

稀土二膦酸配合物的合成、结构和荧光性质

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摘要: 合成并表征了 3 个同构的稀土二膦酸化合物 $\text{Ln}(\text{hpyedpH}_2)(\text{hpyedpH}_3) \cdot 2\text{H}_2\text{O}$ [$\text{Ln}=\text{Gd}$ (**1**), Eu (**2**), Tb (**3**); $\text{hpyedpH}_4=1\text{-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid}$, $\text{C}_7\text{H}_{11}\text{NO}_7\text{P}_2$], 测定了化合物 **1** 的单晶结构。发现它们具有链状结构, 其中 Ln 通过 3 个或 4 个 O-P-O 基团交替连接, 链与链之间存在氢键和 $\pi\text{-}\pi$ 堆积作用。探讨了化合物 **2** 和 **3** 的荧光性质。

关键词: 稀土; 二膦酸; 链状结构; 荧光性质

中国分类号: O614.33*9; O614.33*8; O614.341

文献标识码: A

文章编号: 1001-4861(2007)11-1851-06

Syntheses, Crystal Structure and Luminescent Properties of Lanthanide Diphosphonates

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Abstract: Three isomorphous complexes $\text{Ln}(\text{hpyedpH}_2)(\text{hpyedpH}_3) \cdot 2\text{H}_2\text{O}$ [$\text{Ln}=\text{Gd}$ (**1**), Eu (**2**), Tb (**3**)], where hpyedpH_4 is 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid ($\text{C}_7\text{H}_{11}\text{NO}_7\text{P}_2$), have been prepared under hydrothermal conditions. All show a one-dimensional linear chain structure in which the Ln atoms are alternatively bridged by four and three O-P-O units. The chains are held together through extensive hydrogen bond interactions and $\pi\text{-}\pi$ contacts between the pyridyl groups, hence generating a three-dimensional network. The luminescent properties of complexes **2** and **3** are investigated. CCDC: 642506.

Key words: rare earth; diphosphonate; chain structure; luminescent property

0 Introduction

Lanthanide ions are appealing for the design of functional molecular entities and materials because of their intrinsic chemical, magnetic and spectroscopic properties which are often not matched by the other transition metal ions^[1,2]. On the other hand, the metal phosphonate chemistry has received rapid developments in the past two decades primarily owing to their potential applications in catalysis, ion exchange, and proton conductivity etc.^[3-6]. A majority of work have

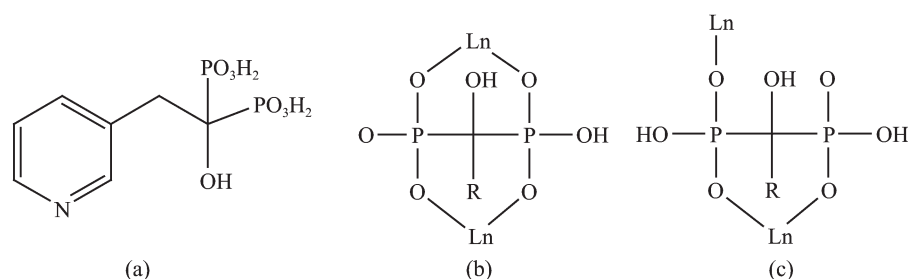
been concentrated on the phosphonate complexes with group IV metal ions or transition metal ions. In recent years, it has been extended to the lanthanide phosphonate chemistry. New lanthanide phosphonate complexes have been prepared and crystallographically characterized, some of which show interesting magnetic or luminescent properties^[7-13]. In this paper, we employ 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid (hpyedpH_4) (Scheme 1a) to react with the lanthanide(III) salts under hydrothermal conditions. Three new isomorphous Ln diphosphonates, $\text{Ln}(\text{hpyedpH}_2)(\text{hpyedpH}_3)$

收稿日期: 2007-04-19。收修改稿日期: 2007-06-26。

国家自然科学基金资助项目(No.20325103)。

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Scheme 1 HpyedpH₄ (a) and its coordinate modes (b and c) in **1**

·2H₂O [Ln=Gd (**1**), Eu (**2**), Tb (**3**)], are obtained which show one-dimensional structures.

