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Constructions of a Set of New Lanthanide-Based Coordination Polymers with Hatza Ligands (Hatza = 5-Aminotetrazole–1-Acetic Acid)

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ABSTRACT: Reaction of $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ with 5-aminotetrazole-1-acetic acid (Hatza) under the presence of KOH produced a set of new Ln(III)/atza complexes, $[\text{Ln(atza)}_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{Cl}][\text{Ln} = \text{Pr (1), Nd (2), Sm (3)}]$, $[\text{Ln(atza)}_2(\text{H}_2\text{O})_3]\text{Cl} [\text{Ln} = \text{Eu (4), Gd (5)}]$, and $[\text{Tb(atza)}_2(\text{H}_2\text{O})_4]\text{Cl (6)}$. These compounds were structurally characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The complexes **1–3** are isostructural and display two-dimensional frameworks, the isostructural complexes **4–5** show one-dimensional (1D) structures, and complex **6** forms a 1D framework. Furthermore, the luminescence properties of **4** and **6** were investigated at room temperature in the solid state.

Introduction

In the past decade, the design and synthesis of tetrazole-based coordination compounds have been of an attractive area of research due to their intriguing topological structures and their potential applications in advanced materials.¹ Among numerous tetrazole-based ligands, 5-methyl-, 5-ethyl-, 5-amino-, 5-pyrazinyl-, 5-(2-pyridyl)-, 5-(3-pyridyl)-, and 5-(4-pyridyl)tetrazolato, 1-methyl-, 1-ethyl-, and 1-propyltetrazole, 1,5-diaminotetrazole, 1,4-benzeneditetrazolate, 1,3,5-benzenetris-tetrazolate, 1,2-bis(tetrazol-1-yl)ethane, 1,4-bis(tetrazol-1-yl)-butane, 1,6-bis(tetrazol-1-yl)hexane, etc., have already been studied, and a number of complexes containing these ligands have been reported.¹ However, adducts of another class of carboxylate–tetrazole ligands have only been the subject of limited study with metal ions; typical examples are coordination compounds with the Htza ligand (Htza = tetrazole-1-acetic acid).² As is well-known, carboxylate O atoms and tetrazolyl ring N atoms have good coordination capacities.^{1,3} So, carboxylate–tetrazole ligands are excellent and versatile building blocks for the construction of novel coordination compounds. For some time, we have been interested in the synthesis and characterization of coordination complexes containing carboxylate–tetrazole ligands.⁴ In this work, we selected a carboxylate–tetrazole ligand, 5-aminotetrazole-1-acetic acid (Hatza), to construct novel lanthanide-based coordination compounds. The selection of this ligand was based on the following considerations: (i) 5-aminotetrazole-1-acetic acid, with both carboxylate group and tetrazole ring, is expected to exhibit more varied coordinating patterns in the construction of multidimensional coordination frameworks; (ii) the $-\text{CH}_2-$ spacer between the tetrazole ring and carboxylate donor group offers flexible orientations of the carboxylate arm, favoring the formation of varied framework structures; (iii) the amido group ($-\text{NH}_2$) of the Hatza may form a hydrogen bond, stabilizing the supramolecular assemblies; (iv) the lanthanide-based complexes of Hatza have not been reported before, to the best of our knowledge. In previous

reports, we have described the synthesis and structures of $[\text{Co(atza)}_2(\text{H}_2\text{O})_4]$, $[\text{Cd(atza)}_2]_n$, $\{\text{Cu(atza)}_2\} \cdot 2\text{H}_2\text{O}_n$, $[\text{Cu(atza)}_2(4,4'\text{-bipy})_{0.5}\text{H}_2\text{O}]_n$, and $[\text{Mn(atza)}_2(\text{H}_2\text{O})_4]$, and four kinds of coordination modes of the atza ligand have been found [Scheme 1 (I–IV)].^{4a–4d} In this report, we have extended the investigation to lanthanide metal ions. Compared to the transition metals, lanthanides have much higher coordination numbers and more flexible coordination geometry. We anticipate that the coordination of Hatza at lanthanide metal ion center may lead to the formation of new coordination polymer with structures different from that of the transition metal/Hatza.

By reacting Hatza with the corresponding lanthanide(III) chlorides under the presence of KOH, we obtained a series of coordination polymers, $[\text{Ln(atza)}_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{Cl}] [\text{Ln} = \text{Pr(1), Nd(2), Sm(3)}]$, $[\text{Ln(atza)}_2(\text{H}_2\text{O})_3]\text{Cl} [\text{Ln} = \text{Eu(4), Gd(5)}]$, and $[\text{Tb(atza)}_2(\text{H}_2\text{O})_4]\text{Cl (6)}$. Herein we report their synthesis, crystal structures, and the luminescent properties of **4** and **6**.

