# Hydrothermal Syntheses, Structures and Luminescent Properties of Lanthanide-Zinc Coordination Polymers, $[Ln_2Zn(pzdc)_4(H_2O)_6 \cdot 2H_2O]_n$ (pzdc = pyrazine-2,3-dicarboxylate, Ln = Gd, Nd, Sm)

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The hydrothermal reactions of $Ln_2O_3$, $Zn(NO_3)_2 \cdot 6H_2O$, pyrazine-2,3-dicarboxylic acid ($H_2$pzdc) and $H_2O$ resulted in the formation of three isostructural coordination polymers $[Ln_2Zn(pzdc)_4(H_2O)_6 \cdot 2H_2O]_n$ (Ln = Gd, **1**; Nd, **2**; and Sm, **3**). The crystal structures of complexes **1** and **2** were determined by X-ray diffraction methods. Compounds **1**, **2** and **3** are isomorphous and crystallize in the monoclinic space group $P2_1/n$ with $a$ = 6.1196(2), $b$ = 22.5318(8), $c$ = 11.9617(1) Å, $\beta$ = 91.766(2), $V$ = 1648.56(8) Å$^3$, $Z$ = 2 for **1**, $a$ = 6.1644(3), $b$ = 22.6577(12), $c$ = 12.0384(6) Å, $\beta$ = 91.513(2), $V$ = 1680.8(2) Å$^3$, $Z$ = 2 for **2**. X-ray diffraction analyses confirm that complexes **1** and **2** possess a 3-D brick-like framework structure, each framework being surround by metal atoms, with a size of 16.37×6.12 Å, accommodating two water molecules as guests. The Ln(III) ions in compounds **1** to **3** are coordinated by seven oxygen and two nitrogen atoms. In addition, the zinc(II) ions are bonded by two carboxyl oxygen, two nitrogen and two apical carboxyl oxygen atoms in an octahedral geometry. The excitation spectrum and luminescent properties of **1** and **3** were studied qualitatively.

Recently, studies on the syntheses, structures and properties of lanthanide–transition metal complexes are of current great interest, not only because they possess abundant structures, but also because there are potential applications to magnetic materials,[1–5] La-doped semiconductor technology,[6] luminescent properties[7] and fiber optical materials[8] in recent rapidly developing fields. In these studies, organic ligands, for instance, carboxylic acid, Schiff bases, and pyridine betaine, were often selected to construct discrete, or infinite, structural complexes by conventional self-assembly reaction methods in solution.[1–5,9–12] However, the study of an aromatic dicarboxylate containing a nitrogen or sulfur hybrid atom as a ligand was not explored. We are currently interested in constructing lanthanide–transition metal–ligand frameworks by solvo-thermal reactions, and have found that rigid aromatic dicarboxylate ligands containing a nitrogen atom are excellent structural members around which to entrain infinite lattices.[13] Our goal is to construct some coordination polymers comprising rare earths and transition metals through a aromatic polycarboxylate ligand type linkage. During the course of study on this system by hydrothermal synthesis, we found that two factors are important concerning the formation of lanthanide-transition metal coordination polymers: (i) the reaction temperature and (ii) the starting material. Since the reaction speed could be controlled by the starting material and the reaction temperature, selecting an appropriate starting material and the reaction temperature are two key factors concerning the formation of a rare-earth and transition-metal coordination polymer. In this paper, we explore the syntheses, structures and properties of lanthanide heterometallic complexes containing d-block element zinc. When rare earth oxides, zinc(II) salt and dicarboxylic acid were used as the starting materials, unfortunately, uncharacterized polymers insoluble in most of the common solvents were obtained. In order to decrease the reaction speed and to grow single crystals suitable for x-ray analysis, rare earth oxide and zinc(II) were employed as the starting materials, and a series of novel lanthanide(III)-zinc(II) coordination polymers were prepared. Herein reported are three coordination polymers containing a pyrazine-2,3-dicarboxylate ligand, $[\{Ln_2Zn(pzdc)_4(H_2O)_6\} \cdot 2H_2O]_n$ (Ln = Gd, (**1**); Ln = Nd, (**2**); and Ln = Sm, (**3**), and luminescent properties for compounds **1** and **3**).

## Experimental

**Syntheses.** All of the chemicals were of reagent grade and used as commercially purchased without further purification.

