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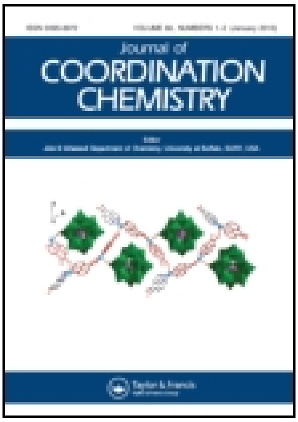

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Ming-Hua He [a] , Cheng Ji [a] , Zhen-Dong Shen [a] , Qiao-Yun Li [a] , Gao-Wen Yang [a] , Wei Shen [a] , Qing-Guo Qiou [a] & Xiao-Feng Shen [a]

[a] Jiangsu Laboratory of Advanced Functional Materials, Department of Chemistry and Materials Engineering , Changshu Institute of Technology , Changshu , P.R. China

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# Three lanthanide-based coordination compounds with 5-[N-acetato(4-pyridyl)]tetrazolate

MING-HUA HE, CHENG JI, ZHEN-DONG SHEN, QIAO-YUN LI*, GAO-WEN YANG, WEI SHEN, QING-GUO QIOU and XIAO-FENG SHEN

Jiangsu Laboratory of Advanced Functional Materials, Department of Chemistry and Materials Engineering, Changshu Institute of Technology, Changshu, P.R. China

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Reaction of 5-[N-acetato(4-pyridyl)]tetrazolate (a4-ptz) potassium salt with lanthanide(III) chlorides, produced three new coordination compounds, $[Ln(a4\text{-}ptz)_2(H_2O)_4]\cdot Cl\cdot 2H_2O$ (Ln = La(**1**), Eu(**2**) and Tb(**3**)). These compounds were characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. Complexes **1**–**3** displayed 1-D structures. Luminescences of **1**–**3** were investigated at room temperature in the solid state.

*Keywords*: Lanthanide(III); 5-[N-acetato(4-pyridyl)]tetrazolate (a4-ptz); Crystal structure; Luminescence

## 1. Introduction

The molecular architecture of coordination compounds is affected by ligands, metal ions, metal–ligand ratio, solvents, counterions, pH, and temperature [1–10], making it a challenge to design metal complexes with the desired topologies and properties. Of these factors, intrinsic geometric preferences of metal centers and various coordination sites of bridging ligands are the pivotal factors in determining supramolecular architectures [11–16]. Among various N-heterocyclic carboxylic acid ligands, heterocyclic nitrogens can coordinate to metal, while carboxylates can coordinate monodentate, chelate or bridging resulting in MOFs with unusual structures and useful properties [17–21]; pyridinecarboxylic acid [6, 22, 23], pyrimidinecarboxylic acid [24–26], pyrazolecarboxylic acid [27, 28], imidazolecarboxylic acid [29, 30], tetrazolecarboxylic acid [31–33], etc. have proved to be good choices.

A new tetrazolecarboxylic acid, 5-[N-acetato(4-pyridyl)]tetrazolate (a4-ptz) with four N and two O potential binding centers have been employed in construction of coordination compounds of various metal ions (Mn, Cu, Cd, Zn, Mg, Ca, Sr, Ba, and Pb) [34–38]. Recently, we extended this investigation to lanthanide metal ions; compared to d/ds- or p-block metals, lanthanides have much higher coordination numbers and more flexible coordination geometry. We anticipate that coordination of a4-ptz with lanthanides may lead

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*Corresponding author. Email: liqiaoyun@cslg.edu.cn to new coordination compounds with different structures from that of the d/ds- or p-block metals with a4-ptz. By reacting a4-ptz potassium salt with the corresponding lanthanide (III) chlorides, we obtained three new coordination compounds, [Ln(a4-ptz)$_2$(H$_2$O)$_4$]·Cl·2H$_2$O (Ln = La(**1**), Eu(**2**) and Tb(**3**)]. Herein, syntheses, crystal structures, and luminescent properties of **1**–**3** are reported.

## 2. Experimental

### 2.1. *Materials and methods*

The a4-ptz potassium salt was prepared according to the literature method [39]. Other chemicals were commercially available reagents of analytical grade and used without purification. Elemental analyzes for C, H, and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. IR spectra were recorded (4000–400 cm$^{-1}$) on a NICOLET 380 spectrometer with pressed KBr pellets. Photoluminescence spectra were performed on a Hitachi F4600 spectrofluorometer.

