

## 由 $\beta$ -二酮和三苯氧膦配体构筑的钕三元配合物的合成、晶体结构和荧光性质

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**摘要:** 在温和条件下合成了 2 种以  $\beta$ -二酮和三苯氧膦为配体的钕三元配合物  $[\text{Nd}(\text{TTA})_3(\text{TPPO})_2]$  (**1**) (TTA=2-噻吩甲酰三氟丙酮, TPPO=三苯氧膦) 和  $[\text{Nd}(\text{BFA})_3(\text{TPPO})_2]$  (**2**) (BFA=4,4,4-三氟-1-苯基-1,3-丁二酮), 获得了单晶并通过 X 射线单晶衍射确定了配合物结构。晶体分析显示, 2 种配合物均为八配位结构, 属于三斜晶系,  $P\bar{1}$  空间群。采用元素分析、红外光谱和热重分析对 2 种配合物进行了结构表征; 通过近红外荧光分析, 探讨了配合物的荧光特征。

**关键词:** 钕配合物; 合成; 晶体结构; 荧光性质

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## Syntheses, Crystal Structures and Luminescence Properties of Nd Complexes with $\beta$ -Diketonate and Triphenylphosphine Oxide

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**Abstract:** Two ternary complexes of neodymium ions,  $[\text{Nd}(\text{TTA})_3(\text{TPPO})_2]$  (**1**) and  $[\text{Nd}(\text{BFA})_3(\text{TPPO})_2]$  (**2**), based on 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (BFA) and triphenylphosphineoxide (TPPO) have been synthesized by mild condition and the single crystals suitable for X-ray measurement were obtained. The structures of the two Nd complexes were determined in solid states by X-ray diffraction. Single crystal analysis revealed that the complexes are both eight-coordinated with one center Nd ion and eight O atoms from ligands and crystallize in triclinic symmetry with  $P\bar{1}$  space group. The complexes were characterized by elemental analysis, IR spectroscopy and thermogravimetric. Furthermore, photophysical studies on the complexes were carried out, which shows luminescence in near-infrared area. CCDC: 1558841, **1**; 1558842, **2**.

**Keywords:** neodymium complex; synthesis; crystal structure; luminescence property

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## 0 Introduction

Lanthanide complexes based on  $\beta$ -diketonate as ligands have attracted much attention over the past decades due to their unusual luminescence properties and potential applications in light-emitting diodes<sup>[1-5]</sup>, catalytic actions<sup>[6-9]</sup> and magnetic materials<sup>[10-13]</sup>, *etc.* As generally known, lanthanide ions have excellent luminescent properties arising from their filling mode of the  $4f$  orbitals. The characterizations of lanthanide ions luminescence, such as sharp emission and high color purity, originate from  $f$ - $f$  electron transitions. However, these transitions are difficult because of the shielding by  $5s$  and  $5p$  shells which are filled by electrons. The  $\beta$ -diketonate molecules are the most effective ligands to increase the electron transitions of center lanthanide ions by constructing coordination geometry. In order to explore the connections between structural and physic-chemical properties, we have synthesized two neodymium complexes with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione (TTA), 4,4,4-trifluoro-1-phenyl-1,3-butanedione(BFA) and triphenylphosphineoxide (TPPO) as ligands, namely  $[\text{Nd}(\text{TTA})_3(\text{TPPO})_2]$  (**1**) and  $[\text{Nd}(\text{BFA})_3(\text{TPPO})_2]$  (**2**), under mild condition. In this report we described the syntheses, structural characterizations and properties of the two Nd ternary complexes.

## 1 Experimental

### 1.1 Materials and instruments

All reagents and solvents employed were used as commercial sources without further purification. Elemental analyses (C, H) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra were recorded on a Nicolet 6700 FTIR spectrometer with KBr disks in the range of  $4\,000\sim 400\text{ cm}^{-1}$ . Thermogravimetric analyses (TGA) were performed on a TGA Pyris 1 PE instrument heating from room temperature to  $800\text{ }^{\circ}\text{C}$  under a flow of  $\text{N}_2$  with a heating rate of  $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ . Solid-state excitation and fluorescence spectra for crystals were recorded at room temperature on a Fluorolog-3 spectrofluorometer (Horiba Jobin Yvon) with a 450W Xenon Lamp as the

excitation source and a PMT (H10330-75, Hamamatsu) as the detector.

