



# Optimized single molecule magnet in double-decker hetero-metallic complexes



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## ABSTRACT

Two new hetero-metallic complexes  $[\text{LnNa}_2(\text{L})_2(\text{bta})(\text{CH}_3\text{OH})] \cdot n\text{H}_2\text{O} \cdot m\text{CH}_3\text{OH}$  ( $\text{Ln} = \text{Dy}$  (**1**),  $n = 1, m = 0$ ; Er (**2**),  $n = 0, m = 1$ ) supported by rigid hexadentate salen-type ( $\text{H}_2\text{L} = N, N'$ -bis(2-oxy-3-methoxybenzylidene)-1,2-phenylenediamine) and  $\beta$ -diketonate ( $\text{bta} = \text{benzoyltrifluoroacetone}$ ) ligands have been designed and synthesized. Structural analysis reveals that the  $\text{Ln}^{3+}$  ion has a typical double-decker sandwich structure with a distorted bicapped triangular prism. The magnetic analysis unveils that both complexes **1** and **2** are of single molecule magnet behavior, and both of them can be regarded as rare SMMs based on the salen-type ligand with a double-decker structure.

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## 1. Introduction

The design of new single-molecule magnets (SMMs) with high energy barrier ( $\Delta E_a$ ) and blocking temperature ( $T_B$ ) has remained an active field domain because of their potential applications in high-density magnetic memories [1–3], magnetic refrigeration [4–6] and quantum computing devices [7,8]. Among which a growing amount of Ln-based SMMs from mononuclear [9–11] to multinuclear [12–15], and to chain [16,17] have been documented. It is attributed to the large unquenched orbital angular momentum of  $\text{Ln}^{3+}$  ions which may bring significant anisotropy to the system [18–22]. In particular, the mononuclear lanthanide complexes in which the anisotropic  $\text{Ln}^{3+}$  ion lies in an axial ligand-field environment can exhibit slow relaxation of the magnetization which has been rapidly development due to the simplification of the analysis of local anisotropy [23]. It has been demonstrated that the local anisotropy of the  $\text{Ln}^{3+}$  ions lies in the ligand-field (LF) and the coordination geometry dominate magnetism of the SMMs [24,25]. Therefore, a suitable ligand may promote the anisotropic energy barrier for the mononuclear Ln-based SMMs. Previously, phthalocyanine [26,27],  $\beta$ -diketone [28–30] and polyoxometalate [31–33] have been proven to be particularly suitable for the synthesis of pure mononuclear Ln-based SMMs which usually reveals a double-decker structure and/or high-order single axis  $C_n$

( $n \geq 3$ ) defining the local symmetry. However, the use of multi-dentate salen-type ligand in building the pure mononuclear Ln-based SMMs is relatively rare because of the multi-coordination donors and flexible bonding modes which apt to form polynuclear lanthanide complexes [34–36]. Nevertheless, the introduction of the suitable metal and/or the secondary ligands is an effective way to obtain a SMMs which comprising a single  $\text{Ln}^{3+}$  ion based on the salen-type ligand. E.g. in 2011, Kajiwara et al. have reported a salen-type ligand and salicylaldehyde complex  $[\text{ZnBr}(\text{Hsal})(\text{L})\text{Dy}(\text{NO}_3)(\text{CH}_3\text{OH})] (\text{H}_2\text{L} = N, N'$ -bis(2-oxy-3-methoxybenzylidene)-1,3-2,2-dimethylpropanediamine) which shows SMMs behavior with a extremely high barrier of 333 K [37]. In 2013, Tang et al. presented two hetero-metallic complexes  $[\text{DyML}(\text{OAc})_2(\text{NO}_3)] \cdot \text{CH}_3\text{OH}$  ( $\text{M} = \text{Zn}/\text{Cu}$ ,  $\text{H}_2\text{L} = N, N'$ -bis(3-methoxy-salicylidene) cyclohexane-1,2-diamine) which reveals field-induced SMMs behavior [38]. In 2014, Kou et al. reported four dinuclear 3d–4f complexes  $[\text{M}^{\text{II}}\text{Ln}^{\text{III}}(\text{L})(\text{DBM})_3]$  ( $\text{M} = \text{Zn}/\text{Co}$ ,  $\text{Ln} = \text{Dy}/\text{Y}$ ,  $\text{H}_2\text{L} = N, N'$ -dimethyl- $N, N'$ -(2-hydroxy-3-methoxy-5-methyl-benzyl) ethylenediamine) which were introduced the transition metal and the secondary ligand of 1,3-diphenyl-propane-1,3-dione (DBM) to synthesis the SMMs with containing a single  $\text{Dy}^{3+}$  ion [39]. Obviously, with the introduction of the transition metals, it is usually coordinated by the  $\text{N}_2\text{O}_2$  set of the salen-type ligand which led to the  $\text{Ln}^{3+}$  ion locate in the  $\text{O}_2\text{O}_2$  set with an equator package structure. While it is well known that the double-decker ligands geometry for the  $\text{Dy}^{3+}$  ion would maximize the anisotropy of an oblate ion which may obtain a highly anisotropic ground state with a large  $\pm m_j$  [40]. Thus, it may be of interest to explore the salen-type double-decker

