

一个双核 β -二酮镝(III)配合物的超声化学合成、晶体结构和磁性

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摘要: 用超声波辅助的方法合成得到了一个双核 β -二酮镝配合物 $\text{Dy}_2(\text{Hpdm})_2(\text{dbm})_4 \cdot 2\text{EtOH}$ (**1**) (H_2pdm =2,6-吡啶二甲醇, Hdbm =二苯甲酰甲烷)。单晶 X-射线衍射结构分析表明双核镝(III)结构单元通过 2,6-吡啶二甲醇配体中去质子化的羟基氧原子桥联, 每个镝(III)离子呈现不规则的八面体配位构型。磁学性质研究表明, 该配合物中镝(III)离子之间存在着反铁磁性耦合作用, 但没有出现磁弛豫行为。

关键词: 双核镝(III)配合物; 晶体结构; 磁性质; 超声化学合成

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Ultrasonic Synthesis, Crystal Structure and Magnetic Properties of a Dinuclear Dysprosium(III) β -Diketonate Complex

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Abstract: A new dinuclear Dy(III) β -diketonate complex, $\text{Dy}_2(\text{Hpdm})_2(\text{dbm})_4 \cdot 2\text{EtOH}$ (**1**, H_2pdm =2,6-pyridinedimethanol, Hdbm =dibenzoylmethane), has been successfully prepared by ultrasonic method. Single crystal X-ray crystallographic analysis revealed that the two Dy(III) ions are bridged by the deprotonated alkoxide arm of the pdmH-ligand. Variable-temperature magnetic susceptibility measurements showed that there exists a weak antiferromagnetic interaction between the two Dy(III) ions, but no relaxation process of magnetization was observed, even when a 2000 Oe dc field was applied. CCDC: 950414.

Key words: dinuclear dysprosium(III) complex; crystal structure; magnetic properties; ultrasonic synthesis

0 Introduction

By virtue of the large magnetic anisotropy of single ion and weak magnetic interaction among ions, lanthanide coordination complexes are often designed and constructed to explore new single molecular magnets (SMMs) or single ion magnets (SIMs)^[1-2]. The SMMs can exhibit superparamagnet-like behavior of

slow magnetic relaxation at low temperature, which are thus viewed as potential candidates for high-density storage devices, quantum information processing and spintronics. On the other hand, the lanthanide coordination complexes also find applications in fluorescence materials and luminescent probes for their unique photophysical properties^[3-7]. Hence, the lanthanide complexes have received more

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and more attention.

We are also very interested in the lanthanide molecular materials^[8-14], and have explored several Dy(III) β -diketonate SMMs/SIMs^[12-13] recently. Notably, as good bidentate chelating ligands, β -diketonates have provided special opportunities to investigate the SMMs/SIMs properties of simple lanthanide complexes^[15-22]. To extend the lanthanide coordination chemistry based on the β -diketonate ligands, we chose 2, 6-pyridinedimethanol (H_2pdm), which can work as not only the capping ligand but also the excellent bridge, to construct new Dy(III) β -diketonate complexes. Herein we describe the ultrasonic synthesis, crystal structure, and magnetic properties of the first lanthanide β -diketonate complex derived from the 2, 6-pyridinedimethanol ligand, $Dy_2(Hpdm)_2(dbm)_4 \cdot 2EtOH$ (**1**, dbm^- =dibenzoylmethanato). Remarkably, the work represents a rare example that ultrasonic is successfully used to synthesize lanthanide complex crystals.

1 Experimental

1.1 Materials and methods

All reagents were obtained from commercial sources and used without further purification. $Dy(dbm)_3 \cdot H_2O$ was prepared according to references method.^[23] Elemental analyses for C, H and N were performed on a Heraeus Chn-Rapid instrument. The magnetic susceptibility measurements were carried out on a polycrystalline sample with a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range

2 ~300 K. Diamagnetic corrections were estimated from Pascals constants.

1.3 Preparation of $Dy_2(pdmH)_2(DBM)_4 \cdot 2EtOH$ (**1**)

A mixture of pyridine-2,6-diylldimethanol (H_2L) (0.2 mmol), $Dy(dbm)_3 \cdot H_2O$ (0.2 mmol) in 30 mL of C_2H_5OH/Me_2CO (1:2, V/V) was sonicated for 10 min, the resultant light-yellow solution was evaporated for several days, light-yellow crystals of **1** were obtained (yield 15% based on Dy). Anal. Calcd. (%) for $C_{78}H_{72}Dy_2N_2O_{14}$ (**1**): C, 59.05; H, 4.57; N, 1.77. Found (%): C, 58.99; H, 4.61; N, 1.74. IR (KBr, cm^{-1}): 3 061w, 3 027w, 2 973w, 2 895w, 2 811w, 1 599s, 1 554s, 1 522s, 1 478m, 1 460s, 1 411s, 1 309w, 1 285w, 1 219w, 1 179w, 1 157w, 1 103w, 1 071w, 1 051w, 1 025w, 941w, 780w, 743w, 722m, 690w, 655w, 609w, 521w.