### 1.2 Syntheses of the complexes

$\beta$ -diketonate ligand (1.5 mmol) was dissolved in 10 mL ethanol, and aqueous solution of neodymium acetate monohydrate (1 mL, 0.5 mmol) was added dropwise into the  $\beta$ -diketonate ligand solution. The mixtures were stirred for 4 h at room temperature, and then followed by the addition of triphenylphosphine oxide (TPPO) ethanol solution (5 mL, 1.0 mmol). After stirring overnight, crystalline precipitates were formed. The products were filtered and washed several times with ethanol, then dried under vacuum at  $70\text{ }^{\circ}\text{C}$  for 24 h. The complexes were dissolved in ethyl acetate/ethanol (1:1, V/V) and stilled several days. Pink crystals were obtained in the form of single crystals which are suitable for X-ray measurements. The obtained crystals are hardly soluble in water or ethanol but soluble in ethyl acetate, DMF, THF and DMSO.

$[\text{Nd}(\text{TTA})_3(\text{TPPO})_2]$  (**1**): Yield: 92.5% based on the Nd. Main IR bands ( $\text{cm}^{-1}$ ): 1 625(s), 1 535(m), 1 502(m), 1 472(w), 1 438(w), 1 415(m), 1 297(s), 1 236(w), 1 168(s), 1127(s), 783(w), 721(m), 693(w), 541(m). Anal. Calcd. for  $\text{C}_{60}\text{H}_{42}\text{F}_9\text{NdO}_8\text{P}_2\text{S}_3(\%)$ : C, 52.82; H, 3.10. Found(%): C, 52.42; H, 3.01.

$[\text{Nd}(\text{BFA})_3(\text{TPPO})_2]$  (**2**): Yield: 86.6% based on the Nd. Main IR bands ( $\text{cm}^{-1}$ ): 1 625(s), 1 579(m), 1 532(m), 1 486(m), 1 438(m), 1 314(m), 1 297(s), 1 240(w), 1 170(s), 1 128(s), 760(w), 723(m), 695(m), 541(m). Anal. Calcd. for  $\text{C}_{66}\text{H}_{48}\text{F}_9\text{NdO}_8\text{P}_2(\%)$ : C, 58.88; H, 3.59. Found(%): C, 58.30; H, 3.35.

### 1.3 X-ray crystallography analysis

The single-crystal diffraction measurements for complexes were performed on a Xcalibur Eos four-circle diffractometer with monochromatic  $\text{Mo K}\alpha$  radiation source ( $\lambda=0.071\,073\text{ nm}$ ) at  $143\text{ K}$ . The structures were solved by a direct method using the program SHELXS-2013 and refined anisotropically by the full-matrix least squares on  $F^2$  using the SHELXL-2013 crystallographic software package to the non-hydrogen atoms<sup>[14-15]</sup>. Hydrogen atoms based on carbon were generated geometrically and refined using the riding

model. The summary of crystal data and refinement details are listed in Table 1, and the selected bond lengths and bond angles are given in Table 2. CCDC: 1558841, **1**; 1558842, **2**.