### 2.2. *Synthesis of [Ln(a4-ptz)$_2$(H$_2$O)$_4$]·Cl·2H$_2$O (Ln = La(1), Eu(2) and Tb(3)]*

Potassium salt of a4-ptz (0.0486 g, 0.2 mmol) was dissolved in distilled water (5 mL). Then LnCl$_3$·6H$_2$O [0.0707 g (Ln = La), 0.0733 g (Ln = Eu), 0.0747 g (Ln = Tb), 0.2 mmol] was added. The mixture was stirred at 80 °C for 1 h and then cooled to room temperature and filtered. Diethyl ether (40 mL) was allowed to diffuse into the filtrate at ambient temperature for two weeks, forming colorless crystals of **1**, **2,** and **3**, respectively. For **1**, yield: 39% based on La. Anal. Calcd for $C_{16}H_{24}ClLaN_{10}O_{10}$: C, 27.82; H, 3.50; N, 20.28%. Found: C, 28.01; H, 3.60; N, 20.42%. IR (KBr, cm$^{-1}$): 3409(s), 1642(s), 1587(s), 1471 (m), 1429(m), 1401(m), 1383(s), 843(w), 1011(w), 732(w), and 673(w). For **2**, yield: 42% based on Eu. Anal. Calcd for $C_{16}H_{24}ClEuN_{10}O_{10}$: C, 27.30; H, 3.44; N, 19.90%. Found: C, 27.49; H, 3.51; N, 20.11%. IR (KBr, cm$^{-1}$): 3400(s), 1641(s), 1601(s), 1539(m), 1473 (m), 1432(w), 1399(m), 1341(m), 1316(m), 1022(m), 868(w), 734(w), and 698(w). For **3**, yield: 45% based on Tb. Anal. Calcd for $C_{16}H_{24}ClTbN_{10}O_1$: C, 27.04; H, 3.40; N, 19.71%. Found: C, 27.28; H, 3.52; N, 19.53%. IR (KBr, cm$^{-1}$): 3415(s), 1640(s), 1603(s), 1538(s), 1470(s), 1426(s), 1389(s), 1289(m), 1202(w), 1153(w), 1054(w), 870(w), 732(w), and 695(w).

### 2.3. *X-ray crystallography*

Single crystal X-ray crystal data were collected on a Rigaku SCX mini charge-coupled device diffractometer equipped with graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.071073$ Å). The intensity data were collected by the $\omega$ scan technique and reduced using the CrystalClear program [40]. An empirical absorption correction based on scans was applied. The structure was solved by direct methods and refined by full-matrix least-squares on $F^2$ using SHELXTL [41]. All non-hydrogen atoms were refined anisotropically and hydrogens were included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Crystallographic data are summarized in table 1.

Table 1. Crystallographic data and structure refinements for **1**–**3**.

| Compounds | **1** | **2** | **3** |
|---|---|---|---|
| Empirical formula | $C_{16}H_{24}ClLaN_{10}O_{10}$ | $(C_{16}H_{24}ClEuN_{10}O_{10})_2$ | $(C_{16}H_{24}ClTbN_{10}O_{10})_2$ |
| Formula mass | 690.81 | 1407.72 | 1421.66 |
| Crystal system | Monoclinic | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ |
| $a$ (Å) | 9.3161(9) | 15.078(3) | 15.012(3) |
| $b$ (Å) | 22.563(4) | 23.010(5) | 22.928(5) |
| $c$ (Å) | 13.023(5) | 16.897(7) | 16.895(7) |
| $\beta$ (°) | 117.22(2) | 118.58(2) | 118.46(2) |
| $V$ (Å$^3$) | 2434.3(12) | 5148(3) | 5112(3) |
| $Z$ | 4 | 4 | 4 |
| $T$ (K) | 291(2) | 291(2) | 291(2) |
| $D_{calcd}$ (g·cm$^{-3}$) | 1.885 | 1.816 | 1.847 |
| $\mu$ (mm$^{-1}$) | 1.939 | 2.610 | 2.942 |
| Reflections collected | 24,995 | 50,617 | 52,527 |
| Unique reflections ($R_{int}$) | 5571 (0.0591) | 11,779 (0.0954) | 11,703 (0.0675) |
| No. observations ($I > 2\sigma$(I)) | 4532 | 8106 | 8166 |
| No. variables | 325 | 631 | 694 |
| $R$[a], w$R$[b] | 0.0421, 0.0865 | 0.0846, 0.1993 | 0.0482, 0.1096 |
| GOF[c] | 1.104 | 1.238 | 1.000 |
| $\Delta/\rho_{max}$ (e/Å$^3$) | 1.654 | 1.779 | 1.912 |
| $\Delta/\rho_{min}$ (e/Å$^3$) | −0.689 | −4.617 | −0.917 |

[a] $R = \Sigma||F_o| - |F_c|/\Sigma|F_o|$. [b] $Rw = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma w((F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$, where $n$ = number of reflections and $p$ = total numbers of parameters refined.

## 3. Results and discussion

### 3.1. *Preparation and characterization of 1–3*

Treatment of $LnCl_3$ (Ln = La, Eu and Tb) with a4-ptz potassium salt in water produced **1**–**3** in modest yields. They were stable toward oxygen and moisture. Elemental analyzes of **1**–**3** were consistent with their chemical formulas. In IR spectra of **1**–**3**, a strong absorption at 1642–1640 cm$^{-1}$ corresponds to ν(COO) of carboxylate [37, 42, 43]. IR spectra of the products showed typical peaks (1426–1601 cm$^{-1}$) of the tetrazole and pyridyl in the corresponding a4-ptz. A peak at 3400–3415 cm$^{-1}$ is that of coordinated water and perhaps uncoordinated water as well. The identities of **1**–**3** were finally confirmed by X-ray crystallography.

### 3.2. *Description of crystal structures of 1–3*

Carboxylate and tetrazolate are multifunctional ligands in that they have potential to coordinate in a number of different ways [44]. Single crystal X-ray analysis reveals **1–3** crystallize in monoclinic space group $P2_1/c$. Selected bond lengths and angles for **1**, **2,** and **3** are given in table 2.