1 Experimental section

1.1 Materials and methods

All the starting materials were obtained from commercial sources and were used without further purification. The hpyedpH₄·H₂O (formula C₇H₁₁NO₇P₂·H₂O) was purchased from Changzhou Watson Fine Chemicals Co., Ltd, China. Elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. The fluorescent spectra were recorded on a SHIMADZU VF-320 spectrometer with polycrystalline samples.

1.2 Synthesis of Ln(hpyedpH₂)(hpyedpH₃)·2H₂O [Ln=Gd (**1**), Eu (**2**), Tb (**3**)]

The three complexes were synthesized under very similar experimental conditions. For complex **1**, a mixture of Gd₂(SO₄)₃·6H₂O (0.019 g, 0.025 mmol), hpyedpH₄ (0.030 g, 0.1 mmol), 1 mol·L⁻¹ H₂SO₄ (0.05 mL) and water (8 mL) was sealed in a 25 mL Teflon-lined stainless autoclave, which was heated to 140 °C and held for 48 h. After slow cooling to room temperature, colorless needlelike crystals of complex **1** were collected as a monophasic material, judged by powder XRD measurements. For complexes **2** and **3**, 0.05 mmol EuCl₃ (23 mg) and 0.05 mmol Tb(NO₃)₃ (23 mg), respectively, were used as reactants. Monophasic colorless needlelike crystals of complexes **2** and **3** were also obtained.

For complex **1**: Yield: 47% based on Gd. Anal. Calcd for C₁₄H₂₃GdN₂O₁₆P₄: C, 22.23; H, 3.06; N, 3.70. Found: C, 22.09; H, 2.99; N, 3.82. IR (KBr, cm⁻¹):

3 492m, 3 090w, 2 864br, 1 629w, 1 565w, 1 478w, 1 442w, 1 346w, 1 307w, 1 143s, 1 089s, 1 059s, 978m, 928w, 888w, 832w, 797w, 698w, 676w, 618w, 546m, 485w, 452w.

For complex **2**: Yield: 43% based on Eu. Anal. Calcd for C₁₄H₂₃EuN₂O₁₆P₄: C, 22.38; H, 3.09; N, 3.73. Found: C, 22.12; H, 3.05; N, 3.70. IR (KBr, cm⁻¹): 3 493m, 3 091w, 2 863br, 1 629w, 1 562w, 1 478w, 1 442w, 1 345w, 1 307w, 1 142s, 1 089s, 1 059s, 978m, 926w, 889w, 832w, 797w, 698w, 676w, 618w, 547m, 485w, 452w.

For complex **3**: Yield: 38% based on Tb. Anal. Calcd for C₁₄H₂₃TbN₂O₁₆P₄: C, 22.18; H, 3.06; N, 3.69. Found: C, 22.20; H, 3.13; N, 3.73. IR (KBr, cm⁻¹): 3 489m, 3 091w, 2 864br, 1 630w, 1 565w, 1 478w, 1 443w, 1 345w, 1 307w, 1 144s, 1 089s, 1 060s, 979m, 928w, 889w, 833w, 797w, 699w, 677w, 618w, 547m, 485w, 453w.

1.3 X-ray crystallographic analysis

A crystal with dimensions 0.2 mm × 0.2 mm × 0.3 mm of **1** was selected for indexing and intensity data collection at 293(2) K on a Bruker SMART APEX CCD diffractometer with monochromatized Mo Kα radiation (λ=0.071 073 nm). A hemisphere of data (1 271 frames at 5 cm detector distance) was collected using a narrowframe method with scan widths of 0.30° in ω and an exposure time of 15 s/frame. The data were integrated using the Siemens SAINT program^[14], with the intensities corrected for the Lorentz and polarization factors, air absorption, and absorption due to variation in the path length through the detector faceplate. An empirical absorption was applied. The structure was solved by Paterson method and difference Fourier synthesis, and refined on F² by full-matrix least squares

using SHELXTL^[15]. All the nonhydrogen atoms were refined anisotropically. All the hydrogen atoms were refined isotropically. Selected crystallographic data and

structure determination parameters are given in Table 1, and selected bond lengths and angles in Table 2.

