

# Dy<sub>2</sub> and Dy<sub>4</sub> hydroxo clusters assembled using o-vanillin based Schiff bases as ligands and b-diketone co-ligands: Dy<sub>4</sub> cluster exhibits slow magnetic relaxation

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## abstract

The reaction of DyCl<sub>3</sub>·6H<sub>2</sub>O with the mixed ligand system consisting of o-vanillin based Schiff base ligand H<sub>2</sub>L [2-(2-hydroxy-3-methoxybenzylideneamino) phenol], dibenzoylmethane (Ph<sub>2</sub>acac) and acetylacetonate (Acac) in the presence of triethylamine as the base afforded, di and tetranuclear dysprosium hydroxo clusters having formulae [Dy<sub>2</sub>(L)<sub>2</sub>(Ph<sub>2</sub>acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>3</sub> (1) and [Dy<sub>4</sub>(L)<sub>4</sub>(acac)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(C<sub>6</sub>H<sub>5</sub>N)<sub>4</sub>] (2) respectively. The solid state structures of these products were established by Single Crystal X-ray diffraction technique. Magnetism studies reveal Dy<sub>4</sub> exhibits slow magnetic relaxation behavior.

## 1. Introduction

Since the isolation of first Single Molecule Magnet (SMM) based on lanthanides in 2003 by Ishikawa et al. [1] continuous efforts are going on to synthesize lanthanide based SMMs due to their potential applications in high density data storage [2], quantum computing [3], spintronics [4], magnetic cooling at low temperatures [5]. Till date, many of the pure mononuclear (SIMs) [6] and polynuclear 4f based SMMs [7] have been isolated with heavier metals like Tb, Dy, and Ho. However, molecular compounds SMMs based on dysprosium have been used to synthesize SMMs possessing high-energy barriers ( $U_{\text{eff}}$ ) and high blocking temperatures (TB)

compare to the 3d [8] and 3d-4f [9] based SMMs, because of large Ising-type magnetic anisotropy of Dy<sup>III</sup> ion and also due to the large magnetic moment of Kramers ground state (<sup>6</sup>H<sub>15/2</sub>) [10]. In recent years large number of dysprosium based SMMs have been reported with nuclearity ranging from Dy1-11 [6,11,12] and Dy26 [13]. Among these SMMs tetranuclear Dy-SMMs with different structural topologies have received special attention since they have been displaying high energy barrier for magnetic relaxation

pathways. For example, a centrosymmetric defect dicubane [Dy<sub>4</sub>(m<sub>3</sub>-OH)<sub>2</sub>(bmh)<sub>2</sub>(msh)<sub>4</sub>Cl<sub>2</sub>](bmh: 1, 2-bis(2-hydroxy-3-methoxybenzylidene) hydrazine, msh: 3-methoxysalicylaldehyde hydrazine) is found to show remarkably large anisotropic barrier of 170 K [12n]. Recently a potassium doped oxo centered octahedral dysprosium cluster [Dy<sub>4</sub>K<sub>2</sub>O(O-tBu)<sub>12</sub>] was reported for its record highest energy barrier of 842 K [12o] for reversal of spin magnetization. The above examples brings inquisitiveness among various experimental chemists to synthesize novel tetranuclear Dy based (SMM) molecules with higher anisotropic barriers and blocking temperatures. Further 4f-element based dinuclear N<sub>2</sub> radical bridged terbium complex [K(18-crown-6)(THF)<sub>2</sub>][{(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>2</sub>(THF)Tb)<sub>2</sub>(**1-g**<sup>2</sup>:g<sup>2</sup>-N<sub>2</sub>)] has shown SMM behavior with blocking temperature of 13.9 K [12p]. Very recently Goodwin and coworkers have reported a mononuclear dysprosium complex [Dy(Cp<sup>III</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] [6q] {(Cp<sup>III</sup>=C<sub>5</sub>H<sub>2</sub>-tBu<sub>3</sub>-1,2,4, tBu=C(CH<sub>3</sub>)<sub>3</sub>} that exhibits blocking temperature up to 60 K and an effective energy barrier for magnetization reversal ( $U_{\text{eff}}$ ) 1760 K. Most of the lanthanide based hydroxo complexes/clusters have been mainly synthesized via a well-established ligand controlled hydrolytic approach [14], in which lanthanide salts in organic solvents is treated with a base in the presence of suitable coordinating approach a large number of lanthanide oxo-hydroxo clusters have been reported with nuclearity ranging

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$\text{Ln}_2\text{-60}$  [6,11,12,13] by the utilization of wide variety of ligand systems like beta diketones [14c–e,15], carboxylates [16], alkoxides [17], aminoacids [18], Schiff bases [19] and *o*-vanillin based Schiff bases [20]. However, isolation of lanthanide oxo-hydroxo clusters involving two different ligand systems is slightly difficult compared to that of transition metal complexes because of their stereochemical preferences, high coordination number and formation of insoluble polymers. Recently, interesting results regarding isolation of novel lanthanide oxo-hydroxo clusters have been achieved by using mixed ligand systems with lanthanide salts, for example, b-diketones with orthonitrophenols [ $\text{Ln}_2(\text{OH})_4(\text{Ph}_2\text{acac})_7(\text{o-O}_2\text{N-C}_6\text{H}_4\text{-O})_3\text{Cl}$ ]-( $\text{Ln} = \text{Er, Tm}$ ;  $\text{o-O}_2\text{N-C}_6\text{H}_4\text{O} = \text{o-nitro-phenolate}$ )[15 g] and b-diketones with amino acids [ $\text{Y}_5(\text{OH})_5(\text{a-AA})_4(\text{Ph}_2\text{acac})_6$ ] ( $\text{a-AA} = \text{D-phenyl glycine, L-proline, L-valine, and L-tryptophan}$ ;  $\text{Ph}_2\text{acac} = \text{dibenzoylmethane}$ ) [18i] has opened up many interesting possibilities. In another recent report, a hexanuclear lanthanide hydroxo cluster  $\{[\text{Ln}_6(\text{teaH})_2(\text{teaH}_2)_2(\text{CO}_3)(\text{NO}_3)_2(\text{chp})_7(\text{H}_2\text{O})]^+$  ( $\text{Ln} = \text{Gd, Dy, Tb}$ .  $\text{tea} = \text{triethanolamine}$ ,  $\text{chp} = 6\text{-chloro-2-hydroxypyridine}$ ); [11q] containing triethanolamine and 6-chloro-2-hydroxy pyridine ligand systems has been reported. Some of these complexes have shown interesting structural and magnetic properties. Reaction of lanthanide salts independently with various Schiff bases and b-diketones have been thoroughly investigated yielding fascinating structural diversities and remarkable physical properties [15,19,20] being inspired by these results, *o*-vanillin based Schiff base ( $\text{H}_2\text{L}$ ), and b-diketones dibenzoylmethane ( $\text{Ph}_2\text{-acacH}$ )/acetylacetone ( $\text{acacH}$ ) as mixed ligand systems were used to assemble dysprosium hydroxo clusters and the results are reporting here.