**Table 1** Crystallographic data of complexes **1** and **2**

Empirical formula	C <sub>60</sub> H <sub>42</sub> F <sub>9</sub> NdO <sub>8</sub> P <sub>2</sub> S <sub>3</sub>	C <sub>66</sub> H <sub>48</sub> F <sub>9</sub> NdO <sub>8</sub> P <sub>2</sub>
Formula weight	1 364.29	1 346.22
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
$a$ / nm	1.117 01(5)	1.123 44(4)
$b$ / nm	1.212 22(4)	1.227 63(3)
$c$ / nm	2.351 37(7)	2.369 10(8)
$\alpha$ / (°)	80.094(3)	79.778(3)
$\beta$ / (°)	76.759(3)	76.477(3)
$\gamma$ / (°)	70.521(4)	71.603(3)
$V$ / nm <sup>3</sup>	2.905 9(18)	2.995 33(19)
$Z$	2	2
$D_c$ / (g·cm <sup>-3</sup> )	1.559	1.493
Crystal size / mm	0.35×0.35×0.30	0.40×0.35×0.30
Absorption coefficient / mm <sup>-1</sup>	1.139	1.004
$F(000)$	1 370	1 358
$\theta$ range / (°)	3.021~26.372	2.975~26.371
Reflection collected, unique ( $R_{int}$ )	23 442, 11 852 (0.026 4)	25 676, 12 229 (0.033 4)
Goodness of fit on $F^2$	1.036	1.042
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.035$ 7, $wR_2=0.076$ 7	$R_1=0.037$ 4, $wR_2=0.081$ 6
Largest diff. peak and hole / (e·nm <sup>-3</sup> )	670 and -490	490 and -450

**Table 2** Selected bond lengths (nm) and bond angle (°) of complexes **1** and **2**

<b>1</b>					
Nd1-O1	0.240 39(19)	Nd1-O2	0.241 91(19)	Nd1-O3	0.248 59(18)
Nd1-O4	0.240 9(2)	Nd1-O5	0.248 2(19)	Nd1-O6	0.239 7(2)
Nd1-O7	0.248 8(2)	Nd1-O8	0.240 6(2)		
O1-Nd1-O2	145.02(7)	O3-Nd1-O4	69.96(7)	O5-Nd1-O6	70.68(7)
O7-Nd1-O8	69.11(7)	O1-Nd1-O3	75.53(7)	O1-Nd1-O4	87.46(7)
O1-Nd1-O5	78.80(7)	O1-Nd1-O6	143.77(7)	O1-Nd1-O7	79.92(7)
O1-Nd1-O8	83.44(7)	O2-Nd1-O3	71.76(7)	O2-Nd1-O4	84.83(7)
O2-Nd1-O5	129.70(7)	O2-Nd1-O6	71.21(7)	O2-Nd1-O7	125.06(7)
O2-Nd1-O8	84.15(7)	O3-Nd1-O5	132.63(7)	O3-Nd1-O6	142.40(7)
O3-Nd1-O7	138.08(7)	O3-Nd1-O8	76.03(7)	O4-Nd1-O5	71.15(7)
O4-Nd1-O6	100.32(8)	O4-Nd1-O7	141.02(7)	O4-Nd1-O8	145.99(7)
O5-Nd1-O7	70.26(7)	O5-Nd1-O8	137.81(7)	O6-Nd1-O7	71.83(7)
O6-Nd1-O8	106.32(8)				
<b>2</b>					
Nd1-O1	0.247 66(19)	Nd1-O2	0.241 3(2)	Nd1-O3	0.249 9(2)
Nd1-O4	0.239 6(2)	Nd1-O5	0.244 57(19)	Nd1-O6	0.241 9(2)
Nd1-O7	0.242 3(2)	Nd1-O8	0.240 58(19)		

Continued Table 2

O1-Nd1-O2	69.54(7)	O3-Nd1-O4	69.07(7)	O5-Nd1-O6	70.06(7)
O7-Nd1-O8	146.54(7)	O1-Nd1-O3	136.25(7)	O1-Nd1-O4	75.66(7)
O1-Nd1-O5	130.94(7)	O1-Nd1-O6	144.98(7)	O1-Nd1-O7	73.46(7)
O1-Nd1-O8	73.28(7)	O2-Nd1-O3	142.84(7)	O2-Nd1-O4	144.98(7)
O2-Nd1-O5	70.86(7)	O2-Nd1-O6	100.43(7)	O2-Nd1-O7	82.33(8)
O2-Nd1-O8	89.49(7)	O3-Nd1-O5	72.39(7)	O3-Nd1-O6	71.61(7)
O3-Nd1-O7	125.85(7)	O3-Nd1-O8	78.11(7)	O4-Nd1-O5	140.22(7)
O4-Nd1-O6	105.84(7)	O4-Nd1-O7	84.22(8)	O4-Nd1-O8	84.20(7)
O5-Nd1-O7	127.70(7)	O5-Nd1-O8	78.62(7)	O6-Nd1-O7	71.93(7)
O6-Nd1-O8	141.52(7)				