In **1**, each La(III) is nine-coordinate by O1, O2A, O3, O4, and O4B from four a4-ptz, O5, O6, O7, and O8 of four waters, forming a distorted monocapped square-antiprism coordination geometry ($LaO_9$) (figure 1 and Supplementary material). La–O bond lengths 2.445(5)–2.831(3) Å are observed in analogous complexes [45]. In **1**, two coordination modes of a4-ptz have been found: two neighboring $La^{3+}$ (La1, La1A) are bridged by two carboxylates from two a4-ptz ligands in a $\mu_{1,3}$-COO *syn–syn* bridging mode and another

Table 2. Selected bond distances (Å) and angles (°) for **1**–**3**.

| | | | |
|---|---|---|---|
| *Compound* **1** | | | |
| La(1)–O(1) | 2.445(5) | La(1)–O(6) | 2.550(3) |
| La(1)–O(2A) | 2.552(5) | La(1)–O(7) | 2.557(3) |
| La(1)–O(8) | 2.565(3) | La(1)–O(5) | 2.588(3) |
| La(1)–O(3) | 2.598(5) | La(1)–O(4B) | 2.623(3) |
| La(1)–O(4) | 2.831(3) | | |
| O(1)–La(1)–O(6) | 81.05(16) | O(1)–La(1)–O(2A) | 91.64(18) |
| O(6)–La(1)–O(2A) | 136.63(15) | O(1)–La(1)–O(7) | 80.36(15) |
| O(6)–La(1)–O(7) | 67.91(6) | O(2A)–La(1)–O(7) | 68.73(14) |
| O(1)–La(1)–O(8) | 77.74(16) | O(6)–La(1)–O(8) | 138.17(10) |
| O(2A)–La(1)–O(8) | 79.85(14) | O(7)–La(1)–O(8) | 140.86(11) |
| O(1)–La(1)–O(5) | 149.25(16) | O(6)–La(1)–O(5) | 72.86(6) |
| O(2A)–La(1)–O(5) | 96.21(14) | O(7)–La(1)–O(5) | 74.99(7) |
| O(8)–La(1)–O(5) | 132.90(11) | O(1)–La(1)–O(3) | 72.69(18) |
| O(6)–La(1)–O(3) | 67.97(15) | O(2A)–La(1)–O(3) | 149.50(18) |
| O(7)–La(1)–O(3) | 130.95(14) | O(8)–La(1)–O(3) | 71.44(15) |
| O(5)–La(1)–O(3) | 110.71(14) | O(1)–La(1)–O(4B) | 142.94(16) |
| O(6)–La(1)–O(4B) | 133.27(5) | O(7)–La(1)–O(4) | 144.30(10) |
| O(8)–La(1)–O(4) | 74.75(7) | O(8)–La(1)–O(4) | 74.78(7) |
| O(3)–La(1)–O(4) | 47.84(13) | O(4)–La(1)–O(4B) | 61.69(9) |
| *Compound* **2** | | | |
| Eu(1)–O(3) | 2.302(6) | Eu(1)–O(5) | 2.324(3) |
| Eu(1)–O(6A) | 2.420(6) | Eu(1)–O(11) | 2.424(3) |
| Eu(1)–O(12) | 2.442(3) | Eu(1)–O(9) | 2.457(5) |
| Eu(1)–O(2) | 2.464(7) | Eu(1)–O(10) | 2.473(3) |
| Eu(2)–O(1) | 2.329(7) | Eu(2)–O(8B) | 2.369(7) |
| Eu(2)–O(7) | 2.380(5) | Eu(2)–O(16) | 2.404(5) |
| Eu(2)–O(14) | 2.441(3) | Eu(2)–O(4) | 2.450(6) |
| Eu(2)–O(15) | 2.479(3) | Eu(2)–O(13) | 2.485(3) |
| O(3)–Eu(1)–O(5) | 149.24(19) | O(3)–Eu(1)–O(6A) | 82.8(2) |
| O(5)–Eu(1)–O(6A) | 91.86(16) | O(3)–Eu(1)–O(11) | 105.61(19) |
| O(5)–Eu(1)–O(11) | 96.17(9) | O(6A)–Eu(1)–O(11) | 144.78(17) |
| O(3)–Eu(1)–O(12) | 69.12(19) | O(5)–Eu(1)–O(12) | 139.67(12) |
| O(6A)–Eu(1)–O(12) | 79.17(17) | O(11)–Eu(1)–O(12) | 72.58(7) |
| O(3)–Eu(1)–O(9) | 74.7(2) | O(5)–Eu(1)–O(9) | 74.74(14) |
| O(6A)–Eu(1)–O(9) | 74.2(2) | O(11)–Eu(1)–O(9) | 140.91(14) |
| O(12)–Eu(1)–O(9) | 137.14(14) | O(3)–Eu(1)–O(2) | 89.0(2) |
| O(5)–Eu(1)–O(2) | 78.17(17) | O(6A)–Eu(1)–O(2) | 145.1(2)) |
| O(11)–Eu(1)–O(2) | 70.04(17) | O(12)–Eu(1)–O(2) | 129.01(17) |
| O(9)–Eu(1)–O(2) | 70.89(19) | O(3)–Eu(1)–O(10) | 134.97(19) |
| O(5)–Eu(1)–O(10) | 72.52(8) | O(6A)–Eu(1)–O(10) | 78.96(16) |
| O(11)–Eu(1)–O(10) | 71.01(7) | O(12)–Eu(1)–O(10) | 67.19(7) |
| O(9)–Eu(1)–O(10) | 136.47(14) | O(2)–Eu(1)–O(10) | 127.51(16) |
| O(1)–Eu(2)–O(8B) | 83.6(3) | O(1)–Eu(2)–O(7) | 78.3(2) |
| O(7)–Eu(2)–O(8B) | 74.8(2) | O(1)–Eu(2)–O(16) | 145.0(2 |
| O(16)–Eu(2)–O(8B) | 100.6(2) | O(16)–Eu(2)–O(7) | 69.65(17) |
| O(1)–Eu(2)–O(14) | 75.8(2) | O(14)–Eu(2)–O(7) | 144.76(14) |
| O(14)–Eu(2)–O(8B) | 78.93(18) | O(14)–Eu(2)–O(16) | 139.14(13) |
| O(1)–Eu(2)–O(4) | 84.2(2) | O(4)–Eu(2)–O(7) | 77.2(2) |
| O(4)–Eu(2)–O(8B) | 151.2(2) | O(16)–Eu(2)–O(4) | 75.59(18) |
| O(14)–Eu(2)–O(4) | 122.85(17) | O(1)–Eu(2)–O(15) | 111.1(2) |
| O(15)–Eu(2)–O(8B) | 140.85(17) | O(15)–Eu(2)–O(7) | 142.27(14) |
| O(16)–Eu(2)–O(15) | 87.58(13) | O(14)–Eu(2)–O(15) | 70.60(7) |
| O(4)–Eu(2)–O(15) | 67.95(17) | O(1)–Eu(2)–O(13) | 144.24(19) |
| O(7)–Eu(2)–O(13) | 122.86(14) | O(16)–Eu(2)–O(13) | 68.80(13) |
| O(14)–Eu(2)–O(13) | 71.55(7) | O(4)–Eu(2)–O(13) | 126.02(16) |
| O(13)–Eu(2)–O(15) | 71.26(7) | O(1)–Eu(2)–O(13) | 144.24(19) |