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mononuclear lanthanide SMMs which may exhibit unusual magnetic behavior.

In view of recent important progress in mononuclear lanthanide SMMs [41–45] as well as our longstanding research on the structure and physical properties of salen-type sandwich multiple-decker lanthanide complexes [46–48]. The rigid hexadentate salen-type ligand of *N,N'*-bis(2-oxy-3-methoxybenzylidene)-1,2-phenylenediamine and benzoyltrifluoroacetone were jointly employed to construct the SMMs. As a result, two new heterometallic complexes with a double-decker structure of complexes **1** and **2** have been isolated. Their crystal structures have been determined and their static and dynamic magnetic properties have been studied.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals except  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{Dy}$  and  $\text{Er}$ ) and  $\text{H}_2\text{L}$  were obtained from commercial sources and used without further purification.  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  was prepared by the reactions of  $\text{Ln}_2\text{O}_3$  and hydrochloric acid in aqueous solution. The ligand  $\text{H}_2\text{L}$  was prepared according to the literature [49]. Elemental (C, H and N) analyses were performed on a PerkinElmer 2400 analyzer. FT-IR data were collected on a PerkinElmer 100 spectrophotometer by using KBr disks in the range of 4000–500  $\text{cm}^{-1}$ . UV spectra (in methanol) were recorded on a PerkinElmer 35 spectrophotometer. Thermal analyses were carried out on a STA-6000 with a heating rate of 20  $^\circ\text{C min}^{-1}$  in a temperature range from 300  $^\circ\text{C}$  to 800  $^\circ\text{C}$  in atmosphere. The Powder X-ray diffraction (PXRD) patterns were obtained with a Rigaku D/Max-3B X-ray diffractometer with  $\text{Cu-K}\alpha$  radiation, the scanning rate is 4 $^\circ/\text{s}$ , 2 $\theta$  ranging from 5 to 40 $^\circ$ . The magnetic susceptibilities of complexes **1** and **2** were measured with a superconducting quantum interference device (SQUID) magnetometer of Quantum Design VSM. The magnetic corrections were made by using Pascal's constants.

### 2.2. Synthesis of $[\text{DyNa}_2(\text{L})_2(\text{bta})(\text{CH}_3\text{OH})] \cdot \text{H}_2\text{O}$ (**1**)

$\text{NaOH}$  (0.04 g, 1 mmol) and *bta* (0.22 g, 1 mmol) in methanol was stirred for 5 min. Then,  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.19 g, 0.5 mmol) and  $\text{H}_2\text{L}$  (0.37 g, 1 mmol) were added to the solution and the mixture was stirred for 1 h at room temperature. Diethyl ether was allowed to diffuse slowly into the above mixture, and pale yellow single crystals of **1** suitable for single crystal X-ray diffraction experiment were obtained in about 2 days. Yield: 0.325 g (54%); Elemental analysis (%) calcd for  $\text{C}_{55}\text{H}_{47}\text{N}_4\text{F}_3\text{O}_{12}\text{Na}_2\text{Dy}$  (1221.46): C, 54.08; H, 3.88; N, 4.59. found: C, 54.02; H, 3.81; N, 4.55; IR (KBr,  $\text{cm}^{-1}$ ): 3394 (w), 2923(m), 1619(s), 1480(m), 1294(s), 1184(m), 1133(m), 756(w). UV-vis [MeOH,  $\lambda$ ]: 242, 311 and 389 nm.

### 2.3. Synthesis of $[\text{ErNa}_2(\text{L})_2(\text{bta})(\text{CH}_3\text{OH})] \cdot \text{CH}_3\text{OH}$ (**2**)

Complex **2** was prepared with the identical procedure to complex **1** except  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  was used instead of  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ . Yield: 0.378 g (60%); Elemental analysis (%) calcd for  $\text{C}_{56}\text{H}_{49}\text{N}_4\text{F}_3\text{O}_{12}\text{Na}_2\text{Er}$  (1240.24): C, 54.23; H, 3.98; N, 4.52. found: C, 54.18; H, 3.89; N, 4.50; IR (KBr,  $\text{cm}^{-1}$ ): 3407(w), 2928(m), 1619 (s), 1481(m), 1292(s), 1180(m), 1132(m), 757(w). UV-vis [MeOH,  $\lambda$ ]: 241, 311 and 390 nm.