CCDC: 642506.

Table 1 Crystal data and structure refinement for 1

Formula	C ₁₄ H ₂₃ GdN ₂ O ₁₆ P ₄	$\gamma / (^{\circ})$	87.869(4)
M_r	756.47	V / nm^3	1.136 4(3)
Crystal system	Triclinic	Z	2
Space group	$P\bar{1}$	$D_c / (\text{g} \cdot \text{cm}^{-3})$	2.211
a / nm	0.830 26(16)	$F(000)$	746
b / nm	1.053 90(19)	$\mu (\text{Mo } K\alpha) / \text{mm}^{-1}$	3.287
c / nm	1.369 1(2)	Goodness of fit on F^2	0.969
$\alpha / (^{\circ})$	76.869(5)	$R_1, wR_2 [I > 2\sigma(I)]$	0.067 0, 0.122 6
$\beta / (^{\circ})$	76.949(4)	$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} / (\text{e} \cdot \text{nm}^{-3})$	1 630, -1 100

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

Gd(1)-O(4)	0.230 9(7)	Gd(1)-O(1A)	0.231 5(6)	Gd(1)-O(2)	0.232 8(6)
Gd(1)-O(9B)	0.232 8(7)	Gd(1)-O(11)	0.234 3(7)	Gd(1)-O(5A)	0.235 3(7)
Gd(1)-O(8)	0.239 4(7)	O(1)-P(1)	0.149 7(7)	O(2)-P(1)	0.151 6(7)
O(3)-P(1)	0.153 0(7)	O(4)-P(2)	0.149 6(7)	O(5)-P(2)	0.149 2(7)
O(6)-P(2)	0.154 5(8)	O(8)-P(3)	0.150 2(7)	O(9)-P(3)	0.150 5(7)
O(10)-P(3)	0.155 3(7)	O(11)-P(4)	0.149 9(7)	O(12)-P(4)	0.147 7(7)
O(13)-P(4)	0.158 2(7)				
O(4)-Gd(1)-O(2)	78.1(2)	O(1A)-Gd(1)-O(2)	122.5(2)	O(4)-Gd(1)-O(9B)	108.5(2)
O(1A)-Gd(1)-O(9B)	78.1(2)	O(2)-Gd(1)-O(9B)	159.4(2)	O(4)-Gd(1)-O(11)	78.1(2)
O(1A)-Gd(1)-O(11)	141.3(2)	O(2)-Gd(1)-O(11)	80.7(2)	O(9B)-Gd(1)-O(11)	81.7(2)
O(4)-Gd(1)-O(5A)	123.3(2)	O(1A)-Gd(1)-O(5A)	75.4(2)	O(2)-Gd(1)-O(5A)	76.2(2)
O(9B)-Gd(1)-O(5A)	113.2(3)	O(11)-Gd(1)-O(5A)	143.3(2)	O(4)-Gd(1)-O(8)	152.1(2)
O(1A)-Gd(1)-O(8)	130.1(2)	O(2)-Gd(1)-O(8)	86.5(2)	O(9B)-Gd(1)-O(8)	79.1(2)
O(11)-Gd(1)-O(8)	76.5(2)	O(5A)-Gd(1)-O(8)	74.0(2)	O(4)-Gd(1)-O(1A)	77.6(2)

^a Symmetry codes: A: $x+1, y+1, z+2$; B: $x+1, y, z+2$.

2 Result and discussion

2.1 Crystal structure

Complexes **1**~**3** are isostructural based on the XRD measurements (Fig.1). The single crystal structure analysis on complex **1** reveals that it crystallizes in triclinic space group $P\bar{1}$. The asymmetric unit of **1** consists of one Gd³⁺ ion, one hpyedpH₂²⁻, one hpyedpH₃⁻, and two lattice water molecules (Fig.2). Each Gd atom is seven-coordinated, surrounded by phosphonate oxygen atoms O(2), O(4), O(8), O(11), O(1A), O(5A) and O(9B) from two hpyedpH₂²⁻ and a pair of hpyedpH₃⁻ ligands. The Gd-O bond lengths fall between 0.230 9(7) and 0.239 4(7) nm with an average of 0.233 8(7) nm.

