一例具有显著单分子磁体行为的双核镝配合物

辛晓艳¹ 张雪瑾¹ 陈凤姣¹ 王 瑜¹ 杨 晨¹ 乔 娜¹ 石 瑛^{*,2} 王文敏^{*,1,2} (¹太原师范学院化学系,晋中 030619) (²太原师范学院,碳中和研究院,晋中 030619)

摘要:使用多齿席夫碱H₂L(H₂L=(*E*)-*N*'-(3-乙氧基-2-羟基亚苄基)-3-羟基吡啶甲酰肼)为配体,与Ln(dbm)₃·2H₂O(Ln=Dy (1)、Nd (2);dbm⁻=1,3-dioxo-1,3-diphenylpropan-2-ide)反应,通过溶剂热法,成功得到了2例新的双核稀土配合物[Ln₂(dbm)₂(L)₂(C₂H₅OH)₂]。单晶X射线衍射结构表明:配合物1和2的结构主要由2个Ln(m离子、2个dbm⁻、2个L²⁻及2个C₂H₅OH组成,中心Ln(m离子通过2个 μ_2 -O原子相互连接,形成一个平行四边形的Ln₂O₂核心。磁性研究表明,配合物1中Dy(m离子间存在铁磁耦合作用,且1表现出显著的单分子磁体行为。

关键词:稀土配合物;单晶结构;磁性;铁磁耦合作用;单分子磁体
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A Dy₂ Complex Showing Outstanding Single-Molecule Magnet Behavior

XIN Xiao-Yan¹ ZHANG Xue-Jin¹ CHEN Feng-Jiao¹ WANG Yu¹ YANG Chen¹ QIAO Na¹ SHI Ying^{*,2} WANG Wen-Min^{*,1,2} (¹Department of Chemistry, Taiyuan Normal University, Jinzhong, Shanxi 030619, China) (²Institute for Carbon Neutrality, Taiyuan Normal University, Jinzhong, Shanxi 030619, China)

Abstract: Two new binuclear Ln(III)-based complexes with the formula $[Ln_2(dbm)_2(L)_2(C_2H_5OH)_2]$ (Ln=Dy (1), Nd (2); dbm⁻=1,3-dioxo-1,3-diphenylpropan-2-ide) have been synthesized via the solvothermal method by using a polyden-tate Schiff base ligand (H₂L=(*E*)-*N'*-(3-ethoxy-2-hydroxybenzylidene)-3-hydroxypicolinohydrazide) reacting with Ln(dbm)₃·2H₂O. Single-crystal X-ray structures reveal that complexes 1 and 2 are mainly composed of two Ln(III) ions, two dbm⁻ ions, two L²⁻ ions, and two C₂H₅OH molecules, and the two central Ln(III) ions are connected by two μ_2 -O atoms forming a "parallelogram-shaped" Ln₂O₂ core. Magnetic studies show that the ferromagnetic interaction exists between the adjacent two Dy(III) ions and single-molecule magnet behavior occurs in 1. CCDC: 2100188, 1; 2133336, 2.

Keywords: rare-earth-based complexes; crystal structures; magnetic properties; ferromagnetic interaction; single-molecule magnet

In recent years, a large number of Ln (III) - based complexes have been synthesized and used in the study of single - molecule magnets (SMMs), including binuclear^[1], trinuclear^[2], tetranuclear^[3], pentanuclear^[4], hexanuclear^[5], heptanuclear^[6], and octanuclear^[7] Dy(III)- based complexes SMMs. Because the low nuclear complexes are easy to design and synthesize, the magnetic moment is easier to be an axial, and relatively large number of low nuclear Dy(III)-based complexes showing SMMs behaviors have been reported^[8-10]. Binuclear

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^{*}通信联系人。E-mail:wangwenmin0506@126.com,ucia0812@163.com

Dy (III) - based SMMs are an important model system, which can be used to answer whether the relaxation of the system comes from the relaxation of a single ion or the whole molecule^[11]. Therefore, a large number of binuclear Dv(III)-based SMMs have been reported^[12-14]. In 2011, Tang group prepared an asymmetric Dy (III) binuclear complex [Dv₂(ovph)₂Cl₂(MeOH)₃]^[15]. Through experimental tests and theoretical calculations, it is found that there is a ferromagnetic coupling between Dy(III) in this complex. Feng group^[16] reported a series of binuclear lanthanide complex, [Dy₂(Mq)₄(NO₃)₆] (Mq= 2 - methyl - 8 - hydroxyquinoline), which has exhibited SMM behavior. These binuclear Dy (III) - based SMMs studies help to promote and stimulate the development of Ln(III)-based single molecular magnetic materials and attract more inorganic chemists and materials scientists to design and construct Dy(III)-based SMMs.