(*Continued*)

Table 2. (*Continued*).

| | | | |
|---|---|---|---|
| *Compound* **3** | | | |
| Tb(1)–O(1) | 2.279(4) | Tb(1)–O(4) | 2.286(4) |
| Tb(1)–O(3) | 2.381(4) | Tb(1)–O(10) | 2.402(5) |
| Tb(1)–O(16) | 2.429(5) | Tb(1)–O(9) | 2.431(4) |
| Tb(1)–O(15) | 2.444(5) | Tb(1)–O(8) | 2.457(4) |
| Tb(2)–O(7) | 2.291(5) | Tb(2)–O(5) | 2.344(4) |
| Tb(2)–O(6) | 2.358(4) | Tb(2)–O(14) | 2.378(5) |
| Tb(2)–O(12) | 2.412(6) | Tb(2)–O(2) | 2.412(4) |
| Tb(2)–O(11) | 2.433(7) | Tb(2)–O(13) | 2.434(6) |
| O(1)–Tb(1)–O(14) | 149.33(18) | O(1)–Tb(1)–O(3) | 84.00(15) |
| O(4)–Tb(1)–O(3) | 91.97(15) | O(1)–Tb(1)–O(10) | 104.26(19) |
| O(4)–Tb(1)–O(10) | 96.57(17) | O(3)–Tb(1)–O(10) | 144.62(16) |
| O(1)–Tb(1)–O(16) | 69.85(18) | O(4)–Tb(1)–O(16) | 139.01(18) |
| O(3)–Tb(1)–O(16) | 78.10(18) | O(10)–Tb(1)–O(16) | 72.99(18) |
| O(1)–Tb(1)–O(9) | 74.54(17) | O(4)–Tb(1)–O(9) | 75.10(16) |
| O(3)–Tb(1)–O(9) | 74.40(15) | O(10)–Tb(1)–O(9) | 140.95(16) |
| O(16)–Tb(1)–O(9) | 136.70(17) | O(1)–Tb(1)–O(15) | 135.56(17) |
| O(4)–Tb(1)–O(15) | 72.52(16) | O(3)–Tb(1)–O(15) | 79.07(15) |
| O(10)–Tb(1)–O(15) | 71.03(17) | O(16)–Tb(1)–O(15) | 66.58(18) |
| O(9)–Tb(1)–O(15) | 136.91(16) | O(1)–Tb(1)–O(8) | 87.24(16) |
| O(4)–Tb(1)–O(8) | 78.88(16) | O(3)–Tb(1)–O(8) | 145.25(15) |
| O(10)–Tb(1)–O(8) | 70.11(16) | O(16)–Tb(1)–O(8) | 129.55(19) |
| O(9)–Tb(1)–O(8) | 70.85(15) | O(15)–Tb(1)–O(8) | 127.87(15) |
| O(7)–Tb(2)–O(5) | 83.89(18) | O(7)–Tb(2)–O(6) | 78.38(18) |
| O(5)–Tb(2)–O(6) | 74.86(15) | O(7)–Tb(2)–O(14) | 144.89(19) |
| O(5)–Tb(2)–O(14) | 102.0(2) | O(6)–Tb(2)–O(14) | 70.13(18) |
| O(7)–Tb(2)–O(12) | 77.5(2) | O(5)–Tb(2)–O(12) | 78.9(2) |
| O(6)–Tb(2)–O(12) | 145.88(18) | O(14)–Tb(2)–O(12) | 137.6(2) |
| O(7)–Tb(2)–O(2) | 82.52(16) | O(5)–Tb(2)–O(2) | 151.02(15) |
| O(6)–Tb(2)–O(2) | 77.40(15) | O(14)–Tb(2)–O(2) | 75.94(18) |
| O(12)–Tb(2)–O(2) | 122.4(2) | O(7)–Tb(2)–O(11) | 144.1(3) |
| O(5)–Tb(2)–O(11) | 75.7(2) | O(6)–Tb(2)–O(11) | 122.6(2) |
| O(14)–Tb(2)–O(11) | 69.4(2) | O(12)–Tb(2)–O(11) | 69.9(3) |
| O(2)–Tb(2)–O(11) | 127.7(2) | O(7)–Tb(2)–O(13) | 112.6(3) |
| O(5)–Tb(2)–O(13) | 140.32(19) | O(6)–Tb(2)–O(13) | 141.93(18) |
| O(14)–Tb(2)–O(13) | 85.0(2) | O(12)–Tb(2)–O(13) | 70.6(2) |
| O(2)–Tb(2)–O(13) | 68.65(19) | O(11)–Tb(2)–O(13) | 70.4(3) |