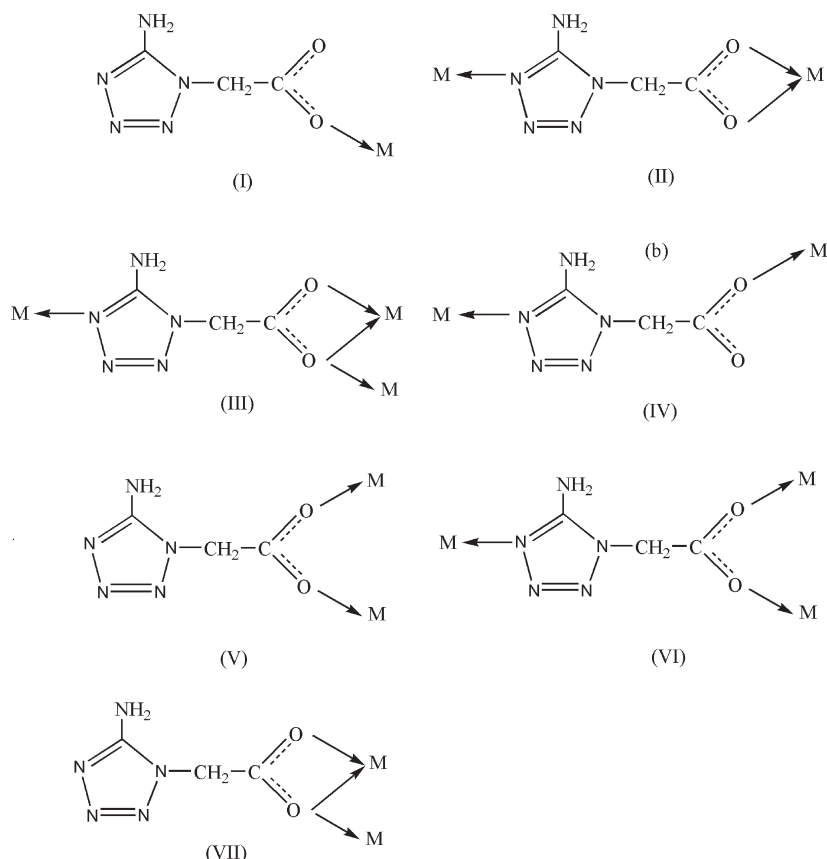
Experimental Section

Materials and Apparatus. The ligand Hatza was prepared according to the literature method.⁵ Other chemicals were commercially available reagents of analytical grade and were used without further purification. The elemental analysis for C, H, and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. IR spectra were recorded on a thermo NICOLET-380 instrument as KBr disk ($4000\text{--}400\text{ cm}^{-1}$). The photoluminescent spectra were performed on a Hitachi F4600 spectrofluorometer.

Synthesis of $[\text{Ln(atza)}_2(\text{CH}_3\text{OH})(\text{H}_2\text{O})\text{Cl}]$ ($\text{Ln} = \text{Pr(1), Nd(2), Sm(3)}$). Hatza (0.0572 g, 0.4 mmol) and KOH (0.0224 g, 0.4 mmol) was dissolved in MeOH (8 mL). Then $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ [0.0711 g ($\text{Ln} = \text{Pr}$), 0.0717 g ($\text{Ln} = \text{Nd}$), 0.0730 g ($\text{Ln} = \text{Sm}$), 0.2 mmol] was added. The mixture was stirred at 70°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 2 weeks, forming green crystals of **1**, purple crystals of **2**, and buff crystals of **3**, respectively. For **1**, yield: 60.4 mg (59% based on Pr). Anal. Calcd. for $\text{C}_7\text{H}_{14}\text{ClN}_{10}\text{PrO}_6$: C, 16.47; H, 2.76; N, 27.43%. Found: C, 16.51; H, 2.65; N, 27.49%. IR (KBr, cm^{-1}): 1650 (s), 1592 (s), 1440 (m), 1397 (m), 1323 (w), 1283 (w), 1114 (w), 1011 (w), 829 (w), 682 (w). For **2**, yield: 64.5 mg (63% based on Nd). Anal. Calcd for

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Scheme 1. Coordination Modes of the atza Ligand



$C_7H_{14}ClN_{10}NdO_6$: C, 16.36; H, 2.75; N, 27.25%. Found: C, 16.43; H, 2.61; N, 27.39%. IR (KBr, cm^{-1}): 1651 (s), 1591 (s), 1441 (m), 1399 (m), 1323 (w), 1283 (w), 1117 (w), 1012 (w), 827 (w), 681 (w). For **3**, yield: 63.4 mg (61% based on Sm). Anal. Calcd for $C_7H_{14}ClN_{10}SmO_6$: C, 16.17; H, 2.71; N, 26.93%. Found: C, 16.48; H, 2.58; N, 27.12%. IR (KBr, cm^{-1}): 1650 (s), 1593 (s), 1442 (m), 1399 (m), 1324 (w), 1284 (w), 1115 (w), 1012 (w), 828 (w), 682 (w).

