两个双核稀土–自由基化合物的合成、结构及磁性

梅雪兰*,1　杜敏杰2　胡　鹏3　李宗群1

(1 蚌埠学院材料与化学工程学院,蚌埠　233030)
(2 南京军代局驻合肥地区军代室,合肥　230041)
(3 肇庆学院环境与化学工程学院,肇庆　526061)

摘要: 以乙酰丙酮为共配体的稀土配合物与 2-羟基苯取代的自由基配体进行反应得到 2 个新颖的稀土–自由基配合物 [Ln$_2$(acac)$_4$(NIT-PhO)$_2$](Ln=Tb (**1**),Y (**2**);acac=乙酰丙酮,NIT-PhOH=2-(2′-hydroxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide)。2 个配合物的结构相同,均是通过 2 个自由基体上的羟基氧原子桥联 2 个稀土离子构成双核结构。直流磁化率的研究表明配合物 **2** 具有弱的反铁磁性质。

关键词: 稀土配合物;晶体结构;磁性质;自由基

Syntheses, Structures and Magnetic Properties of Two Binuclear Lanthanide Complexes Bridged by Nitronyl Nitroxide Radical Ligands

MEI Xue-Lan*,1　　DU Min-Jie2　　HU Peng3　　LI Zong-Qun1

(1College of Materials Science and Chemical Engineering, Bengbu University, Bengbu, Anhui 233030, China)
(2Military Representative Bureau of Nanjing of the PLA Army, Hefei 230041, China)
(3College of Environment and Chemical Engineering, Zhaoqing University, Zhaoqing, Guangdong 526061, China)

Abstract: The reaction of Ln(acac)$_3$·3H$_2$O with NIT-PhOH radical yielded two new Ln-radical complexes [Ln$_2$(acac)$_4$(NIT-PhO)$_2$] (Ln=Tb (**1**), Y (**2**); acac=acetylacetonato, NIT-PhOH=2-(2′-hydroxyphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide). Two complexes are isostructural and have binuclear structure in which two lanthanide ions are bridged by two radical ligands through their phenoxo-O atoms. DC magnetic susceptibility studies indicated that there exists weak antiferromagnetic interaction in complex **2**. CCDC: 1878666, **1**; 1878665, **2**.

Keywords: lanthanide complexes; crystal structure; magnetic properties; radical

0　Introduction

Lanthanide-based complexes are attracting an increasing attention over the past decades because of their enchanting and potential applications in the realm of molecular magnetic materials[1-4].

The lanthanide ions are excellent candidates for developing molecular magnetic materials because of their outstanding single-ion anisotropy and large magnetic moments[5-6]. To date, a large number of lanthanide-based complexes such as pure lanthanide complexes[7-9] and mixed transition metal-4f complexes[10-11] or radical-4f complexes[12-15] have been obtained and characterized in terms of structures and

magnetic properties, and plenty of them exhibit novel structures and good magnetic properties[16-19]. It should be noted that in contrast to 3d-4f or pure 4f systems, fewer Ln-radical complex has been reported so far. The research demonstrates that the magnetic properties of Ln-radical based complexes have a broad variation, among which both antiferromagnetic[20-21] and ferromagnetic[22-23] interactions between the radical ligand and the lanthanide ions center have been observed. Some of them have been observed to exhibit slow magnetic relaxation behaviors[21,23]. For the applied radical ligands, the nitronyl nitroxide radicals (NITR) are one of the most explored owing to their stability and ease chemical modification[24]. Especially, since the first Dy(Ⅲ)-radical based molecule [Dy(hfac)$_3$NITpPy]$_2$ showing single-molecule magnetic behavior was discovered in 2007[25], much attention has been attracted by the nitronyl nitroxide-4f complexes[26-27]. Recently, a few Ln-nitronyl nitroxide complexes revealing magnetic relaxation have been described. To explore new Ln-nitronyl-nitroxide-based complexes, herein we employ the NIT-PhOH (Scheme 1) radical containing a hydroxyl group to build new Ln-radical complexes. Herein, the synthesis, crystallography and magnetic characterization of two new phenoxo-bridged lanthanide-radical binuclear complexes [Ln$_2$(acac)$_4$(NIT-PhO)$_2$] (Ln=Tb (1), Y (2)) are reported. Before this, several complexes have been obtained through NIT-PhOH radical already[28-30], some of which have excellent magnetic property. In order to get more novel complexes with good magnetic property, we study further.
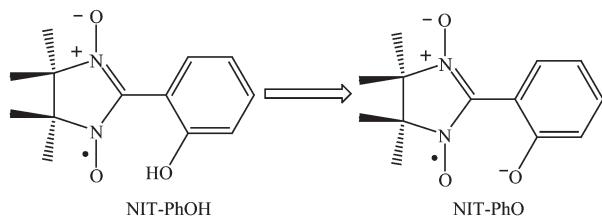
Scheme 1   Nitronyl nitroxide radicals NIT-PhOH and NIT-PhO

