



## Two one-dimensional lanthanide compounds with pentagonal bipyramidal Er<sup>III</sup> centers showing slow magnetic relaxation

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### ABSTRACT

Two one-dimensional (1D) erbium compounds based on the pentadentate ligand N1, N3-bis(3-methoxy-salicylidene) diethylenetriamine (H<sub>2</sub>valdien) and a bulky anion diphenyl phosphate ([PhO<sub>2</sub>PO<sub>2</sub>]<sup>-</sup>) of [ErNa(valdien)Cl((PhO)<sub>2</sub>PO<sub>2</sub>)<sub>n</sub>] (1) and [Er(valdien)((PhO)<sub>2</sub>PO<sub>2</sub>)<sub>n</sub>] (2) have been synthesized and characterized by single-crystal X-ray diffraction analysis. For both compounds 1 and 2, each Er<sup>III</sup> ion adopts a seven-coordinate ligand set and has a distorted pentagonal bipyramidal geometry with pseudo-*D*<sub>5h</sub> symmetry. The Er<sup>III</sup> centers are bridged by Cl and/or diphenyl phosphate anions to form 1D chains along the b axis. Furthermore, detailed magnetic measurements indicate that both compounds 1 and 2 exhibit field-induced slow magnetic relaxation behavior. The energy barrier *U*<sub>eff</sub> of compound 1 was determined to be (14.19 ± 0.73) cm<sup>-1</sup> ((20.41 ± 1.05) K) for only Orbach process. And the spin–lattice relaxation of both Raman and Orbach processes was considered for compound 1 and the observed energy barrier in whole region was (36.01 ± 5.03) cm<sup>-1</sup> ((51.82 ± 7.23) K). These results demonstrated that the lanthanide compounds with pentagonal bipyramidal geometry (pseudo-*D*<sub>5h</sub>) could be effectively designed and synthesized by using a suitable pentadentate ligand.

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### 1. Introduction

The rocketing development in the area of lanthanide single-molecule magnets (SMMs) has been encouraged by their promising applications in information storage [1] and spintronic devices [2]. Despite many mono- and polynuclear lanthanide SMMs have been reported so far, great interest still remains constrained to heavy lanthanide ions, such as Dy<sup>III</sup>, Tb<sup>III</sup>, Er<sup>III</sup> and Ho<sup>III</sup>, due to their strong spin–orbit coupling and leading to large magnetic anisotropy [3]. Till now, monometallic SMMs (or called single-ion magnets (SIMs)) with specific symmetry related to single-ion magnetic anisotropy have become the requirement and criterion to gain the large energy barriers (*U*<sub>eff</sub>) and high blocking temperature (*T*<sub>B</sub>). A striking approach to gain the excellent magnetic properties can be achieved by means of controlling the symmetry of simple monometallic lanthanide compounds. The following illustration provides some typical examples, mononuclear Tb porphyrins compounds with pseudo-*D*<sub>4d</sub> symmetry and Tb radical-bridged compounds have the large *U*<sub>eff</sub> of 652 cm<sup>-1</sup> [4] and *T*<sub>B</sub> of 14 K [5] and keep the record for a long time. Recently, Dy SIMs with pentagonal bipyramid geometry (*D*<sub>5h</sub>) have the energy barrier exceeded 1000