## 2 Results and discussion

### 2.1 Infrared spectroscopy

IR spectra of the two complexes were similar at main bands depending on their similar structures. The strong IR band of  $1\ 625\ \text{cm}^{-1}$  is attributed to the stretching vibrations of C=C-C=O conjugate system in Nd complexes. Other same groups, such as C-O, P=O and  $\text{CF}_3$ , have strong bands in the range from  $1\ 350$  to  $1\ 100\ \text{cm}^{-1}$ . In these IR spectra, strong bands at  $1\ 297$ ,  $1\ 168$  and  $1\ 127\ \text{cm}^{-1}$  probably belong to aforesaid groups.

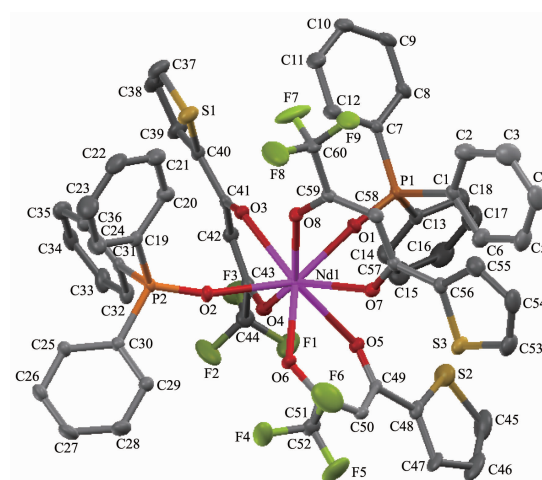
The slight differentia between each other are the middling bands at  $1\ 502$  and  $1\ 415\ \text{cm}^{-1}$  (for complex **1**) owing to the thienyl in 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione ligands, as well as the band of  $1\ 579\ \text{cm}^{-1}$  (for complex **2**) owing to the phenyl in 4,4,4-trifluoro-1-phenyl-1,3-butanedione ligands.

### 2.2 Structural investigations

The crystal system and unit cell of complexes were determined by single-crystal X-ray diffraction analysis. The results reveal that the two complexes both crystallize in triclinic symmetry with  $P\bar{1}$  space group, which are shown in Fig.1 and 2.

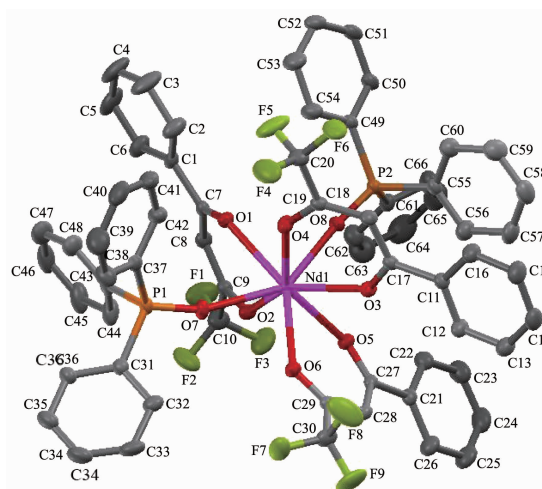
The complexes of **1** and **2** have eight-coordinated Nd ions with six O atoms (O3, O4, O5, O6, O7, O8 for **1**; O1, O2, O3, O4, O5, O6 for **2**) from the three  $\beta$ -diketonate ligand molecules and the other two O atoms (O1, O2 for **1**; O7, O8 in for **2**) afforded by two triphenylphosphineoxide molecules. In addition, no solvent molecules participate in the crystal structure of complexes. The Nd-O<sub>TFA</sub> distances range from