Based on the above considerations, in this work, we try to find an efficient synthetic strategy for constructing two new Ln (III) - based complexes showing remarkable magnetic behaviors. As shown in Scheme 1, a multidentate Schiff-base ligand H_2L ($H_2L=(E)-N'-$ (3-ethoxy-2-hydroxybenzylidene)-3-hydroxypicolinohydrazide) with abundant coordination atoms and multiple coordination modes has been used to synthesize Ln(II)-based binuclear complex. To further explore and study the relationship between the structure and magnetic properties of binuclear Ln(III)-based complex, we designed and synthesized two new binuclear Ln (III) based complexes with the formula $[Ln_2(dbm)_2(L)_2]$ $(C_2H_5OH)_2$] (Ln=Dy (1), Nd (2); dbm⁻=1, 3 - dioxo - 1, 3 diphenylpropan-2-ide) via the solvothermal method by using H₂L and Ln(dbm)₃·2H₂O. Structural analysis reveals that two central Ln(III) ions are connected by two μ_2 -O atoms forming a "parallelogram - shaped" Ln₂O₂



Scheme 1 Structure of H₂L

core. Magnetic analysis shows that the ferromagnetic interaction exists between the adjacent two $Dy(\mathbb{II})$ ions and **1** has SMM behavior.

1 Experimental

1.1 Materials and measurements

1,3-Diphenyl-1,3-propanedione, 3-ethoxysalicylaldehyde, 3-hydroxy-2-picolinyl hydrazide, and $Ln(NO_3)_3 \cdot 6H_2O$ (Ln=Dy, Nd) were bought from Energy Chemical Co., Ltd., and the common solvents (ethanol, acetonitrile, and dichloromethane) were purchased from Komeo Reagent Co., Ltd. According to the previously reported method^[17], the multidentate Schiff base ligand H_2L was synthesized. $Ln(dbm)_3 \cdot 2H_2O$ was prepared according to the method reported in the literature^[18].

Elemental analyses for complexes 1 and 2 were performed on a Perkin-Elmer 2400 analyzer. Infrared spectra data were measured with a Bruker TENOR 27 spectrophotometer. Powder X - ray diffraction (PXRD) data were collected using a Rigaku Ultima IV instrument with Cu $K\alpha$ radiation (λ =0.154 056 nm) in a 2 θ range from 5° to 50°. The operating voltage and current were 40 kV and 25 mA, respectively. Thermogravimetric analysis (TGA) data were recorded using a NETZSCHTG 409 PC thermal analyzer. The magnetic measurements were performed through a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. **1.2 Preparations of H₂L and complexes 1 and 2**

1.2.1 Synthesis of H_2L

To a suspension of 3-ethoxysalicylaldehyde (20.0 mmol, 3.32 g) in 10 mL methanol was added 3-hydroxy-2-picolinyl hydrazide (20.0 mmol, 3.08 g). The resulting reaction mixture was stirred at room temperature for 4 h. The white precipitate was collected by filtration and washed with methanol. The crude product was dried under vacuum for 48 h to give the ligand (H₂L) (Scheme 2). Yield: 3.99 g (63%). Elemental analysis Calcd. for C₁₆H₁₉N₃O₄ (%): C, 60.50; H, 5.90; N, 13.23. Found(%): C, 60.55; H, 5.93; N, 13.24. IR (KBr, cm⁻¹): 3 291(m), 2 980(w), 2 929(w), 2 875(w), 2 834(w), 1 660 (s), 1 623(m), 1 577(m), 1 532(m), 1 451(s), 1 388(w), 1 330(w), 1 267(w), 1 246(s), 1 172(w), 1 089(w), 1 077 (m), 1 116(w), 1 010(w), 950(w), 967(m), 900(m), 833





(m), 802(m), 783(m), 741(s).