K (1815 K) [6,7] and the blocking temperature of 20 K [8]. Remarkably, to date, an organometallic compound [Dy(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] exhibits magnetic hysteresis at temperatures of up to 60 K [9,10]. Indeed, Er<sup>III</sup> ion is also a Kramers ion like Dy<sup>III</sup> with a *J* = 15/2 ground state, which also has large magnetic anisotropy. For instance, the POM-containing compounds [Er(W<sub>5</sub>O<sub>18</sub>)<sub>2</sub>]<sup>9-</sup> and [Er(SiW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>13-</sup> with *D*<sub>4d</sub> symmetry show SMM properties [11]. And the organometallic sandwich compounds with COT systems, [(Cp<sup>\*</sup>)Er(COT)] was the first organometallic Er<sup>III</sup> compounds with high performance SIM behavior [12], [Er(COT)<sub>2</sub>]<sup>-</sup> has been demonstrated to be the blocking temperature at 10 K [13], [Er(COT<sup>o</sup>)] exhibits the hysteresis loops up to 8 K with an energy barrier of 187(1) K [14], and [(C<sub>5</sub>H<sub>5</sub>BH)Er(COT)] obtained the highest energy barrier (300 cm<sup>-1</sup>) among all the reported erbium SIMs [15]. The exceptional slow relaxation observed for the compounds can be rationalized by considering that large conjugated  $\pi$ -system formed by the [Cp<sup>\*</sup>]<sup>-</sup>, C<sub>5</sub>H<sub>5</sub>BH<sup>-</sup>, COT<sup>2-</sup> and COT<sup>o2-</sup> ligands creates a strong equatorial ligand field to stabilize *m*<sub>J</sub> = ±15/2. In addition, a series of Er<sup>III</sup> silazanes compounds with C<sub>3v</sub> and *D*<sub>3h</sub> symmetry, such as Er(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> with a trigonal planar geometry [16], [Li(THF)<sub>4</sub>{Er[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>Cl}·2THF with a trigonal–pyramidal geometry [17], also showed high performance of SMM behaviors under a zero dc field. Furthermore, the air-stable Er complexes based on the Schiff-base ligands such as [Er(HL)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] [18] and [Er(N<sub>5</sub>)<sub>2</sub>]<sup>3+</sup>

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[19] also show the field-induced SIM behavior. A series of air-stable Er<sup>III</sup>  $\beta$ -diketonate complexes [20–22] and a layered erbium phosphonate [Er(notpH<sub>4</sub>(H<sub>2</sub>O))ClO<sub>4</sub>·3H<sub>2</sub>O [23] show the field-induced SIM behavior and luminescent properties, which provide an approach to design and obtain multifunctional molecule-based materials combining magnetism with luminescence, and other properties.

As mentioned above, the mononuclear lanthanide compounds with an appropriate spherical coordination geometry showed the slow magnetic relaxation behavior. It is worth noting that the specific symmetry of the crystal field could stabilize the  $m_J$  ground state. Consequently, it has a great possibility to gain the SIM behavior by controlling the symmetry of the lanthanide centers, especially for the simple mononuclear lanthanide compounds. Generally speaking, the coordination number of lanthanide complexes are eight-coordinate or more. Importantly, the mononuclear seven-coordinated lanthanide compounds with pentagonal bipyramidal geometry have the great potentials for constructing suitable crystal field environment to design the SIMs. To gain a pentagonal bipyramidal geometry (seven-coordinate), one of the effective synthetic strategy is to design a nearly coplanar pentadentate ligand with fruitful O atoms.

Recently, we reported a series of 1D Ln<sup>III</sup> coordination polymers with pentagonal bipyramidal Ln<sup>III</sup> centers by using a simple pentadentate ligand and carefully studied the SMM behaviors of the Dy<sup>III</sup> compounds [24]. Herein, we continue to focus on the rare Er<sup>III</sup> compounds compare with the Dy<sup>III</sup> SMMs. Interestingly enough, the two 1D Er<sup>III</sup> coordination polymers also display SMM behavior.

## 2. Materials and methods

### 2.1. Materials

All preparations and manipulations were performed under aerobic conditions. The ligand H<sub>2</sub>valdien (H<sub>2</sub>valdien = N1, N3-bis(3-methoxysalicylidene) diethylenetriamine) was prepared according to a method described previously [25].

**Preparation of Na(PhO)<sub>2</sub>PO<sub>2</sub>.** Diphenyl phosphate (PhO)<sub>2</sub>PO<sub>2</sub>H (10 mmol, 0.25 g) was added to the solution of NaOH (10 mmol, 0.4 g) in MeOH (20 mL), then the mixture was vigorously stirred for 2 h at room temperature, concentrated up to dryness under reduced pressure and then washed several times with MeOH and Et<sub>2</sub>O to give the white solid (Na(PhO)<sub>2</sub>PO<sub>2</sub>) without further purification for use directly. Yield, 96%.

