

# Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## ARTICLE

# Probing the magnetic and magnetothermal properties of M(II)-Ln(III) complexes (where M(II) = Ni or Zn; Ln(III) = La or Pr or Gd)

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Naushad Ahmed,<sup>a</sup> Chinmoy Das,<sup>a</sup> Shefali Vaidya,<sup>a</sup> Anant K Srivastava,<sup>c</sup> Stuart K Langley,<sup>b</sup> Keith S Murray<sup>b</sup> and Maheswaran Shanmugam<sup>\*a</sup>

We have established the coordination potential of the Schiff base ligand (2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenolate (H<sub>2</sub>L)) via the isolation of various M(II)-Ln(III) complexes (where M(II) = Ni or Zn and Ln(III) = La or Pr or Gd). Single crystals of these five complexes were isolated and their solid state structures determined by single crystal X-ray diffraction. Structural determination revealed molecular formulas of [NiGd(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**1**), [NiPr(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**2**) and [Ni<sub>2</sub>La(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**3**), [Zn<sub>2</sub>Gd(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**4**), and [Zn<sub>2</sub>Pr(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**5**). Complexes **1** and **2** were found to be neutral heterometallic dinuclear compounds, whereas **3** - **5** are found to be linear heterometallic trinuclear cationic complexes. Direct current (dc) magnetic susceptibility and magnetization measurements conclusively reveal that complexes **1** and **4** possess a spin ground state of  $S = 9/2$  and  $7/2$  respectively. Empirically calculated  $\Delta\chi_M T$  derived from the variable temperature susceptibility data of all complexes, undoubtedly indicates that the Ni(II) ion is coupled ferromagnetically to the Gd(III) ion, and antiferromagnetically to the Pr(III) ion in **1** and **2** respectively. The extent of the exchange interaction for **1** was estimated by fitting the magnetic susceptibility data using the parameters ( $g = 2.028$ ,  $S = 9/2$ ,  $J = 1.31 \text{ cm}^{-1}$  and  $zJ = +0.007$ ) and supporting the phenomenon observed in an empirical approach. Similarly using a HDVV Hamiltonian, the magnetic data of **3** and **4** were fitted, yielding parameters of  $g = 2.177$ ,  $D = 3.133 \text{ cm}^{-1}$ ,  $J = -0.978 \text{ cm}^{-1}$ , (for **3**) and  $g = 1.985$ ,  $D = 0.508 \text{ cm}^{-1}$  (for **4**). The maximum change in magnetic entropy ( $-\Delta S_m$ ) estimated from the isothermal magnetization data for **1** was found to be  $5.7 \text{ J K g}^{-1} \text{ K}^{-1}$  ( $\Delta B = 7 \text{ Tesla}$ ) at  $7.0 \text{ K}$ , which is larger than the  $-\Delta S_m$  value extracted from **4** of  $3.5 \text{ J K g}^{-1} \text{ K}^{-1}$  ( $\Delta B = 7 \text{ Tesla}$ ) at  $15.8 \text{ K}$ , revealing the importance of the exchange interaction in increasing the overall ground state of a molecule for better MCE efficiency.

## Introduction

Coordination chemistry is a fascinating area of research as a large number of potential applications throughout various fields are possible, such as catalysis,<sup>1</sup> biomedical applications,<sup>2</sup> novel magnetic materials,<sup>3</sup> particularly molecular magnetism<sup>4</sup> etc. A plethora of polynuclear transition metal clusters have appeared in the literature after the discovery of single-molecule magnet (SMM) behaviour in a {Mn<sub>12</sub>} cluster in 1993.<sup>4,5</sup> In transition metal clusters, the total ground spin state ( $S$ ) and Ising type magnetic anisotropy ( $D$ ) associated with the molecule dictates the SMM behaviour of the molecule. This results in an anisotropy barrier ( $U_{eff}$ ) blocking the reversal of the magnetization vector and in turn is related to the blocking temperature ( $T_b \propto U_{eff} = |D|S^2$  for an integer spin and  $|D|S^2 - 1/4$  for a non-integer spin). The enhancement of the blocking temperature, however, remains a significant challenge for

chemists as  $D$  and  $S$  are in reality inversely proportional to each other.<sup>6</sup> A small magnetic anisotropy is observed in the majority of large oligonuclear transition metal clusters due to the partial and/or complete quenching of the orbital angular momentum. This is due to the ligand field interaction with the d<sup>n</sup> electrons, as well as the random orientation of the single ion anisotropic axes within the molecule due to the absence of the necessary synthetic control.

To overcome this issue and to enhance the magnetic anisotropy associated with these molecules, lanthanide ions, which contain inherently large anisotropy, are now used in conjunction with transition metal ions. Much interest was shown in 3d-4f complexes in the past due to the observation of ferromagnetic coupling between Cu(II) and Gd(III) ions.<sup>7</sup> In 2004, the first 3d-4f SMM was reported,<sup>8</sup> and this was subsequently followed by a range of further examples.<sup>9</sup> Although, the use of lanthanide ions with 3d metal ions appears

to be beneficial in gaining the magnetic anisotropy required, when SMM behaviour is observed in the majority of complexes the magnetization vector relaxes via quantum tunnelling of magnetization (QTM).<sup>10</sup> This therefore also obstructs the effort towards increasing the blocking temperature. In an unrelated study, homologous dinuclear lanthanide complexes bridged by a radical ligand revealed the importance of strong magnetic exchange interactions, which resulted in the suppression of the QTM. The combination of the large anisotropy and strong exchange resulted in a record blocking temperature (14 K) known for any SMM.<sup>11</sup> On a similar note, we have proved recently that strong exchange can be brought into a molecular system by incorporating 3d metal ions such as Cr(III).<sup>12</sup> This reveals a more versatile and robust synthetic method compared to the difficult goal of achieving stable and reactive radical containing complexes. Apart from SMM behaviour, there is a growing interest in probing the cooling efficiency of molecular complexes, which is exclusively based on its intrinsic magneto caloric effect (MCE).<sup>13</sup> The MCE is simply the change in temperature of material with the aid of external magnetic field. The change in magnetic entropy ( $-\Delta S_m$ ) and adiabatic temperature ( $\Delta T_{ad}$ ) are the two key parameters which determine the effectiveness of the MCE. These parameters depend on the overall ground state of the molecule, which should be isotropic in nature, as well as being dependent on the exchange interaction, which are preferably weak. These criteria are often satisfied in Gd<sup>III</sup> containing complexes.

In this line of interest we are focussed on a new generation of Ni-4f metal complexes as these are likely to display favourable (ferro)magnetic exchange interactions similar to the Cu(II)-4f congeners, using the Schiff base ligand, (2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenolate (H<sub>2</sub>L)). We will use these compounds to probe the nature of the magnetic exchange and determine the strength in both isotropic and anisotropic complexes, which will be of great interest to the SMM and MCE community. Moreover we reveal how the use of appropriately substituted diamagnetic metal complexes can be used to extract information on the nature of the exchange interaction between the metal centres.

The ligand in question (H<sub>2</sub>L) has been scarcely used, with only two transition metal complexes reported in the literature, these being a {Cu<sub>4</sub>} and a monomeric Mo(VI) complex.<sup>14</sup> In this article, we have established the coordination potential of the H<sub>2</sub>L ligand, isolating five different heterometallic 3d-4f (where 3d = Ni or Zn; 4f = La or Pr or Gd) complexes of formulae [NiGd(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**1**), [NiPr(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**2**) and [Ni<sub>2</sub>La(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**3**), [Zn<sub>2</sub>Gd(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**4**), and [Zn<sub>2</sub>Pr(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**5**). We have performed detailed magnetic measurements, probing the exchange interactions and the MCE properties of selected complexes (*vide infra*).