Note: Symmetry code for **1**: A $-x, -y, 1-z$; B $1-x-y, 1-z$; for **2**: A $3-x, -y, 1-z$; B $2-x, -y, -z$.

two neighboring $La^{3+}$ (La1, La1B) are bridged by two carboxylates from two a4-ptz ligands in a $\mu_{1,1,3}$-COO bridging mode, giving a 1-D polymeric chain extending along the *a* axis with La···La distance of 4.6845 or 5.4138 Å and the La···La···La bite angle of 134.5° (figure 2).

These 1D chains are connected by coordinated waters (O5, O6, O7, and O8) and crystallization waters (O9 and O10) via hydrogen-bonding interactions (table 3) into a 3-D supramolecular network structure (Supplementary material).

The X-ray structure analysis reveals that **2** and **3** are isomorphic; here, complex **3** is taken as the example to depict the 1D structure. In **3**, the asymmetric unit contains one $[Tb(a4\text{-}ptz)_2(H_2O)_4]\cdot Cl\cdot 2H_2O$. Two crystallographically independent Tb(1) and Tb(2) are observed. Each Tb1 and Tb2 is eight-coordinate by four oxygens from four a4-ptz and four waters, forming a distorted square-antiprism coordination geometry (figure 3(a), (b), and Supplementary material). Tb–O bond lengths of 2.279(4)–2.457(4) Å are observed in related complexes [31]. Two neighboring $Tb^{3+}$ ions are doubly bridged by two carboxylates from two a4-ptz in a $\mu_{1,3}$-COO *syn-syn* bridging mode, forming a 1-D chain with Tb···Tb distances of 5.2894, 5.3111, and 5.7576 Å, respectively, and the Tb···Tb···Tb bite angle of 100.92° or 146.22° (figure 4). The Tb···Tb separation in **3** is somewhat

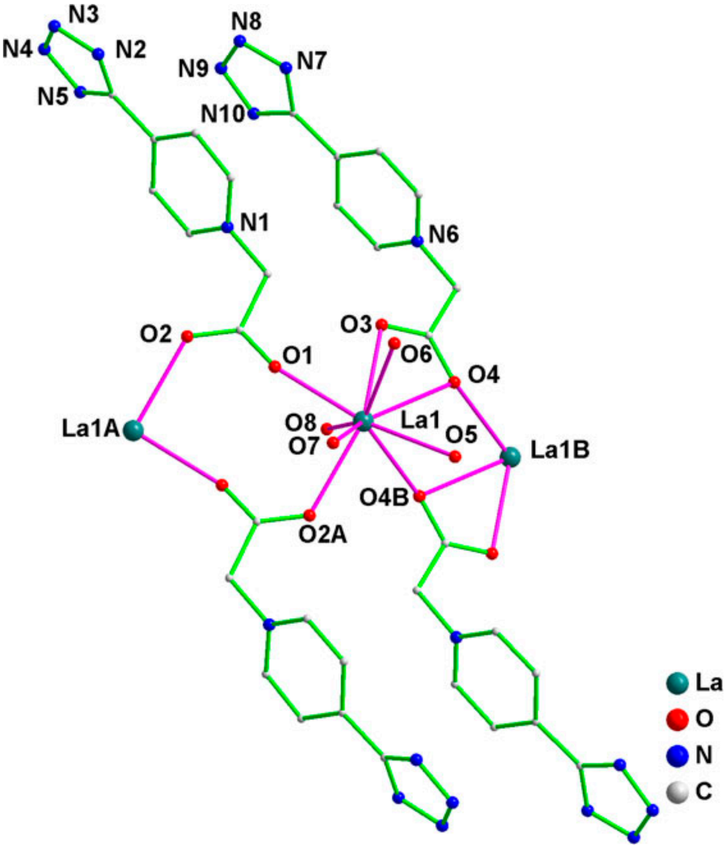

Figure 1. The coordination environment of La(III) and coordination mode of a4-ptz$^-$ in **1** (hydrogens are omitted for clarity).

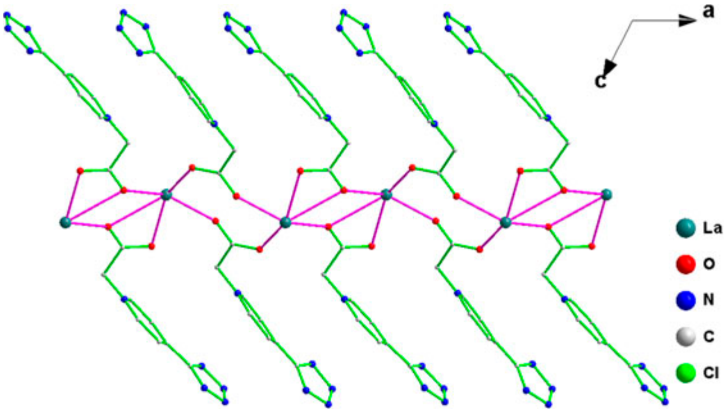

Figure 2. 1-D polymeric chain of **1**.

longer than La···La distance in **1** because a4-ptz uses only one $\mu_{1,3}$-COO bidentate bridging coordination mode in **3**.