## 2. Experimental section

### 2.1. Materials and physical measurements

The dysprosium trichloride hexahydrate was synthesized from corresponding oxide by neutralizing with concentrated HCl, followed by evaporation to dryness. Ligand  $\text{H}_2\text{L}$  [2-(2-hydroxy-3-methoxybenzylideneamino) phenol], was prepared based on reported procedure [28]. Common organic solvents, dibenzoylmethane, acetylacetone 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. Magnetic measurements were carried out on polycrystalline samples (circa 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.

### 2.2. Synthesis

Dysprosium trichloride hexahydrate  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ , the ligands  $\text{H}_2\text{L}$ ,  $\text{Ph}_2\text{acacH}$  (for 1) and  $\text{H}_2\text{L}$ ,  $\text{AcacH}$  (for 2) were taken into 30 mL of methanol/acetonitrile (1:1) mixture and stirred at room temperature for 10 min during which time a clear solution was obtained. To this clear solution triethylamine was added drop wise which resulted in a yellow clear solution and the stirring was continued for a period of 20 h at room temperature. The yellow precipitate obtained was filtered and dried in air. X-ray quality crystals were grown from mixture of pyridine and toluene diffused by hexane at room temperature in two weeks' time. The compounds 1–2 were characterized using standard analytical and spectroscopic

techniques. The stoichiometry and amounts of the reagent used are as follows.

1:  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.20 g, 0.530 mmol),  $\text{H}_2\text{L}$  (0.128 g, 0.530 mmol),  $\text{Ph}_2\text{acac}$  (0.118 g, 0.530 mmol) and  $\text{Et}_3\text{N}$  (0.160 g, 1.59 mmol), Yield: 0.18 g, 52.63%. Anal. Calcd for  $\text{C}_{174}\text{H}_{144}\text{N}_6\text{O}_{36}\text{Dy}_6$ : C, 54.00%; H, 3.75%; N, 2.17%. Found: C, 54.13%; H, 3.65%; N, 2.21%. IR (KBr,  $\text{cm}^{-1}$ ): 3606 (m), 3057(m), 1600(s), 1545(s), 1518(s), 1479(s), 1452(m), 1392(s), 1304(m), 1283(s), 1216(s), 1178(m), 1063(m), 822(s), 734(s).

2:  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.300 g, 0.796 mmol),  $\text{H}_2\text{L}$  (0.193 g, 0.796 mmol),  $\text{acac}$  (0.0796 g, 0.796 mmol) and  $\text{Et}_3\text{N}$  (0.24 g, 2.38 mmol); Yield: 0.25 g, 53.30%. Anal. Calcd for  $\text{C}_{76}\text{H}_{74}\text{N}_6\text{O}_{20}\text{Dy}_4$ : C, 44.71%; H, 3.65%; N, 4.12%. Found: C, 44.85%; H, 3.58%; N, 4.21%. IR(KBr,  $\text{cm}^{-1}$ ): 3600(s), 1600(s), 1578(w), 1540(m), 1474(m), 1381(s), 1293(m), 1216(s), 1172(s), 1079(m), 959(m), 867(s), 811(s), 729(s).

### 2.2.1. X-ray structure determination

Single-crystal X-ray data collection for compounds 1–2 were carried out at 100(2) K on Oxford CCD X-ray diffractometer (Yarnton, Oxford, UK) equipped with Mo K $\alpha$  radiation ( $k = 0.71073 \text{ \AA}$ ) source. Data reduction was performed using CrysAlisPro 171.33.55 software [29]. The structures were solved using SHELXS-97 and refined using SHELXL-2014/7 [30]. All non-hydrogen atoms were refined anisotropically.

## 3. Results and discussion

### 3.1. Synthesis

The compounds 1–2 were synthesized by using well established ligand controlled hydrolytic approach, in which lanthanide salts are treated with a base in the presence of suitable organic ligands to generate soluble and finite sized lanthanide oxo-hydroxo clusters. In the present study the aforementioned method was employed to obtain dysprosium hydroxo clusters by using Schiff base and b-diketone as mixed ligand system (Chart 1). The dysprosium hydroxo clusters (Scheme 1) were synthesized by using mixture of one equivalent dysprosium trichloride hexahydrate ( $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ ), one equivalent of the Schiff base ligand  $\text{H}_2\text{L}$  and one equivalent of b-diketone ( $\text{Ph}_2\text{acacH}$  for 1,  $\text{AcacH}$  for 2) followed by drop wise addition of three equivalents triethylamine ( $\text{Et}_3\text{N}$ ) base in methanol/acetonitrile as solvent. The reaction mixture was stirred for period of 20 h at room temperature and filtered to isolate the precipitate. Triethylamine removes proton from the ligand  $\text{H}_2\text{L}$  and b-diketone to form  $[\text{HEt}_3\text{N}]\text{Cl}$ . As a result dianionic Schiff base ligand ( $\text{L}^{2-}$ ) and monoanionic b-diketone ligand ( $\text{Ph}_2\text{-acac}^{1-}/\text{acac}^{1-}$ ) ready to chelate or bridge the dysprosium ions are formed. Further the excess triethylamine deprotonates coordinated water molecules of dysprosium chloride salt to form hydroxo bridges which is responsible for the building up of cluster core via bridging the dysprosium metal ion centers. X-ray quality yellow block like crystals were grown from solvent mixture of pyridine and toluene in 1:1 ratio with hexane as diffusing solvent in 1–2 weeks at room temperature. Compounds 1–2 were characterized by standard analytical and spectroscopic techniques. In the IR spectra of 1–2 a strong peak around  $1620 \text{ cm}^{-1}$  indicates presence of coordinated imine ( $-\text{C}=\text{N}$ ) nitrogen to metal centers. A broad peak around  $3000\text{--}3600 \text{ cm}^{-1}$  represents presence of hydroxyl groups in the structure. A peak at around  $1220 \text{ cm}^{-1}$  indicates ( $-\text{C}-\text{O}$ ) coordination through the phenolic oxygen atom. A peak at  $1595\text{--}1610 \text{ cm}^{-1}$  corresponds to  $\text{C}-\text{O}$  stretch in coordinated b-diketone (Chart 2).