**$[\{Gd_2Zn(pzdc)_4(H_2O)_6\} \cdot 2H_2O]_n$ (1).** Heating a mixture of $Gd_2O_3$ (0.09 g, 0.25 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.150 g, 0.5 mmol), pyrazine-2,3-dicarboxylic acid (0.168 g, 1 mmol), and $H_2O$ (14.0 mL, 777 mmol) in a 25 mL stainless-steel reactor with Teflon liner at 120 °C for 72 h resulted in colorless crystals of **1**. Yield: 60% based on the Gd. Calcd for $C_{24}H_{24}Gd_2N_8O_{24}Zn$ (1188.38): C, 24.26; H, 2.04; N, 9.43%. Found: C, 23.82; H, 2.12; N, 9.00%. IR (KBr) 3610 (m), 3246 (br, m), 1657 (vs), 1628 (s), 1591 (s), 1564 (s), 1389 (s), 1362 (s), 1171 (m), 1130 (m), 1119 (s), 901 (m), 850 (m), 841 (m), 785 (m), 750 (m), 550 cm$^{-1}$ (m).

**$[\{Nd_2Zn(pzdc)_4(H_2O)_6\} \cdot 2H_2O]_n$ (2).** A mixture of $Nd_2O_3$

(0.084 g, 0.25 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.150 g, 0.5 mmol), pyrazine-2,3-dicarboxylic acid (0.167 g, 1.0 mmol) and $H_2O$ (14.0 mL, 777 mmol) was sealed in a 25 mL stainless-steel reactor with a Teflon liner and heated directly at 120 °C from room temperature and at a constant temperature for 72 h, then slowly cooled to 35 °C in 48 h. Colorless crystals of **2** were obtained in a yield 65% based on the Nd. Calcd for $C_{24}H_{24}N_8Nd_2O_{24}Zn$ (1162.36): C, 24.80; H, 2.08; N, 9.64%. Found: C, 24.57; H, 2.14; N, 9.51%. IR (KBr pellet) 3611 (m), 3325 (br, m), 1653 (vs), 1632 (s), 1589 (vs), 1566 (s), 1389 (vs), 1362 (vs), 1171 (m), 1130 (m), 1119 (s), 901 (m), 850 (m), 839 (m), 785 (m), 750 (m), 552 cm$^{-1}$ (m).

**$[\{Sm_2Zn(pzdc)_4(H_2O)_6\}{\cdot}2H_2O]_n$ (3).** The same procedure as that for an analogous compound **2** was applied to the preparation of **3**, except for replacing $Nd_2O_3$ by $Sm_2O_3$. Yield: 75% based on the Sm. Calcd for $C_{24}H_{24}N_8O_{24}Sm_2Zn$ (1174.60): C, 24.54; H, 2.06; N, 9.54%. Found: C, 24.25; H, 2.01; N, 9.45%. IR (KBr): 3608 (m), 3246 (br, m), 1655 (vs), 1630 (s), 1589 (vs), 1564 (s), 1389 (vs), 1362 (vs), 1171 (m), 1130 (m), 1119 (s), 903 (m), 850 (m), 839 (m), 785 (m), 750 (m), 550 cm$^{-1}$ (m).

**Instrumentation.** Elemental analyses of C, H, and N were carried out by a chemical analysis group of this institute with a Perkin-Elmer model 240C automatic instrument. The IR spectra were recorded on a Magna750 FT-IR spectrophotometer using the KBr pellet technique. The excitation spectra and the luminescent properties of the compounds were measured on an AMIN CO. BOWMAN Series 2(AB2) Luminescent Spectrometer at 298 K.

