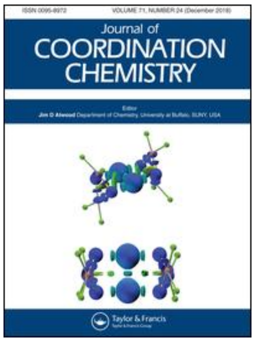

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Synthesis, characterization and magnetic studies of dinuclear lanthanide complexes constructed with a Schiff base ligand

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ABSTRACT

A series of seven isostructural homometallic dinuclear lanthanide metal complexes having the general formula $[Ln_2(L)_2(NO_3)_4]\cdot 2CH_3OH$, where L = 6-methoxy-2-(2-pyridylmethyliminomethyl) phenol Ln = Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), Tm (**5**), Yb (**6**), and Lu (**7**), are described. Compounds **1**–**7** were obtained from the reactions of Schiff base ligand (L) with the respective metal nitrates in the presence of triethylamine in MeOH. The structure of **2** was determined by single-crystal X-ray diffraction and the remaining compounds were characterized from X-ray powder diffraction patterns and found to be isostructural. The magnetic properties of **1**–**7** have been investigated using dc and ac susceptibility measurements. All these compounds show antiferromagnetic behavior between adjacent paramagnetic centers. Out of these seven compounds, only **2** displays an out-of-phase ac susceptibility signal which is attributed to the presence of the anisotropic Dy^{III} ions.

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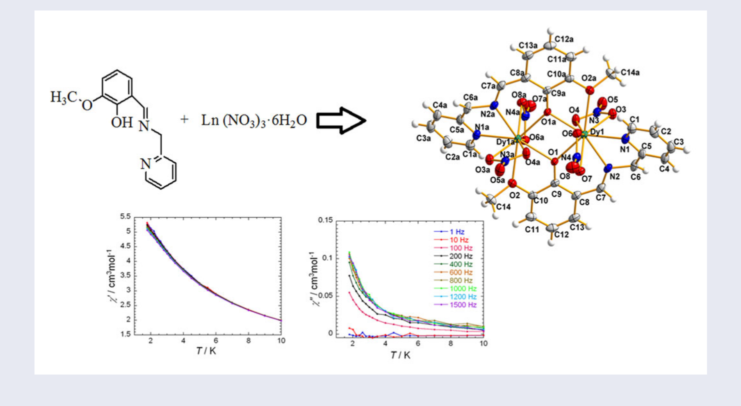


1. Introduction

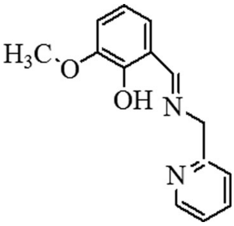
Single molecule magnets (SMMs) in the field of research are attractive for both physicists and chemists because of their promising applications in high-density information storage, molecular spintronics and quantum computing [1, 2]. Large negative axial magnetic anisotropy (*D*) and high spin values (*S*) are fundamental requirements and useful to increase the anisotropic energy barrier (U_{eff}) to reversal of the molecular magnetization [3]. Recently, attention has been diverted to lanthanide systems due to the significant magnetic anisotropy of lanthanide ions arising from their large, unquenched orbital angular momentum [4]. The significance of homonuclear lanthanide complexes in molecular magnetism has increased with the discovery of the $\{Dy_5\}$ [5] and $\{Dy_4K_2\}$ [6] complexes which display the highest barriers of energy for reversal of magnetization in any system so far. Up to now, various nuclearity lanthanide clusters have been reported [7–11] but proper ligand design system to synthesis polynuclear Ln(III) complexes with interesting properties is still a synthetic challenge.

Therefore, herein a tetradentate N,O-donor Schiff-base ligand, *i.e.* 6-methoxy-2-(2-pyridylmethyliminomethyl) phenol (HL) (Scheme 1), synthesized by condensation of o-vaniline and 2-(aminomethyl)pyridine, has been used to generate a series of isostructural dinuclear Ln compounds. The synthesized ligand has only been used previously to report Cu [12] and Pd [13] complexes. We are introducing this ligand for the first time in lanthanide chemistry.

2. Experimental

2.1. Materials and methods

All chemicals and solvents were obtained from commercially available sources and used as received without purification. o-Vanillin, 2-(aminomethyl)pyridine and $Ln(NO_3)_3·6H_2O$ (Ln = Tb, Dy, Ho, Er, Tm, Yb and Lu) were obtained from Sigma Aldrich and methanol was received from Merck. All manipulations were performed under aerobic conditions.



Scheme 1. 6-Methoxy-2-(2-pyridylmethyliminomethyl) phenol (HL).