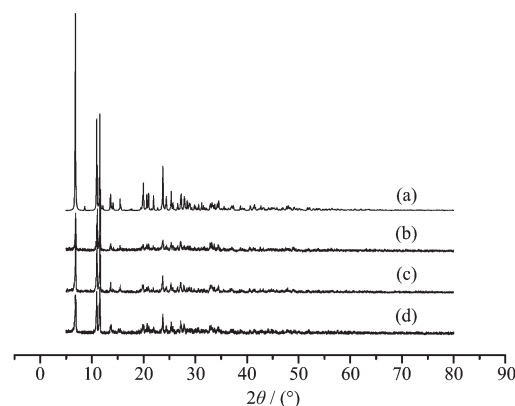
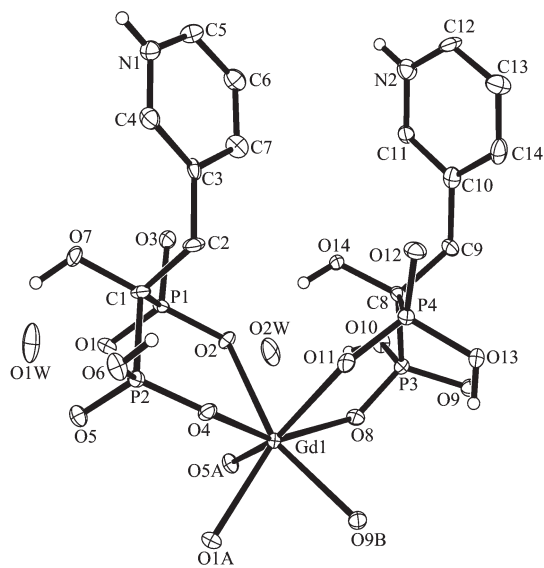


Fig.1 XRD patterns: (a) simulated XRD pattern of compound **1** from crystallographic data, (b) compound **1**, (c) compound **2**, (d) compound **3**

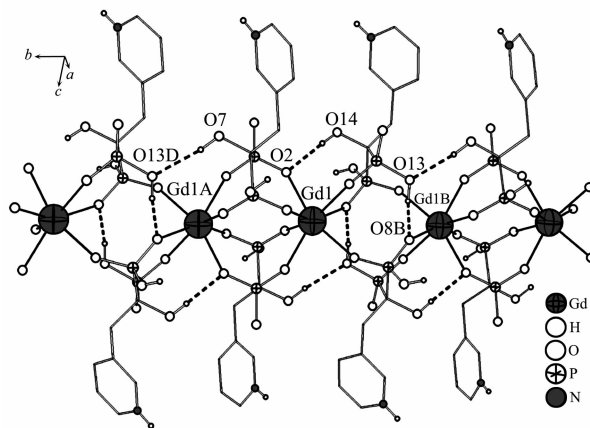
The hpyedpH_2^{2-} with protonated O(6) and dangling O(3) behaves as a tetra-dentate bis(chelating) bridging ligand by using its four phosphonate oxygen atoms O(1), O(2), O(4) and O(5) (Scheme 1b). Two equivalent hpyedpH_2^{2-} links the neighboring equivalent Gd atoms through two pairs of O-P-O bridges, forming a dimer of $\{\text{Gd}_2(\text{hpyedpH}_2)_2\}$. The Gd \cdots Gd distance within the dimer is 0.476 8(1) nm. An inversion center lies in the middle of this dimer. The hpyedpH_3^- with protonated O(10) and O(13), and dangling O(12) is tri-dentate (Scheme 1c). It connects the adjacent $\{\text{Gd}_2(\text{hpyedpH}_2)_2\}$ dimers via phosphonate oxygens O(8), O(9) and O(11), hence leading to an alternating linear chain with composition $\text{Gd}_2(\text{hpyedpH}_2)_2(\text{hpyedpH}_3)_2$ (Fig.2). The Gd \cdots Gd distance over the O(8)-P(3)-O(9) bridge is 0.597 1(1) nm. Such a chain structure may be compared with that observed in $[\text{Tb}(\text{H}_3\text{hedp})(\text{H}_2\text{hedp})] \cdot 5\text{H}_2\text{O}$ ^[8], where a similar diphosphonate ligand except with a different organic tail is involved. It is interesting that the chain is further stabilized by the intra-chain hydrogen bonds between the hydroxyl group [O(7)] or protonated phosphonate oxygens [O(13)] and the coordinated phosphonate oxygens [O(8), O(2)]. The O \cdots O contacts 0.307 7(10) nm for O(7) \cdots O(13), 0.263 1(10) nm for O(13) \cdots O(8) and 0.281 1(9) nm for O(14) \cdots O(2) (Fig.3).