**X-ray Structural Analyses of Complexes 1 and 2.** Each single crystal of complexes **1** and **2** was mounted on a glass fiber and coated with epoxy resin. The crystal data and data collection parameters to **1** and **2** are summarized in Table 1. Only the special features of the analysis are noted here. The intensity data of **1** and **2** were collected on a SIEMENS SMART CCD diffractometer with graphite-monochromated Mo $K\alpha(\lambda = 0.71073$ Å) radiation in the $\omega$–$2\theta$ scanning mode at room temperature. The data were corrected for Lorentz and polarization effects as well as absorption. The structure was solved by direct methods and the positions of the H atoms were generated geometrically (C–H bond fixed at 0.96 Å), assigned isotropic thermal parameters, and allowed to ride on their parent carbon atoms before the final cycle of the refinement. The weight atom was located from the E-map. Other non-hydrogen atoms were derived from successive difference Fourier syntheses. The structure was refined on $F^2$ by full-matrix least-squares methods using the SHELXTL-93 program package on a legend 586 computer. All non-hydrogen atoms were refined anisotropically. The atomic coordinates of the non-hydrogen atoms of compounds **1** and **2** are given out in supplementary materials. Selected bond lengths and angles of complexes **1** and **2** are given in Table 2. Crystallographic data, excluding structural factors for the structures reported in this paper, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-154851–154852. Copies of the data can be obtained free of charge by applying to CCDC, 12 Union Road, Cambridge CB1Ez, UK fax: (+44)1223-336-033; email: deposit@ccdc.cam.ac.uk. The data also were deposited as Document No. 75032 at the Office of the Editor of Bull. Chem. Soc. Jpn.

## Results and Discussion

Compounds **1**, **2** and **3** were obtained as colorless crystals in ca. 60–75% yield based on lanthanide oxide from the reaction of $Ln_2O_3$ (Ln = Gd, Nd, Sm), $Zn(NO_3)_2{\cdot}6H_2O$, and pyrazine-2,3-dicarboxylic acid ($H_2pzdc$) in the molar ratio of 1:2:4 at 120 °C in water. We found that the ratio of the starting materi-

Table 1. Summary of Crystal Data and Data Collection Parameters of **1** and **2**

| Compound | **1** | **2** |
|---|---|---|
| Formula | $C_{24}H_{24}Gd_2N_8O_{24}Zn$ | $C_{24}H_{24}N_8Nd_2O_{24}Zn$ |
| Formula weight | 1188.38 | 1162.36 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ |
| $a$/Å | 6.1196(2) | 6.1644(3) |
| $b$/Å | 22.5318(8) | 22.6577(12) |
| $c$/Å | 11.96170(10) | 12.0384(6) |
| $\beta$/° | 91.766(2) | 91.513(2) |
| $V$/Å$^3$ | 1648.56(8) | 1680.8(2) |
| $Z$ | 2 | 2 |
| $D_c$/g cm$^{-3}$ | 2.394 | 2.297 |
| $\mu$/cm$^{-1}$ | 4.815 | 3.886 |
| $F(000)$ | 1148 | 1132 |
| Crystal dimensions/mm$^3$ | 0.30×0.10×0.07 | 0.18×0.04×0.04 |
| Scan mode | $\omega$ | $\omega$ |
| Scan range $2\theta$/° | 3.62 to 50.14 | 3.60 to 50.02 |
| Reflections measured | 5991 | 6530 |
| Independent reflections | 2914 ($R_{int}$ = 0.0705) | 2949 ($R_{int}$ = 0.0697) |
| Observed reflections ($I > 2\sigma(I)$) | 2910 | 2944 |
| Parameters | 268 | 268 |
| S | 1.048 | 1.039 |
| $\Delta\rho_{min}$ and $\Delta\rho_{max}$/e Å$^3$ | −1.432 and 2.190 | −0.769 and 0.850 |
| R($I > 2\sigma(I)$) | 0.0496 | 0.0448 |
| R$_W$($I > 2\sigma(I)$) | 0.0970 | 0.0767 |

Table 2. Selected Bond Lengthes (Å) and Bond Angles (°) of Complex **1** and **2**