2.2. Syntheses

The Schiff base ligand (HL) was obtained by condensation of o-vanillin (2-hydroxy-3-methoxybenzaldehyde) with 2-(aminomethyl)pyridine in methanol [14].

2.2.1. $[Tb_2(L)_2(NO_3)_4]\cdot 2CH_3OH$ (1)

To a solution containing HL (0.1 mmol, 24.2 mg), dissolved in 10 mL methanol, was added triethylamine (0.1 mmol, 10.1 mg) and the resulting mixture was stirred for about 5 min before adding slowly 10 mL of a methanolic solution containing $Tb(NO_3)_3\cdot 6H_2O$ (0.1 mmol, 45.3 mg). After 1 h of stirring, the resultant solution was filtered and left undisturbed for one week, yielding pale yellow rectangular-block crystals of the complex by slow evaporation which were collected in ~78% yield (0.086 g). Elemental analysis (%) Found (calc. for $C_{30}H_{32}Tb_2N_8O_{18}$) (1110.48 g mol^{-1}) (**1**): C, 31.92 (32.44); H, 2.98 (2.90); N, 9.86 (10.09). Selected IR data (KBr): υ cm^{-1} = 3314 (br), 1644 (s), 1609 (m), 1565 (w), 1477 (m), 1424 (w), 1379 (vs), 1265 (w), 1229 (m), 956 (m), 841 (m), 745 (s), 655(w), 576 (m), 446 (w).

2.2.2. Preparation of 2–7

Compounds **2**–**7** were obtained by the same procedure using $Dy(NO_3)_3\cdot 6H_2O$ (45.6 mg), $Ho(NO_3)_3\cdot 6H_2O$ (46.9 mg), $Er(NO_3)_3\cdot 6H_2O$ (46.1 mg), $Tm(NO_3)_3\cdot 6H_2O$ (46.3 mg), $Yb(NO_3)_3\cdot 6H_2O$ (46.7 mg) and $Lu(NO_3)_3\cdot 6H_2O$ (46.9 mg) in place of $Tb(NO_3)_3\cdot 6H_2O$, respectively. Their IR spectra are nearly identical.

2.2.2.1. $[Dy_2(L)_2(NO_3)_4]\cdot 2CH_3OH$ (2). Yield: 70% (0.077 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Dy_2N_8O_{18}$) (1117.64 g mol^{-1}) (**2**): C, 31.82 (32.24); H, 2.98 (2.88); N, 9.80 (10.02). Selected IR data (KBr): υ cm^{-1} = 3314 (br), 1644 (s), 1609 (m), 1565 (w), 1477 (m), 1424 (w), 1379 (vs), 1265 (w), 1229 (m), 956 (m), 841 (m), 745 (s), 655(w), 576 (m), 446 (w).

2.2.2.2. $[Ho_2(L)_2(NO_3)_4]\cdot 2CH_3OH$ (3). Yield: 83% (0.092 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Ho_2N_8O_{18}$) (1122.49 g mol^{-1}) (**3**): C, 31.84 (32.10); H, 2.76 (2.87); N, 9.84 (9.98). Selected IR data (KBr): υ cm^{-1} = 3323 (br), 1631 (s), 1597 (m), 1538 (w), 1465 (m), 1421 (w), 1358 (vs), 1247 (w), 1228 (m), 946 (m), 845 (m), 727 (s), 637(w), 573 (m), 429 (w).

2.2.2.3. $[Er_2(L)_2(NO_3)_4]\cdot 2CH_3OH$ (4). Yield: 60.5% (0.073 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Er_2N_8O_{18}$) (1127.15 g mol^{-1}) (**4**): C, 31.91 (31.96); H, 2.74 (2.86); N, 9.68 (9.94). Selected IR data (KBr): υ cm^{-1} = 3323 (br), 1635 (s), 1612 (m), 1546 (w), 1459 (m), 1432 (w), 1381 (vs), 1258 (w), 1225 (m), 942 (m), 843 (m), 721 (s), 643 (w), 564 (m), 422(w).

2.2.2.4. [$Tm_2(L)_2(NO_3)_4$]·2CH_3OH (5). Yield: 54% (0.059 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Tm_2N_8O_{18}$) (1130.5 g mol^{-1}) (**5**): C, 31.73 (31.87); H, 2.68 (2.85); N, 9.83 (9.91). Selected IR data (KBr): υ cm^{-1} = 3321 (br), 1645 (s), 1604 (m), 1535 (w), 1465 (m), 1420 (w), 1383 (vs), 1248 (w), 1234 (m), 946 (m), 838 (m), 737 (s), 661 (w), 565 (m), 438 (w).