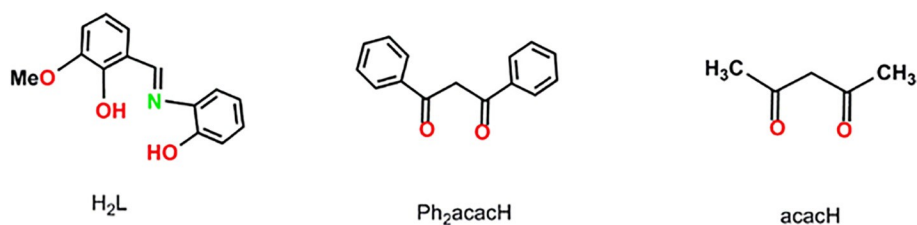
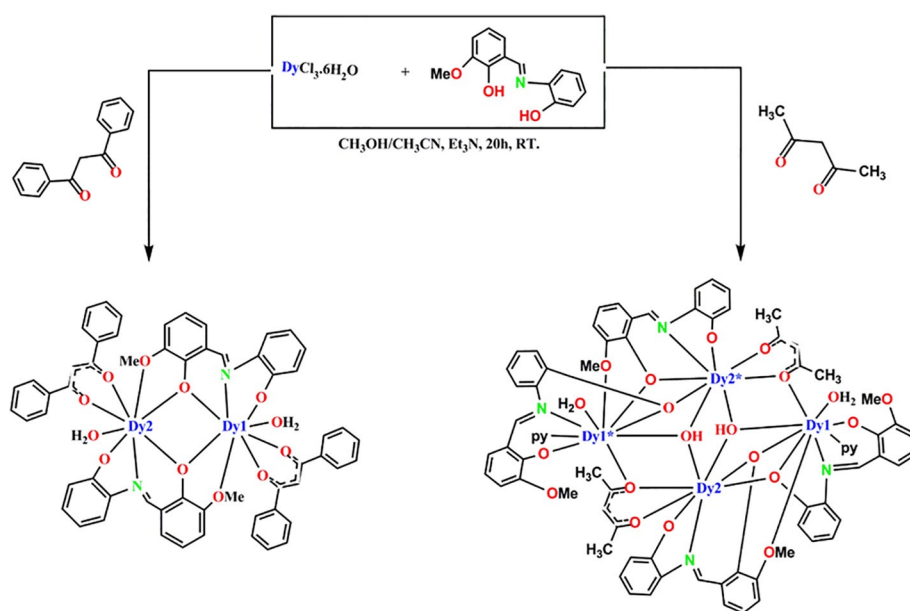


Chart 1. Ligands used.



Scheme 1. Synthesis of 1 and 2.

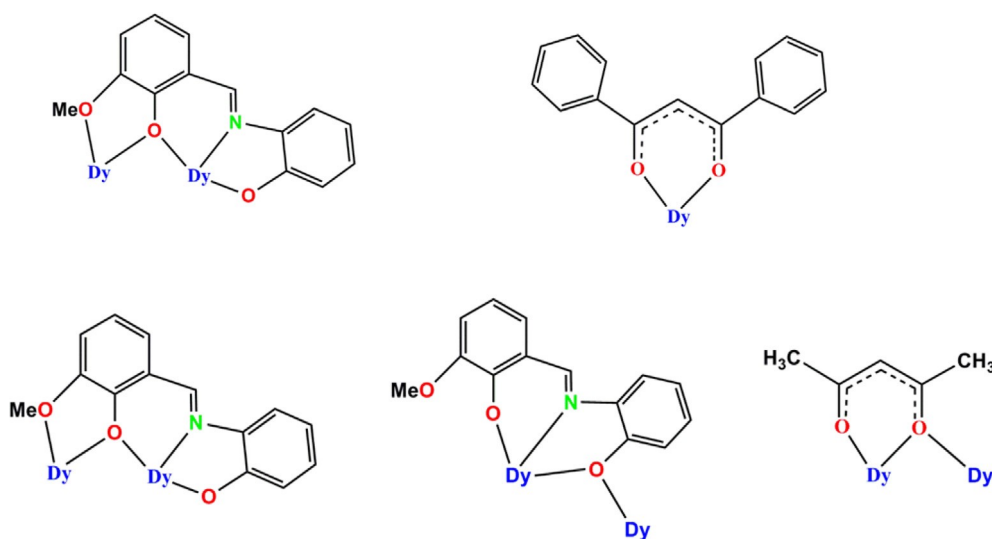


Chart 2. Binding modes of ligands in the compound 1 and 2.

### 3.2. Description of the crystal structure

The solid state structures of compounds 1–2 were established by single crystal X-ray diffraction. X-ray data parameters and selected metric parameters for 1 and 2 are given in Tables 1 and 2.

### 3.3. Dinuclear dysprosium cluster (1)

Single crystal X-ray analysis reveals the formation of a neutral dinuclear dysprosium hydroxo cluster  $[\text{Dy}_2(\text{L})_2(\text{Ph}_2\text{acac})_2(\text{OH})_2]_3$ , which crystallized in triclinic space group  $P\bar{1}$  (Fig. 1). In the

Table 1  
Crystallographic data and structural refinement for compounds 1 and 2.