Synthesis of $[Ln(atza)_2(H_2O)_3]Cl$ [$Ln = Eu(4), Gd(5)$]. An procedure identical to that for **1–3** was followed to prepare **4** and **5** (colorless crystals for **4** and **5**), except that lanthanide(III) chlorides were replaced by $LnCl_3 \cdot 6H_2O$ [$Ln = Eu(4), Gd(5)$]. For **4**, yield: 60.5 mg (58% based on Eu). Anal. Calcd. for $C_6H_{14}ClEuN_{10}O_7$: C, 13.71; H, 2.68; N, 26.65%. Found: C, 13.85; H, 2.61; N, 26.94%. IR (KBr, cm^{-1}): 1646 (s), 1596 (s), 1443 (m), 1400 (m), 1324 (w), 1277 (w), 1118 (w), 1018 (w), 825 (w), 693 (w). For **5**, yield: 62.7 mg (59% based on Gd). Anal. Calcd for $C_6H_{14}GdN_{10}O_7Cl$: C, 13.57; H, 2.66; N, 26.38%. Found: C, 13.47; H, 2.56; N, 26.22%. IR (KBr, cm^{-1}): 1643 (s), 1598 (s), 1447 (m), 1399 (m), 1327 (w), 1281 (w), 1113 (w), 1014 (w), 826 (w), 686 (w).

Synthesis of $[Tb(atza)_2(H_2O)_4]Cl$ (6**).** An procedure identical to that of **1–3** was followed to prepare **6** (colorless crystals), except that lanthanide(III) chlorides were replaced by $TbCl_3 \cdot 6H_2O$. Yield: 71.6 mg (65% based on Tb). Anal. Calcd for $C_6H_{16}ClN_{10}TbO_8$: C, 13.09; H, 2.93; N, 25.44%. Found: C, 13.38; H, 2.78; N, 25.13%. IR (KBr, cm^{-1}): 1643 (s), 1599 (s), 1450 (m), 1399 (m), 1317 (w), 1276 (w), 1114 (w), 1015 (w), 825 (w), 687 (w).

X-ray Single-Crystal Determination. Suitable single crystals of complexes **1–6** were mounted on a Rigaku SCXmini-CCD diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 291 K. All absorption corrections were performed using the CrystalClear programs. The crystal structures of **1–6** were solved by direct methods and refined on F^2 by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms.⁶ For **1–6**, important crystal data and collection and refinement parameters are summarized in Table 1,

and selected bond lengths and angles are given in Table S1, Supporting Information.

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-716889(**1**), -716892(**2**), -716890(**3**), -739904 (**4**), -716896 (**5**), -716895(**6**). 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].

Results and Discussion

Crystal Structures of $[Ln(atza)_2(CH_3OH)(H_2O)Cl]$ ($Ln = Pr(1), Nd(2), Sm(3)$). The X-ray structure analysis reveals that **1–3** are isomorphic; here, complex **1** is taken as an example to depict the two-dimensional structure in detail. Complex **1** crystallizes in triclinic space group $P\bar{1}$ and the asymmetric unit contains one $[Pr(atza)_2(CH_3OH)(H_2O)Cl]$ molecule. Each Pr atom in **1** is eight-coordinated by four O atoms from four atza ligands, one N atom from one atza ligand, one O atom from one water molecule, one O atom from one methanol molecule, and one Cl^- anion, forming a distorted square-antiprism coordination geometry (Figure 1). There are two kinds of coordination modes for atza ligands in the structure [Scheme 1 (V–VI)]. Two neighboring Pr^{3+} ions are doubly bridged by two carboxylate groups from two atza ligands in a $\mu_{1,3}$ -COO *syn-syn* bridging mode, forming a 1D chain extending along the *c* axis with a $Pr \cdots Pr$ distance of 5.7450 or 5.2449 Å and a $Pr \cdots Pr \cdots Pr$ bite angle of 136°. While the tridentate atza ligand coordinates one Pr^{3+} ion of the adjacent chain through one of its tetrazole N atoms to yield an interesting 2D layer network extending along the