0.239 7 to 0.248 8 nm, Nd-O<sub>BFA</sub> distances from 0.239 6 to 0.249 9 nm and the Nd-O<sub>TPPO</sub> distances from 0.240 4



Thermal ellipsoids are drawn at 30% probability level; All H atoms are omitted for clarity

Fig.1 Molecular structure of complex **1**



Thermal ellipsoids are drawn at 30% probability level; All H atoms are omitted for clarity

Fig.2 Molecular structure of complex **2**

to 0.242 3 nm. All the bond lengths are within the range of those found in the other analogical Nd complexes<sup>[16-18]</sup>. The O-Nd-O bond angles in the complexes range from 69.07° to 146.54° (Table 2).

The complexes of **1** and **2** possess 3D structures with analogical mode. The crystallographic description will be focused on complex **1** (Fig.1). Single-crystal X-ray diffraction analysis reveals that the bond lengths based on center Nd ion and O atoms (O4, O6, O8) which are near by the trifluoromethyl group are longer than the others based on center ion and O atoms (O3, O5, O7) which are near by the thienyl group. It should be attributed to the strong action of attracting electron with trifluoromethyl group of the ligand, which results in adding electron cloud density of O atoms and enhancing its ability of coordination with Nd ion. Three TTA ligands distribute on an approximate plane including the center Nd ion. And two TPPO ligands lie in the opposite positions of this plane with O<sub>TPPO</sub>-Nd-O<sub>TPPO</sub> bond angle of 145.01°, which results in reducing the repulsion to each other.

Owing to the absence of solvate molecules and additional hydrogen bonds, the crystal lattices of complexes are dominated by van der Waals forces. In addition, it was found that a weak interaction ( $\pi$ - $\pi$  stacking interaction) exists in crystal units of complexes. As shown in Fig.3a, in complex **1**, the face to face  $\pi$ - $\pi$  stacking interactions occur between the two benzene rings (from C19 to C24 for each benzene ring) by the different TPPO ligands contained in the two adjacent molecules. The centroid-to-centroid distance of 0.390 7 nm and the dihedral angle of 0.007° belong to effective  $\pi$ - $\pi$  stacking interactions. Similar structures are also found in complex **2** (Fig. 3b). Two benzene rings (from C37 to C42 for each benzene ring) form face to face  $\pi$ - $\pi$  stacking interactions with the centroid-to-centroid distance of 0.406 3 nm and the dihedral angle of 0°. More units connect each other via these weak  $\pi$ - $\pi$  interaction and van der Waals forces, thus, three-dimensional coordination frameworks are constructed.

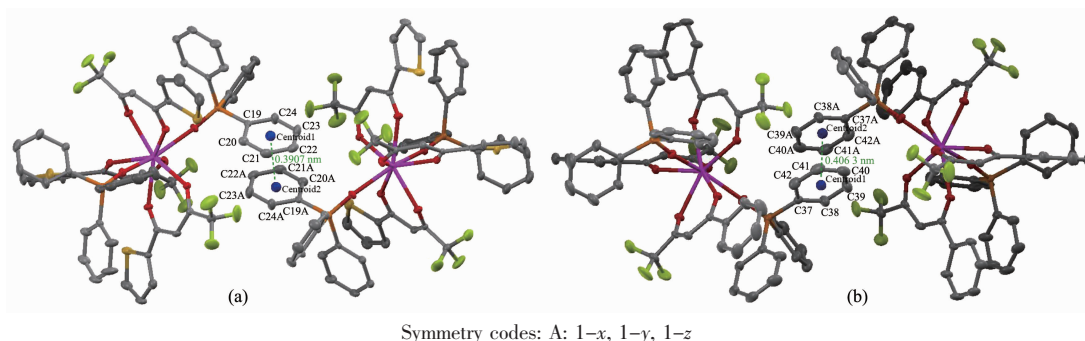


Fig.3  $\pi$ - $\pi$  interactions of crystal units in complexes **1** (a) and **2** (b)