1.4 Crystal structure determination

Crystal data collection for complex **1** is performed on a Bruker SMART APEX-CCD with $Mo-K\alpha$ radiation ($\lambda = 0.071\ 073$ nm). The data were corrected for Lorentz-polarization effects, and absorption corrections were applied. All nonhydrogen atoms were refined anisotropically and all of the hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms. The structure **1** was solved by direct methods. The structure was refined by using SHELXL 97^[24]. The crystallographic details about data collection and refinement parameters are given in Table 1. Selected bond lengths and angles for the complex **1** are given in Table 2.

CCDC: 950414.

Table 1 Crystallographic data for **1**

Chemical formula	$C_{78}H_{72}Dy_2N_2O_{14}$	μ / mm^{-1}	2.215
Formula weight	1 586.38	$F(000)$	1596
Crystal system	monoclinic	θ Ranges (data collection) / (°)	3.02 to 26.00
Space group	$P2_1/c$	Indices range (h, k, l)	$-12 \leq h \leq 13, -28 \leq k \leq 28, -17 \leq l \leq 18$
a / nm	1.070 0(2)	Reflections collected	20 720
b / nm	2.306 5(5)	Independent collections(Rint)	6 753(0.0421)
c / nm	1.499 4(6)	Reflections observed($I > 2\sigma(I)$)	6 369
$\beta / (^\circ)$	111.10(2)	GOF on F^2	1.125
V / nm^3	3.452 3(17)	R_1, wR_2 ($I > 2\sigma(I)$)	0.033 1, 0.070 4
Z	2	R_1, wR_2 (all data)	0.036 2, 0.072 1
$D_c / (g \cdot cm^{-3})$	1.526	$\Delta\rho_{max}, \Delta\rho_{min} / (e \cdot nm^{-3})$	822, -540

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for **1**

Dy1-N1	0.2506(3)	Dy1-O1	0.2421(2)	Dy1-O2	0.2338(2)
Dy1-O3	0.2313(2)	Dy1-O4	0.2372(2)	Dy1-O5	0.2303(2)
Dy1-O5 ⁱ	0.2268(2)	Dy1-O6	0.2403(2)		
Dy1 ⁱ -O5-Dy1	110.88(9)	O1-Dy1-N1	74.94(9)	O2-Dy1-N1	131.66(9)
O2-Dy1-O1	70.10(8)	O2-Dy1-O4	72.11(8)	O2-Dy1-O6	81.61(9)
O3-Dy1-N1	69.39(9)	O3-Dy1-O1	143.78(8)	O3-Dy1-O2	141.39(9)
O3-Dy1-O4	70.85(9)	O3-Dy1-O6	83.86(9)	O4-Dy1-N1	129.91(9)
O4-Dy1-O1	141.76(8)	O4-Dy1-O6	83.61(8)	O5-Dy1-N1	67.06(8)
O5 ⁱ -Dy1-N1	135.89(9)	O5-Dy1-O1	78.12(8)	O5 ⁱ -Dy1-O1	100.98(8)
O5-Dy1-O2	132.94(8)	O5 ⁱ -Dy1-O2	83.66(8)	O5-Dy1-O3	82.66(9)
O5 ⁱ -Dy1-O3	100.38(9)	O5-Dy1-O4	134.86(8)	O5 ⁱ -Dy1-O4	80.27(8)
O5 ⁱ -Dy1-O5	69.12(9)	O5-Dy1-O6	130.01(8)	O5 ⁱ -Dy1-O6	160.86(8)
O6-Dy1-N1	63.12(9)	O6-Dy1-O1	85.41(9)		

Symmetry code: ⁱ $-1-x, -y, -z$

2 Results and discussion

2.1 Synthesis

Ultrasonic is seldom utilized to prepare coordination complexes. In 2001, eight lanthanide complexes with lactam type open chain crown ethers have ever been synthesized by ultrasonic method, but no related structures reported [25]. In our experiment, ultrasonic reaction of 6-pyridinedimethanol (H_2L) and Dy (dbm)₃H₂O in C₂H₅OH/Me₂CO mixed solvents yielded the pure yellow single crystals of the dinuclear complex Dy₂(pdmH)₂(dbm)₄·2EtOH (**1**). It is note worthy that during reaction one dbm⁻ anion of Dy (dbm)₃·H₂O was replaced by the pdmH⁻ ligand, which also worked as the bridging ligand to connect with another Dy³⁺ ion. Such a case is unusual because most lanthanide β -diketonate complexes are constructed from the 1+1 additive reaction. To our knowledge, complex **1** represent the first lanthanide β -diketonate complex containing the 2, 6-pyridinedimethanol ligand, although several 3d-4f tertranuclear cluster complexes [26-27], one mononuclear Sm(III) complex [28] and one linear tertranuclear Dy(III) complex [29] have been constructed from the 2, 6-pyridinedimethanol ligand recently.