Table 1. Crystallographic Data and Structure Refinement for 1–6

compound	1	2	3
molecular formula	C ₇ H ₁₄ ClPrN ₁₀ O ₆	C ₇ H ₁₄ ClNdN ₁₀ O ₆	C ₇ H ₁₄ ClSmN ₁₀ O ₆
formula weight	510.64	513.97	520.09
crystal system	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.9630(18)	8.9228(18)	8.8778(18)
<i>b</i> (Å)	10.197(2)	10.135(2)	10.083(2)
<i>c</i> (Å)	10.197(2)	10.156(2)	10.093(2)
α (°)	65.14(3)	65.05(3)	65.05(3)
β (°)	70.43(3)	84.41(3)	84.49(3)
γ (°)	84.41(3)	70.52(3)	70.63(3)
<i>V</i> (Å ³)	795.9(4)	784.1(4)	771.8(4)
<i>Z</i>	2	2	2
<i>T</i> /K	291(2)	291(2)	291(2)
<i>D</i> _{calc} (g·cm ^{−3})	2.131	2.177	2.238
λ (Mo K α) (Å)	0.71073	0.71073	0.71073
μ (cm ^{−1})	3.281	3.535	4.032
total reflections	8353	8280	8139
unique reflections	3626 (<i>R</i> _{int} = 0.0272)	3584 (<i>R</i> _{int} = 0.0317)	3524 (<i>R</i> _{int} = 0.0277)
no. observations	3353 (<i>I</i> > 2.00 σ (<i>I</i>))	3291 (<i>I</i> > 2.00 σ (<i>I</i>))	3277 (<i>I</i> > 2.00 σ (<i>I</i>))
no. parameters	254	254	254
<i>R</i> ^a	0.0248	0.0248	0.0260
<i>wR</i> ^b	0.0513	0.0562	0.0493
GOF ^c	1.048	1.050	0.796
$\Delta\rho_{\max}$ (e Å ^{−3})	0.538	0.988	1.156
$\Delta\rho_{\min}$ (e Å ^{−3})	−0.971	−1.012	−0.908
compound	4	5	6
molecular formula	C ₆ H ₁₄ ClEuN ₁₀ O ₇	C ₆ H ₁₄ ClGdN ₁₀ O ₇	C ₆ H ₁₆ ClTbN ₁₀ O ₈
formula weight	525.68	530.97	550.67
crystal system	triclinic	triclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
<i>a</i> (Å)	9.3219(19)	9.3156(19)	4.9573(10)
<i>b</i> (Å)	10.141(2)	10.118(2)	18.121(4)
<i>c</i> (Å)	10.197(2)	10.184(2)	19.338(4)
α (°)	60.34(2)	60.41(3)	90.00
β (°)	76.87(3)	76.80(3)	92.28(3)
γ (°)	86.754(18)	86.80(3)	90.00
<i>V</i> (Å ³)	813.9(3)	810.8(4)	1735.8(6)
<i>Z</i>	2	2	4
<i>T</i> /K	291(2)	291(2)	291(2)
<i>D</i> _{calc} (g cm ^{−3})	2.145	2.175	2.107
λ (Mo K α) (Å)	0.71073	0.71073	0.71073
μ (cm ^{−1})	4.074	4.312	4.289
total reflections	7432	8526	17986
unique reflections	3202 (<i>R</i> _{int} = 0.0367)	3704 (<i>R</i> _{int} = 0.0267)	4140 (<i>R</i> _{int} = 0.0346)
no. observations	2874 (<i>I</i> > 2.00 σ (<i>I</i>))	3462 (<i>I</i> > 2.00 σ (<i>I</i>))	3986 (<i>I</i> > 2.00 σ (<i>I</i>))
no. parameters	226	258	3468
<i>R</i> ^a	0.0420	0.0211	0.0258
<i>wR</i> ^b	0.0964	0.0424	0.0494
GOF ^c	1.078	1.071	1.079
$\Delta\rho_{\max}$ (e Å ^{−3})	0.793	0.724	0.566
$\Delta\rho_{\min}$ (e Å ^{−3})	−1.570	−0.776	−1.052

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

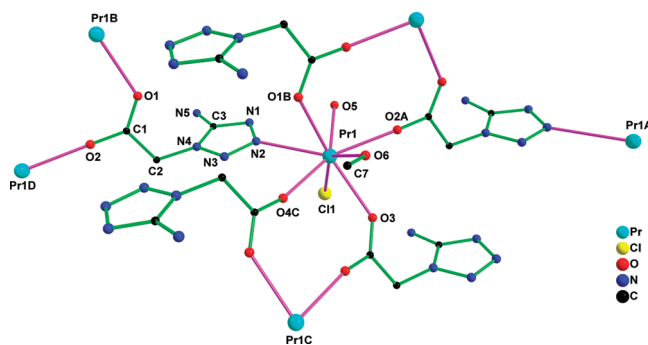


Figure 1. The coordination environment of Pr atom of complex 1. Hydrogen atoms are omitted for clarity.