2.2.2.5. [$Yb_2(L)_2(NO_3)_4$]·2CH_3OH (6). Yield: 54% (0.06 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Yb_2N_8O_{18}$) (1138.71 g mol^{-1}) (**6**): C, 31.58 (31.64); H, 2.72 (2.83); N, 9.68 (9.84) Selected IR data (KBr): υ cm^{-1} = 3314 (br), 1652 (s), 1607 (m), 1562 (w), 1468 (m), 1428 (w), 1377 (vs), 1256 (w), 1234 (m), 945 (m), 837 (m), 738 (s), 655 (w), 571 (m), 438 (w).

2.2.2.6. [$Lu_2(L)_2(NO_3)_4$]·2CH_3OH (7). Yield: 54% (0.06 g); Elemental analysis (%) Found (calc. for $C_{30}H_{32}Lu_2N_8O_{18}$) (1142.56 g mol^{-1}) (**7**): C, 31.47 (31.53); H, 2.66 (2.82); N, 9.74 (9.80). Selected IR data (KBr): υ cm^{-1} = 3323 (br), 1646 (s), 1621 (m), 1557 (w), 1477 (m), 1421 (w), 1369 (vs), 1247 (w), 1232 (m), 961 (m), 844 (m), 738 (s), 647 (w), 580 (m), 451 (w).

2.3. Physical measurements

The elemental analyses (C, H, N) were performed using an Elementar Vario EL analyser. FT-IR spectra were measured on a Perkin-Elmer *Spectrum One* spectrometer with samples prepared as KBr discs. X-ray powder diffraction patterns for **1**–**7** were measured at room temperature using a Stoe STADI-P diffractometer with a Cu K_α radiation. Single-crystal X-ray crystallographic data were collected for **2** at 130 K on a Stoe IPDS II diffractometer using graphite-monochromated Mo Kα radiation. Crystallographic data and details of measurement and refinement are summarized in Table 1. The structure was solved using direct methods, followed by full-matrix least-squares refinement against F^2 (all data) using SHELX [15]. Anisotropic refinement was used for all non-H atoms of **2**; hydrogens were placed in calculated positions.

Magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer, MPMS-XL. The magnetometer operates between 1.8 and 400 K for dc applied fields of −7 to +7 T. Measurements were performed on polycrystalline samples of 9.6 mg (**1**), 22.7 mg (**2**), 8.9 mg (**3**), 7.8 mg (**4**), 29.9 mg (**5**), 22.7 mg (**6**), and 35.6 mg (**7**). Ac susceptibility measurements were measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. The magnetic data were corrected for the sample holder and the diamagnetic contribution referenced from the Lu_2 compound **7**.

3. Results and discussion

3.1. Synthesis

The room temperature reaction of $Ln(NO_3)_3 \cdot xH_2O$, HL, and triethylamine with a molar ratio of 0.1/0.1/0.1 in methanol led to formation of rectangular-block pale yellow crystals of **1**–**7** in *ca.* 54–78% yield after one week by slow evaporation. Compounds **1**–**7**

Table 1. Crystallographic data and structure refinement for **2**.

Formula	$C_{30}H_{32}Dy_2N_8O_{18}$
FW [g mol^{-1}]	1117.64
Crystal dimensions [mm^3]	$0.15 \times 0.13 \times 0.10$
Color	Yellow
Crystal system	Triclinic
Space group	*P*-1
T [K]	180(2)
a [Å]	9.7117(19)
b [Å]	9.907(2)
c [Å]	11.010(2)
α [°]	71.96(3)
β [°]	68.20(3)
γ [°]	88.48(3)
V [Å^3]	930.5(4)
Z	1
ρ_{calcd} [g cm^{-3}]	1.995
μ(Mo-Kα) [mm^{-1}]	4.074
F(000)	544
Data measured	11633
Unique data	3779
R_{int}	0.0492
Data with $I > 2\sigma(I)$	3690
Parameters/restraints	255/0
wR_2 (all data)	0.0565
Gof on F^2 (all data)	1.108
R_1 [data with $I > 2\sigma$(I)]	0.0202
Largest difference peak/hole [e Å^{-3}]	0.897/−1.248
CCDC number	823654

are stable, retain their crystallinity on exposure to air and are soluble in common organic solvents such as methanol, acetone, acetonitrile, tetrahydrofuran and *N,N′*-dimethylformamide.