	1	2
Formula	3(C <sub>58</sub> H <sub>44</sub> N <sub>2</sub> O <sub>12</sub> Dy <sub>2</sub> ) 14py. 2H <sub>2</sub> O	C <sub>96</sub> H <sub>94</sub> N <sub>10</sub> O <sub>20</sub> Dy <sub>4</sub>
Fw.g mol <sup>-1</sup>	5013.37	2357.81
Cryst syst	triclinic	triclinic
Cryst size.mm	0.30 X 0.22 X 0.14	0.18 X 0.14 X 0.10
Space group	P-1	P-1
<i>Unit cell dimensions</i>		
a (Å)	13.3006(5)	12.341(3)
b (Å)	13.5253(4)	13.614(3)
c (Å)	34.0280(10)	15.155(3)
a (°)	93.118(2)	98.28(3)
b (°)	91.605(3)	108.83(3)
c (°)	118.562(4)	106.47(3)
v, Å <sup>3</sup>	5358.3(4)	2231.6(8)
Z	1	1
Dcacl.d.Mgm <sup>-3</sup>	1.554	1.754
T.K	100(2)	100(2)
<i>I</i> (mm <sup>-1</sup> )	2.146	3.388
F(000)	2522	1164
h (0)	2.845 to 26.000	2.644 to 26.372
No. of. refln colled	39 107	16 859
Completeness to h max (%)	99.9	99.9
No. of. indep refln/R <sub>int</sub>	21 051(0.0487)	9102(0.0522)
GooF (F <sup>2</sup> )	1.077	1.041
R <sub>1</sub> (F) (I > 2σ(I))	0.0546	0.0477
wR <sub>2</sub> (F <sup>2</sup> ) (All data)	0.1017	0.1024
Largest diff peak/hole (e Å <sup>-3</sup> )	2.915/−2.103	2.446/−1.149

Table 2  
Bond length and bond angle parameters for compound 1 and 2.

1		2	
Dy1-O1	2.325(4)	Dy1-O1	2.423(4)
Dy1-O2	2.254(4)	Dy1-O2	2.407(4)
Dy1-O6	2.384(4)	Dy1-O4*	2.477(4)
Dy1-O7	2.386(4)	Dy1-O7	2.202(4)
Dy1-O8	2.514(4)	Dy1-O8	2.639(4)
Dy1-N1	2.491(4)	Dy1-O10	2.452(5)
Dy2-O1	2.372(4)	Dy1-N1	2.537(6)
Dy2-O7	2.315(4)	Dy1-N3	2.596(6)
Dy2-N2	2.512(4)	Dy2-O1	2.338(4)
Dy2-O12	2.379(4)	Dy2-O1*	2.327(4)
Dy1-O1-Dy2	105.59(14)	Dy2-O2	2.328(4)
O1-Dy1-N1	75.20(14)	Dy2-O4	2.392(4)
O4-Dy1-O5	75.75(13)	Dy2-N2	2.529(5)
O6-Dy1-O7	80.73(13)	Dy1-O1-Dy2	97.83(16)
O7-Dy1-O8	64.17(12)	Dy1-O2-Dy2	98.59(14)
O10-Dy2-O11	73.14(13)	Dy1-O6-Dy2	98.43(17)
Dy1.....Dy2	3.374	Dy1-O1-Dy2*	111.90(16)
		Dy2-O1-Dy2*	107.52(16)
		Dy2-O4-Dy1*	107.87(15)
		O1-Dy1-O2	67.34(14)
		O1-Dy2-O2	70.06(14)
		O1-Dy2-O1*	72.48(16)
		O1*-Dy2-O4	71.11(14)
		O1-Dy1-O4*	68.11(13)
		O2-Dy1-O6	66.50(14)
		Dy1.....Dy2	3.589(11)
		Dy1.....Dy2*	3.936(10)

\* Represents symmetry generated atom.

asymmetric unit one full dysprosium dimer, one half dimer, one water molecule and seven solvent pyridine molecules and were crystallized. The dimeric metal phenoxo core (Dy<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub>) is surrounded by two Schiff base ligands (L) and two dibenzoylmethane (Ph<sub>2</sub>acacH) ligands with each metal center being eight coordinate. The coordination sphere of each dysprosium metal ion is [DyO<sub>7</sub>N]. Each Schiff base ligand serves as tetra dentate chelate to dysprosium atoms through two phenoxide oxygens, one imine

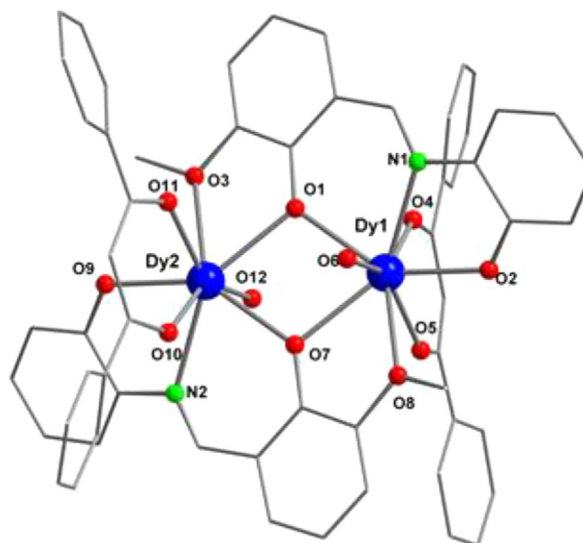


Fig. 1. The solid state structure of 1; hydrogen atoms and solvents of crystallization are omitted for clarity.