bc plane (Figure 2). In the 2D layer of **1**, three kinds of hydrogen bonds are formed between the water molecule and the O atom of methanol molecule [O(5)···O(6) 2.975(5) Å/168(5)°, $-x + 1, -y + 1, -z + 2$], between the methanol molecule and the N atom of the tetrazolate group [O(6)···N(8) 2.735(6) Å/167(4)°, $-x + 1, -y + 2, -z + 1$], and between the amino group and the Cl[−] anion [N(10)···Cl(1) 2.473(5) Å/150(5)°]. The adjacent 2D layers are further linked through four kinds of hydrogen bonding interactions between the amino group and the Cl[−] anion [N(5)···Cl(1) 3.360(5) Å/170(4)°, $-x, -y, -z + 2$], and the N atom of the tetrazolate group [N(5)···N(9) 2.957(6) Å/171(5)°, $-x, -y + 1, -z + 2$; N(10)···N(2) 3.140(6) Å/169(5)°, $-x, -y + 1, -z + 2$] and between the water molecule

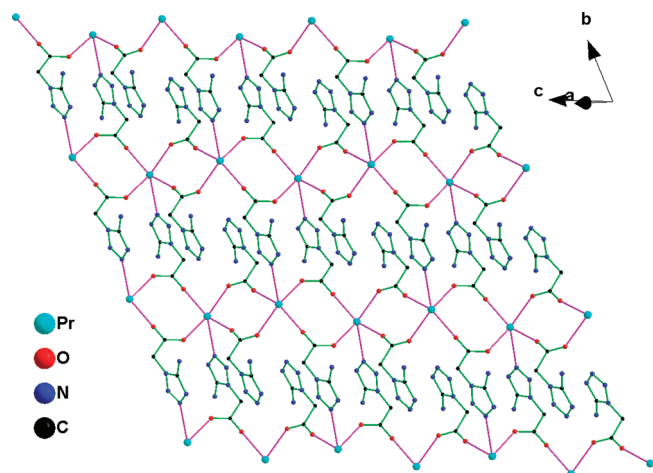


Figure 2. The 2D layer structure of **1** extending along the *bc* plane. Hydrogen atoms, water molecules, and methanol molecules are omitted for clarity.

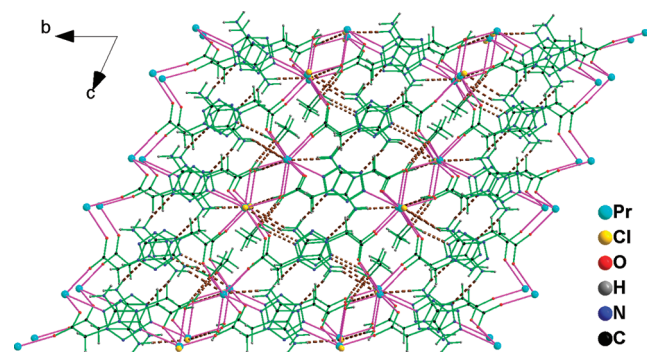


Figure 3. The 3D network structure of **1** formed via H-bonding interactions.

and the Cl^- anion $[\text{O}(5) \cdots \text{Cl}(1) \ 2.199(4) \text{ \AA}/172(4)^\circ, -x, -y + 1, -z + 2]$ to afford a 3D supramolecular structure (Figure 3).

Crystal Structures of $[\text{Ln}(\text{atza})_2(\text{H}_2\text{O})_3]\text{Cl}$ [$\text{Ln} = \text{Eu}(4), \text{Gd}(5)$]. The two complexes are also isostructural, and complex **5** is taken as an example to describe the crystal structure. Complex **5** crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains one $[\text{Gd}(\text{atza})_2(\text{H}_2\text{O})_3]\text{Cl}$ molecule. In complex **5**, each Gd atom is nine-coordinated by five O atoms from four atza ligands, one N atom from one atza ligand, three O atoms from three water molecules, forming a distorted monocapped square–antiprism coordination geometry (Figure 4). There are two kinds of coordination modes for atza ligands in **5** [Scheme 1 (VI–VII)]. Two neighboring Gd^{3+} ions are quadruply bridged by two carboxylate groups from two atza ligands in a $\mu_{1,3}$ -COO *syn-syn* bridging mode and two carboxylate group from the atza ligand in a $\mu_{1,1,3}$ -COO bridging mode, giving rise to a “paddle-wheel” dimer with a $\text{Gd} \cdots \text{Gd}$ distance of 4.0491 Å. The tridentate atza ligand coordinates one Gd^{3+} ion of the adjacent dimer through its a tetrazole N atom to yield a 1D chain extending along the *b* axis (Figure 5). Within this 1D chain, there is one hydrogen bonding interaction between the amino group and the O atom of carboxylate group $[\text{N}(10) \cdots \text{O}(1) \ 2.927(4) \text{ \AA}/151(4)^\circ]$. The adjacent 1D chains are further connected by seven kinds of hydrogen bonding interactions between the amino group and the Cl^- anion