3.2. Description of the structure

X-ray powder diffraction indicates that all seven compounds are isostructural (Figure 1), thus only the full structure of **2** was determined by single crystal X-ray diffraction. Dinuclear complex **2** crystallizes in the triclinic space group *P*-1 with $Z = 1$ with two molecules of lattice bound methanol per formula unit. Selected interatomic distances are listed in Table 2. A perspective view of the dinuclear unit is depicted in Figure 2. The complex consists of two dysprosium(III) ions which are linked by phenoxo oxygen atoms of two Schiff base ligands with Dy–O distances Dy(1)–O(1) = 2.3036(19) Å and Dy(1)–O(1a) = 2.357(2) Å and a Dy(1)–O(1)–Dy(1a) angle of 105.86(8). The Dy(1) … Dy(1a) distance is 3.7186(12) Å. The dinuclear aggregate is centrosymmetric. Each Dy(III) ion is nine-coordinate by three oxygens and two nitrogens from the Schiff base ligand and four oxygens belonging to two nitrate anions in the bidentate coordination mode. The Dy–O bond lengths are in the range of 2.3036(19)–2.428(2) Å. The Dy–N bond lengths are 2.42(2) and 2.907(3) Å. The bond angles and bond lengths are shown in Table 2. The coordination polyhedron of the nine-coordinate Dy(III) ions can be approximated as a distorted three-capped trigonal prism (Figure 3). A literature review indicates that various [Dy_2] clusters with their bond lengths and bond angles are comparable with our synthesized compound. For example, Powell *et al.* reported

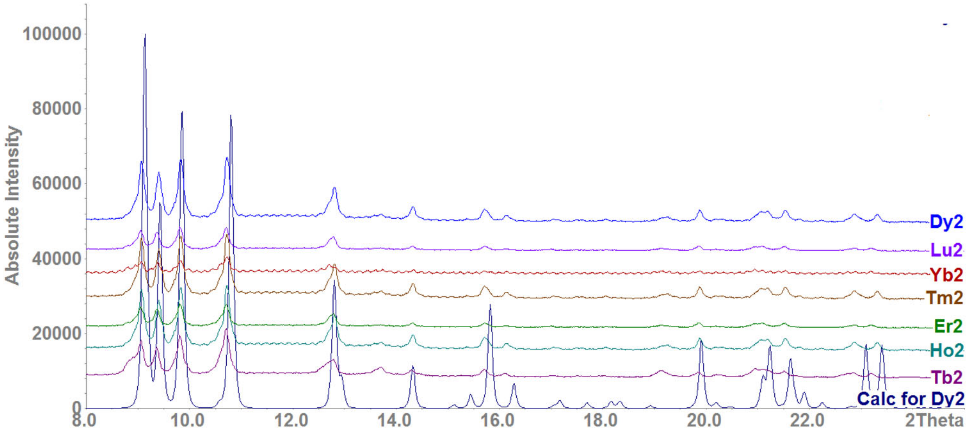


Figure 1. Comparison of simulated powder X-ray diffraction (PXRD) pattern of **2** (Dy_2) with experimental pattern of **1**–**7**.

[16] three centrosymmetric dinuclear Dy complexes with the Dy–O (bridged) bond lengths: Dy1–O1a = 2.255(5) and Dy1–O1 = 2.277 Å for $[Dy_2(HL_1)_2(NO_3)_4]$, where HL_1 = 2-[(2-hydroxy-ethyl)-pyridin-2-ylmethylamino]ethanol; Dy1–O1a = 2.259(7) and Dy1–O1 = 2.266(7) Å for $[Dy_2(L_2)_2(NO_3)_4]$, where HL_2 = 2-(bis-pyridin-2-ylmethylamino)-ethanol; Dy1–O1a = 2.257(17) and Dy1–O1 = 2.265(17) Å for $[Dy_2(HL_3)_2(NO_3)_4]$, where HL_3 = 2-(bis-pyridin-2-ylmethylamino)-propane-1,3-diol. While their Dy1–O–Dy1a bonds angles are: 109.83(18)°, 109.71(15)°, and 110.65(7)°, respectively. Similarly, Baskar *et al.* [17] reported $[Dy_2(L)_2(Ph_2acac)_2(OH_2)_2]_3$ cluster using Schiff base ligand with bond lengths, Dy1–O1 = 2.325(4) and Dy1–O2 = 2.254(4) Å and bond angles, Dy1–O1–Dy1a = 105.6(14)°.