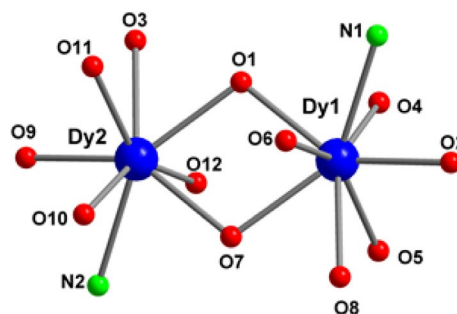


Fig. 2. The dysprosium oxo core of the cluster 1 omitting carbon and hydrogen atoms.

nitrogen and one methoxy oxygen atom. Dy1 and Dy2 atoms are bridged through a phenoxide oxygen atom of each Schiff base ligand leading to the formation of a four membered Dy<sub>2</sub>(μ<sub>2</sub>-O)<sub>2</sub> core. The bond angle of Dy1-O1-Dy2 is 105.60 (14) and bond lengths of Dy1-O1, Dy2-O7, Dy1-N1 and Dy1-Dy2 are 2.325(4) Å, 2.315(4) Å, 2.491(4) Å and 3.741(5) Å respectively. Each dibenzoylmethane is again chelated to a dysprosium atom, further one water molecule coordinated to each metal center. These bond lengths and bond angles fall within the range reported for dinuclear complexes of lanthanides [Ln<sub>2</sub>(HL)<sub>2</sub>(H<sub>2</sub>L)(NO<sub>3</sub>)(py)(H<sub>2</sub>O)] [(Ln = Y, Ce-Nd, Sm-Yb)] [21] [Dy<sub>2</sub>(ovph)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] [22] (Fig. 2).

### 3.4. Tetranuclear dysprosium cluster (2)

Compound 2 crystallize in the triclinic space group P-1 with the asymmetric unit containing half the cluster which lies on inversion centre (Fig. 3). The asymmetric unit consists of dysprosium dimer coordinated to two Schiff base ligands (L), one acetylacetonate ligand (acac), one oxygen, one water molecule and one coordinated pyridine solvent molecule as well as two non-coordinated pyridine solvent molecules. On a whole the dysprosium metal core made up four Dy<sup>III</sup> ions (Dy1, Dy2 and their symmetry equivalents Dy1<sup>+</sup>, Dy2<sup>+</sup>). The four dysprosium ions of cluster core are lies on almost same plane (RMS D/A = 0) and exhibits a planar butterfly type structural topology. The metal centers Dy2, its symmetry

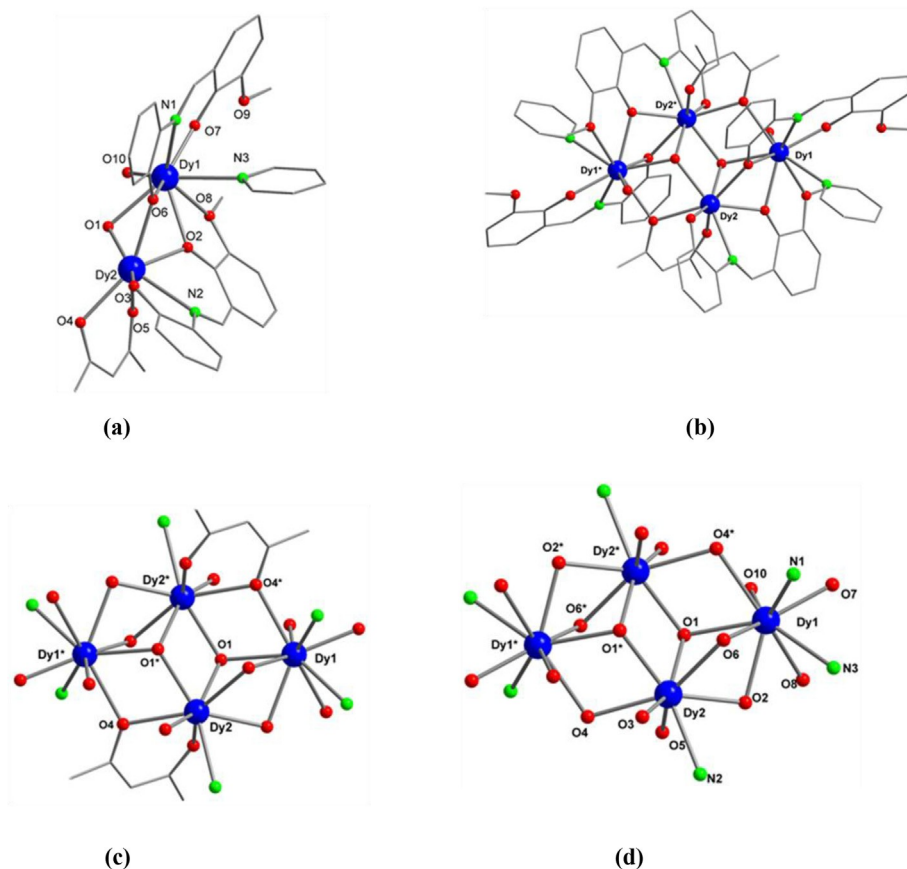


Fig. 3. (a) Asymmetric unit of 2 (b) Full structure of 2; hydrogen atoms and solvents of crystallization are omitted for clarity, (symmetry code) 1-x, 1-y, -z. (c) the dysprosium oxo core with acetylacetonate (acac) ligands. (d) The dysprosium oxo core of the cluster 2, omitting carbon and hydrogen atoms.