1.2.2 Synthesis of complexes **1** and **2**

The synthesis method of complexes 1 and 2 was similar. $Ln(dbm)_3 \cdot 2H_2O$ (0.025 mmol, 0.021 g) was added to a solution of H_2L (0.025 mmol, 0.008 g) in 15 mL of $CH_3OH/CH_2Cl_2/CH_3CN$ (3:1:1, *V/V*), and then the mixture was stirred for 30 min at room temperature. Whereafter, the mixture was sealed and packed in a glass sample vase (20 mL), which was heated at 80 °C for 24 h under autogenous pressure. Thereafter, it was cooled to room temperature, and yellow block crystals of 1 or 2 suitable for X - ray crystallography were obtained. The synthesis diagram of complexes 1 and 2 is shown in Scheme 3.

 $[Dy_2(dbm)_2(L)_2(C_2H_5OH)_2]$ (1). Yield: 35% (based on $Dy(dbm)_3 \cdot 2H_2O$). Elemental analysis Calcd. for

 $C_{64}H_{60}Dy_2N_6O_{14}(\%)$: C, 52.52; H, 4.10; N, 5.74. Found (%): C, 52.51; H, 4.09; N, 5.75. IR (KBr, cm⁻¹): 3 639 (w), 2 973(m), 2 693(w), 1 594(s), 1 549(s), 1 515(m), 1 479(s), 1 444(s), 1 379(s), 1 334(m), 1 293(s), 1 250 (s), 1214(w), 1 148(s), 1 113(w), 1 073(w), 1 036(w), 972(w), 935(w), 899(w), 850(m), 809(w), 746(m), 684 (m), 609(m), 552(w), 434(w).

 $[Nd_2(dbm)_2(L)_2(C_2H_5OH)_2]$ (2). Yield: 36% (based on $Nd(dbm)_3 \cdot 2H_2O$). Elemental analysis Calcd. for $C_{64}H_{60}Nd_2N_6O_{14}$ (%): C, 53.87; H, 4.20; N, 5.89. Found (%): C, 53.76; H, 4.19; N, 5.78. IR (KBr, cm⁻¹): 3 644 (w), 3 056(w), 2 973(m), 2 693(w), 1 594(s), 1 549(s), 1 515(m), 1 479(s), 1 444(s), 1 379(s), 1 334(m), 1 293 (s), 1 250(s), 1 214(w), 1 148(s), 1 113(w), 1 073(w), 1 036 (w), 972(w), 935(w), 899(w), 850(m), 809(w), 746(m), 684(m), 609(m), 552(w), 462(w).



Scheme 3 Synthesis of complexes 1 and 2

1.3 X-ray crystallography

Single crystal X - ray diffraction data of 1 and 2 were collected on a computer-controlled Rigaku Saturn CCD area detector diffractometer, equipped with confocal monochromatized Mo $K\alpha$ radiation with a radiation wavelength of 0.071 073 nm, using the $\varphi - \omega$ scan technique. The structures of 1 and 2 were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 using the SHELXTL programs. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Crystallographic data and structure refinement parameters of complexes 1 and 2 are listed in Table 1. Selected bond lengths and angles are given in Table S1 and S2 (Supporting information).

CCDC: 2100188, 1; 2133336, 2.

2 Results and discussion

2.1 Crystal structures of 1 and 2

Single-crystal X-ray diffraction analysis revealed that complexes **1** and **2** are isostructural and crystallize in the triclinic space group $P\overline{1}$ with Z=2. Therefore, only the structure of **1** is described here in detail as a representative. As depicted in Fig. 1, complex **1** contains two Dy (III) ions, two L²⁻ ions, two coordinated