Table 3. Hydrogen-bonding geometry (Å and °) for **1–3**.

| D-H···A | D-H | H···A | D···A | ∠D-H···A |
|---|---|---|---|---|
| *Complex* **1** | | | | |
| O(5)–H(5A)···N(10)$^{\#1}$ | 0.85 | 2.02 | 2.8525 | 167 |
| O(5)–H(5B)···O(8)$^{\#2}$ | 0.85 | 1.99 | 2.8253 | 168 |
| O(6)–H(6A)···N(2)$^{\#3}$ | 0.85 | 2.00 | 2.8466 | 173 |
| O(6)–H(6B)···N(9)$^{\#1}$ | 0.85 | 2.00 | 2.8256 | 164 |
| O(7)–H(7A)···N(5)$^{\#1}$ | 0.85 | 2.06 | 2.8991 | 167 |
| O(7)–H(7B)···Cl(1)$^{\#4}$ | 0.85 | 2.29 | 3.1033 | 160 |
| O(8)–H(8A)···O(9)$^{\#5}$ | 0.85 | 1.80 | 2.6377 | 169 |
| O(8)–H(8B)···Cl(1) | 0.85 | 2.24 | 3.0907 | 173 |
| O(9)–H(9A)···N(7)$^{\#6}$ | 0.85 | 2.11 | 2.9274 | 162 |
| O(10)–H(10C)···O(5) | 0.85 | 2.12 | 2.9337 | 159 |
| *Complex* **2** | | | | |
| O(9)–H(9A)···N(7)$^{\#1}$ | 0.85 | 2.04 | 3.2035 | 159 |
| O(9)–H(9B)···Cl(1)$^{\#2}$ | 0.85 | 2.39 | 3.2035 | 159 |
| O(10)–H(10D)···Cl(1) | 0.85 | 2.30 | 3.1478 | 173 |
| O(11)–H(11C)···N(14)$^{\#3}$ | 0.85 | 1.98 | 2.8191 | 169 |
| O(11)–H(11D)···O(17)$^{\#4}$ | 0.85 | 1.98 | 2.7637 | 152 |
| O(12)–H(12C)···Cl(2)$^{\#1}$ | 0.85 | 2.23 | 3.0597 | 166 |
| O(12)–H(12D)···O(17) | 0.85 | 1.95 | 2.7591 | 158 |
| O(13)–H(13C)···O(19)$^{\#4}$ | 0.85 | 2.10 | 2.7735 | 136 |
| O(13)–H(13D)···N(11)$^{\#4}$ | 0.85 | 2.15 | 2.9977 | 176 |
| O(14)–H(1B)···N(3)$^{\#3}$ | 0.85 | 2.24 | 2.9599 | 142 |
| O(14)–H(14C)···N(4)$^{\#3}$ | 0.85 | 2.56 | 3.3973 | 169 |
| O(14)–H(14D)···N(11)$^{\#4}$ | 0.85 | 2.04 | 2.8005 | 149 |
| O(15)–H(15D)···N(11)$^{\#4}$ | 0.85 | 2.35 | 3.0316 | 138 |
| O(15)–H(15D)···N(12)$^{\#4}$ | 0.85 | 2.54 | 3.3763 | 167 |
| O(15)–H(15E)···Cl(2)$^{\#4}$ | 0.85 | 2.39 | 3.1745 | 153 |
| O(16)–H(16A)···N(18)$^{\#3}$ | 0.82 | 2.04 | 2.1793 | 140 |
| O(16)–H(16B)···O(20) | 0.82 | 2.39 | 3.1963 | 167 |
| O(19)–H(19C)···N(1)$^{\#4}$ | 0.85 | 2.52 | 3.3606 | 170 |
| O(19)–H(19D)···Cl(1)$^{\#5}$ | 0.85 | 2.39 | 3.1663 | 152 |
| O(20)–H(20C)···N(19)$^{\#3}$ | 0.82 | 2.28 | 3.0818 | 164 |
| *Complex* **3** | | | | |
| O(9)–H(9C)···N(2)$^{\#1}$ | 0.85 | 2.18 | 2.856(7) | 136 |
| O(11)–H(11B)···N(9)$^{\#2}$ | 0.85 | 2.25 | 3.022(14) | 151 |
| O(11)–H(11C)···O(19)$^{\#3}$ | 0.85 | 2.07 | 2.777(14) | 140 |
| O(12)–H(12B)···N(8)$^{\#2}$ | 0.85 | 2.33 | 2.945(12) | 130 |
| O(13)–H(13B)···N(8)$^{\#2}$ | 0.85 | 2.59 | 3.338(10) | 147 |
| O(13)–H(13B)···N(9)$^{\#2}$ | 0.85 | 2.33 | 2.974(11) | 133 |
| O(13)–H(13C)···Cl(2A) | 0.85 | 2.69 | 3.465(12) | 151 |
| O(15)–H(15B)···N(1)$^{\#4}$ | 0.85 | 2.01 | 2.851(7) | 173 |
| O(15)–H(15C)···Cl(1)$^{\#5}$ | 0.85 | 2.33 | 3.139(6) | 158 |
| O(17)–H(17B)···O(18)$^{\#6}$ | 0.85 | 1.87 | 2.722(11) | 179 |
| O(17)–H(17C)···N(14)$^{\#7}$ | 0.85 | 2.16 | 2.841(10) | 137 |
| O(18)–H(18C)···O(16) | 0.85 | 2.16 | 2.791(7) | 131 |
| O(18)–H(18D)···N(3)$^{\#2}$ | 0.85 | 2.60 | 3.418(7) | 161 |
| O(18)–H(18D)···N(4)$^{\#2}$ | 0.85 | 2.03 | 2.847(8) | 161 |
| O(19)–H(19B)···Cl(1) | 0.85 | 2.41 | 3.229(14) | 162 |