3.3. Magnetic properties

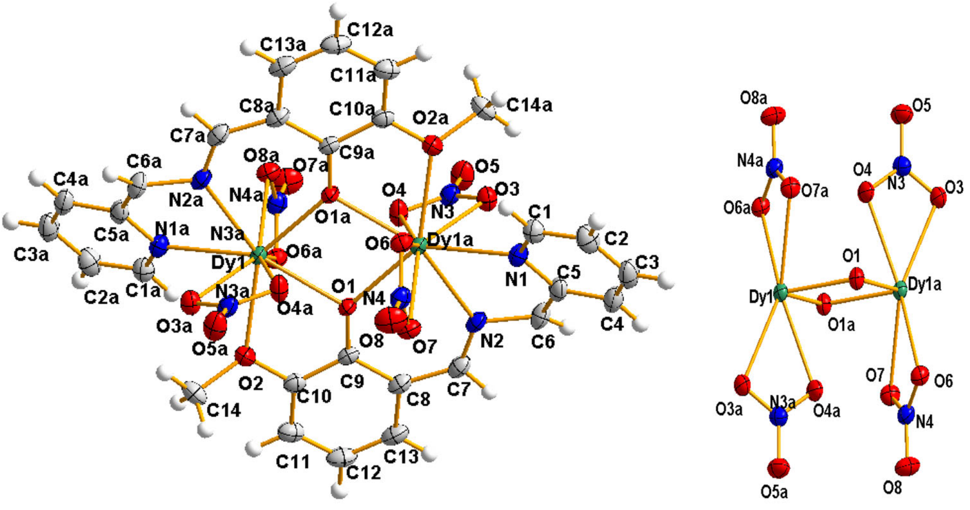
Variable-temperature dc magnetic susceptibility data for **1**–**7** were collected in the temperature range 1.8–300 K under an applied field of 0.1 T (Figure 4). Of this series of compounds, Lu_2 (**7**) is a diamagnetic compound; thus its magnetic susceptibility ($\chi_{Lu2} = \chi_{dia} = -3.9 \times 10^{-4}\,cm^3\ mol^{-1}$) was used for diamagnetic correction for the other complexes (**1**–**6**). The dc magnetic data of **1**–**6** are summarized in Table 3. The observed χT products at room temperature are in good agreement with the expected values for two non-interacting Ln^{III} ions. On lowering the temperature, the χT products decrease steadily down to 30 K and then undergo a more abrupt decrease down to 1.8 K. The continuous decrease of χT product mainly results from the thermal depopulation of the Stark sublevels of the anisotropic Ln^{III} (Tb, Dy, Ho, Er, Tm, and Yb) ions since the Ln···Ln interactions are probably insignificant by comparison to other Ln complexes with similar superexchange bridges [18–20].

The field dependence of the magnetization of **1**–**6** at low temperatures shows that the magnetization increases smoothly with increasing applied dc field without saturation even at 7 T (Figure S1). The magnitude of magnetization at 1.8 K is also given in Table 3. This behavior indicates the presence of magnetic anisotropy and/or the lack

Table 2. Selected bond distances (Å) and angle parameters (°) for **2**.

Dy1–O1	2.3036(19)	Dy1–N4	2.882(3)	Dy1–O1–Dy1a	105.86(8)
Dy1–O1a	2.357(2)	Dy1–N3	2.907(3)	O1–Dy–N2	77.82(8)
Dy1–O2a	2.428(2)	Dy1–Dy1a	3.7186(12)	O1–Dy–O1a	74.14(8)
Dy1–N2	2.428(2)	O1–Dy1a	2.357(2)	$O1^i$–Dy1–O2a	66.88(7)
Dy1–O4	2.454(2)	O2–Dy1a	2.428(2)	$O1^i$–Dy1–O2a	66.88(7)
Dy1–O7	2.457(2)	Dy1–O3	2.497(2)	O1–Dy1–O2a	140.30
Dy1–N1	2.489(3)	Dy1–O6	2.448(2)	N2–Dy1–N1	67.79(9)

Symmetry code: (i) $-x+1$, $-y+1$, $-z$.



(a) (b)

Figure 2. Thermal ellipsoid structure of $[Dy_2(L)_2(NO_3)_4]\cdot 2CH_3OH$ (a) nitrate ligands relative to the cluster cores (b).

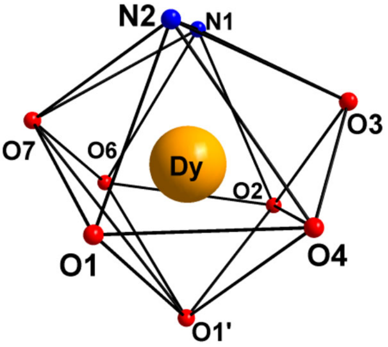


Figure 3. Distorted three-capped trigonal prism environment.

of a well-defined ground state, suggesting the presence of low-lying excited states that might be populated when a field is applied.