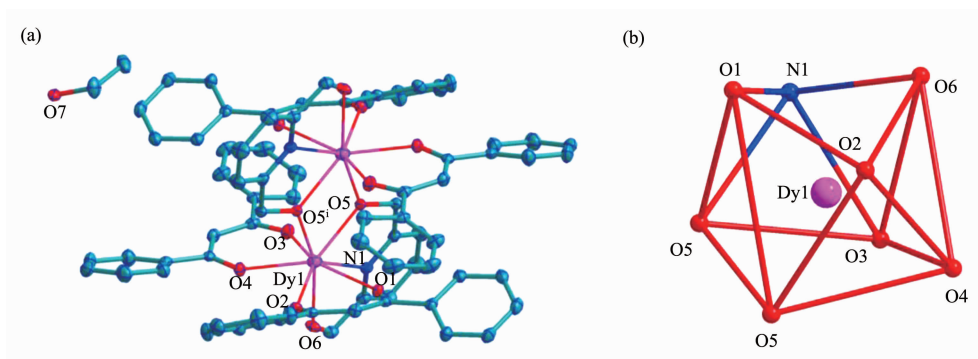
2.2 Description of crystal structure

Complex **1** crystallizes in the monoclinic space

group $P2_1/c$. As shown in Fig.1, this complex possesses a crystallographically centrosymmetric dinuclear Dy₂ core, with the Dy···Dy edges of 0.376 4 nm(Table 2). The two Dy³⁺ ions are bridged by two η^2 -CH₂O⁻ arm oxygen atoms (O5 and O5ⁱ, ⁱ $-1-x, -y, -z$) of two pdmH⁻ ligands, with the Dy1-O5-Dy1ⁱ angle of 110.88°. Because of centrosymmetry, the central core Dy₂O₂ exhibits a parallelogram motif, with the Dy-O distance of 0.226 9 and 0.230 2 nm, respectively. The Dy1 atom is eight-coordinate and bounded by the {NO₅} environment from two η^2 -pdmH⁻ bridging ligands and two β -diketonate terminal ligands. An analysis of coordination geometry by the creased angles of two approximate square planes was employed to accesses the eight-coordinate polyhedron conformations [30]. For the Dy1 atom of **1**, the two approximate square planes defined by O3-O4-O5-O5ⁱ and N1-O1-O2-O6 are creased about the respective diagonals O4-O5 and N1-O2 with angles of 36.3° and 128.9°, respectively. These two angle values are obviously deviated from the standard values for a dodecahedron (the corresponding angles are 29.5° and 29.5°), for a square antiprism (0° and 0°), and for a bicapped trigonalprism (21.8° and 0°) [30]. Therefore, the polyhedron defined by the Dy1 ion and its bound atoms can be best described as an irregular polyhedron geometry.

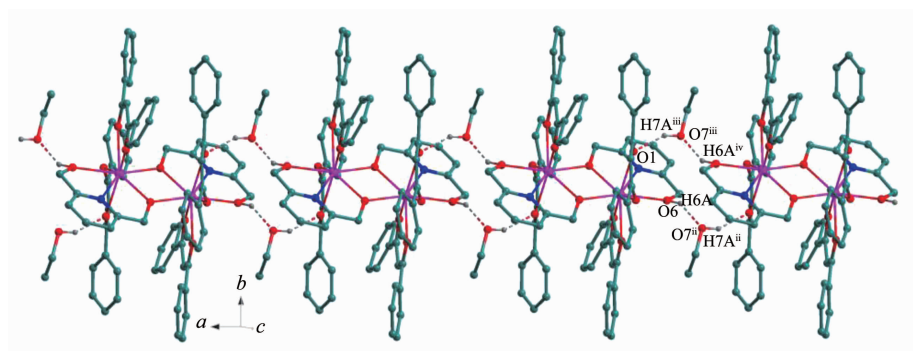
Each $\text{Dy}_2(\text{pdmH})_2(\text{dbm})_4 \cdot 2\text{EtOH}$ molecule contains two crystalline ethanol molecules. There are two type of strong intramolecular hydrogen bonds between the crystalline ethanol molecule and the pdmH^- ligand from neighboring $\text{Dy}_2(\text{pdmH})_2(\text{dbm})_4$ ($\text{O7}^{\text{ii}} \cdots \text{O6}$ 0.260 2 nm, $^{\text{ii}}x-1, -y-1/2, z-1/2$) as well as between the crystalline ethanol molecule and the β diketonate terminal ligand from adjoining $\text{Dy}_2(\text{pdmH})_2$

($\text{dbm})_4$ ($\text{O7}^{\text{iii}} \cdots \text{O1}$ 0.276 0 nm, $^{\text{iii}}-x-1, y+1/2, -z+1/2$). Therefore a couple of crystalline ethanol molecules connect with adjacent $\text{Dy}_2(\text{pdmH})_2(\text{dbm})_4$ molecules through these weak interactions, generating a supramolecular chain along the a -axis (Fig.2). The shortest intermolecular Dy-Dy distance is 1.279 4 nm, which reveals that the intermolecular exchange interaction is negligible.