## Experimental

### Materials and Methods

All the reactions were carried out under aerobic conditions. Analytical grade solvents and reagents were purchased from commercial sources (Alfa Aesar and Aldrich) and used without further purification. Infrared spectra were collected for the solid samples using KBr pellets on a Perkin-Elmer FT-IR spectrometer between 400 and 4000 cm<sup>-1</sup>. Single crystal data were collected on a Rigaku Saturn CCD diffractometer using a graphite monochromator (MoK<sub>α</sub>, λ = 0.71073 Å). The selected crystals were mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced with an Oxford Cryo-cooling device. Complete hemispheres of data were collected

using ω and φ-scans (0.3°, 16 s per frame). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software and they were corrected for absorption correction. Structure solution and refinement was performed with the SHELX-package. The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F<sup>2</sup>. The diffused electron density for the solvate molecule does not allow us to model these in some cases, hence the SQUEEZE routine was employed to calculate the number of electrons present in the void. The resultant loop created in the platon software is appended at the end of cif file for the corresponding crystal structure. See Table 1 for the crystallographic parameters for **1** – **5**. CCDC numbers: 1013525 and 1017181-1017184. The magnetic susceptibility measurements were obtained with the use of a MPMS SQUID magnetometer. Measurements were performed on polycrystalline samples and the magnetic data were corrected for the sample holder and diamagnetic contribution. The magnetic data were fitted for the selected complexes using PHI software.<sup>15</sup> The ligand was synthesized via a modified literature approach, resulting in an improved yield of the ligand.<sup>16</sup>

### Synthetic Procedures

#### Synthesis of complex **1**:

The Schiff base ligand H<sub>2</sub>L (0.200 g, 0.777 mmol) was deprotonated using sodium methoxide (0.042 g, 0.777 mmol) in 40 mL of methanol. Into this solution Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.133 g, 0.3889 mmol) was added, which was stirred for 15 minutes before nickel acetate hydrate (0.0965 g, 0.3889 mmol) was introduced. Upon addition of the nickel salt, the solution changed from light orange to green. The solution was stirred for 24 h at room temperature, after which the volume was reduced to 4.0 mL. To this 2.0 mL of THF was then added and the solution filtered. X-ray quality green single crystals were grown after allowing the filtrate to stand at room temperature undisturbed for one week. Yield for **1** (based on nickel): 0.09 g (26 %). FTIR-1621 cm<sup>-1</sup>(ν<sub>C=N</sub>), Ar-H, 2925 cm<sup>-1</sup> (ν<sub>Ar-H</sub>).

#### Synthesis of complexes **2** - **5**:

A similar synthetic procedure to **1** was followed. In the case of complexes **2** and **3** Gd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was replaced by praseodymium nitrate hydrate (0.168g, 0.3889 mmol) and lanthanum nitrate hydrate (0.167g, 0.3889 mmol) respectively. Yield for **2** (based on nickel): 0.08 g (23 %). FTIR-1620 cm<sup>-1</sup>(ν<sub>C=N</sub>), Ar-H, 2924 cm<sup>-1</sup> (ν<sub>Ar-H</sub>). Yield for **3** (based on nickel): 0.100g (17%). FTIR-1617cm<sup>-1</sup>(ν<sub>C=N</sub>), Ar-H, 2942 cm<sup>-1</sup> (ν<sub>Ar-H</sub>). In the case of **4** and **5**, nickel acetate hydrate was replaced by zinc acetate hydrate (0.0852g, 0.3889 mmol) which was treated with its corresponding chemical equivalence of the required lanthanide nitrate salt (Gd (**4**) and Pr (**5**)). Block shaped pale yellow single crystals of **4** and **5** were grown from the filtrate. Yield for **4** (based on zinc): 0.160 g (27%) FTIR, (1614 cm<sup>-1</sup>(ν<sub>C=N</sub>), 2940 cm<sup>-1</sup> (ν<sub>Ar-H</sub>). Yield for **5** (based on zinc): 0.150 g (27%) FTIR, (1614 cm<sup>-1</sup>(ν<sub>C=N</sub>), 2941 cm<sup>-1</sup> (ν<sub>Ar-H</sub>).

### Results and discussion

The deprotonated Schiff base ligand was reacted with Ln(NO<sub>3</sub>)<sub>3</sub> hydrate and nickel acetate hydrate (where Ln = La, Pr, Gd) in methanol under aerobic conditions. Green single crystals were isolated in all the cases (Scheme 1), with single crystal X-ray diffraction revealing the molecular formulae for these complexes as [NiGd(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**1**), [NiPr(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] (**2**) and [Ni<sub>2</sub>La(HL)<sub>4</sub>(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> (**3**). Compounds **1** - **3** crystallize in the monoclinic space group, P2<sub>1</sub>/n.

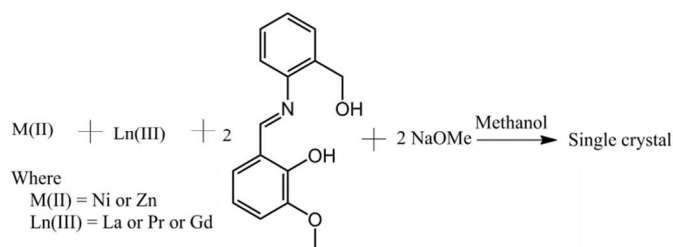
## ARTICLE

**Table 1.** Crystallographic parameters for complexes 1-5.

	1	2	3	4	5
Formula	NiGdC <sub>31.25</sub> H <sub>33</sub> O <sub>16.25</sub> N <sub>5</sub>	NiPrC <sub>31.25</sub> H <sub>33.5</sub> O <sub>16.5</sub> N <sub>5</sub>	Ni <sub>2</sub> LaC <sub>60</sub> H <sub>56</sub> O <sub>21</sub> N <sub>7</sub>	Zn <sub>2</sub> GdC <sub>61</sub> H <sub>60</sub> O <sub>22</sub> N <sub>7</sub>	Zn <sub>2</sub> PrC <sub>61.25</sub> H <sub>61</sub> O <sub>22.25</sub> N <sub>7</sub>
Size [mm]	0.14 × 0.12 × 0.07	0.13 × 0.11 × 0.07	0.14 × 0.12 × 0.07	0.16 × 0.16 × 0.09	0.09 × 0.09 × 0.07
System	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>	<i>P-1</i>	<i>P-1</i>
<i>a</i> [Å]	11.286(3)	11.303(2)	20.056(5)	12.714(3)	12.809(7)
<i>b</i> [Å]	26.990(8)	27.142(5)	14.595(3)	13.200(3)	13.227(7)
<i>c</i> [Å]	12.817(4)	12.804(3)	24.624(6)	21.782(6)	21.704(10)
$\alpha$ [°]	90	90	90	85.876(12)	92.342(4)
$\beta$ [°]	98.722(5)	98.45(3)	102.582(3)	87.692(12)	91.904(6)
$\gamma$ [°]	90	90	90	61.678(5)	118.684(7)
<i>V</i> [Å <sup>3</sup> ]	3859.2(19)	3885.6(14)	7035(3)	3209.6(14)	3217(3)
<i>Z</i>	4	4	4	2	2
$\rho_{\text{calcd}}$ [g/cm <sup>3</sup> ]	1.640	1.608	1.386	1.580	1.567
$2\theta_{\text{max}}$	53.46	56.68	52.74	50	50
radiation	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$	MoK $\alpha$
$\lambda$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
<i>T</i> [K]	100	100	100	100	100
reflns	61924	38661	76720	35802	43900
Ind. reflns	8178	9689	14331	11271	11297
reflns with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	7552	7861	10726	9758	9576
<i>R</i> <i>I</i>	0.0727	0.0523	0.0793	0.0443	0.0794
<i>wR</i> <i>2</i>	0.1956	0.1483	0.2685	0.1049	0.2284

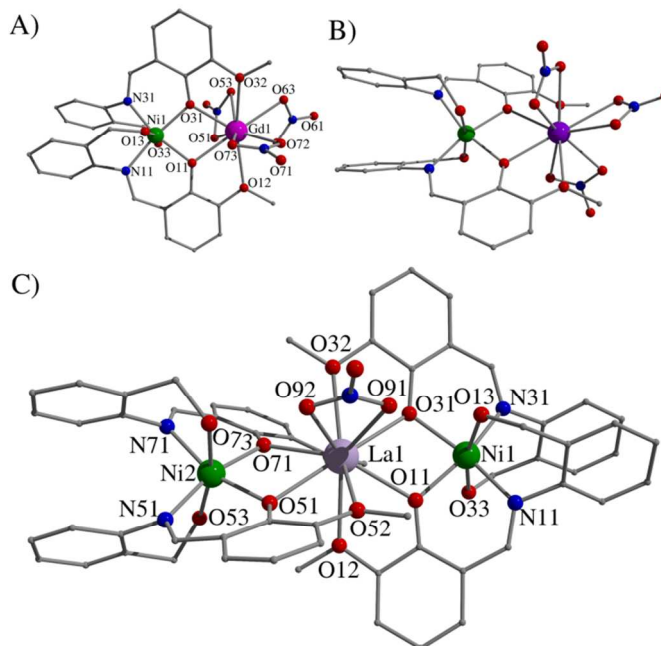
It is found that complexes **1** and **2** are isostructural, both containing a divalent nickel ion and a trivalent lanthanide ion, thus forming a heterometallic dinuclear complex (Figure 1). The Ni and Ln metal ions are linked exclusively by two  $\mu$ -phenoxo oxygen atoms derived from two partially deprotonated Schiff base ligands.