Notes: Symmetry codes for **1**: $^{(\#1)}$ $1+x, y, 1+z$; $^{(\#2)}$ $1-x, -y, 1-z$; $^{(\#3)}$ $1+x, 1/2-y, 1/2+z$; $^{(\#4)}$ $-x, -y, 1-z$; $^{(\#5)}$ $-1-x, -y, -z$; $^{(\#6)}$ $-1+x, 1/2-y, -1/2+z$; for **2**: $^{(\#1)}$ $x, 1/2-y, 1/2+z$; $^{(\#2)}$ $3-x, -y, 1-z$; $^{(\#3)}$ $x, -1/2-y, -1/2+z$; $^{(\#4)}$ $x, y, -1+z$; $^{(\#5)}$ $-1+x, y, z$; for **3**: $^{(\#1)}$ $x, 1/2-y, -1/2+z$; $^{(\#2)}$ $-1-x, -y, 1-z$; $^{(\#3)}$ $x, -1/2-y, 1/2+z$; $^{(\#4)}$ $-1-x, -1/2+y, 1/2-z$; $^{(\#5)}$ $-1+x, -1/2-y, -1/2+z$; $^{(\#6)}$ $1+x, -1/2-y, 1/2+z$; $^{(\#7)}$ $x, -1/2-y, -1/2+z$.

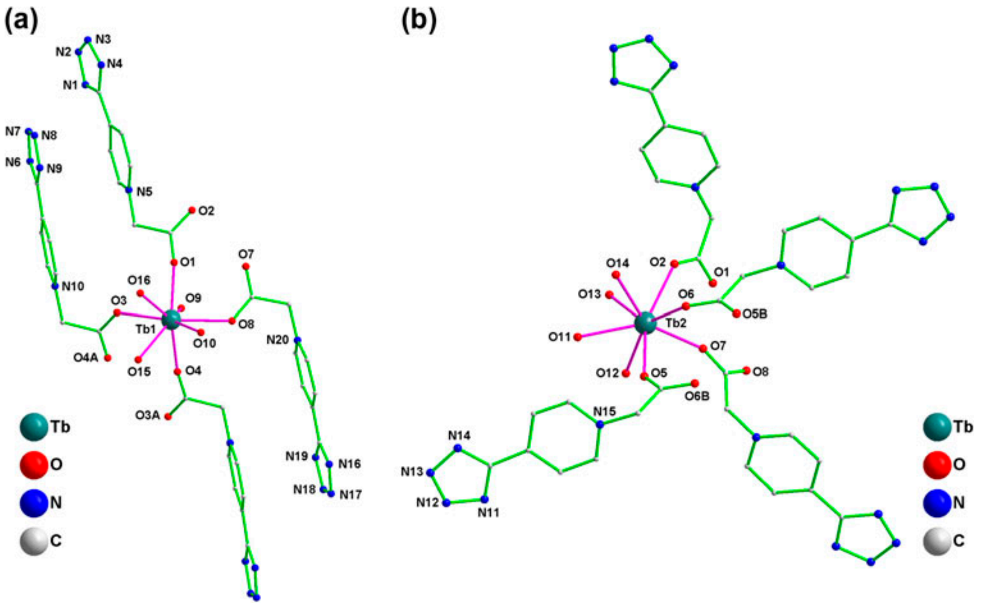

Figure 3. The coordination environment of Tb(III) and coordination mode of a4-ptz$^-$ (hydrogens are omitted for clarity) in **3** (figure 3(a) for table 1, figure 3(b) for table 2).

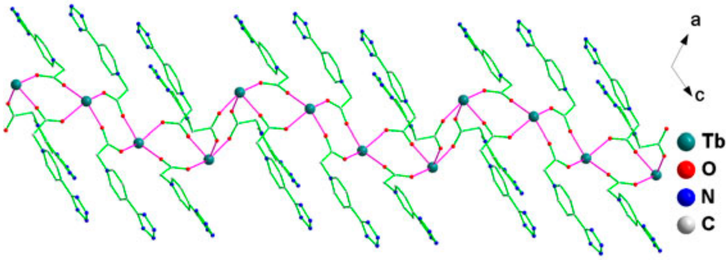

Figure 4. The 1D structure of **3**.

Lanthanide(III) (La, Eu, and Tb) a4-ptz complexes contain a4-ptz with $\mu_{1,3}$-COO and $\mu_{1,1,3}$-COO bridges to connect different lanthanide(III) ions. Compared with other metal/a4-ptz complexes, the coordination modes of the a4-ptz are different; a4-ptz is a bidentate bridge to two transition metal ions via its tetrazole N and one carboxylate O.