All H atoms were omitted for clarity; ellipsoids at 30% probability; symmetry code: $^{\text{i}}-1-x, -y, -z$

Fig.1 (a) Crystal structure of **1** and (b) coordination geometry of the Dy1 atom



Symmetry codes: $^{\text{ii}}x-1, -y-1/2, z-1/2$; $^{\text{iii}}-x-1, y+1/2, -z+1/2$; $^{\text{iv}}-x-2, -y, -z$

Fig.2 A supramolecular chain formed by strong intramolecular hydrogen bonds between the crystalline ethanol molecule and the $\text{Dy}_2(\text{pdmH})_2(\text{dbm})_4$ molecule

2.3 Magnetic properties

Variable-temperature magnetic susceptibility of complex **1** was measured over the temperature range 2~300 K in an applied field of 1 000 Oe. As shown in Fig.3, the observed χ_{T} value of $27.66 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at room temperature is in agreement with the theoretical value of $28.34 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ calculated for two magnetically isolated $\text{Dy}(\text{III})$ ions ($^6\text{H}_{15/2}$, $S=5/2$, $L=5$, $g=4/3$, $\chi_{\text{T}}=14.17 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$). Upon cooling, the χ_{T}

product slightly decreases until 50 K, then it shows a sharp drop to a value of $9.95 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2.0 K. The fitting of $1/\chi$ versus T by Curie-Weiss law gives the Curie constant $C=27.62 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ and Weiss constant $\theta=-5.88 \text{ K}$. The negative θ value suggests the presence of weak antiferromagnetic interactions between the two $\text{Dy}(\text{III})$ ions mediated by the $\eta^2\text{-CH}_2\text{O}^-$ arm oxygen atom of the pdmH^- ligand, although magnetic anisotropy and the thermal

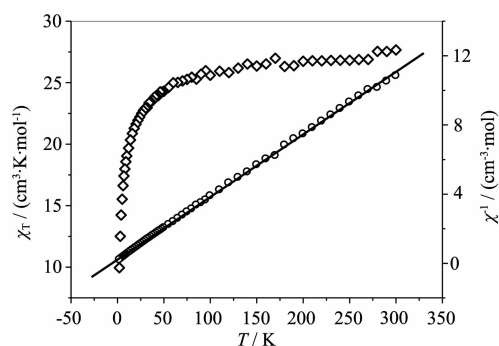


Fig.3 Plots of the dependence of χ_T (\diamond) and $1/\chi$ (\circ) on temperature for complex **1**

depopulation of the Dy (III) excited states (Stark sublevels of the ${}^6H_{15/2}$ state) might be partially included in the Weiss constant value^[31].

The alternating current magnetic susceptibility measurements indicated that down to 2 K, slow relaxation of magnetization was not observed under a 2.5 Oe oscillating field at frequencies up to 997 Hz (Fig.4). The application of a dc field such as 2 000 Oe, which probably may remove the ground state degeneracy and induce the quantum tunneling effects^[32], did not bring any slow relaxation of magnetization too. These results indicate that complex **1** is not a SMM. It is believed that the high symmetry of the eight-coordinate Dy(III) conformation (such as T_{4d}) is beneficial to show SMM properties^[19]. As mentioned above, the Dy(III) ion in complex **1** has an irregular polyhedron conformation, therefore, the lack of symmetry of the Dy(III) coordination geometry maybe causes no SMM behavior of **1**.

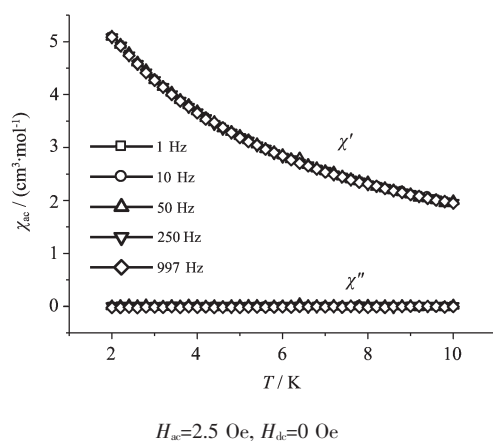


Fig.4 Ac susceptibilities measured in a 2.5 Oe ac magnetic field for **1**

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