The pyridyl groups of hpyedpH_2^{2-} and hpyedpH_3^- ,



Thermal ellipsoids at the 30% probability

Fig.2 ORTEP representation of the asymmetry unit of compound 2



Hydrogens connected to carbon atoms are omitted for clarity

Hydrogen bond is described by dashed line

Fig.3 A fragment of chain in structure 1

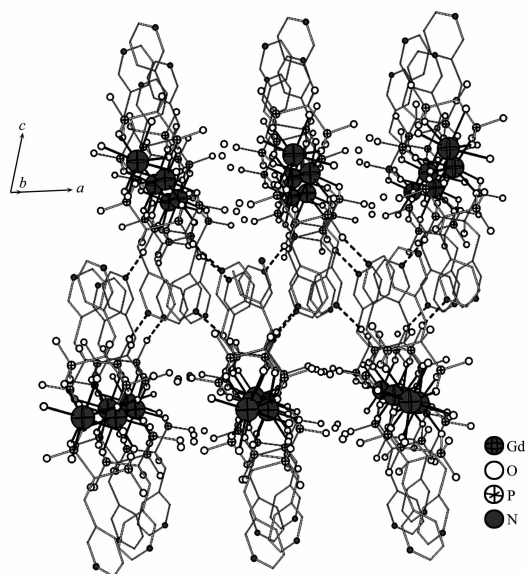
which are referred to py1 and py2 respectively, are both protonated at nitrogen. Strong inter-chain hydrogen bond interactions are found between the pyridyl nitrogens from one chain to the phosphonate oxygens from the other [N(1) \cdots O(12): 0.255 9(12) nm, N(2) \cdots O(3): 0.249 9(11) nm]. Additionally, π - π contacts are observed between the pyridyl groups of the adjacent chains. The π - π interactions between the py1 groups are stronger than those between the py2 groups (plane-plane distance: 0.329 vs 0.347 nm; centroid-centroid distance: 0.358 vs 0.392 nm; angle between the ring normal of the pyridyl plane and the centroid vector: 23.1° vs 27.8°)^[16]. Inter-chain hydrogen bonds are also found among the lattice water molecules and the phosphonate oxygens (Table 3). Therefore, a three-

Table 3 Hydrogen bond interactions in 1^b

D(H) \cdots A	Distance / nm	Angle / (°)
N(1) \cdots O(12G)	0.255 9(12)	167.7
N(2) \cdots O(3H)	0.249 9(11)	171.2
O(6) \cdots O(2WC)	0.307 0(10)	128.1
O(7) \cdots O(13D)	0.307 7(10)	171.2
O(10) \cdots O(2W)	0.251 2(10)	140.5
O(13) \cdots O(8B)	0.263 1(10)	172.2
O(14) \cdots O(2)	0.281 1(9)	157.1
O(1W) \cdots O(13E)	0.295 8(12)	145.0
O(1W) \cdots O(6F)	0.255 1(11)	142.4
O(2W) \cdots O(4F)	0.288 7(11)	164.9
O(2W) \cdots O(5A)	0.312 6(10)	166.6

^b Symmetry codes: A: $x+1, y+1, z+2$; B: $x+1, y, z+2$; C: $x+1, y, z$; D: $x, y+1, z$; E: $x-1, y+1, z$; F: $x-1, y, z$; G: $x+2, y+1, z+1$; H: $x+1, y+1, z+1$.

dimensional network structure is constructed (Fig.4).