Hydrogen-bonding interactions (table 3) among the coordinated waters (O9, O11, O12, and O13) and crystallization waters (O16, O17, O18, and O19), tetrazole-N and Cl$^-$ led to formation of a 3-D hydrogen-bond network structure (Supplementary material).

### 3.3. *Luminescent properties of 1–3*

Luminescent properties of free a4-ptz potassium salt and **1**–**3** were investigated at room temperature in the solid state. Complexes **1**–**3** show a strong emission at 368, 381, and 380 nm upon excitation at 322, 329, and 333 nm, respectively (figure 5 and Supplementary

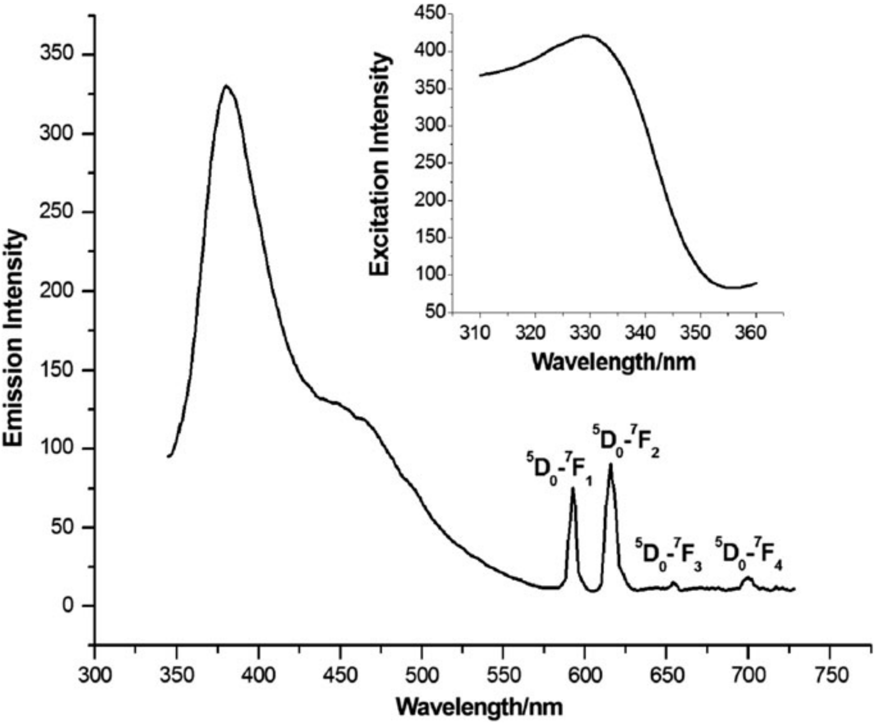

Figure 5. Solid-state fluorescent excitation and emission spectra of **2** ($\lambda_{ex} = 329$ nm).

material). The emissions of **1**–**3** can probably be assigned to intraligand fluorescent emission since a similar emission ($\lambda_{em} = 372$ nm, $\lambda_{ex} = 333$ nm) is also observed for free a4-ptz potassium salt (Supplementary material). In addition, emission spectra of **2** and **3** exhibit characteristic emissions of $Eu^{3+}$ and $Tb^{3+}$, respectively. For **2**, four characteristic peaks are shown in figure 5, which belong to the transitions $^5D_0 \rightarrow {}^7F_1$ (593 nm), $^5D_0 \rightarrow {}^7F_2$ (616 nm), $^5D_0 \rightarrow {}^7F_3$ (654 nm), and $^5D_0 \rightarrow {}^7F_4$ (700 nm) [46]. The intensity of the $^5D_0 \rightarrow {}^7F_2$ transition (electric dipole) is stronger than that of the $^5D_0 \rightarrow {}^7F_1$ transition (magnetic dipole), indicating that the coordination environment of $Eu^{3+}$ is asymmetric [47], confirmed by crystallographic analyzes. For **3**, there are four characteristic peaks (Supplementary material) assigned to $^5D_4 \rightarrow {}^7F_6$ (490 nm), $^5D_4 \rightarrow {}^7F_5$ (546 nm), $^5D_4 \rightarrow {}^7F_4$ (586 nm), and $^5D_4 \rightarrow {}^7F_3$ (623 nm) transitions [48].

The emission spectra of **2** and **3** exhibit the characteristic narrow bands of Eu(III) and Tb(III) and an intense broad band of the ligand was evident, indicating poor sensitization of the ligand toward Eu(III) and Tb(III). In excitation spectra of **2** and **3**, narrow absorptions from the f–f transitions of Ln(III) were absent, which prove that luminescence sensitization via excitation of the ligand is efficient.

## 4. Conclusions

We are the first to investigate lanthanide-based coordination compounds containing a4-ptz. Three new lanthanide-based complexes $[Ln(a4\text{-}ptz)_2(H_2O)_4]\cdot Cl\cdot 2H_2O$ (Ln = La(**1**), Eu(**2**) and Tb(**3**)), with a4-ptz have been constructed and displayed 1-D structures. The structures of **1**–**3** are different from Ca/Sr(II) and Zn/Mn(II) metal/a4-ptz complexes with the 1-D coordination compounds that may be attributed to different coordination modes of the a4-ptz ligands [35, 37, 38]. The structures of **1**–**3** and Ba(II)/a4-ptz coordination compounds are similar [37, 49]. The promising new multifunctional ligand, a4-ptz, has potential in coordination compounds, and further exploration of a4-ptz complexes is underway in our group.

## Supplementary material

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC-871853 (**1**), -871852 (**2**) and -871854 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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