### 2.3 Thermal analysis

Fig.4 shows the results of thermal stability of the complexes, which were investigated by thermal gravimetric analyses (TGA) at a heating rate of 10 °C · min<sup>-1</sup> under flowing N<sub>2</sub> gas. The TG curves of both complexes show only one sharp weight loss step that occur in the range from 280 to 380 °C by weight loss of 82.86% and 84.85%, respectively. It demonstrates that the complexes decomposed by the escaping of  $\beta$ -diketonate and TPPO ligands without difference owing to that all the Nd-O bands (such as Nd-O<sub>TTA</sub>, Nd-O<sub>BFA</sub> and Nd-O<sub>TPPO</sub>) have the approximate bond energy. The

quite high decomposition temperatures mean that the obtained complexes have the favorable thermal stabilities.

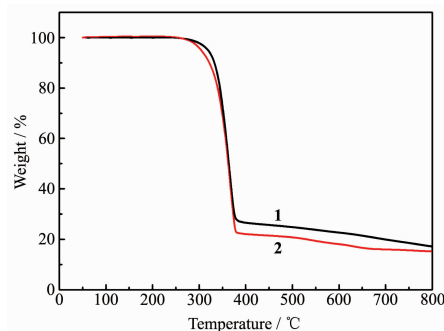


Fig.4 Thermogravimetric curves of complexes **1** and **2**



## 2.4 Luminescent properties

The luminescent properties in near-infrared region of complexes were investigated with solid state at room temperature. In the excitation spectra (Fig.5), there are three main peaks in each complex. Two peaks are almost in the same wavelengths at 524 and 582 nm for complexes **1** and **2**, while the third peak is visibly different for the two complexes at 388 and 371 nm, respectively. The results are similar to the UV absorption spectra of Nd ion but red-shifted about 30, 2 and 8 nm<sup>[19]</sup>, respectively, attributed to the energy transfer from ligands to the center Nd ions. The emission spectra are shown in Fig.6. With excitation at 360 nm, the complexes show same emission bands at 1 057 and 1 329 nm which are the characteristic emissions of Nd ion. The strongest band at about 1 057 nm is applicable for laser emission.

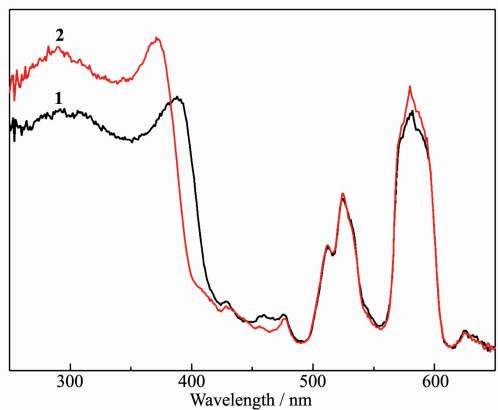


Fig.5 Excitation spectra of complexes **1** and **2**

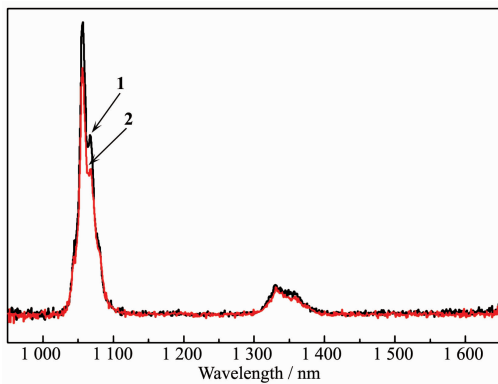


Fig.6 Emission spectra of complexes **1** and **2**

## 3 Conclusions

Two neodymium ternary complexes involving  $\beta$ -diketonate and triphenylphosphineoxide as ligands

have been synthesized by mild conditions. The complexes have good thermal stabilities and typical near infrared fluorescence properties. The absences of coordinated water molecules in their frameworks avoid the high frequency vibration of the OH groups in water molecules, which prevents the energy losing. So, the Nd complexes possess remarkable fluorescence properties.

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