The magnetic relaxation was tested for all compounds using ac susceptibility measurements under zero dc field. We found that only **2** exhibits a non-zero out-of-phase component below 10 K, indicating slow relaxation of its magnetization under these conditions (Figure 5). The in-phase component of ac susceptibility is weakly frequency

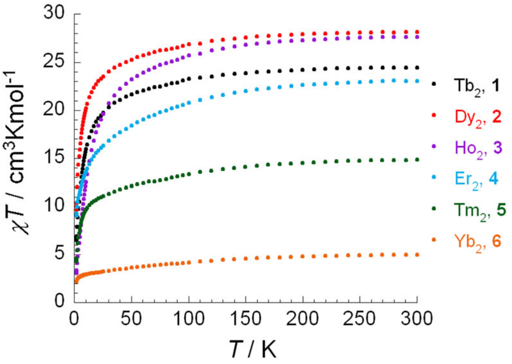


Figure 4. Temperature dependence of the χT products for **1**–**6** at 0.1 T (with χ being the molar susceptibility defined as *M*/*H*).

Table 3. Summary of the dc magnetic data for **1**–**6**.

Compounds	**1** (Tb)	**2** (Dy)	**3** (Ho)	**4** (Er)	**5** (Tm)	**6** (Yb)
Ground state term of Ln^{III} ion	$^7F_6$	$^6H_{15/2}$	$^5I_8$	$^4I_{15/2}$	$^3H_6$	$^2F_{7/2}$
S	3	5/2	2	3/2	1	1/2
L	3	5	6	6	5	3
g	3/2	4/3	5/4	6/5	7/6	8/7
C (cm^3 K mol^{-1}) for each Ln ion[9]	11.82	14.17	14.07	11.5	7.15	2.57
χT (cm^3 K mol^{-1}) expected value for 2 non-interacting Ln$_2$ at RT	23.64	28.34	28.14	23.00	14.30	5.14
χT (cm^3 K mol^{-1}) experimental value for Ln$_2$ at RT	24.44	28.15	27.65	23.09	14.85	4.99
χT (cm^3 K mol^{-1}) experimental value for Ln$_2$ at 1.8 K	6.49	9.70	3.10	9.04	4.28	2.20
Magnetization (μ_B) observed at 7 T and 1.8 K	11.4	11.0	9.4	9.8	7.1	4.0

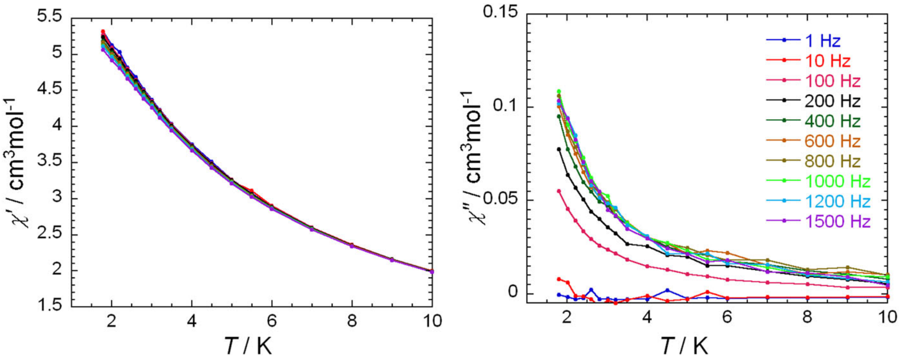


Figure 5. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') components of the ac magnetic susceptibility at indicated frequencies for **2** under zero dc field.

dependent but that of out-of-phase component is strongly frequency dependent, suggesting that this compound is a SMM. However, the energy barrier for the relaxation process cannot be determined from this set of data because the maxima of the χ'' peaks are out of the ranges available (lowest temperature 1.8 K and highest frequency 1500 Hz) on the SQUID. The barrier for the reversal of the magnetization is generated by the presence of magnetic anisotropy of the Dy^{3+} ions as is often observed in many such compounds [18–20], but it is impossible to discuss it more without any further measurements, for instance hysteresis measurements using a micro-SQUID magnetometer.

In order to study the relaxation behavior further and check for quantum tunneling effects above 1.8 K, the frequency dependence of the ac susceptibility of **1** and **2** at 1.8 K was also measured with application of small dc fields up to 2000 Oe. In SMMs with a relaxation partially influenced by quantum effects, the application of a dc field removes the ground state degeneracy and thus the possibility of quantum tunneling, inducing a slowing down of the magnetization relaxation. For Tb compound **1**, there is no field-induced magnetic relaxation appearing under an external field (Figure S2); however, for Dy compound **2**, the slow relaxation process is not significantly influenced by applying an external dc field (Figure S3), indicating that no appreciable quantum tunneling effect is observed above 1.8 K.