| | | | |
|---|---|---|---|
| | **1** | | |
| Gd–O(21) | 2.328(8) | Gd–O(1) | 2.556(8) |
| Gd–O(11) | 2.343(8) | Gd–N(2D) | 2.714(9) |
| Gd–O(13D) | 2.392(7) | Gd–N(1) | 2.801(9) |
| Gd–O(2) | 2.394(8) | Zn–N(4) | 2.062(9) |
| Gd–O(3) | 2.416(8) | Zn–O(24) | 2.080(8) |
| Gd–O(14E) | 2.459(8) | Zn–O(22B) | 2.220(8) |
| O(21)–Gd–O(11) | 77.3(3) | O(13D)–Gd–N(2D) | 63.5(3) |
| O(21)–Gd–O(13D) | 79.6(3) | O(2)–Gd–N(2D) | 146.9(3) |
| O(11)–Gd–O(13D) | 75.5(3) | O(3)–Gd–N(2D) | 72.6(3) |
| O(21)–Gd–O(2) | 80.6(3) | O(14E)–Gd–N(2D) | 72.2(3) |
| O(11)–Gd–O(2) | 131.5(3) | O(1)–Gd–N(2D) | 118.4(3) |
| O(13D)–Gd–O(2) | 140.9(3) | O(21)–Gd–N(1) | 76.5(3) |
| O(21)–Gd–O(3) | 133.3(3) | O(11)–Gd–N(1) | 60.9(3) |
| O(11)–Gd–O(3) | 137.9(3) | O(13D)–Gd–N(1) | 133.7(3) |
| O(13D)–Gd–O(3) | 82.5(3) | O(2)–Gd–N(1) | 72.2(3) |
| O(2)–Gd–O(3) | 87.2(3) | O(3)–Gd–N(1) | 141.0(3) |
| O(21)–Gd–O(14E) | 145.5(3) | vO(14E)–Gd–N(1) | 72.1(2) |
| O(11)–Gd–O(14E) | 99.1(3) | O(1)–Gd–N(1) | 133.7(3) |
| O(13D)–Gd–O(14E) | 133.4(3) | N(2D)–Gd–N(1) | 107.5(3) |
| O(2)–Gd–O(14E) | 76.5(3) | N(4)–Zn–N(4A) | 180.000(3) |
| O(3)–Gd–O(14E) | 71.1(3) | N(4)–Zn–O(24) | 79.8(3) |
| O(21)–Gd–O(1) | 68.4(3) | N(4A)–Zn–O(24) | 100.2(3) |
| O(11)–Gd–O(1) | 133.6(3) | O(24A)–Zn–O(24) | 180.000(1) |
| O(13D)–Gd–O(1) | 68.4(3) | N(4)–Zn–O(22B) | 96.6(3) |
| O(2)–Gd–O(1) | 73.1(3) | O(24)–Zn–O(22B) | 101.3(3) |
| O(3)–Gd–O(1) | 64.9(3) | N(4)–Zn–O(22C) | 83.4(3) |
| O(14E)–Gd–O(1) | 126.8(3) | O(24)–Zn–O(22C) | 78.7(3) |
| O(21)–Gd–N(2D) | 132.3(3) | O(22B)–Zn–O(22C) | 180.000(2) |
| O(11)–Gd–N(2D) | 65.5(3) | | |
| | **2** | | |
| Nd–O(21) | 2.392(6) | Nd–O(1) | 2.578(5) |
| Nd–O(11) | 2.396(6) | Nd–N(2D) | 2.769(6) |
| Nd–O(13D) | 2.444(5) | Nd–N(1) | 2.817(7) |
| Nd–O(2) | 2.467(5) | Zn–N(4) | 2.062(6) |
| Nd–O(3) | 2.475(6) | Zn–O(24) | 2.092(5) |
| Nd–O(14E) | 2.504(5) | Zn–O(22B) | 2.222(6) |
| O(21)–Nd–O(11) | 76.9(2) | O(21)–Nd–O(2) | 80.6(2) |
| O(21)–Nd–O(13D) | 80.6(2) | O(11)–Nd–O(2) | 131.4(2) |
| O(11)–Nd–O(13D) | 75.4(2) | O(13D)–Nd–O(2) | 141.5(2) |
| O(21)–Nd–O(3) | 133.5(2) | O(14E)–Nd–N(2D) | 72.3(2) |
| O(11)–Nd–O(3) | 137.9(2) | O(1)–Nd–N(2D) | 118.7(2) |
| O(13D)–Nd–O(3) | 81.8(2) | O(21)–Nd–N(1) | 76.4(2) |
| O(2)–Nd–O(3) | 87.4(2) | O(11)–Nd–N(1) | 60.8(2) |
| O(21)–Nd–O(14E) | 145.7(2) | O(13D)–Nd–N(1) | 133.9(2) |
| O(11)–Nd–O(14E) | 99.2(2) | O(2)–Nd–N(1) | 72.3(2) |
| O(13D)–Nd–O(14E) | 132.1(2) | O(3)–Nd–N(1) | 141.2(2) |
| O(2)–Nd–O(14E) | 76.9(2) | O(14E)–Nd–N(1) | 72.2(2) |
| O(3)–Nd–O(14E) | 71.1(2) | O(1)–Nd–N(1) | 133.4(2) |
| O(21)–Nd–O(1) | 68.3(2) | N(2D)–Nd–N(1) | 107.3(2) |
| O(11)–Nd–O(1) | 133.3(2) | N(4A)–Zn–N(4) | 180.0 |
| O(13D)–Nd–O(1) | 69.2(2) | N(4)–Zn–O(24A) | 100.5(2) |
| O(2)–Nd–O(1) | 72.7(2) | N(4)–Zn–O(24) | 79.5(2) |
| O(3)–Nd–O(1) | 65.2(2) | O(24A)–Zn–O(24) | 180.0 |
| O(14E)–Nd–O(1) | 127.0(2) | N(4)–Zn–O(22B) | 95.4(2) |
| O(21)–Nd–N(2D) | 131.7(2) | O(24)–Zn–O(22B) | 100.9(2) |
| O(11)–Nd–N(2D) | 65.3(2) | N(4)–Zn–O(22C) | 84.6(2) |
| O(13D)–Nd–N(2D) | 62.2(2) | O(24)–Zn–O(22C) | 79.1(2) |
| O(2)–Nd–N(2D) | 147.4(2) | O(22B)–Zn–O(22C) | 180.0 |
| O(3)–Nd–N(2D) | 72.8(2) | | |