Parameter	1	2	
Formula	$\rm C_{64}H_{60}Dy_2N_6O_{14}$	$\rm C_{64}H_{60}Nd_2N_6O_{14}$	
Formula weight	1 462.18	1 425.66	
<i>T /</i> K	150.0	150	
Crystal system	Triclinic	Triclinic	
Space group	PĪ	$P\overline{1}$	
<i>a /</i> nm	1.303 26(4)	1.311 32(10)	
<i>b</i> / nm	1.421 83(4)	1.427 74(10)	
<i>c</i> / nm	1.880 84(5)	1.880 80(12)	
α / (°)	100.036 0(12)	99.822(4)	
β/(°)	102.275 7(12)	102.555(5)	
γ / (°)	114.247 9(12)	113.953(5)	
V / nm^3	2.968 23(15)	3.005 9(4)	
Ζ	2	2	
Crystal size / mm	0.36×0.31×0.28	0.37×0.26×0.13	
$D_{\rm c} /({\rm g}{\cdot}{\rm cm}^{-3})$	1.636	1.575	
μ / mm $^{-1}$	2.570	13.619	
Limiting indices	$-16 \leq h \leq 16, -17 \leq k \leq 17, -23 \leq l \leq 23$	$-16 \leq h \leq 16, -17 \leq k \leq 17, -23 \leq l \leq 17$	
Reflection collected	74 997	37 740	
Unique reflection	12 159	12 168	
Parameter	787	787	
$R_{ m int}$	0.045 1	0.078 4	
GOF on F^2	1.073	1.006	
$R_1, wR_2 [I > 2\sigma(I)]$	0.026 4, 0.068 6	0.054 4, 0.140 8	
R_1, wR_2 (all data)	0.036 5, 0.073 3	0.068 0. 0.154 8	

Table 1 Crystallographic data and structure refinements for complexes 1 and 2

C₂H₅OH molecules, and two dbm⁻ ions. Each Dy(III) ion center is eight-coordinated (Fig.2), the central Dy1 ion is coordinated by two nitrogen atoms (N4 and N6) and six oxygen atoms (014, 09, 012, 013, 010, and 010a) from two L2- ions, a C2H5OH molecule and two dbm ions. The eight-coordinated center Dy(III) ion shows a triangular dodecahedron. These geometrical configurations were confirmed by using the SHAPE 2.0 software (Table S3). The coordination modes of L²⁻ and dbm⁻ are shown in Fig.3. L²⁻ packages two central Dy(III) ions by the mode of multidentate chelation, and dbm- connects each central Dy(III) ions by the mode of bidentate chelation. Two central Dy(III) ions are bridged by two μ_2 -O atoms (O10 and O10a) of two L²⁻ ligands forming a parallelogram Dy₂O₂ core. In the Dy₂O₂ core, the distance of Dy1...Dy1a is 0.397 44(5) nm, the angles of Dy1-010-Dy1a and 010-Dy1-010a are 114.101° and 65.899°, respectively. Moreover, in complex 1, the bond distances of Dy-O are in a range of 0.217 2(2)- 0.244 4(3) nm, and the Dy—N bond lengths are in a range of 0.248 5(3)-0.254 5(3) nm, respectively. The O—Dy—O bond angles are in a range of $65.61(9)^{\circ}$ -148.30(9)°, which are comparable to those of the reported binuclear Dy(III)-based complexes^[19-20].



All hydrogen atoms are omitted for clarity; Symmetry code: a: -x, -y, 1-z

Fig.1 Molecular structure of **1** shown with 30% probability displacement ellipsoids



Symmetry code: a: -x, -y, 1-z

Fig.2 (a) Coordination environment of Dy₂; (b) Geometric polyhedron of Dy₂ ions observed in complex 1



Symmetry code: a: -x, -y, 1-z

Fig.3 Coordination modes for L²⁻ and dbm⁻

2.2 PXRD and TGA for the complexes

The purity of the crystal samples was checked by using PXRD. As shown in Fig. S2, the experimental PXRD patterns of **1** and **2** were almost identical to the corresponding simulated ones, which suggests that the purities of crystal samples **1** and **2** are high.

The thermal stability of complexes 1 and 2 was studied using the crystalline samples under an air atmosphere from 25 to 800 °C. The TGA curves of complexes 1 and 2 are shown in Fig.S3, and they exhibited similar thermal behaviors because they are isostructural. Herein, complex 1 is selected as a representative illustration. Between 40 and 223 °C, a weight loss of 6.17% took place, which corresponds to the loss of two coordinated ethanol molecules (Calcd. 6.29%). Subsequently, a weight loss of 66.16% was observed from 223 to about 650 °C, which is related to the loss of another twenty - one coordinated ethanol molecules (Calcd. 69.21%). Thereafter, complex 1 decomposed gradually in a temperature range of 450-800 °C.