**Scheme 1.** Schematic representation of synthetic method followed for the isolation various complexes.



The average  $\angle$ Ni1-O11-Ln1 and  $\angle$ Ni1-O31-Ln1 bond angle of 107.2° is found to be same for both **1** and **2**. The Ni1-O11-Ln1-O31 dihedral angle of 6.59° and 6.75° for **1** and **2** respectively reveals a small deviation from planarity. The nickel ion in both complexes is six coordinate, with a {N<sub>2</sub>O<sub>4</sub>} octahedral coordination environment. These coordination sites are provided by the O- and N-atoms of the two Schiff base ligands. The average Ni1-O and Ni-N bond distance is found to be (2.070 and 2.035 Å for **1**) and (2.065 Å 2.024 Å for **2**). In both

complexes the Gd(III) and Pr(III) ions are ten coordinate, displaying distorted bicapped square antiprismatic geometries.



**Fig 1.** Ball and stick representation of crystal structure of complexes **1** (A); **2** (B) and **3** (C). For complex **2**, the same labelling scheme is followed as in figure 1A.

Two of the sites are occupied by the bridging phenoxo O-atoms, while three chelating nitrate ions provide six of the sites, the remaining two are completed by methoxo O-atoms of the Schiff base ligand. The average Ln1-O bond distance is 2.489 Å and 2.549 Å, for **1** and **2** respectively. Selected bond lengths and bond angles for both complexes are given in Table 2.

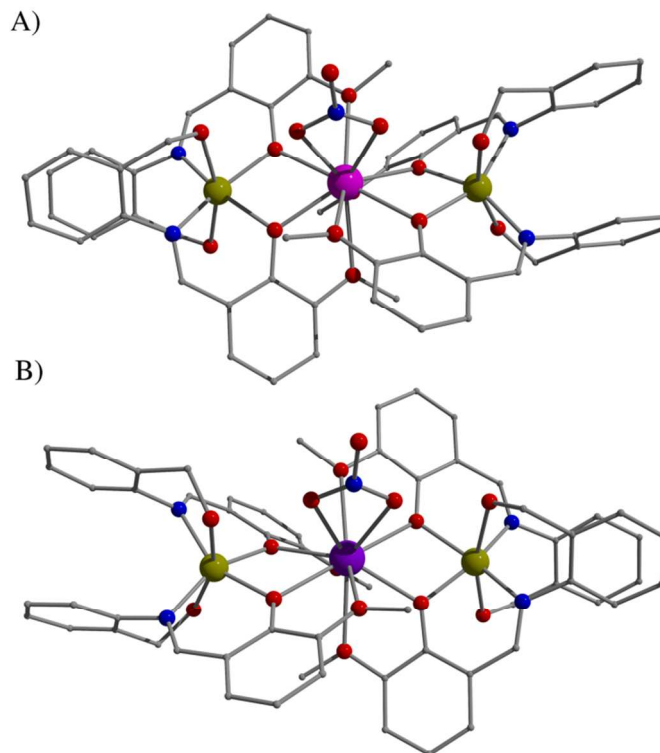
**Table 2.** Selected bond lengths and angles for complexes **1-3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Ni1-O11	2.013(5)	2.009(3)	2.022(5)
Ni2-O51	-	-	2.030(5)
Ni1-O13	2.108(5)	2.102(3)	2.140(6)
Ni2-O53	-	-	2.176(5)
Ni1-O31	2.038(5)	2.033(3)	2.045(5)
Ni2-O71	-	-	2.025(5)
Ni1-O33	2.122(5)	2.123(3)	2.131(6)
Ni2-O73	-	-	2.128(5)
Ni1-N11	2.034(6)	2.017(4)	2.054(7)
Ni2-N51	-	-	2.036(7)
Ni1-N31	2.030(6)	2.030(4)	2.038(7)
Ni2-N71	-	-	2.038(7)
Ln1-O11	2.397(5)	2.479(3)	2.463(5)
Ln1-O12	2.550(6)	2.608(4)	2.697(5)
Ln1-O31	2.341(5)	2.413(4)	2.565(6)
Ln1-O32	2.554(5)	2.598(4)	2.634(6)
Ln1-O52	2.441(17)	2.516(4)	2.663(5)
Ln1-O53	2.599(19)	2.507(4)	-
Ln1-O51	-	-	2.586(6)
Ln1-O62	2.483(7)	2.564(4)	-
Ln1-O63	2.596(7)	2.647(4)	-
Ln1-O72	2.421(6)	2.564(4)	2.687(5)
Ln1-O73	2.454(6)	2.604(5)	-
Ln1-O71	-	-	2.449(5)
Ln1-O91	-	-	2.610(6)
Ln1-O92	-	-	2.586(6)
Bond angle			
Ni1-O11-Ln1	106.6(2)	106.34(14)	109.9(2)
Ni2-O51-Ln1	-	-	104.8(2)
Ni1-O31-Ln1	107.8(2)	107.99(15)	105.5(2)
Ni2-O71-Ln1	-	-	110.1(2)

Complex **3**, on the other hand, while following the same synthetic procedure used to isolate **1** and **2**, resulted in a linear trinuclear heterometallic Ni(II)-La(III)-Ni(II) complex (Figure 1, C). All three metal ions are arranged in a near linear fashion, with a  $\angle$ Ni1-La1-Ni2 angle of 169.2°. Often this deviation from linearity is brought about by ligands such as nitrate and/or solvate molecules coordinated to the Ln(III) ions, witnessed in similar types of complexes.<sup>17</sup> It is found, however, that **3** maintains a similar magnetic core as in **1** or **2**, that being the Ni(II) and La(III) ions are linked solely by phenoxo oxygen bridging atoms. This results in the presence of two dihedral planes (Ni1-O11-La1-O31 and Ni2-O51-La1-O71) with dihedral angles of 12.524° and 10.399°. These two dihedral planes are not coplanar and are twisted by an angle of 36.951°. The structural parameters suggest that the magnetic core (dihedral plane) is more distorted compared to complexes **1** and **2** (Table 2).

In an attempt to replace the paramagnetic nickel(II) ion in **1** and **2** by a diamagnetic ion, we performed the equivalent reaction utilizing zinc acetate hydrate as the transition metal. Pale yellow single crystals suitable for X-ray diffraction revealed two complexes of general molecular formula

$[Zn_2Ln(HL)_4(NO_3)](NO_3)_2$  where Ln = Gd (**4**), Pr (**5**) (Figure 2). Both **4** and **5** are isostructural and are unexpectedly found to be linear heterometallic trinuclear complexes similar to **3**. Although **4** and **5** are analogous to **3**, both **4** and **5** crystallize in the triclinic space group, *P*-1, differing from **3**.



**Fig 2.** Molecular structure of complexes **4** (panel A) and **5** (panel B). The same labelling scheme has been followed as in Figure 1C. Dark yellow, magenta and purple represents the Zn(II), Gd(III) and Pr(III) respectively.

The ligand bonding arrangement for **4** and **5** is identical to that found for **3**. The zinc(II) ions exhibit distorted  $\{N_2O_4\}$  octahedral geometries, while the lanthanide ions (Gd(III) or Pr(III)) are ten coordinate, with distorted bicapped square antiprismatic geometries. The twist angle between the two dihedral planes in **4** and **5** are found to be 30.958° and 31.263° respectively, which are smaller than that found in **3**. Selected bond lengths and bond angles for **4** and **5** are given in Table 3.