1   Experimental

1.1   Materials and physical measurement

All chemicals were used as received without any further purification. The starting materials Ln(acac)$_3$·3H$_2$O were synthesized by the methods in the literature[31]. The radical ligand NIT-PhOH was prepared by the reported methods[32-33]. Elemental analyses for C, H, and N were obtained at the Institute of Elemental Organic Chemistry, Nankai University. The infrared spectra of the complexes in KBr pellets were obtained on a Bruker Tensor 27 IR spectrometer in a range of 4 000~400 cm^{-1} region. Magnetic measurements were performed on a SQUID MPMS XL-7 magnetometer. Diamagnetic corrections were made with Pascal′s constants for all of the constituent atoms.

1.2   Syntheses of the complexes

1.2.1   Preparation of [Tb(acac)$_2$(NIT-PhO)]$_2$ (1)

Tb(acac)$_3$·3H$_2$O (0.103 g, 0.2 mmol) in 30 mL dry n-heptane was heated to reflux for 3 h. Then the solution was cooled to 60 ℃, and a dry CH$_2$Cl$_2$ solution of NIT-PhOH (0.050 g, 0.2 mmol) was added. The resulting mixture was stirred for 15 min at 60 ℃, then cooled to room temperature and filtered. After 2 days, the little azury rectangular crystals was obtained. Yield: 60%. Anal. Calcd. for C$_{46}$O$_{14}$N$_4$H$_{60}$Tb$_2$ (%): C, 45. 63; H, 4.99; N, 4.63. Found (%): C, 45.12; H, 4.86; N, 4.56. FT-IR (KBr, cm^{-1}): 2 991 (w), 1 603(s), 1 518(s), 1 392(s), 1 258(s), 1 173(m), 1 017(m), 922 (m), 819(m), 766(m), 624(m), 537(w).

1.2.2   Preparation of [Y(acac)$_2$(NIT-PhO)]$_2$ (2)

The preparation was similar to that of 1 but Y(acac)$_3$·3H$_2$O (0.089 g, 0.2 mmol) was used in place of Tb(acac)$_3$·3H$_2$O. Yield: 70%. Anal. Calcd. for C$_{46}$O$_{14}$N$_4$H$_{60}$Y$_2$ (%): C, 51.59; H, 5.65; N, 5.23. Found (%): C, 51.93; H, 6.09; N, 5.23. FT-IR (KBr, cm^{-1}): 2 988(w), 1 603(s), 1 519(s), 1 397(s), 1 238(m), 1 169 (m), 1 016(s), 919(s), 869(m), 811(s), 763(s), 653(w), 536(w).

1.3 X-ray crystallography

X-ray single-crystal diffraction of complexes 1 and 2 was performed on a Rigaku mercury CCD diffractometer with graphite-mono-chromated Mo Kα radiation (λ=0.071 073 nm) at 113(2) K. In each case, absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares technique using the SHELXS-97

and SHELXL-97 programs[34-35]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added theoretically and refined isotropically using a riding mode. Crystallographic data and structure refinement results of the complexes **1** and **2** were listed in Table 1.

CCDC: 1878666, **1**; 1878665, **2**.