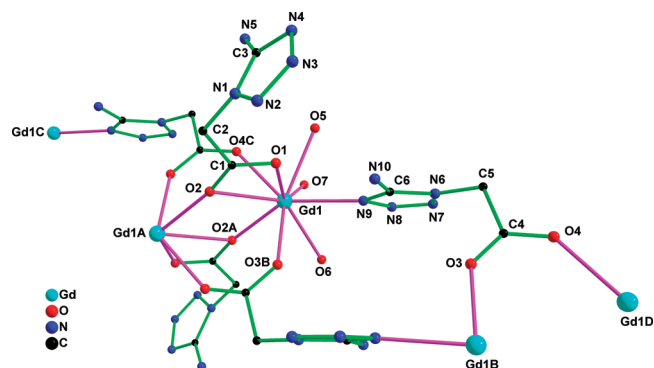


Figure 4. The coordination environment of Gd atom of complex **5**. Hydrogen atoms are omitted for clarity.

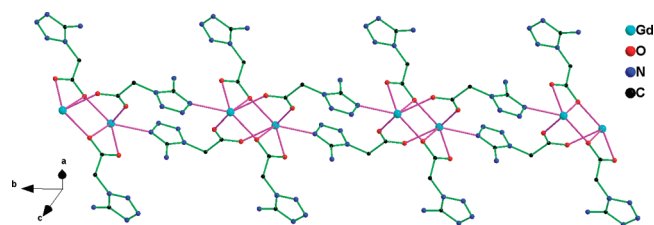


Figure 5. The 1D chain structure of **5** extending along the *b* axis. Hydrogen atoms and water molecules are omitted for clarity.

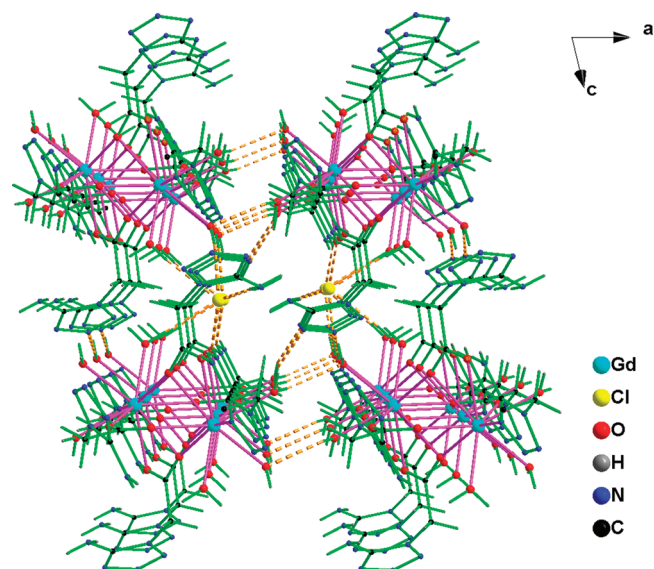


Figure 6. The 3D network structure of **5** formed via H-bonding interactions.

$[\text{N}(5) \cdots \text{Cl}(1) \ 3.498(4) \text{ \AA}/175(3)^\circ, -x + 1, -y, -z + 1; \text{N}(10) \cdots \text{Cl}(1) \ 3.355(4) \text{ \AA}/156(3)^\circ, -x + 1, -y + 1, -z + 1]$, between the water molecule and the Cl^- anion $[\text{O}(6) \cdots \text{Cl}(1) \ 3.221(2) \text{ \AA}/163(3)^\circ, -x + 1, -y, -z + 2; \text{O}(6) \cdots \text{Cl}(1) \ 3.122(2) \text{ \AA}/171(3)^\circ, -x - 1, y, z + 1; \text{O}(7) \cdots \text{Cl}(1) \ 3.161(2) \text{ \AA}/172(4)^\circ, -x + 1, -y, -z + 2]$ and between the water molecule and the N atom of the tetrazolate group $[\text{O}(5) \cdots \text{N}(4) \ 2.823(4) \text{ \AA}/159(3)^\circ, -x + 1, -y + 1, -z + 1; \text{O}(7) \cdots \text{N}(3) \ 2.822(4) \text{ \AA}/169(3)^\circ, x, y - 1, z + 1]$ to form a 3D network (Figure 6).