equivalent  $Dy2'$  defining the hinge or body of the butterfly and  $Dy1$ , its symmetry equivalent  $Dy1'$  defines the wing tips of butterfly motif. The two parts body and wing tips of butterfly core is connected through the two  $m_3$ -OH bridges. The two  $m_3$ -hydroxy ligands are displaced above and below the plane (defined from four  $Dy1$ ,  $Dy1'$ ,  $Dy2$  and  $Dy2'$  dysprosium metal ions) by 0.917(3) Å. The peripheral part of the metal hydroxo core is surrounded by four Schiff base ligands and two acetylacetonate ligands via bridging and chelation mode of binding.  $Dy2$  is connected through  $Dy1$  via two phenoxide oxygens (O2 and O6) of two independent Schiff base ligands.  $Dy2$  metal center further coordinated to one hydroxide ion (O1) and one deprotonated acetylacetonate ligand (O4, O5). The hydroxide ion O1 and O4 of acetylacetonate are responsible for the symmetry generation of full molecule. The bond distances of  $Dy2-O1$  and  $Dy1-O1$  are 2.338(4) Å and 2.423(4) Å respectively. Bond angles of  $Dy2-O1-Dy2'$ ,  $Dy2-O1-Dy1$ ,  $Dy2-O2-Dy1$ , and  $Dy2-O4-Dy1'$  are 111.900 (16), 97.830 (16), 98.590 (14) and 107.870 (15) respectively. The bond distances between metal centers  $Dy1-Dy2$ ,  $Dy1-Dy2'$  are 3.589(11), 3.936(10) Å respectively. The central two dysprosium ions  $Dy2$  and  $Dy2'$  are eight coordinate (seven oxygens, one nitrogen) and display distorted antiprismatic geometry. The outer two dysprosium ions  $Dy1$  and  $Dy1'$  are nine coordinate (seven oxygens, two nitrogen) exhibit distorted tricapped trigonal prismatic geometries. The bond lengths and bond angles of compound 2 are fall in the range of recently reported planar tetranuclear lanthanide hydroxo clusters. examples:  $[Dy_4(l_3-OH)_2(hmmpH)_2(hmmp)_2(Cl)_4]$ ,  $[Dy_4(l_3OH)_2(hmmpH)_2(-hmmp)_2(N_3)_4]\{hmmpH_2 = 2-[(2-hydroxyethylimino)methyl]-6-methoxyphenol\}$  [20a]  $[Ln_4(m_3-OH)_2(o-van)_4(O_2CC(CH_3)_3)_4(NO_3)_2]$  ( $Ln = Gd, Dy$ ) ( $o-van = 3$ -methoxysalicylaldehydato anion)] [23]

and  $[Ln_4(l_3-OH)_2(mdeaH)_2(piv)_8]$  ( $mdeaH_2 = N$ -methyldiethanolaamine;  $piv =$  pivalate;  $Ln = Tb, Dy, Ho, Er, Tm$ ) [24].

### 3.5. Magnetism studies

Magnetic susceptibility data were collected at an applied field of 3000 Oe in the 2–300 K temperature range for samples 1 and 2. The data for 1 are shown in Fig. 4 as a  $\chi T$  versus T plot. The  $\chi T$  product has a value at 300 K of 29.86  $cm^3 K mol^{-1}$ , in agreement with the theoretical value for two isolated  $Dy(III)$  ions ( ${}^6H_{15/2}$ ,  $S = 5/2$ ,  $L = 5$ ,  $J = 15/2$  and  $g_J = 4/3$ ) [25]. As temperature

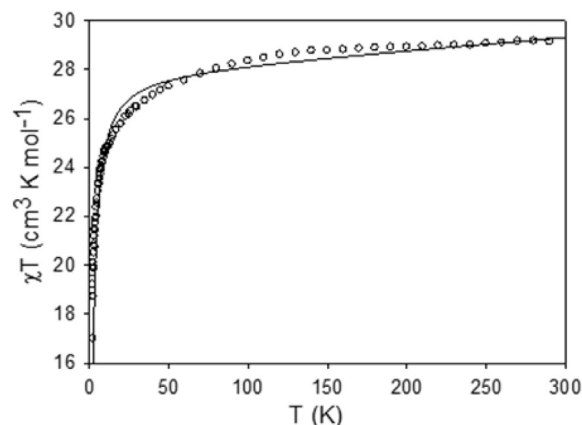


Fig. 4.  $\chi T$  vs. T plot for 1 ( $Dy_2$ ) at 3000 Oe applied dc field.

decreases, the  $\nu T$  product decreases slightly until below 50 K the decrease is more acute.  $\nu T$  product reaches a value of  $17 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. The decrease can be ascribed to the depopulation of the Stark sublevels of the two Dy ions, as well as some weak anti ferromagnetic interaction through the two monoatomic oxo bridges. The data were fitted to a dinuclear model of two Dy(III) centers with strong spin-orbit coupling and a small exchange interaction between them using the software PHI [26]. The best fit is shown in Fig. 4 as a solid line and the fitting parameters were the exchange constant  $J = -0.25 \text{ cm}^{-1}$  and an orbital reduction parameter of  $r = 1.25$ . As expected for lanthanide ions, the exchange coupling is very weak, resulting in a  $S = 0$  ground state which is not isolated from the next excited states. This is reflected in the magnetization versus field plot, (Fig. 5) which shows the Zeeman population of an excited state at 2 K. AC magnetic susceptibility data show that 1 is not an SMM since out-of-phase signals are not observed.

The data for 2 are shown in Fig. 6 as a  $\nu T$  versus T plot. The  $\nu T$  product has a value at 300 K of  $58 \text{ cm}^3 \text{ K mol}^{-1}$ , in agreement with the theoretical value for four isolated Dy(III) ions ( ${}^6\text{H}_{15/2}$ ,  $S = 5/2$ ,  $L = 5$ ,  $J = 15/2$  and  $g_J = 4/3$ ).<sup>1</sup> As temperature decreases, the  $\nu T$  product decreases slightly until below 15 K the decrease is more acute.  $\nu T$  product reaches a value of  $22 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. As in 1, the decrease can be ascribed to the depopulation of the Stark sublevels of the two Dy ions, as well as weak antiferromagnetic interaction between the Dy(III) ions. The central unit in 2 is geometrically very similar to 1, and thus a weak antiferromagnetic exchange as that found in 1 is expected. The two central Dy(III) ions will be in turn coupled to the wing-tip Dy(III), and by examination of the structural parameters this coupling should also be weak and antiferromagnetic: this situation would lead to a spin frustrated system. The magnetization versus field behavior for complex 2 is shown in Fig. 7 at 2 K. AC susceptibility data were collected for both samples with a 4 Oe oscillating field at frequencies between 100 and 1500 Hz.