4. Conclusion

A series of dinuclear lanthanide complexes formulated as $[Ln_2(L)_2(NO_3)_4]\cdot 2CH_3OH$, where Ln is Tb (**1**), Dy (**2**), Ho (**3**), Er (**4**), Tm (**5**), Yb (**6**), and Lu (**7**), was constructed from Schiff base ligand. Magnetic studies of these compounds revealed antiferromagnetic behavior between adjacent paramagnetic centers and Dy containing compound exhibit slow relaxation. This type of ligand, therefore, provides an avenue to obtain a dinuclear compound having interesting magnetic properties.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

[1] (a) J. Wang, M. Feng, M.N. Ahtar, M.-L. Tong. *Coord. Chem. Rev.*, **387**, 129 (2019). (b) R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, F. Balestro. *Nature*, **488**, 357 (2012). (c) S. Loth, S. Baumann, C.P. Lutz, D.M. Eigler, A.J. Heinrich. *Science*, **335**, 196 (2012).

[2] (a) A. Ardavan, O. Rival, J.J.L. Morton, S.J. Blundell, A.M. Tyryshkin, G.A. Timco, R.E.P. Winpenny. *Phys. Rev. Lett.*, **98**, 57 (2007). (b) G.-Z. Huang, Z.-Y. Ruan, J.-Y. Zheng, J.-Y. Wu, Y.-C. Chen, Q.-W. Li, M.N. Akhtar, J.-L. Liu, M.-L. Tong. *Sci. China Chem.*, **61**, 1399 (2018).

[3] (a) M.N. Akhtar, Y. Lan, M.A. Aldamen, Y.-Z. Zheng, C.E. Anson, A.K. Powell. *Dalton Trans.*, **47**, 348 (2018). (b) B.H. Koo, K.S. Lim, D.W. Ryu, W.R. Lee, E.K. Koh, C.S. Hong. *Chem. Commun.*, **48**, 2519 (2012). (c) M.N. Akhtar, Y. Lan, V. Mereacre, M.A. AlDamen, C.E. Anson, A.K. Powell. *Monatsh. Chem.*, **148**, 887 (2017). (d) M.N. Akhtar, Y. Zheng, Y. Lan, V. Mereacre, C.E. Anson, A.K. Powell. *Inorg. Chem.*, **48**, 350 (2009).

[4] (a) F.-S. Guo, B.M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R.A. Layfield. *Science*, **362**, 1400 (2018). (b) M.N. Akhtar, X.-F. Liao, Y.-C. Chen, J.-L. Liu, M.-L. Tong. *Dalton Trans.*, **46**, 2981 (2017). (c) J.-L. Liu, Y.-C. Chen, M.-L. Tong. *Chem. Soc. Rev.*, **47**, 2431 (2018).

[5] R.J. Blagg, C.A. Muryn, E.J.L. McInnes, F. Tuna, R.E.P. Winpenny. *Angew. Chem. Int. Ed.*, **50**, 6530 (2011).

[6] R.J. Blagg, L. Ungur, F. Tuna, J. Speak, P. Comar, D. Collison, W. Wernsdorfer, E.J.L. McInnes, L.F. Chibotaru, R.E.P. Winpenny. *Nat. Chem.*, **5**, 673 (2013).

[7] (a) G.F. Xu, Q.L. Wang, P. Gamez, Y. Ma, R. Clérac, J.K. Tang, S.P. Yan, P. Cheng, D.Z. Liao. *Chem. Commun.*, **46**, 1506 (2010). (b) R.A. Layfield, J.J.W. McDouall, S.A. Sulway, F. Tuna, D. Collison, R.E.P. Winpenny. *Chem. Eur. J.*, **16**, 4442 (2010). (c) Y.N. Guo, G.F. Xu, W. Wernsdorfer, L. Ungur, Y. Guo, J.K. Tang, H.J. Zhang, L.F. Chibotaru, A.K. Powell. *J. Am. Chem. Soc.*, **133**, 11948 (2011). (d) F. Habib, P.-H. Lin, J. Long, I. Korobkov, W. Wernsdorfer, M. Murugesu. *J. Am. Chem. Soc.*, **133**, 8830 (2011). (e) F. Habib, M. Murugesu. *Chem. Soc. Rev.*, **42**, 3278 (2013).

[8] (a) I.J. Hewitt, Y. Lan, C.E. Anson, J. Luzon, R. Sessoli, A.K. Powell. *Chem. Commun.*, 6765 (2009). (b) J. Luzon, K. Bernot, I.J. Hewitt, C.E. Anson, A.K. Powell, R. Sessoli. *Phys. Rev. Lett.*, **100**, 247205 (2008). (c) M.U. Anwar, S.S. Tandon, L.N. Dawe, F. Habib, M. Murugesu, L.K. Thompson. *Inorg. Chem.*, **51**, 1028 (2012). (d) F.S. Guo, J.L. Liu, J.D. Leng, Z.S. Meng, Z.J. Lin, M.L. Tong, S. Gao, L. Ungur, L.F. Chibotaru. *Chem. Eur. J.*, **17**, 2458 (2011). (e) J.K. Tang, I. Hewitt, N.T. Madhu, G. Chastanet, W. Wernsdorfer, C.E. Anson, C. Benelli, R. Sessoli, A.K. Powell. *Angew. Chem. Int. Ed.*, **45**, 1729 (2006). (f) P. Zhang, L. Zhang, S.-Y. Lin, S. Xue, J.K. Tang. *Inorg. Chem.*, **52**, 4587 (2013).