In all five complexes intermolecular H-bonding is facilitated by nitrate ions and the aromatic protons from adjacent molecules. The closest intermolecular 3d-3d (either Ni-Ni or Zn-Zn) distance in **1** – **5** is found to range from 7.901 to 8.774 Å. The closest intermolecular Ln-Ln distance are in the range 8.79 to 11.84 Å.

Direct current (dc) magnetic susceptibility measurements were performed on polycrystalline samples for all five complexes between 2 to 300 K, using an applied magnetic field of 1 kOe (Figure 3). The room temperature (RT)  $\chi_M T$  value of 9.34, 2.63, 2.51, 7.79 and 1.62  $\text{cm}^3 \text{K mol}^{-1}$  is found for **1** - **5** respectively. These observed  $\chi_M T$  values are slightly higher for **1** and **3** than the expected value of 8.875 and 2.00  $\text{cm}^3 \text{K mol}^{-1}$  for a magnetically dilute system ( $g = 2$ ) which is usual for complexes containing Ni(II) ion as its  $g$ -values are always

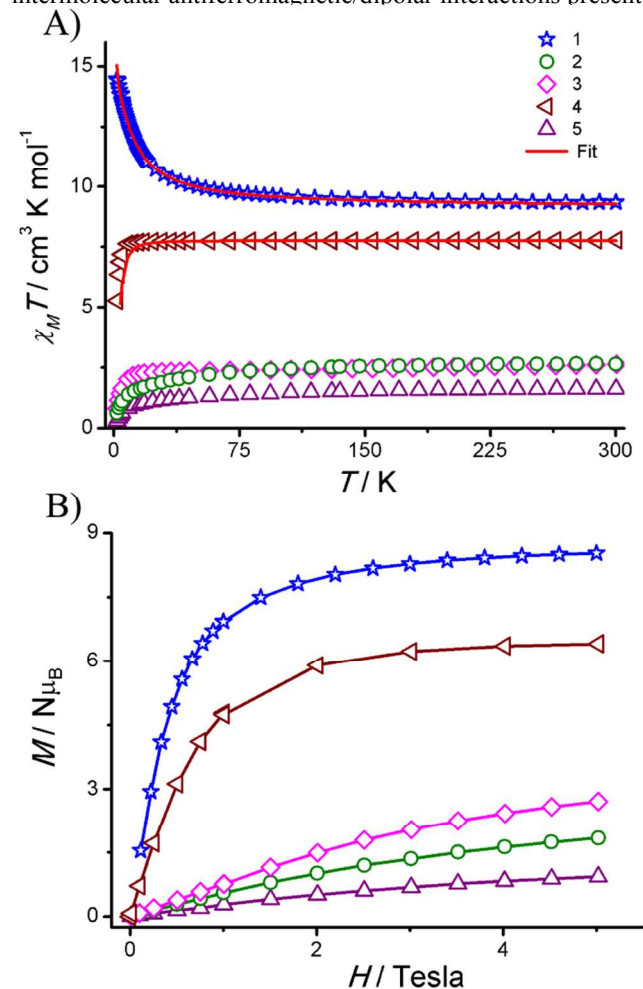
larger than 2.0. For **2**, **4** and **5**, the  $\chi_M T$  values are consistent with that of non-interacting ions of 2.6, 7.875 and 1.6 cm<sup>3</sup> K mol<sup>-1</sup> respectively ( $g_{Pr} = 4/5$ , <sup>3</sup>H<sub>4</sub>). For complex **1**, upon lowering the temperature from RT, the  $\chi_M T$  value steadily increases, reaching a maximum value of 14.46 cm<sup>3</sup> K mol<sup>-1</sup> at 1.9 K. This behaviour reveals that the Ni(II) ion is coupled ferromagnetically with the Gd(III) ion. The low temperature  $\chi_M T$  value signifies an overall spin ground state of  $S = 9/2$  for complex **1**.

**Table 3.** Selected bond lengths and bond angles of complexes **4** and **5**.

	<b>4</b>	<b>5</b>
Zn1-O11	2.068(4)	2.038(5)
Zn2-O51	2.051(4)	2.073(5)
Zn1-O13	2.338(4)	2.288(5)
Zn2-O53	2.285(4)	2.344(6)
Zn1-O31	2.018(4)	2.066(5)
Zn2-O71	2.029(4)	2.019(5)
Zn1-O33	2.226(4)	2.267(5)
Zn2-O73	2.287(4)	2.236(5)
Zn1-N11	2.033(5)	2.082(6)
Zn2-N51	2.048(4)	2.041(6)
Zn1-N31	2.092(5)	2.056(6)
Zn2-N71	2.080(5)	2.019(6)
Ln1-O11	2.459(4)	2.397(5)
Ln1-O12	2.616(4)	2.686(5)
Ln1-O31	2.349(4)	2.535(5)
Ln1-O32	2.620(4)	2.675(5)
Ln1-O51	2.498(4)	2.500(5)
Ln1-O52	2.644(4)	2.656(5)
Ln1-O71	2.344(4)	2.403(5)
Ln1-O72	2.649(4)	2.665(5)
Ln1-O91	2.486(4)	2.544(5)
Ln1-O92	2.459(4)	2.538(6)
Bond angle		
Zn1-O11-Ln1	106.7(6)	111.7(2)
Zn2-O51-Ln1	105.8(5)	106.6 (19)
Zn1-O31-Ln1	112.7 (8)	105.6(19)
Zn2-O71-Ln1	112.4 (4)	112.1(2)

On the contrary to **1**, the iso-structural complex **2** displays markedly different temperature dependence. The  $\chi_M T$  value decreases gradually from RT down to 45 K before falling sharply below this temperature. The steady decrease in  $\chi_M T$  from RT is likely due to depopulation of the stark levels and/or an antiferromagnetic interaction between the Ni(II) and Pr(III) ions. For **3**, the  $\chi_M T$  value gradually decreases from RT down to 23 K before falling drastically below this temperature. The gradual decrease could likely be due to a very weak exchange interaction between the Ni(II) ions (Ni...Ni (7.325 Å) via La(III) ion) and/or depopulation of energy levels arise due to the single ion anisotropy. Complex **4** displays a temperature independent  $\chi_M T$  value from RT down to 25 K. This signifies the simple paramagnetic nature of **4**. For both complexes **3** and **4**, however, the  $\chi_M T$  value decreases sharply below 25 and 23 K respectively, which is likely due to the magnetic anisotropy and/or intermolecular antiferromagnetic interactions. The anisotropic metal complex **5** reveals a continual decrease of the  $\chi_M T$  value from RT down to 80 K, before a larger drop is

observed. This profile is due to the magnetic anisotropy and/or intermolecular antiferromagnetic/dipolar interactions present.



**Fig 3.** A) Variable temperature  $\chi_M T$  plots on polycrystalline samples of **1** - **5** measured at 1 kOe. The solid line represents the best fit obtained for complexes **1** and **4** using the parameters discussed in the main text. B) Field dependent magnetization data of **1** - **5** measured at 2.0 K using the same labelling scheme as A). Solid lines represent a guideline for the eye.

Isothermal field dependent magnetization measurements were performed for all the complexes at 2 K, and shown in Figure 3B (see also Figure S1 of ESI for the 2 – 20 K temperature range). Complexes **2** - **3** and **5**, show a near linear response at low temperature in the entire magnetic field range. Complexes **1** and **4** shows a sharp increase in magnetization value at low field and low temperature, implying that the ground state is predominantly populated. At high magnetic fields both complexes saturate with values of 8.6 (for **1**) and 6.4 N $\mu_B$  (for **4**). The observed saturation values unambiguously confirms that **1** and **4** possess a  $S = 9/2$  and  $S = 7/2$  ground state respectively; consistent with the ground state suggested via the low temperature  $\chi_M T$  values (see Figure 3A). The non-overlap of the reduced magnetization curves for all the complexes, except **1** and **4**, suggests that the complexes possess significant magnetic anisotropy (see Figure S2 of ESI).