2.3 Magnetic properties

Under an external field of 1 000 Oe, the static direct (dc) magnetic susceptibility study of complex **1** was performed in a temperature range of 2.0-300.0 K. As shown in Fig.4, the room-temperature $\chi_{\rm M}T$ value of complex **1** was 28.75 cm³·K·mol⁻¹. This is in good agreement with the expected values for two isolated Dy(III) ions (${}^{6}H_{15/2}$, g=4/3) of 28.34 cm³·K·mol⁻¹ for **1**.



Fig.4 Temperature dependence of $\chi_{M}T$ at 1 000 Oe for complex 1

When the temperature decreased, the $\chi_{\rm M}T$ value of complex **1** decreased slowly in a range of 300.0-20.0 K. Then, the $\chi_{\rm M}T$ value of complex **1** increased rapidly at 2.0 K, reaching the maximum value of 30.85 cm³·K· mol⁻¹. This indicates the possible existence of ferromagnetic coupling between the adjacent Dy(III) ions in **1**^[21].

For complex 1, due to both factors of spin-orbit coupling and electronic interaction, the $4f^n$ electronic configuration of Dy(III) ions can be split into ${}^{2S+1}L_I$ spectral branches. Affected by the crystal field perturbation, each ${}^{2S+1}L_J$ spectral term will be further split into multiple Stark sublevels, and these Stark sublevels are thermally populated. The population at these sublevels decreases with decreasing temperature, resulting in a decrease in the dc temperature - dependent magnetic susceptibility values of Dy(III) with decreasing temperature. The $\chi_{\rm M}T$ vs T curve of complex 1 increased with decreasing temperature, indicating a ferromagnetic interaction between the Dy(III) ions, which counteracts or surmounts the decreasing trend of the $\chi_{\rm M}T$ value caused by the thermal depopulation of the Dy(III) Stark sublevels, and occupies a dominant position at low temperature^[22-23].

To investigate the slow magnetic relaxation behavior of complex 1, alternating - current (ac) magnetic susceptibility was measured at 3.0 Oe ac field under a zero dc field and in a frequency range of 111-2 311 Hz (Fig. S4). Complex 1 exhibited remarkable frequencydependent out-of-phase (χ'') signals and more than two peaks are observed in both in-phase (χ') and χ'' . This indicates multiple magnetic relaxation behavior, typical of SMM behavior in 1. To check the quantum tunneling of magnetization (QTM) effect above 2.0 K in 1, the variable-temperature ac susceptibilities were determined under an extra dc field of 5 000 Oe (Fig. 5). In the out - of - phase, remarkable shoulder peaks were observed in the frequency region (10-999 Hz) and temperature region (4.0-10.0 K), and the rising tail of χ'' at the low-temperature region was not observed. It proves that the quantum tunneling effect in complex **1** is pronounced and the QTM effect is suppressed under an external 5 000 Oe dc field. As shown in Fig.6, we analyzed the frequency-dependent relaxation time and fitted the ln τ vs T^{-1} plot of **1** by using the Arrhenius law^[24]: $\tau = \tau_0 \exp[\Delta E/(k_{\rm B}T)]$. The energy barrier ($\Delta E/k_{\rm B}$) of 56.77 K and the pre-exponential factor (τ_0) of 1.10× 10⁻⁷ s were obtained. The τ_0 of complex **1** was in the normal range of some reported values of 10⁻⁶-10⁻¹² s for SMMs^[25-28]. The $\Delta E/k_{\rm B}$ value of **1** was higher than some



Fig.5 Temperature-dependence of χ' and χ'' components of the ac magnetic susceptibility for **1** under 5 000 Oe dc field with an oscillation of 3.0 Oe



Fig.6 Plot of $\ln \tau$ vs T^{-1} fitting to the Arrhenius law for complex **1**

of the reported dinuclear dysprosium complexes^[29-36] (Table 2).