Table 1　Crystallographic data for complexes 1 and 2

Complex	1	2
Empirical formula	$C_{46}H_{60}N_4O_{14}Tb_2$	$C_{46}H_{60}N_4O_{14}Y_2$
Molecular weight	1 210.84	1 070.80
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.047 8(4)	1.043 4(5)
b / nm	1.127 1(2)	1.124 8(6)
c / nm	1.182 3(3)	1.189 1(5)
α / (°)	104.01(2)	104.520(4)
β / (°)	98.761(17)	98.864(2)
γ / (°)	114.616(12)	114.079(7)
V / nm³	1.179 8(6)	1.180 4(10)
Z	2	2
D_c / (g·cm⁻³)	1.704	1.506
μ / mm⁻¹	3.043	2.516
θ range / (°)	1.85~25.02	1.85~25.01
$F(000)$	606	554
Reflection collected	9 380	9 732
Unique reflection	4 149	4 146
R_{int}	0.060 0	0.067 7
GOF (F^2)	1.063	1.058
R_1 [$I>2\sigma(I)$]	0.043 3	0.055 0
wR_2 [$I>2\sigma(I)$]	0.101 9	0.107 9
R_1 (all data)	0.049 2	0.070 2
wR_2 (all data)	0.104 9	0.114 9

2　Results and discussion

2.1　Crystal structures of 1 and 2

Single-crystal X-ray diffraction analysis reveals that complexes **1** and **2** are isostructural and crystallize in the triclinic space group $P\bar{1}$. Selected bond parameters for complexes **1** and **2** are listed in Table 2. Both complexes have centrosymmetric binuclear structure bridged by two phenoxo groups. For their identical structural motifs, only the structure of complex **1** is described herein as representative. In the asymmetric unit of **1**, there are crystallographically independent one Tb(acac)₂ unit and one radical anion ligand (Fig.1). As shown in Fig.1, to each Tb(Ⅲ) ion, there are seven coordination sites, which are occupied by four oxygen atoms from two acac ligands, two phenoxo-O atoms and one NO group from one radical ligand. Coordination geometry around the Tb(Ⅲ) ions is analyzed by using the program of SHAPE[36] and the lower CShM values of the shape measure are found relative to capped octahedron (C_{3v}) (Table 3). The coordination geometry of Tb(Ⅲ) ions is shown in Fig.2. The two nitronyl nitroxide radical ainons act as bridge ligands to link two Tb(Ⅲ) ions through two μ_2-O atoms of the phenoxo groups, leading to a binuclear Tb₂O₂ unit with the intramolecular Tb(Ⅲ)···Tb(Ⅲ) distance of 0.393 86(16) nm. The Tb-O$_{acac}$ bond lengths are in a range of 0.227 3(4)~0.233 4(4) nm. The Tb-O$_{radical}$

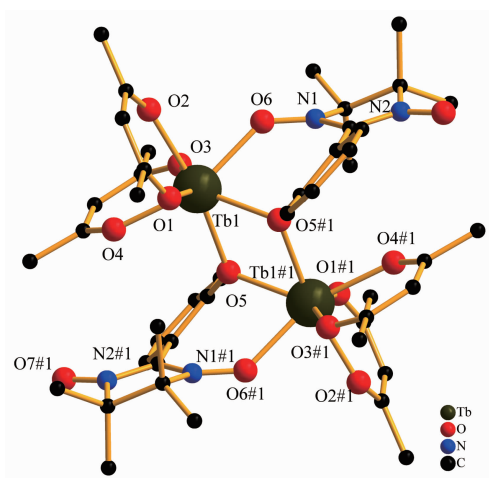**Table 2 Selected important bond lengths (nm) and angles (°) for complexes 1 and 2**