In most cases it is straightforward to predict the nature of the exchange interaction in an isotropic dinuclear metal complex. It is however difficult to predict the interaction upon utilizing anisotropic ions, which is consequence of the first

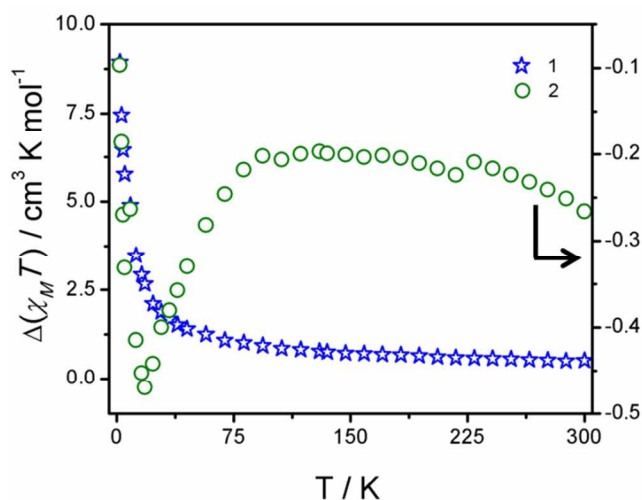
order orbital angular momentum present and the very weak super exchange interaction.

For example in the case of **2** with the replacement of the Gd(III) ion by Pr(III) the exchange is not as clear cut, even though a decrease in  $\chi_M T$  is observed over the entire temperature range. Often a very weak exchange interaction between the 3d-4f ions is masked by the depopulation effect of the stark levels. To further prove the existence of ferro- or antiferro-magnetic exchange in these complexes we have followed an empirical approximation approach, using complexes **3**, **4** and **5** which contain the appropriately substituted diamagnetic analogue, and the following equations.

$$J_{Ni-Gd} \approx \chi_M T_{(1)} - \frac{\chi_M T_{(3)}}{2} - \chi_M T_{(4)} \dots \text{ (Eq 1)}$$

$$J_{Ni-Pr} \approx \chi_M T_{(2)} - \frac{\chi_M T_{(3)}}{2} - \chi_M T_{(5)} \dots \text{ (Eq 2)}$$

This approach will exclusively shed light on the nature of exchange interaction between the Ni(II) and Gd(III) or Pr(III) ions (Figure 4).



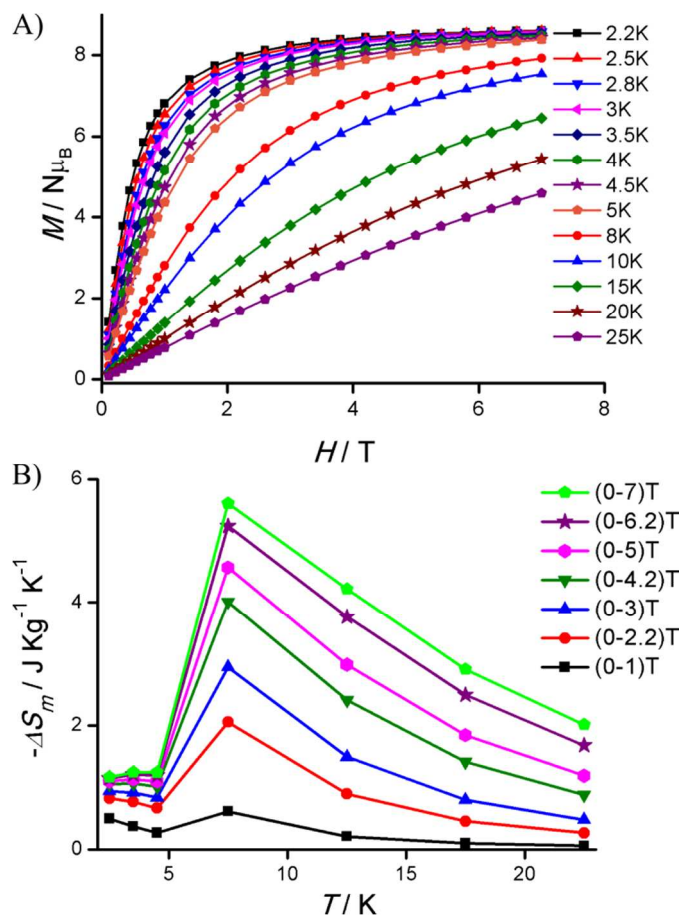
**Fig 4.** Temperature dependent  $\Delta\chi_M T$  plots for **1** and **2** derived from Equations 1 and 2 given in main text.

From figure 4 it is evident that for **1** the  $\Delta\chi_M T$  value remains positive from RT to low temperature, unambiguously signifying that the exchange interaction is ferromagnetic between the Ni(II) and Gd(III) ions. However, for **2** the  $\Delta\chi_M T$  values remain negative for the entire temperature range and below 100 K a pronounced decrease in  $\Delta\chi_M T$  is consistent with an antiferromagnetic interaction between the Ni(II) and Pr(III) ions. This situation could lead to a pseudo singlet ground state for **2**. Further, below 20 K,  $\Delta\chi_M T$  rises, and could be due to intermolecular interactions. The empirical approximation given for **2** is consistent with the exchange correlation that has been developed revealing that a lanthanide ion with  $< 4f^7$  electrons will couple antiferromagnetically with the Ni(II) ion.<sup>18</sup>

In order to validate this empirical approach, we attempted to fit the experimental  $\chi_M T(T)$  data using the PHI program<sup>15</sup> for the isotropic metal complexes **1** as well as for **3** and **4**. An excellent fit was obtained with the following spin Hamiltonian

parameters  $g = 2.028$ ,  $S = 9/2$ ,  $J = 1.31 \text{ cm}^{-1}$  and  $zJ = +0.007$  (for **1**) where  $zJ$  is the intermolecular interaction. A perfect fit of the data could only be obtained upon inclusion of the intermolecular interaction. Indirect evidence for the existence of intermolecular interactions in **2** is clearly reflected from Figure 4, where at lower temperatures  $\Delta\chi_M T$  begins to increase below 20 K. The positive  $J$  value of **1** confirms that the Ni(II) and Gd(III) ions are coupled ferromagnetically, consistent with the empirical approach we have followed, validating our methodology.

Using the following SH parameters,  $g = 2.177$ ,  $D = 3.133 \text{ cm}^{-1}$ ,  $J = -0.978 \text{ cm}^{-1}$ , (for **3**) and  $g = 1.985$ ,  $D = 0.508 \text{ cm}^{-1}$  (for **4**) the magnetic data of **3** and **4** could also be fitted (Figure 3). For complex **3**, we have fitted the  $\chi_M T$  value from 150 K to 2.0 K, as the inclusion of the higher temperature data resulted in poor fits of the data (see Figure S3 of ESI).



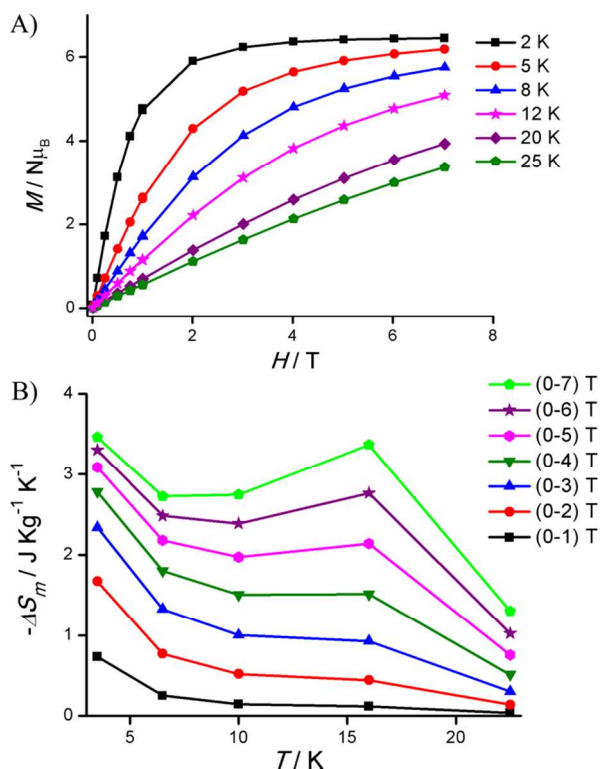
**Fig 5.** A) Field dependent magnetization measurements performed on a polycrystalline sample of **1** at the indicated temperatures. B) The change in magnetic entropy extracted from isothermal magnetization measurement of **1**.