### 2.2. Preparation of compounds 1 and 2

[ErNa(valdien)Cl((PhO)<sub>2</sub>PO<sub>2</sub>)<sub>n</sub>] (1). To a solution of H<sub>2</sub>valdien (0.15 mmol, 55 mg), Et<sub>3</sub>N (0.30 mmol, 41.8  $\mu$ L) in MeOH (3 mL) was added a MeOH solution (2 mL) of ErCl<sub>3</sub>·6H<sub>2</sub>O (0.15 mmol, 57 mg). The solution was stirred for 3 min, and then a MeOH solution (2 mL) of Na(PhO)<sub>2</sub>PO<sub>2</sub> (0.15 mmol, 40.5 mg) was added to the mixture. The resulting clear yellow solution was stirred briefly and filtered. The yellow block crystals suitable for X-ray diffraction studies were obtained by slow diffusion of isopropyl ether vapor into the yellow solution after 3 days. Yield: ca. 45%. Elemental analysis (%) calculated for C<sub>32</sub>H<sub>33</sub>ClErN<sub>3</sub>NaO<sub>8</sub>P: C, 45.52; H, 3.94; N, 4.98. Found: C, 45.48; H, 3.99; N, 4.96. IR (KBr, cm<sup>-1</sup>): 3439 (m), 3203 (w), 2918 (w), 1628 (vs), 1602 (w), 1489 (w), 1471 (s), 1455 (s), 1440 (w), 1252 (vs), 1220 (s), 1099 (s), 1079 (m), 923 (m), 910 (s), 901 (m), 899 (m), 750 (m), 742 (s), 626 (w), 534 (m).

[Er(valdien)((PhO)<sub>2</sub>PO<sub>2</sub>)<sub>n</sub>] (2). To a solution of H<sub>2</sub>valdien (0.15 mmol, 55 mg), Et<sub>3</sub>N (0.30 mmol, 41.8  $\mu$ L) and ErCl<sub>3</sub>·6H<sub>2</sub>O (0.15 mmol, 57 mg) in DMF/MeOH (5 mL, v/v = 1/4) was added a DMF/MeOH (2 mL, v/v = 1/4) solution of (PhO)<sub>2</sub>PO<sub>2</sub>H (0.15 mmol, 37.5

mg) and Et<sub>3</sub>N (0.15 mmol, 20.9  $\mu$ L). The resulting clear yellow solution was stirred briefly and filtered. The yellow block crystals suitable for X-ray diffraction studies were obtained by slow diffusion

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

Complex	1	2
Formula	ErNaC <sub>32</sub> H <sub>33</sub> N <sub>3</sub> O <sub>8</sub> ClP	ErC <sub>32</sub> H <sub>33</sub> N <sub>3</sub> O <sub>8</sub> P
Mr [g mol <sup>-1</sup> ]	844.28	785.84
CCDC number	1573742	1573743
Crystal size [mm <sup>3</sup> ]	0.42 × 0.36 × 0.28	0.38 × 0.18 × 0.08
Crystal system	orthorhombic	monoclinic
Space group	<i>P bca</i>	<i>P 2<sub>1</sub>/c</i>
<i>a</i> [Å]	22.078(3)	11.0338(15)
<i>b</i> [Å]	8.3227(14)	11.6491(16)
<i>c</i> [Å]	36.813(6)	27.321(3)
$\alpha$ [°]	90	90
$\beta$ [°]	90	113.819(4)
$\gamma$ [°]	90	90
<i>V</i> [Å <sup>3</sup> ]	6764.3(18)	3212.6(7)
<i>Z</i>	8	4
<i>T</i> [K]	293(2)	293(2)
$\rho_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.658	1.625
$\mu$ (Mo K $\alpha$ ) [mm <sup>-1</sup> ]	2.674	2.717
<i>F</i> (000)	3368	1572
$\theta$ range [°]	2.151–24.998	2.670–27.582
Refl. collected/unique	34633/5922	56915/7411
<i>R</i> (int)	0.0310	0.0236
<i>T</i> <sub>max</sub> / <i>T</i> <sub>min</sub>	0.5214/0.3997	0.7456/0.5987
Data/restraints/parameters	5921/0/426	7411/0/408
<i>R</i> <sub>1</sub> <sup>a</sup> / <i>wR</i> <sub>2</sub> <sup>b</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0604/0.1156	0.0309/0.0770
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all data)	0.0629/0.1169	0.0368/0.0908
GOF on <i>F</i> <sup>2</sup>	1.063	1.068
Max/min [e Å <sup>-3</sup> ]	1.431/−2.905	1.681/−2.871