1					
Tb(1)-O(6)	0.231 9(5)	Tb(1)-O(5)	0.236 5(4)	Tb(1)-O(5)#1	0.236 7(4)
Tb(1)-O(1)	0.227 3(4)	Tb(1)-O(2)	0.233 4(4)	Tb(1)-O(3)	0.229 3(4)
Tb(1)-O(4)	0.231 9(5)	O(6)-N(1)	0.130 4(6)	O(7)-N(2)	0.127 1(7)
N(1)-C(17)	0.134 5(8)	N(1)-C(19)	0.149 2(8)	N(2)-C(18)	0.148 8(8)
N(2)-C(17)	0.137 5(8)				
O(1)-Tb(1)-O(2)	73.89(15)	O(3)-Tb(1)-O(4)	75.94(17)	O(6)-Tb(1)-O(5)	109.76(15)
O(1)-Tb(1)-O(6)	113.78(16)	O(3)-Tb(1)-O(6)	79.59(16)	O(3)-Tb(1)-O(5)#1	129.86(15)
O(6)-Tb(1)-O(5)#1	72.45(15)	N(1)-O(6)-Tb(1)	136.8(4)	O(6)-N(1)-C(17)	126.7(6)
C(11)-O(5)-Tb(1)	125.0(4)	C(11)-O(5)-Tb(1)#1	121.8(3)	Tb(1)-O(5)-Tb(1)#1	112.66(16)
2					
Y(1)-O(1)	0.226 2(3)	Y(1)-O(2)	0.229 1(3)	Y(1)-O(3)	0.231 1(3)
Y(1)-O(4)	0.224 3(3)	Y(1)-O(5)	0.235 7(3)	Y(1)-O(5)#2	0.232 7(3)
Y(1)-O(6)	0.230 0(3)	O(7)-N(2)	0.127 8(4)	O(6)-N(1)	0.130 3(4)
N(1)-C(17)	0.133 3(5)	N(1)-C(18)	0.150 6(6)	N(2)-C(17)	0.136 6(5)
N(2)-C(19)	0.150 3(5)				
O(1)-Y(1)-O(2)	76.89(11)	O(4)-Y(1)-O(3)	74.75(11)	O(6)-Y(1)-O(5)	72.88(10)
C(11)-O(5)-Y(1)	120.6(2)	C(11)-O(5)-Y(1)#2	126.1(2)	O(6)-N(1)-C(17)	126.1(4)
O(6)-N(1)-C(18)	121.1(3)	O(7)-N(2)-C(17)	126.0(4)	O(7)-N(2)-C(19)	121.1(4)
N(1)-O(6)-Y(1)	137.1(3)	O(1)-Y(1)-O(5)	129.75(11)	O(2)-Y(1)-O(5)	133.45(10)

Symmetry codes: #1: −x+1, −y, −z for **1**; #2: −x+2, −y+1, −z+1 for **2**.

Table 3 Coordination geometry analysis for complexes 1 (Tb1) and 2 (Y1)

| Atom	PBPY-7(D_{5h})	COC-7(C_{3v})	CTPR-7(C_{2v})	JPBPY-7(D_{5h})
Tb1	7.685	0.575	2.016	11.834
Y1	7.785	0.521	2.047	11.639

PBPY-7: Pentagonal bipyramid; COC-7: Capped octahedron; CTPR-7: Capped trigonal prism; JPBPY-7: Johnson pentagonal bipyramid J13.

bond distance is 0.231 9(5) nm. The Tb-O-Tb bridge angle is 112.66(16)° (Tb(1)-O5-Tb(1)#1). These bond parameters are comparable to those reported in other lanthanide salicylic aldehyde substituted radical complexes[37]. The shortest separation between the

All hydrogen atoms are omitted for clarity; Symmetry codes:
#1: −x+1, −y, −z

Fig.1　Crystal structure of complex **1**
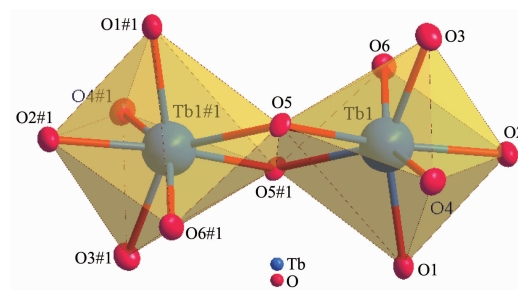
Symmetry codes: #1: −x+1, −y, −z

Fig.2　Local coordination geometry of Tb(Ⅲ) ion

uncoordinated NO groups is 0.545 3 nm. This separation is large enough to convince us to consider the complexes in the solid state as a discrete binuclear Tb(Ⅲ) complex, although the possible weak intermolecular interaction can not be excluded.