Nevertheless, the observation of a weak antiferromagnetic exchange interaction between the Ni(II) ions in **3** via closed shell La(III) ion (Ni...Ni (7.325 Å)) is quite surprising. Moreover we have recently shown that two Ni(II) ions linked via an alkali metal ion at a distance of 6.97 Å displays simple Curie-like behaviour.<sup>19</sup> We therefore attempted to fit the  $\chi_M T(T)$  data without an exchange parameter, but the calculated data deviates significantly from the experimental data (see Figure S3 of ESI). There is precedent for an exchange between Cu(II) ions which are linked through diamagnetic La(III) ion (Cu...Cu

$= 5.886 \text{ \AA}$ ).<sup>7d</sup> The obtained parameters for **3** and **4** are consistent with literature reports confirming the validity of the extracted parameters.<sup>18b, 20</sup> The non-zero magnetic anisotropy ( $D$ ) in both complexes (**3** and **4**) is likely to contribute significantly for the sharp decrease in  $\chi_M T$  value at lower temperature (See Figure 3A). Due to the anisotropy indicated in the  $M$  vs  $H$  plots alternating current magnetic susceptibility measurements were performed only for complex **2** to probe for any SMM behaviour. No out-of-phase susceptibility signals are however observed under both zero and a dc bias (2 kOe) magnetic field. This unfortunately reveals an absence of any slow magnetic relaxation and SMM behaviour.

Molecular complexes which display weak ferromagnetic interactions and which are magnetically isotropic have been proposed as excellent candidates as molecular magnetic coolants.<sup>21</sup> In order to probe the magneto caloric effect (MCE) efficiency of complex **1**, we have performed detailed magnetization measurement from 2.0 K to 25.0 K (Figure 5). Using Maxwell's thermodynamic equation, given below, we have estimated the change in magnetic entropy ( $-\Delta S_m$ ). Upon increasing the magnetic field change, the change in magnetic entropy increases, reaching a maximum value of  $5.65 \text{ J Kg}^{-1} \text{ K}^{-1}$  at 7.5 K ( $\Delta B = 7$  Tesla).

$$\Delta S_m(T, B) = \int_{B_i}^{B_f} \left[ \frac{\partial M(T, B)}{\partial T} \right]_B . dB \dots\dots (Eq 3)$$



**Fig 6.** A) Field dependent magnetization measurements performed on a polycrystalline sample of **4** at the indicated temperatures. B) The change in magnetic entropy extracted from isothermal magnetization measurement of **4** using equation 3.

The observed values are significantly lower than the magnetic entropy estimated for uncoupled Ni(II) and Gd(III) ions ( $3.177R \approx 29.9 \text{ J Kg}^{-1} \text{ K}^{-1}$ ) and is also smaller than other

reported Ni-Gd complexes.<sup>22</sup> This could be likely due to the larger exchange interaction between the Ni(II) and Gd(III) ions in **1** compared to the reported complexes.<sup>22</sup> Moreover, magnetic anisotropy may play a crucial role preventing easy polarization of the magnetization. We have recently shown that a low symmetry environment around the isotropic Gd(III) ion is enough to bring about magnetic anisotropy,<sup>23</sup> although this is not clearly reflected in reduced magnetization plot of **1**. To extract the magnetic anisotropy quantitatively, detailed EPR measurements are required which will be carried out in the future. In order to probe the role of the exchange interaction towards the MCE efficiency, detailed magnetization measurements were performed for **4** and the  $\Delta S_m$  value was extracted from equation 3 (Figure 6) and compared to **1** (Ni-Gd (**1**) vs Gd (**4**)). The maximum change in magnetic entropy is found to be  $3.5 \text{ J Kg}^{-1} \text{ K}^{-1}$  at 15.8 K ( $\Delta B = 7$  Tesla). An approximate two fold increase in the  $\Delta S_m$  value is found for **1**, signifying that the larger ground state contribution to the magnetic entropy ( $S_m = R \ln(2S+1)$  where  $S_m$  = magnetic entropy and  $S$  is overall ground state of a molecule), highlights the importance of the ferromagnetic exchange interaction towards the MCE efficiency.

## Conclusions

We have reported five new 3d-4f metal complexes (**1** - **5**) using the novel Schiff base ligand, 2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenolate. Two types of metallic core arrangements are found. The first is a dinuclear Ni-Ln (**1** and **2**) type and the second a trinuclear Ni-Ln-Ni (**3**) or Zn-Ln-Zn (**4** and **5**) arrangement, all with identical bridging motifs. Detailed dc magnetic measurements suggests that the Ni(II) and Gd(III) ions are coupled ferromagnetically in **1**, while the Ni(II) and Pr(III) ions are coupled antiferromagnetically in **2**. In order to confirm the nature of the interaction between the Ni(II) and Ln(III) (where Ln = Gd or Pr) ions, we synthesized complexes **3** - **5** using appropriately substituted diamagnetic ions. Using the dc magnetic data of these complexes, we have proven the nature of the magnetic interactions, including that found between anisotropic ions, using a recently developed empirical approach. The  $\Delta\chi_M T$  values for **1** remain positive indicating ferromagnetic exchange, while the  $\Delta\chi_M T$  values are negative revealing antiferromagnetic exchange for **2**. To further confirm this approach, the existence of ferromagnetic exchange in the isotropic case **1** was confirmed by fitting the magnetic data using the parameters;  $g = 2.028$ ,  $S = 9/2$ ,  $J = 1.31 \text{ cm}^{-1}$  and  $zJ = +0.007$ .

The change in magnetic entropy was estimated for complex **1** from the isothermal magnetization data (2 - 25 K), revealing a maximum value of  $5.65 \text{ J Kg}^{-1} \text{ K}^{-1}$  at 7 K and  $\Delta T = 7$  T. We then compared the magnetic entropy change to that of **4** which revealed the importance of a ferromagnetic exchange interaction in achieving a larger MCE efficiency.

## Acknowledgements

MS likes to thank the funding agencies DST (SR/S1/IC-32/2011), DST nano-mission (SR/NM/NS-1119/2011), CSIR (01(2768)/13/EMR-II), IIT Bombay for financial support. KSM acknowledge the support of an Australian Research Council Grant and an Australia-India AISRF grant. We thank Dr B. Moubaraki for experimental assistance.



## Notes and references

<sup>a</sup> Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai, Maharashtra, India-400076. Email: eswar@chem.iitb.ac.in; Phone: +91-22-2576-7187; Fax: +91-202-2576-7152

<sup>b</sup> School of Chemistry, Monash University, Clayton, Victoria-3800, Melbourne, Australia.

<sup>c</sup> Department of Chemistry, Indian Institute of Science Education and Research (IISER) Pune, Dr. Homi Bhabha road, Pune, Maharashtra, India-411008.

Electronic Supplementary Information (ESI) available: Relevant magnetic data and crystallographic information files are given in ESI. CCDC numbers: 1013525 and 1017181-1017184. See DOI: 10.1039/b000000x/