For 2 the data are shown in Fig. 8. Two clear relaxation processes can be seen in the ac magnetic susceptibility plot. As the in-phase susceptibility drops around 20 K a rise is observed in the out-of-phase plot, and this overlaps with a second relaxation process centered at 5 K. Both processes are strongly frequency dependent, as expected if the relaxation is of molecular origin. Due to the very weak coupling expected in 2, it is probable that the two relaxation processes observed are related to the fact that there are two very distinct types of Dy(III) ions in the structure, with different coordination environment and thus, different electronic properties. The central unit Dy(III) ions are octacoordinated (seven O, one N), while the wing-tip Dy(III) ions are

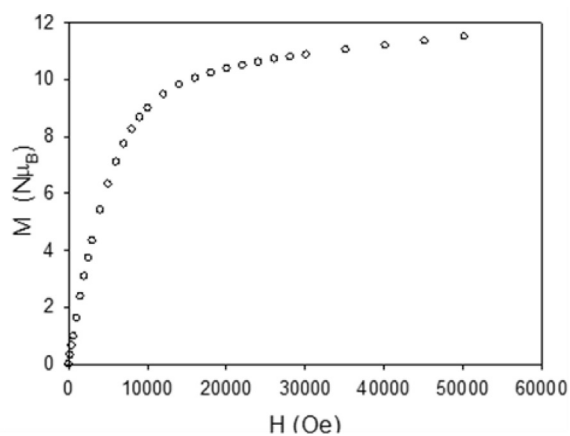


Fig. 5. Magnetization vs. field plot for complex 1 (Dy2) at 2 K.

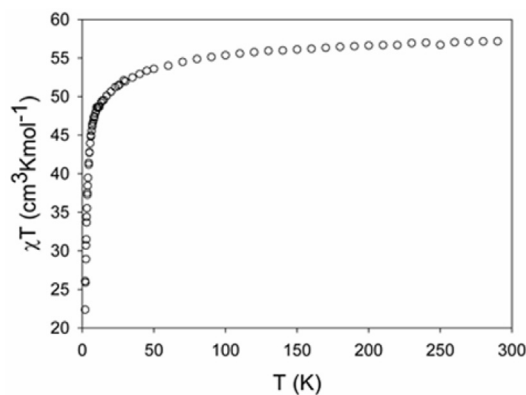


Fig. 6. Magnetic susceptibility as a  $\nu T$  vs. T plot of complex 2 (Dy4) at 3000 Oe applied dc field.

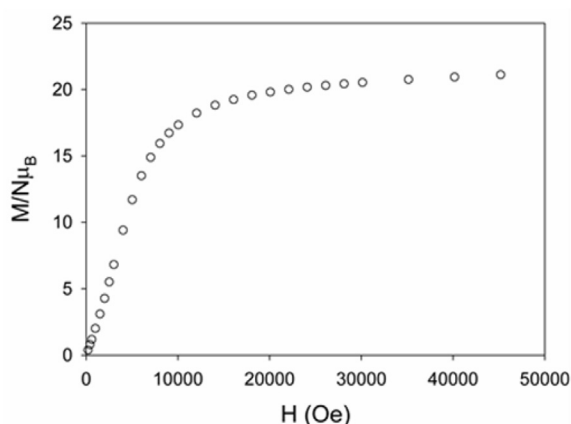


Fig. 7. Magnetization vs. field plot for complex 2 (Dy4) at 2 K.

enneacoordinated (seven O, two N). The relaxation processes were analyzed using the Arrhenius expression Fig. 9, The values obtained for the process centered at 5 K were  $S_0 = 5e-7 \text{ s}^{-1}$  and  $U_{\text{eff}} = 37 \text{ K}$ , while those for the process centered at 15 K were  $S_0 = 7e-7 \text{ s}^{-1}$  and  $U_{\text{eff}} = 78 \text{ K}$ . In both cases the Mydosh parameter [27] was analyzed and has a value of 0.30, in agreement with that expected for a slow relaxation of the magnetization process as that of an SMM. The dynamic properties as a function of frequency were also investigated. The data is shown in Fig. 10 as an Argand or Cole-Cole plot at 10 K. At this temperature only the high-temperature process is observed. The data were fitted to a Debye model with a small distribution of relaxation processes shown by  $a = 0.07$ . The fitting parameters were  $\nu S_0 = 0.92 \text{ cm}^3/\text{mol}$ ,  $\nu T = 3.79 \text{ cm}^3/\text{mol}$ ,  $S_0 = 2e-3 \text{ s}^{-1}$  and  $a = 0.07$ .

Magnetization versus field data were collected at 2, 4 and 10 K but the opening of hysteresis loops was not observed for powdered samples of 2. It is likely that Single crystal experiments with field sweep rate control would be necessary to observe hysteresis for the magnetization.

The orientations of the ground state magnetic anisotropy for each of the Dy(III) ions were calculated using MAGELLAN software. The software uses a purely electrostatic model. The Fig. 11 shows the anisotropy axes on each 1 Dy(III) as a red line. Clearly, the two Dy(III) ions on each Dy2 unit have their anisotropies nearly parallel, at 1.760 and 2.670 for the dinuclear unit Dy1-Dy2 and the dinuclear unit Dy3-Dy3<sup>3</sup> respectively, but in the Dy-O-O-Dy plane. Fig. 12 shows the anisotropy axes on each 2 Dy(III) as a

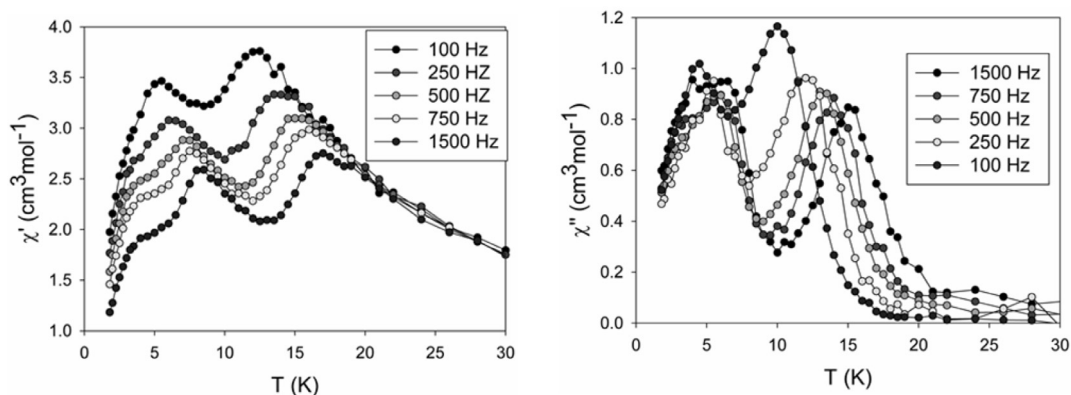


Fig. 8. In-phase and out-of-phase ac magnetic susceptibility plots for complex 2 (Dy4) at the indicated frequencies. The solid lines are only guides for the eye.