2.2　Magnetic properties

Variable temperature (300~2.0 K) direct current (dc) magnetic susceptibility was measured for the crystalline sample of **1** under an applied magnetic field of 2.0 kOe. As shown in Fig.3, the $\chi_M T$ product for **1** was 23.07 cm³·K·mol⁻¹ at 300 K, which is slightly lower than the theoretical value of 24.37 cm³·K·mol⁻¹ for two isolated Tb(Ⅲ) ions ($^7F_6$, $S=3$, $L=3$, $g=3/2$, $C=11.81$ cm³·K·mol⁻¹) and two uncoupled organic radicals ($S=1/2$). The value is comparable with the complex [Tb(hfac)₂(NIT2PhO)][37]. On lowering the temperature, the $\chi_M T$ value gradually decreased before 18 K, then decreased sharply to the value of 10.30 cm³·K·mol⁻¹ at 2.0 K. Based on the crystal structure of **1**, this magnetic behavior may be ascribed to the combination of the depopulation of the Tb(Ⅲ) Stark sublevels, the magnetic exchange between the Tb(Ⅲ) ion and the coordinated NO group, and the Tb⋯Tb magnetic coupling transmitted by double phenolate bridges.
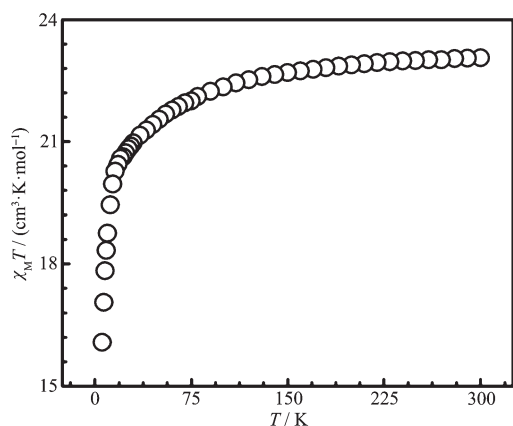

Fig.3　Plot of $\chi_M T$ versus T for complex **1**

The magnetic susceptibility of complex **2** is measured under 5 kOe in a range of 2~300 K and the magnetic behavior is shown in Fig.4. At room temperature, the $\chi_M T$ value of complex **2** was 0.74 cm³·K·mol⁻¹, which is in agreement with the expected value of 0.75 cm³·K·mol⁻¹ for an uncoupled system of
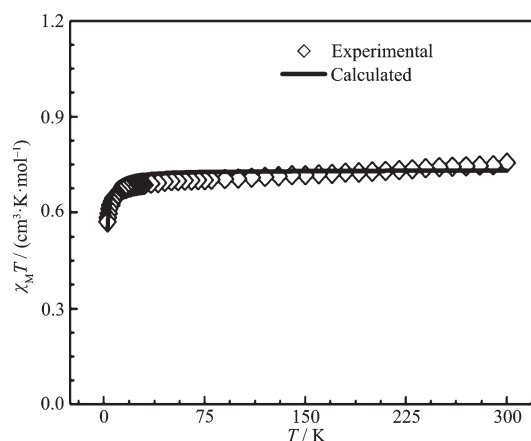

Fig.4　Plot of $\chi_M T$ versus T for complex **2**

two organic radicals ($S=1/2$). When the temperature was decreased, the $\chi_M T$ value decreased gradually and then reached to the minima value 0.58 cm³·K·mol⁻¹ at 2.0 K. The magnetic data was analyzed by a theoretical expression deduced from the spin Hamiltonian $H=-J\hat{S}_{Rad}\cdot\hat{S}_{Rad}$. Considering the weak magnetic coupling between the binuclear units, a correction for a molecular field can be made. The magnetic susceptibility expression is:

$$\chi_M=\frac{Ng^2\beta^2}{kT}\frac{2}{3+\exp[-2J/(kT)]}$$

$$\chi_{total}=\frac{\chi_M}{1-\dfrac{zJ'}{Ng^2\beta^2}\chi_M}$$

The least-squares fit to the data yielded the following parameter values: $g=1.99$, $J=-1.69$ cm⁻¹, $zJ'=-0.067$ cm⁻¹, with an agreement factor $R=9.30\times10^{-4}$. R is defined as $R=\sum(\chi_{M,obs}-\chi_{M,calc})^2/\sum(\chi_{M,obs})^2$. The Y(Ⅲ) ion is a diamagnetic ion, and thus the weak antiferromagnetic coupling should arise from the magnetic interaction of intramoleclur two radical ligands[38-39].

3　Conclusions

Two isostructural Ln-radical complexes are prepared by using the nitronyl nitroxide radical with a phenolate group. These two complexes are binuclear complexes in which the nitronyl nitroxides are the radical anions and act as bridging ligands to bridge two Ln(Ⅲ) ions through two phenoxo groups. This is less common than the usually obtained Ln-nitronyl nitroxide complexes where the radical is neutral

ligand. Magnetic measurements show that complex **2** displays a weak anti-ferromagnetic coupling interaction. This work could represent an important avenue to synthesize polynuclear lantnanide-nitroxide based complexes.

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