- 1 a) R. Al-Oweini, A. Sartorel, B. S. Bassil, M. Natali, S. Berardi, F. Scandola, U. Kortz and M. Bonchio, *Angew. Chem., Int. Ed.* 2014, Ahead of Print; b) C. Atienza, T. Diao, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, J. L. Boyer, A. K. Roy and P. J. Chirik, *J. Am. Chem. Soc.* 2014, Ahead of Print; c) M.-N. Belzile, A. A. Neverov and R. S. Brown, *Inorg. Chem.* 2014, **53**, 7916-7925; d) E. J. Emmett, B. R. Hayter and M. C. Willis, *Angew. Chem., Int. Ed.* 2014, Ahead of Print; e) Y. Liu, J. Cornella and R. Martin, *J. Am. Chem. Soc.* 2014, Ahead of Print; f) K. Natte, A. Dumrath, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.* 2014, Ahead of Print; g) T. Patra, S. Manna and D. Maiti, *Angew. Chem., Int. Ed.* 2011, **50**, 12140-12142; h) S. Rana, R. Haque, G. Santosh and D. Maiti, *Inorg. Chem.* 2013, **52**, 2927-2932; i) U. Sharma, T. Naveen, A. Maji, S. Manna and D. Maiti, *Angew. Chem., Int. Ed.* 2013, **52**, 12669-12673.
- 2 a) T. R. Cook, V. Vajpayee, M. H. Lee, P. J. Stang and K.-W. Chi, *Acc. Chem. Res.* 2013, **46**, 2464-2474; b) S. K. Dash, S. Chattopadhyay, T. Ghosh, S. Tripathy, S. Das, D. Das and S. Roy, *ISRN Oncol.* 2013, 709269/709261-709269/709211; c) M. Lin, Y. Zhao, S. Wang, M. Liu, Z. Duan, Y. Chen, F. Li, F. Xu and T. Lu, *Biotechnol. Adv.* 2012, **30**, 1551-1561; d) Y. Liu, K. Ai and L. Lu, *Chem. Rev.* 2014, **114**, 5057-5115; e) A. Ruggi, F. W. B. van Leeuwen and A. H. Velders, *Coord. Chem. Rev.* 2011, **255**, 2542-2554; f) H. Wille, M. Shanmugam, M. Murugesu, J. Ollesch, G. Stubbs, J. R. Long, J. G. Safar and S. B. Prusiner, *Proc. Natl. Acad. Sci. U. S. A.* 2009, **106**, 3740-3745.
- 3 a) W. Cheng, J. He, T. Yao, Z. Sun, Y. Jiang, Q. Liu, S. Jiang, F. Hu, Z. Xie, B. He, W. Yan and S. Wei, *J. Am. Chem. Soc.* 2014, **136**, 10393-10398; b) Y.-M. Li, H.-J. Lun, C.-Y. Xiao, Y.-Q. Xu, L. Wu, J.-H. Yang, J.-Y. Niu and S.-C. Xiang, *Chem. Commun.* 2014, **50**, 8558-8560; c) N. F. Sciortino, S. M. Neville, J.-F. Letard, B. Moubaraki, K. S. Murray and C. J. Kepert, *Inorg. Chem.* 2014, **53**, 7886-7893; d) H. Shokrollahi, A. Khorramdin and G. Isapour, *J. Magn. Magn. Mater.* 2014, **369**, 176-183; e) S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben and W. Wernsdorfer, *Science* 2014, **344**, 1135-1138; f) L. Ungur, S.-Y. Lin, J. Tang and L. F. Chibotaru, *Chem. Soc. Rev.* 2014, Ahead of Print; g) D. Yang, P. a. Ma, Z. Hou, Z. Cheng, C. Li and J. Lin, *Chem. Soc. Rev.* 2014, Ahead of Print.
- 4 a) R. Sessoli, H. L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.* 1993, **115**, 1804-1816; b) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.* 2003, **42**, 268-297.
- 5 a) G. Aromi and E. K. Brechin, *Struct. Bonding (Berlin, Ger.)* 2006, **122**, 1-67; b) D. Gatteschi, A. Caneschi, L. Pardi and R. Sessoli, *Science* 1994, **265**, 1054-1058.
- 6 a) A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.* 2006, **45**, 4926-4929; b) A. M. Ako, Y. Lan, O. Hampe, E. Cremades, E. Ruiz, C. E. Anson and A. K. Powell, *Chem. Commun.* 2014, **50**, 5847-5850; c) A. M. Ako, V. Mereacre, R. Clerac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson and A. K. Powell, *Chem. Commun.* 2009, 544-546; d) C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.* 2007, **129**, 12505-12511; e) C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.* 2007, **129**, 2754-2755; f) S. Maheswaran, G. Chastanet, S. J. Teat, T. Mallah, R. Sessoli, W. Wernsdorfer and R. E. P. Winpenny, *Angew. Chem., Int. Ed.* 2005, **44**, 5044-5048; g) M. Shanmugam, G. Chastanet, T. Mallah, R. Sessoli, S. J. Teat, G. A. Timco and R. E. P. Winpenny, *Chem.-Eur. J.* 2006, **12**, 8777-8785; h) M. Shanmugam, M. Shanmugam, G. Chastanet, R. Sessoli, T. Mallah, W. Wernsdorfer and R. E. P. Winpenny, *J. Mater. Chem.* 2006, **16**, 2576-2578; i) A. Upadhyay, J. Rajpurohit, M. Kumar Singh, R. Dubey, A. Kumar Srivastava, A. Kumar, G. Rajaraman and M. Shanmugam, *Chem. Eur. J.* 2014, **20**, 6061-6070.
- 7 a) C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.* 1990, **29**, 1750-1755; b) A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *J. Magn. Magn. Mater.* 1986, **54-57**, 1485-1486; c) A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.* 1985, **107**, 8128-8136; d) M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.* 1993, **115**, 1822-1829.
- 8 S. Osa, T. Kido, N. Matsumoto, N. Re, A. Pochaba and J. Mrozinski, *J. Am. Chem. Soc.* 2004, **126**, 420-421.
- 9 a) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.* 2009, **253**, 2328-2341; b) L. Zhao, J. Wu, H. Ke and J. Tang, *Inorg. Chem.* 2014, **53**, 3519-3525; c) Q.-W. Xie, S.-Q. Wu, W.-B. Shi, C.-M. Liu, A.-L. Cui and H.-Z. Kou, *Dalton Trans.* 2014, **43**, 11309-11316; d) M. Ledezma-Gairaud, L. Grangel, G. Aromi, T. Fujisawa, A. Yamaguchi, A. Sumiyama and E. C. Sanudo, *Inorg. Chem.* 2014, **53**, 5878-5880; e) S. K. Langley, D. P. Wielechowski, V. Vieru, N. F. Chilton, B. Moubaraki, L. F. Chibotaru and K. S. Murray, *Chem. Sci.* 2014, **5**, 3246-3256; f) S. M. T. Abtab, M. C. Majee, M. Maity, J. Titis, R. Boca and M. Chaudhury, *Inorg. Chem.* 2014, **53**, 1295-1306; g) L. Ungur, M. Thewissen, J.-P. Costes, W. Wernsdorfer and L. F. Chibotaru, *Inorg. Chem.* 2013, **52**, 6328-6337; h) G. P. Guedes, S. Soriano, L. A. Mercante, N. L. Speziali, M. A. Novak, M. Andruh and M. G. F. Vaz, *Inorg. Chem.* 2013, **52**, 8309-8311; i) H. L. C. Feltham, R. Clerac, L. Ungur, L. F. Chibotaru, A. K. Powell and S. Brooker, *Inorg. Chem.* 2013, **52**, 3236-3240; j) E. Colacio, J. Ruiz, E. Ruiz, E. Cremades, J. Krzystek, S. Carretta, J. Cano, T. Guidi, W. Wernsdorfer and E. K. Brechin, *Angew. Chem., Int. Ed.* 2013, **52**, 9130-9134; k) D. I. Alexandropoulos, T. N. Nguyen, L. Cunha-Silva, T. F. Zafiroopoulos, A. Escuer, G. Christou and T. C. Stamatatos, *Inorg. Chem.* 2013, **52**, 1179-1181; l) L. Zhao, J. Wu, S. Xue and J. Tang, *Chem. - Asian J.* 2012, **7**, 2419-2423, S2419/2411-S2419/2413; m) Y. Liu, Z. Chen, J. Ren, X.-Q. Zhao, P. Cheng and

