinic space group $P\overline{1}$ with Z value of 2. Since the compounds are isostructural, **1** (Figure 1) is considered for discussion. The structure of **1** can be visualized in two ways. First, the metal oxo cluster core can be considered as a triangle consisting of Tb1, Tb2, and Tb3 atoms connected through oxygen atoms forming a puckered six-membered ring system. Of the oxygen atoms involved in the formation of this ring system, O14 and O12 are μ_2-bridging to the metals in the ring while the third oxygen O1 is μ_3-bridging, two to the metal atoms of the ring and the third coordination to the fourth metal atom (Tb4) present outside the ring system. Further the Tb_3O_3 cyclic ring is held together by two μ_3-bridging oxygen atoms which cap the six membered ring on both sides. The distance of these oxygen atoms (O3 and O7) from the plane defined by the six membered ring are 1.325 Å and 1.186 Å, respectively. The fourth metal Tb4 is connected to Tb3 by a μ3-bridging oxygen and two μ_2-bridging oxygen atoms leading to the formation of a Tb_2O_3 subunit. The overall structure of the metal cluster core can be considered as a fusion of the Tb_3O_5 and the Tb_2O_3 units through a Tb−O edge (Figure 2a). Tb1 and Tb2 are eight coordinate while Tb3 and Tb4 are nine coordinate. Another way of visualizing the metal oxo cluster core is the formation of a *ladder* type core builds up of three Tb_2O_2 rings fused along two Tb−O edges (Figure 2b). Five H_3L ligands build up the peripheral part of the cluster. On the basis of the coordination modes observed they are clearly of two types. Three of those ligands are present in dianionic forms which are denoted by HL, and two are present in monoanionic form (denoted by H_2L). These ligands display chelating and chelating−bridging modes of coordination. The various binding modes of the ligand are shown in Chart 1.

Magnetism Studies. Magnetic susceptibility data were collected at applied dc fields of 0.02 and 0.3 T on crushed crystalline samples of the Ln4 complexes between 2 and 300 K. The data are shown in Figure 3 as a χT vs T plots (white, Dy_4; red, Tb_4; blue, Ho_4). The susceptibility is not field dependent. The χT product has a value of 59 cm^3 K mol^{-1} at 300 K, for Dy_4 and Ho_4 complexes in agreement with the expected value of 56 cm^3 K mol^{-1} for four noninteracting Dy(III) ions ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $J = 15/2$, and $g_J = 4/3$) or Ho(III) ions $^5I_8$, $S = 2$, $L = 6$, $J = 8$, and $g_J = 10/8$) and a value of 49 cm^3 K mol^{-1} at 300 K for Tb4, in agreement with that expected for four noninteracting Tb(III) ions ($^7F_6$, $S = 3$, $L = 3$, $J = 6$, and $g_J = 3/2$);[7a] as temperature decreases, so does the χT product, until below 50 K a sharp decrease to a χT value of 37 cm^3 K mol^{-1} for Dy4, 29 cm^3 K mol^{-1} for Tb4, and 23 cm^3 K mol^{-1} for Ho4 is observed, indicating the depopulation of the excited Stark sublevels. The exchange interaction between the Dy(III) centers is very weak, and the behavior of the coordination complexes resembles that of isolated Ln(III) ions in the high temperature region. The magnetization vs field was studied at 2 K, and the results are shown in Figure 4. The magnetization shows a rapid increase at the low fields, which eventually reaches 22 μB at 2 K and 5 T for Dy_4, 21 μB at 2 K and 5 T for Ho_4, and 19 μB at 2 K and 5 T for Tb_4. These values are lower than the expected saturation value for four Dy(III), four Tb(III), or four Ho(III)) ions most likely due to anisotropy and important crystal field effects[31] at the Ln(III) ions that eliminate degeneracy of the ground state. ac magnetic susceptibility data of the samples (**1**−**3**) were collected, and only the Dy_4 cluster showed a signal in the out-of-phase ac susceptibility, indicating slow relaxation of the magnetization. The data are shown in Figure 5. Clearly, as the in-phase ac magnetic susceptibility decreases, the out-of-phase signal increases and a peak is seen in the out-of-phase ac magnetic susceptibility that is frequency dependent. Thus, a slow relaxation process takes place in the sample, which in turn could be related to the single-ion effects observed in Ln(III) ions like Dy(III) or to long-range order. The peak appears too close to 1.8 K, the limit temperature of our commercial SQUID magnetometer; thus, the dynamics of the relaxation process cannot be properly assessed. Dy_4 could be a new example of a polynuclear Ln(III) SMM. The behavior is similar to some earlier reports in literature.[32,6a,k,23a,21e]

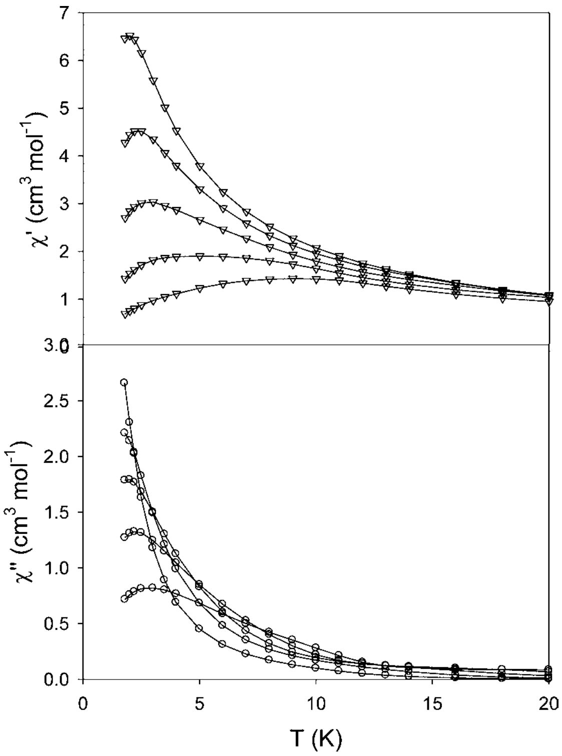


Figure 5. In-phase (top) and out-of-phase ac magnetic susceptibility for Dy_4 at 1500, 426, 121, 35, and 10 Hz oscillating field frequencies. The solid lines are only a guide for the eye.

■ CONCLUSION

In summary, a series of isostructural tetranuclear lanthanide hydroxo cluters using *o*-vanillin based Schiff bases as ligands have been synthesized and structurally characterized. Dy_4 cluster shows slow magnetic relaxation in very low temperatures as shown by frequency dependent ac susceptibility magnetic measurement studies.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

IR, TGA plots, and PXRD patterns for compounds **1**−**3** and ORTEPs of compounds **2** and **3** are given. Crystallographic file. 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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