[9] (a) M.T. Gamer, Y. Lan, P.W. Roesky, A.K. Powell, R. Clérac. *Inorg. Chem.*, **47**, 6581 (2008). (b) J.B. Peng, X.J. Kong, Y.P. Ren, L.S. Long, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **51**, 2186 (2012). (c) R.J. Blagg, C.A. Muryn, E.J.L. McInnes, F. Tuna, R.E.P. Winpenny. *Angew. Chem. Int. Ed.*, **50**, 6530 (2011).

[10] (a) B. Hussain, D. Savard, T.J. Burchell, W. Wernsdorfer, M. Murugesu. *Chem. Commun.*, 1100 (2009). (b) I.J. Hewitt, J.K. Tang, N.T. Madhu, C.E. Anson, Y. Lan, J. Luzon, M. Etienne, R. Sessoli, A.K. Powell. *Angew. Chem., Int. Ed.*, **49**, 6352 (2010). (c) S. Xue, L. Zhao, Y.N. Guo, P. Zhang, J.K. Tang. *Chem. Commun.*, **48**, 8946 (2012). (d) Y.N. Guo, X.H. Chen, S. Xue, J.K. Tang. *Inorg. Chem.*, **51**, 4035 (2012). (e) H. Tian, M. Wang, L. Zhao, Y.N. Guo, Y. Guo, J.K. Tang, Z. Liu. *Chem. Eur. J.*, **18**, 442 (2012). (f) S.-Y. Lin, W. Wernsdorfer, L. Ungur, A.K. Powell, Y.-N. Guo, J.K. Tang, L. Zhao, L.F. Chibotaru, H.-J. Zhang. *Angew. Chem. Int. Ed.*, **51**, 12767 (2012).

[11] (a) J.D. Rinehart, M. Fang, W.J. Evans, J.R. Long. *J. Am. Chem. Soc.*, **133**, 14236 (2011). (b) R.J. Blagg, F. Tuna, E.J.L. McInnes, R.E.P. Winpenny. *Chem. Commun.*, **47**, 10587 (2011). (c) M.A. AlDamen, S. Cardona-Serra, J.M. Clemente-Juan, E. Coronado, A. Gaita-Ariño, C. Martí-Gastaldo, F. Luis, O. Montero. *Inorg. Chem.*, **48**, 3467 (2009). (d) S.D. Jiang, B.W. Wang, H.L. Sun, Z.M. Wang, S. Gao. *J. Am. Chem. Soc.*, **133**, 4730 (2011).

[12] (a) S. Xuan. *Acta Crystallogr. E*, **64**, m33 (2008). (b) C. Maxim, T.D. Pasatoiu, V.C. Kravtsov, S. Shova, C.A. Muryn, R.E.P. Winpenny, F. Tuna, M. Andruh. *Inorg. Chim. Acta*, **361**, 3903 (2008).

[13] S.A. Patil, C.-M. Weng, P.-C. Huang, F.-E. Hong, S.A. Patil. *Tetrahedron*, **65**, 2889 (2009).

[14] Z.-H. Ni, H.-L. Wang. *Acta Crystallogr. E*, **64**, 3799 (2007).

[15] G.M. Sheldrick. *Acta Crystallogr. A*, **64**, 112 (2008).

[16] Y. Peng, V. Mereacre, A. Baniodeh, Y. Lan, M. Schlageter, G.E. Kostakis, A.K. Powell. *Inorg. Chem.*, **55**, 68 (2016).

[17] A. Kumar Jami, J. Ali, S. Mondal, J. Homs-Esquius, E. Carolina Sañudo, V. Baskar. *Polyhedron*, **151**, 90 (2018).

[18] G. Abbas, Y. Lan, G. Kostakis, C.E. Anson, A.K. Powell. *Inorg. Chim. Acta*, **361**, 3494 (2008).

[19] G. Abbas, Y. Lan, G.E. Kostakis, W. Wernsdorfer, C.E. Anson, A.K. Powell. *Inorg. Chem.*, **49**, 8067 (2010).

[20] P.W. Roesky, A. Bhunia, Y. Lan, A.K. Powell, S. Kureti. *Chem. Commun.*, **47**, 2035 (2011).