Table 2Comparison of energy barrier $(\Delta E/k_B)$ of
recently reported Dy_2 SMMs and complex
1 in this work

Dy ₂ -SMM	$\Delta E/k_{ m B}$ /K	Reference
$[\mathrm{Dy}_2(\mathrm{hfac})_4(\mathrm{L})_2]$	6.77	[29]
$[\mathrm{Dy}_2(\mathrm{L}_1)_2(\mathrm{hfac})_6]\!\cdot\!\mathrm{C}_7\mathrm{H}_{16}$	6.81	[30]
$[\mathrm{Dy}_2(\mathrm{tmhd})_2\mathrm{L}_2(\mathrm{CH}_3\mathrm{OH})_2]$	13.14	[31]
$\{[Dy_2(bpda)_3(H_2O)_3]_4\!\cdot\!2H_2O\}$	1.14	[32]
$[Dy(bfa)_2L]_2$	24.3	[33]
$[\mathrm{Dy}_2(\mathrm{dbm})_4\mathrm{L}\boldsymbol{\cdot}\mathrm{CH}_3\mathrm{OH}]$	28	[34]
$[\mathrm{Dy}_2(\mathrm{L}_2)_2]$	33	[35]
$\mathrm{Dy}_2(\mathrm{L}_1)_2(\mathrm{L}_2)_2(\mathrm{CH}_3\mathrm{CH}_2\mathrm{OH})(\mathrm{CH}_3\mathrm{OH})$	61	[36]
$[\mathrm{Dy}_2(\mathrm{dbm})_2(\mathrm{L})_2(\mathrm{C}_2\mathrm{H}_5\mathrm{OH})_2]$	56.77	This work

For further probing and studying the SMM behavior of **1**, in the temperature range of 2.0-14.0 K, the frequency dependence (0-10 000 Hz) of χ' and χ'' magnetic ac susceptibility was measured under an external field of H_{dc} =0 Oe (Fig.7). The χ'' vs ν plot of **1** showed evident peaks, indicating that SMM behavior exists in $\mathbf{1}^{[37-40]}$.



Fig.7 Frequency dependence of χ' and χ'' for 1 at 2.0-14.0 K under a zero dc field

From the frequency dependence of χ'' , we obtained the $\ln \tau$ vs T^{-1} curve (Fig.S5). It is noteworthy that the plot of $\ln \tau$ vs T^{-1} showed an obvious curvature, which indicates that perhaps another relaxation pathway is also operative. In view of this, we fitted the $\ln \tau$ vs T^{-1} plot by using the equation^[41]: $\ln \tau = -\ln\{AT + B + B\}$ $CT^{n} + \tau_{0}^{-1} \exp[\Delta E/(k_{\rm B}T)]$, where AT + B, CT^{n} , and $\tau_{0}^{-1} \exp[\Delta E/(k_{\rm B}T)]$ $[\Delta E/(k_{\rm B}T)]$ represent direct, Raman and Orbach relaxation processes, respectively. The best - fitting was obtained for $\Delta E/k_{\rm B}$ =55.08 K, τ_0 =1.73×10⁻⁷ s, n=4.9, A= 0.387 6 s⁻¹·K^{-4.9}, and C=0.065 43. The small A and C parameters indicate that the relaxation process can dominate by the Orbach mechanism at high temperatures and the Raman mechanism at low temperatures where the curvature of the Arrhenius plot is the transition from Raman to Orbach relaxation.

The Cole - Cole plots of complex **1** are shown in Fig. 8. The Debye model was used to fit the Cole-Cole curves in a temperature range of 2.0 to 14.0 K, and the obtained α values were in a range of 0.17-0.65. However, some curves were not well fitted because there wasn't only one semicircle at these temperatures (*T*=4.0-9.0 K), and good results were also not obtained for double magnetic relaxation fitting. The large α value indicates that there is a wide magnetic relaxation distribution in complex **1**, and there may be multiple magnetic relaxation processes in **1**.



Red solid lines are the best fitting to the experimental data, obtained with the generalized Debye model with α =0.17-0.65 for 1

Fig.8 Cole-Cole plots for **1** measured under a zero dc field

3 Conclusions

In summary, we have designed and synthesized two new binuclear $Ln(\mathbb{II})$ -based complexes by using a flexible polydentate Schiff base ligand (H₂L) and $Ln(dbm)_3 \cdot 2H_2O$ (Ln=Dy, Nd). The structures analysis reveals that the two central $Ln(\mathbb{II})$ ions are connected by two μ_2 - O atoms forming a "parallelogram - shaped" Ln_2O_2 core. Magnetic studies show that the ferromagnetic interaction exists between the adjacent two Dy(\mathbb{II}) ions and the Dy₂ complex has single-molecule magnet behavior. As part of our research interests, the continued study of other $Ln(\mathbb{II})$ -based complexes is currently in progress for exploring outstanding properties.

Supporting information is available at http://www.wjhxxb.cn

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