### 2.4. X-ray crystallography

X-ray single-crystal diffractions of complexes **1** and **2** were performed at 293 K on an Oxford Xcalibur Gemini Ultra diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation

**Table 1**

Crystal data and structures refinement for complexes **1** and **2**.

Complexes	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{55}\text{H}_{47}\text{N}_4\text{F}_3\text{O}_{12}\text{Na}_2\text{Dy}$	$\text{C}_{56}\text{H}_{49}\text{N}_4\text{F}_3\text{O}_{12}\text{Na}_2\text{Er}$
Formula weight	1221.46	1240.24
Color	Buff	Buff
Crystal system	Monoclinic	Monoclinic
Space group	$\text{P}2_1/\text{c}$	$\text{P}2_1/\text{c}$
a (Å)	16.384(5)	16.293(5)
b (Å)	15.625(5)	15.518(5)
c (Å)	23.554(5)	23.340(5)
$\alpha$ (deg)	90	90
$\beta$ (deg)	117.494(4)	117.693(4)
$\gamma$ (deg)	90	90
V (Å <sup>3</sup> )	5349(3)	5225(3)
Z	2	4
$\rho_{\text{calcd}}$ ( $\text{g cm}^{-3}$ )	1.504	1.517
$\mu$ ( $\text{mm}^{-1}$ )	1.488	1.702
F (000)	2440	2488
$R_1$ , [ $I > 2\sigma(I)$ ] <sup>a</sup>	0.0347	0.0313
$wR_2$ , [ $I > 2\sigma(I)$ ]	0.0998	0.0773
$R_1$ , (all data) <sup>b</sup>	0.0457	0.0396
$wR_2$ , (all data)	0.1079	0.0805
GOF on $F^2$	1.112	1.181

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

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

( $l = 0.71073 \text{ \AA}$ ). The structures were solved by the direct methods and refined on  $F^2$  by full-matrix least-squares using the SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. All crystal data and refinement parameters for complexes **1** and **2** are summarized in Table 1.

## 3. Results and discussion

### 3.1. Structural descriptions of complexes **1** and **2**

X-ray crystallographic analysis reveals that complexes **1** and **2** are isomorphous, and crystallized in the monoclinic space group of  $\text{P}2_1/\text{c}$ . In a typical structure of complex **1** (Fig. 1 left), it possesses a hetero-metallic  $[\text{DyNa}_2]^{5+}$  core capped by a *bta* ligand and two salen-type ligands. The  $\text{Dy}^{3+}$  ion has a typical double-decker sandwich structure and is eight-coordinated by two  $\text{N}_2\text{O}_2$  sets of two salen-type ligands. The Na1 ion is six-coordinated by five oxygen atoms from two salen-type ligands and one oxygen atom from a methanol molecule, while the Na2 ion is five-coordinated by three oxygen atoms from the top salen-type ligands and two oxygen atoms from the *bta* ligand. Moreover, the distances range of Dy—O bonds is 2.243 to 2.301 Å (average 2.272 Å), while the Dy—N bond lengths are in the range of 2.483 to 2.515 Å (average 2.500 Å). Further inspection of the packing arrangement reveals the shortest intermolecular Dy...Dy distances is 9.431 Å (Figure S5). According to the semiquantitative method of polytopal analysis [50,51], the coordination geometries of  $\text{Dy}^{3+}$  ion for complex **1** can be described as a distorted bicapped triangular prism (Fig. 1 right, and Table 2). It differs from the reported mixed phthalocyanine and salen-type double-decker hetero-metallic complex  $[\text{KDy}(\text{pc})(\text{L})\text{CH}_3\text{OH}]$  ( $\text{H}_2\text{pc}$  = metal-free phthalocyanine,  $\text{H}_2\text{L} = \text{N,N}'$ -bis(2-oxy-3-methoxybenzylidene)-1,2-phenylenediamine) [52] in which the  $\text{Dy}^{3+}$  ion is a distorted square antiprism geometry (SAP) coordination polyhedron.

### 3.2. Magnetic properties

Direct current (dc) magnetic susceptibility measurements of complexes **1** and **2** have been carried out under a 1000 Oe dc field over the temperature range 1.8–300 K. As shown in Fig. 2 and

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