Crystal Structures of $[\text{Tb}(\text{atza})_2(\text{H}_2\text{O})_4]\text{Cl}$ (6**).** Complex **6** crystallizes in monoclinic space group $P\bar{1}$ and the asymmetric unit contains one $[\text{Tb}(\text{atza})_2(\text{H}_2\text{O})_4]\text{Cl}$ molecule. In

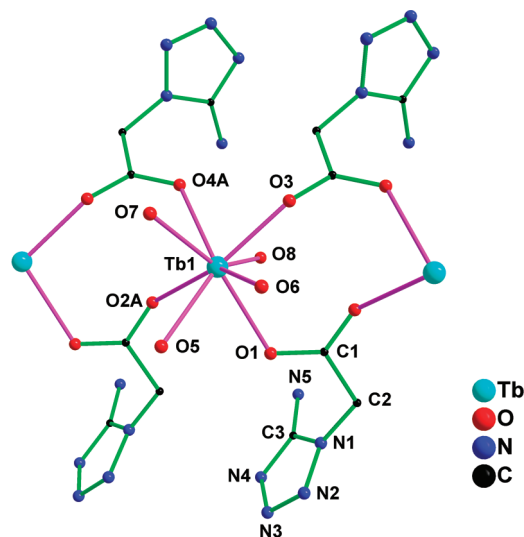


Figure 7. The coordination environment of Tb atom of complex **6**. Hydrogen atoms are omitted for clarity.

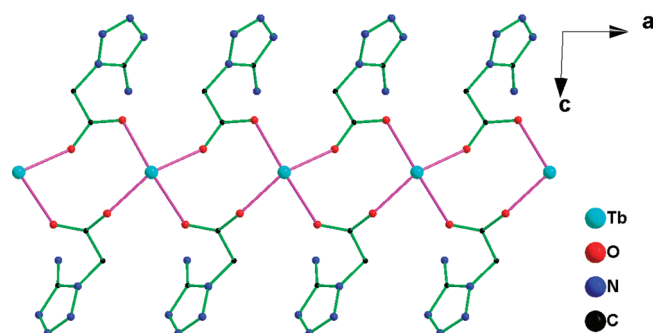


Figure 8. The 1D chain structure of **6** extending along the *a* axis. Hydrogen atoms and water molecules are omitted for clarity.

complex **6**, each Tb atom is eight-coordinated by four O atoms from four atza ligands and four O atoms from four water molecules, forming a distorted square-antiprism coordination geometry (Figure 7). Each atza ligand acts as a bidentate bridging ligand in **6** [Scheme 1 (V)]. Two neighboring Tb(III) ions are doubly bridged by two carboxylate groups from two atza ligands in a $\mu_{1,3}$ -COO *syn-syn* bridging mode, forming a 1D chain extending along the *a* axis with a Tb...Tb distance of 4.9573 Å and a Tb...Tb...Tb bite angle of 180° (Figure 8). As for the 1D chain of **6**, there is one hydrogen bonding interaction between the water molecules [O(6)...O(7) 2.863(3) Å/157(7)°]. The adjacent 1D are held together through 10 kinds of hydrogen bonding interactions between the amino group and the Cl[−] anion [N(5)...Cl(1) 3.585(4) Å/168(3)°; N(10)...Cl(1) 3.570(4) Å/153(3)°], and the N atom of the tetrazolate group [N(5)...N(9) 2.899(5) Å/157(4)°, $x+1, -y-1/2, z-1/2$; N(10)...N(4) 2.961(4) Å/153(4)°, $x-1, -y-1/2, z+1/2$], between the water molecule and the N atom of the tetrazolate group [O(5)...N(3) 2.974(4) Å/154(3)°, $-x+1, -y, -z$; O(5)...N(2) 2.963(4) Å/178(3)°, $-x, -y, -z$; O(7)...N(8) 2.764(4) Å/176.5(12)°, $-x, -y, -z+1$], and between the water molecule and the Cl[−] anion [O(7)...Cl(1) 3.181(3) Å/172(3)°, $-x, y+1/2, -z+1/2$; O(8)...Cl(1) 3.162(3) Å/165(3)°; O(8)...Cl(1) 3.186(3) Å/173(4)°, $x-1, -y-1/2, z+1/2$], and to generate a 3D network (Figure 9).

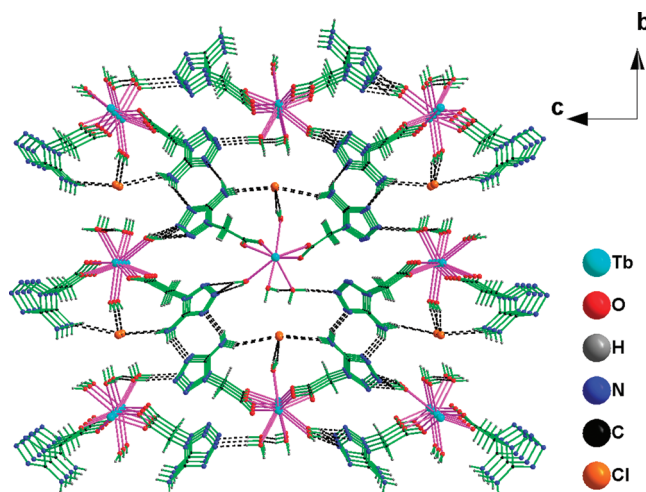


Figure 9. The 3D network structure of **6** formed via H-bonding interactions.