- B. Zhao, *Inorg. Chem.* 2012, **51**, 7433-7435; n) M. Holynska, D. Premuzic, I.-R. Jeon, W. Wernsdorfer, R. Clerac and S. Dehnen, *Chem. - Eur. J.* 2011, **17**, 9605-9610; o) H. L. C. Feltham, R. Clerac, A. K. Powell and S. Brooker, *Inorg. Chem.* 2011, **50**, 4232-4234; p) V. Baskar, K. Gopal, M. Helliwell, F. Tuna, W. Wernsdorfer and R. E. P. Winpenny, *Dalton Trans.* 2010, **39**, 4747-4750.
- 10 a) T. Fukuda, K. Matsumura and N. Ishikawa, *J. Phys. Chem. A* 2013, **117**, 10447-10454; b) Y.-N. Guo, G.-F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J. Tang, H.-J. Zhang, L. F. Chibotaru and A. K. Powell, *J. Am. Chem. Soc.* 2011, **133**, 11948-11951; c) N. Ishikawa, M. Sugita and W. Wernsdorfer, *Angew. Chem., Int. Ed.* 2005, **44**, 2931-2935; d) A. Saha, M. Thompson, A. Abboud Khalil, W. Wernsdorfer and G. Christou, *Inorg Chem* 2011, **50**, 10476-10485; e) T. Yamaguchi, J.-P. Costes, Y. Kishima, M. Kojima, Y. Sunatsuki, N. Brefuel, J.-P. Tuchsagues, L. Vendier and W. Wernsdorfer, *Inorg. Chem.* 2010, **49**, 9125-9135; f) T. C. Stamatatos, S. J. Teat, W. Wernsdorfer and G. Christou, *Angew. Chem., Int. Ed.* 2009, **48**, 521-524; g) A. Okazawa, T. Nogami, H. Nojiri and T. Ishida, *Chem. Mater.* 2008, **20**, 3110-3119; h) F. Mori, T. Nyui, T. Ishida, T. Nogami, K.-Y. Choi and H. Nojiri, *J. Am. Chem. Soc.* 2006, **128**, 1440-1441; i) A. Mishra, W. Wernsdorfer, K. A. Abboud and G. Christou, *J. Am. Chem. Soc.* 2004, **126**, 15648-15649.
- 11 a) S. Demir, J. M. Zadrozny, M. Nippe and J. R. Long, *J Am Chem Soc* 2012, **134**, 18546-18549; b) K. R. Meihaus, J. F. Corbey, M. Fang, J. W. Ziller, J. R. Long and W. J. Evans, *Inorg Chem* 2014, **53**, 3099-3107; c) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *Nat. Chem.* 2011, **3**, 538-542; d) J. D. Rinehart, M. Fang, W. J. Evans and J. R. Long, *J Am Chem Soc* 2011, **133**, 14236-14239.
- 12 S. K. Langley, D. P. Wielechowski, V. Vieru, N. F. Chilton, B. Moubaraki, B. F. Abrahams, L. F. Chibotaru and K. S. Murray, *Angew Chem Int Ed Engl* 2013, **52**, 12014-12019.
- 13 a) E. Colacio, J. Ruiz, G. Lorusso, E. K. Brechin and M. Evangelisti, *Chem Commun (Camb)* 2013, **49**, 3845-3847; b) M. Evangelisti and E. K. Brechin, *Dalton Trans.* 2010, **39**, 4672-4676; c) T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti and E. K. Brechin, *Angew Chem Int Ed Engl* 2012, **51**, 4633-4636; d) T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.* 2012, **51**, 4633-4636; e) G. Karotsis, M. Evangelisti, S. J. Dalgarno and E. K. Brechin, *Angew. Chem., Int. Ed.* 2009, **48**, 9928-9931; f) S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti and K. S. Murray, *Chem. Sci.* 2011, **2**, 1166-1169; g) G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, *Chem. Commun.* 2012, **48**, 7592-7594; h) G. Lorusso, W. Sharples Joseph, E. Palacios, O. Roubeau, K. Brechin Euan, R. Sessoli, A. Rossin, F. Tuna, J. L. McInnes Eric, D. Collison and M. Evangelisti, *Adv. Mater* 2013, **25**, 4653-4656; i) M. Manoli, A. Collins, S. Parsons, A. Candini, M. Evangelisti and E. K. Brechin, *J. Am. Chem. Soc.* 2008, **130**, 11129-11139; j) M. Manoli, R. D. L. Johnstone, S. Parson, M. Murrie, M. Affronte, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.* 2007, **46**, 4456-4460; k) R. S. Shaw, R. H. Laye, L. F. Jones, D. M. Low, C. Talbot-Eeckelaers, Q. Wei, C. J. Milios, S. Teat, M. Helliwell, J. Raftery, M. Evangelisti, M. Affronte, D. Collison, E. K. Brechin and E. J. L. McInnes, *Inorg. Chem.* 2007, **46**, 4968-4978; l) Y. Z. Zheng, M. Evangelisti, F. Tuna and R. E. Winpenny, *J Am Chem Soc* 2012, **134**, 1057-1065.
- 14 a) J.-W. Lu, Y.-H. Huang, S.-I. Lo and H.-H. Wei, *Inorg. Chem. Commun.* 2007, **10**, 1210-1213; b) M. Cindrić, N. Strukan, V. Vrdoljak, T. Kajfež and B. Kamenar, *Z. anorg.allg. Chem.* 2002, **628**, 2113-2117.
- 15 N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini and K. S. Murray, *J. Comput. Chem.* 2013, **34**, 1164-1175.
- 16 N. Ahmed, C. Das, S. Vaidya, S. K. Langley, K. S. Murray and M. Shanmugam, *Chem. Eur. J* 2014, DOI: 10.1002/chem.201404393.
- 17 a) C. A. Barta, S. R. Bayly, P. W. Read, B. O. Patrick, R. C. Thompson and C. Orvig, *Inorg. Chem.* 2008, **47**, 2280-2293; b) V. Chandrasekhar, B. M. Pandian, R. Boomishankar, A. Steiner, J. J. Vittal, A. Houry and R. Clerac, *Inorg. Chem.* 2008, **47**, 4918-4929; c) T. Yamaguchi, Y. Sunatsuki, H. Ishida, M. Kojima, H. Akashi, N. Re, N. Matsumoto, A. Pochaba and J. Mrozinski, *Inorg. Chem.* 2008, **47**, 5736-5745; d) J.-P. Costes, T. Yamaguchi, M. Kojima and L. Vendier, *Inorg. Chem.* 2009, **48**, 5555-5561; e) T. Yamaguchi, Y. Sunatsuki, M. Kojima, H. Akashi, M. Tsuchimoto, N. Re, S. Osa and N. Matsumoto, *Chem. Commun.* 2004, 1048-1049.
- 18 a) M. Towatari, K. Nishi, T. Fujinami, N. Matsumoto, Y. Sunatsuki, M. Kojima, N. Mochida, T. Ishida, N. Re and J. Mrozinski, *Inorg Chem* 2011, **52**, 6160-6178; b) T. D. Pasatoiu, J. P. Sutter, A. M. Madalan, F. Z. Fellah, C. Duhayon and M. Andruh, *Inorg Chem* 2011, **50**, 5890-5898.
- [19] A. Upadhyay, C. Das, M. S. Nagul, S. K. Langley, K. S. Murray and M. Shanmugam, *J. Chem. Sci.* 2014, Ahead of Print.
- 20 a) J.-P. Costes and L. Vendier, *Eur. J. Inorg. Chem.* 2010, 2768-2773; b) N. P. Burkovskaya, E. V. Orlova, M. A. Kiskin, N. N. Efimov, A. S. Bogomyakov, M. V. Fedin, S. V. Kolotilov, V. V. Minin, G. G. Aleksandrov, A. A. Sidorov, V. I. Ovcharenko, V. M. Novotortsev and I. L. Eremenko, *Russ. Chem. Bull.* 2011, **60**, 2490-2503; c) T. Shiga, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa and M. Ohba, *Inorg. Chem.* 2007, **46**, 3492-3501.
- 21 a) M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. N. Hooper, E. K. Brechin and J. J. Alonso, *Angew. Chem. Int. Ed.* 2011, **50**, 6606-6609; b) R. Sessoli, *Angew. Chem., Int. Ed.* 2012, **51**, 43-45.
- 22 a) A. Upadhyay, N. Komatireddy, A. Ghirri, F. Tuna, S. K. Langley, A. K. Srivastava, E. C. Sanudo, B. Moubaraki, K. S. Murray, E. J. McInnes, M. Affronte and M. Shanmugam, *Dalton Trans.* 2014, **43**, 259-266; b) Y. Z. Zheng, M. Evangelisti and R. E. Winpenny, *Angew Chem. Int. Ed.* 2011, **50**, 3692-3695.
- 23 A. Upadhyay, C. Das, M. Shanmugam, S. K. Langley, K. S. Murray and M. Shanmugam, *Eur. J. Inorg. Chem.* 2014, 4320-4325.

## TABLE OF CONTENTS

We have reported a series of Ni(II)-Ln(III) (where Ln = Gd or Pr) and its suitably substituted diamagnetic analogues which are characterized by X-ray diffraction. The detailed dc magnetic susceptibility measurement suggests that Ni(II) ion coupled ferromagnetically with Gd(III) ion while with anisotropic Pr(III) antiferromagnetically. In addition, magnetic coolant properties were investigated and reported for the isotropic metal complexes.