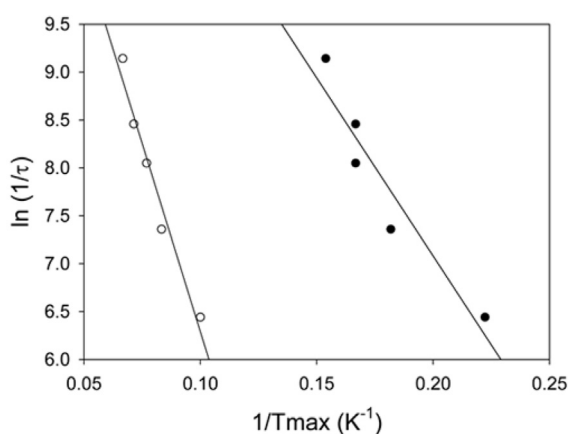


Fig. 9. Arrhenius plot for the two maxima (centered at 5 K (black symbol) and 15 K (white symbol)) observed in the ac susceptibility data of 2 (Dy4). See text for fitting parameters. (Colour online.)

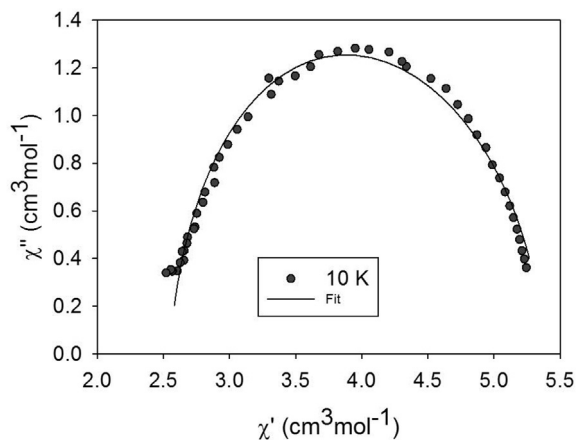


Fig. 10. Argand plot for 2 at 10 K. The line is the best fitting to a Debye model. See text for fitting parameters.

red line. Three of the anisotropy axes are relatively parallel with angles of 30 and 60 (Dy1, Dy2 and Dy2<sup>b</sup>) while the fourth (Dy1<sup>b</sup>) is nearly perpendicular to the other three (840). Thus complex 2 magnetic anisotropy is much larger than that of 1. The dynamic magnetic properties investigated corroborated that 2 is an SMM and 1 is not.

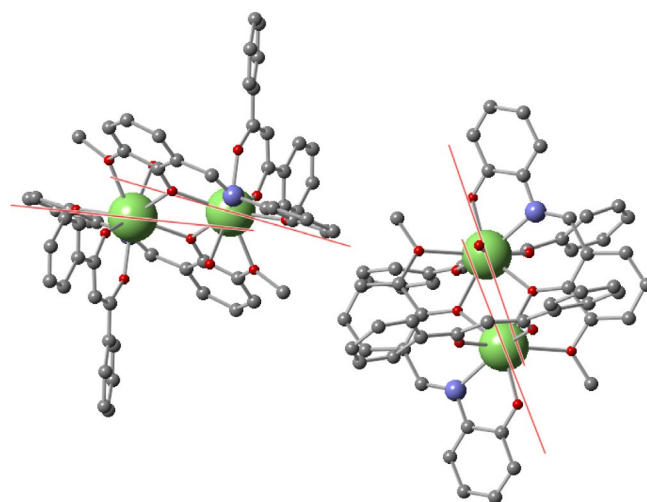


Fig. 11. The two crystallographically distinct dinuclear units of 1 (left Dy3-Dy3', right Dy1-Dy2) following the labelling on the cif file. The red lines are the orientations of the ground state magnetic anisotropy on each Dy(III) calculated with MAGELLAN. (Colour online.)

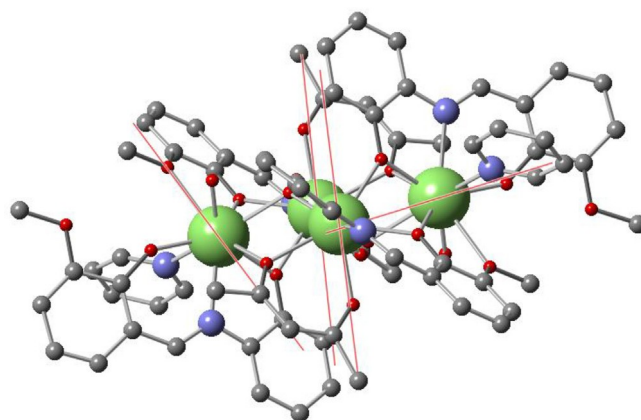


Fig. 12. The structure of 2 with the orientations of the ground state magnetic anisotropy on each Dy(III) calculated with MAGELLAN shown as red lines. (Colour online.)

#### 4. Conclusion

We have successfully synthesized and characterized di and tetranuclear dysprosium hydroxo clusters by employing a mixed



ligand system consisting of Schiff base and b-diketone. Magnetic studies reveal that for compound 1 magnetic data is showing very weak magnetic exchange. For compound 2 frequency dependent AC susceptibility measurements strongly suggestive of SMM behavior.

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## Appendix A. Supplementary data

CCDC reference numbers 1439048–1439049 contain the supplementary crystallographic data for compounds 1 and 2, respectively. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), by emailing [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.poly.2018.05.023>.

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