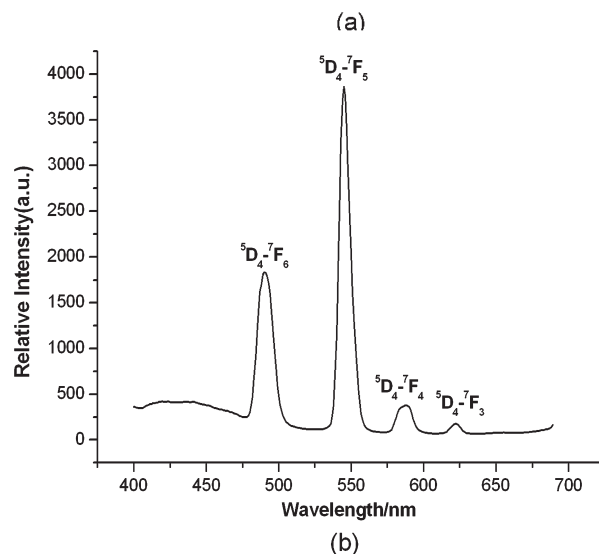
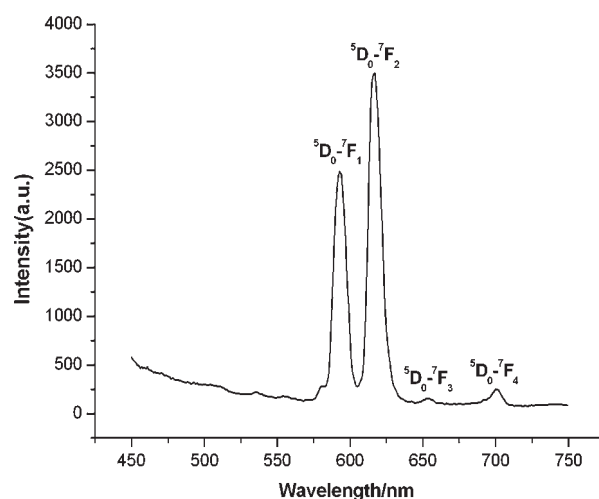


Figure 10. Emission spectra of complexes **4** (a) and **6** (b).

Luminescent Properties of 4 and 6. The luminescent properties of **4** and **6** were investigated in the solid state at room temperature. The emission spectra of the two complexes (Figure 10) at the excited wavelength of 394 nm for **4** and 350 nm for **6** exhibit the characteristic emission of Eu³⁺ and

Tb³⁺, respectively. For **4**, four characteristic peaks are shown in Figure 10a, which belong to the transitions of ⁵D₀ → ⁷F₁ (593 nm), ⁵D₀ → ⁷F₂ (617 nm), ⁵D₀ → ⁷F₃ (654 nm), and ⁵D₀ → ⁷F₄ (700 nm). The intensity of the ⁵D₀ → ⁷F₂ transition (electric dipole) is stronger than that of the ⁵D₀ → ⁷F₁ transition (magnetic dipole), and it indicates that the coordination environment of the Eu³⁺ ion is asymmetric,⁷ which is confirmed by crystallographic analyses. For **6**, there are four characteristic peaks shown in Figure 10b. They are assigned to the ⁵D₄ → ⁷F₆ (490 nm), ⁵D₄ → ⁷F₅ (545 nm), ⁵D₄ → ⁷F₄ (587 nm), and ⁵D₄ → ⁷F₃ (623 nm) transitions.⁷

Conclusions

To the best of our knowledge, we are the first to investigate lanthanide-based coordination polymers containing Hatza. Six new lanthanide-based complexes with Hatza ligands have been successfully constructed. The strong coordinate abilities of flexible acetic groups and nitrogens of the tetrazolate endow Hatza with abundant coordination modes, and three new coordination modes of the atza ligand have been observed in **1–6** [Scheme 1 (V–VII)]. It is worth noting that Eu(**4**), Gd(**5**), and Tb(**6**) whose structures are 1D chains do not solvate methanol, while Pr(**1**), Nd(**2**), and Sm(**3**) whose structures are 2D frameworks solvate methanol. With the comparison in mind, we assume that the solvent inclusion property is one of the important factors in the structural differences in this group of complexes. On the other hand, the amido group (–NH₂) of each atza ligand in complexes **1–6** forms a hydrogen bond with the neighboring tetrazolate-N or Cl[–] anion. These hydrogen bonding interactions are strong and can be regarded as a stabilizing factor for supramolecular assemblies. Furthermore, the complexes of Eu³⁺ (**4**) and Tb³⁺ (**6**) exhibit characteristic lanthanide-centered luminescence. Our research results indicate that, as a promising new type of multifunctional ligand, Hatza has a great potential in the field of coordination polymers, and further endeavors for exploration of Hatza complexes are underway in our workgroup.

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Supporting Information Available: Crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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