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

**Table 2**  
Selected bond distances [Å] and angles [°] for 1 and 2.

1			
Er(1)–O(1)	2.183(5)	Er(1)–N(1)	2.486(7)
Er(1)–O(3)	2.205(5)	Er(1)–N(3)	2.504(8)
Er(1)–O(5)	2.248(5)	Er(1)–Cl(1)	2.606(2)
Er(1)–N(2)	2.459(7)	Er(1)–Na(1)	3.605(4)
O(1)–Er(1)–O(3)	76.3(2)	O(3)–Er(1)–N(2)	139.6(2)
O(1)–Er(1)–O(5)	89.9(2)	O(5)–Er(1)–N(2)	79.72(19)
O(3)–Er(1)–O(5)	89.90(19)	O(1)–Er(1)–N(1)	73.8(2)
O(1)–Er(1)–N(2)	141.7(2)	O(3)–Er(1)–N(1)	150.0(2)
O(5)–Er(1)–N(1)	86.5(2)	O(5)–Er(1)–N(3)	86.6(2)
N(2)–Er(1)–N(1)	68.9(2)	N(2)–Er(1)–N(3)	67.7(2)
O(1)–Er(1)–N(3)	149.0(2)	N(1)–Er(1)–N(3)	136.5(2)
O(3)–Er(1)–N(3)	72.8(2)	O(1)–Er(1)–Cl(1)	103.20(16)
O(3)–Er(1)–Cl(1)	103.30(16)	N(1)–Er(1)–Cl(1)	87.05(18)
O(5)–Er(1)–Cl(1)	163.19(14)	N(3)–Er(1)–Cl(1)	87.42(19)
N(2)–Er(1)–Cl(1)	83.48(15)		
2			
Er(1)–O(3)	2.185(3)	Er(1)–N(3)	2.519(4)
Er(1)–O(1)	2.196(3)	Er(1)–N(1)	2.523(4)
Er(1)–O(6)#1	2.243(3)	Er(1)–N(2)	2.538(4)
Er(1)–O(5)	2.248(3)		
O(3)–Er(1)–O(1)	81.43(13)	O(1)–Er(1)–O(5)	92.01(13)
O(3)–Er(1)–O(6)#1	92.22(13)	O(6)#1–Er(1)–O(5)	163.67(12)
O(1)–Er(1)–O(6)#1	101.14(13)	O(3)–Er(1)–N(3)	72.86(13)
O(3)–Er(1)–O(5)	99.34(13)	O(1)–Er(1)–N(3)	153.33(13)
O(6)#1–Er(1)–N(3)	87.10(13)	O(6)#1–Er(1)–N(1)	85.49(13)
O(5)–Er(1)–N(3)	85.35(13)	O(5)–Er(1)–N(1)	89.47(13)
O(3)–Er(1)–N(1)	152.30(13)	N(3)–Er(1)–N(1)	134.38(14)
O(1)–Er(1)–N(1)	72.00(13)	O(3)–Er(1)–N(2)	140.32(14)
O(1)–Er(1)–N(2)	138.23(13)	N(3)–Er(1)–N(2)	67.66(14)
O(6)#1–Er(1)–N(2)	82.15(13)	N(1)–Er(1)–N(2)	66.74(14)
O(5)–Er(1)–N(2)	81.59(13)		

Symmetry transformations used to generate equivalent atoms: #1  $-x, y - 1/2, -z + 3/2$ .

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