Inter-chain strong hydrogen bonds between pyridyl nitrogen and phosphonate oxygen atoms are represented by the dashed lines
Hydrogen atoms are omitted for clarity

Fig.4 Structure **1** packed along the b-axis

2.2 Luminescent properties

The luminescent properties of complex **2** and **3** are investigated. Complex **2** emits strong red luminescence upon excitation with 395 nm characteristic for the Eu^{3+} ions. The emission bands are attributed to the $^5D_0 \rightarrow ^7F_n$ ($n=1\sim4$) transitions (Fig.5). The absence of the $^5D_0 \rightarrow ^7F_0$ transition is consistent with the low-symmetry environment around the Eu atom. The $^5D_0 \rightarrow ^7F_1$ transition is magnetic dipole in origin, and its intensity varies with the crystal field strength acting on Eu^{3+} , while the transition $^5D_0 \rightarrow ^7F_2$ is electric dipole in nature and is extremely sensitive to chemical bonds in the vicinity of Eu^{3+} ion^[17]. The intensity of $^5D_0 \rightarrow ^7F_2$

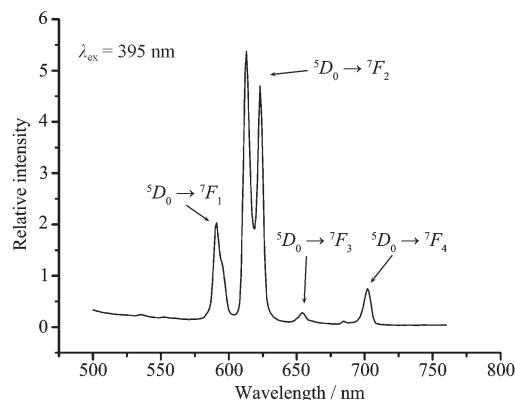


Fig.5 Emission spectra of compound **2** in solid state

increases as the site symmetry of Eu^{3+} decreases. For complex **2**, the strongest emission is $^5D_0 \rightarrow ^7F_2$ transition, the band of which is split into two peaks at 613 nm and 623 nm and about twice that of the next, $^5D_0 \rightarrow ^7F_1$ (591 nm), in agreement with the low-symmetry Eu^{3+} ion.

The emission spectra of complex **3** was excited at 375 nm and the photoluminescence spectrum are depicted in Fig.6. The most intense transition is $^5D_4 \rightarrow ^7F_5$ (542 nm), which implies green emission light characteristic for the Tb^{3+} ion.

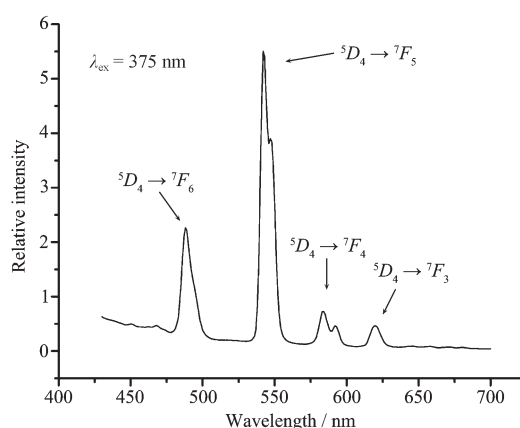


Fig.6 Emission spectra of compound **3** in solid state

3 Conclusion

Based on 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid, three new isomorphous lanthanide diphosphonate complexes $\text{Ln}(\text{hpydpH}_2)(\text{hpydpH}_3) \cdot 2\text{H}_2\text{O}$ [$\text{Ln}=\text{Gd}$ (**1**), Eu (**2**), Tb (**3**)] with a chain structure have been synthesized through hydrothermal technique. Photoluminescence investigations reveal that upon excitation complex **2** emits strong red luminescence while for complex **3** intense green emission light is observed, which are characteristic for the corresponding lanthanide ions. Further work is in progress to search for new lanthanide phosphonate materials by using the other functionalized phosphonate ligands.

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