Symmetry modes: A $-x+2$, $-y$, $-z+2$, B $-x+1$, $-y$, $-z+2$, D $x-1/2$, $-y+1/2$, $z+1/2$, E $x+1/2$, $-y+1/2$, $z+1/2$.

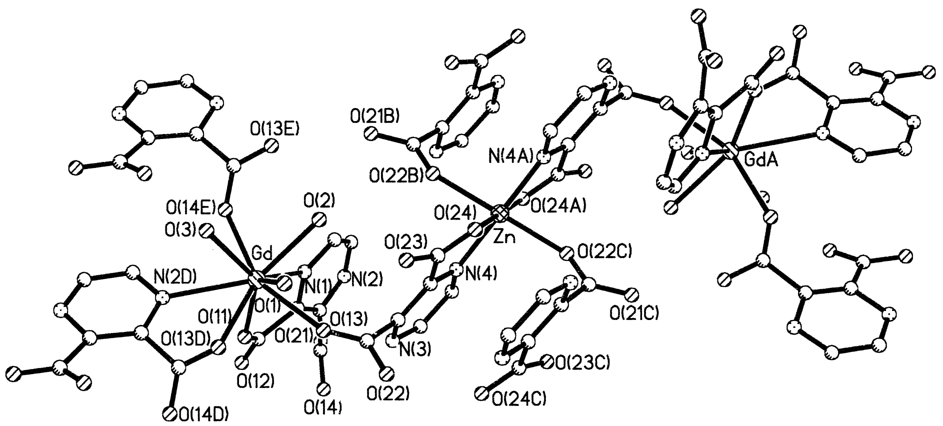
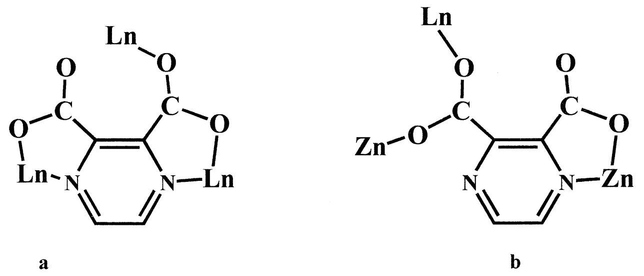


Fig. 1. A view of the basic unit structure of **1**.

als, Ln:Zn of 1:2, led to the formation of a product having a ratio of Ln:Zn = 2:1 In contrast, the 2:1 ratio of Ln and Zn in the starting materials could not give the title complex, but only some white deposition that could not be characterized by an X-ray single-crystal diffraction analysis. We also tried to use different reaction ratio of Ln and Zn (Ln:Zn is 2–1); some microcrystals that were not suitable for an X-ray single-crystal analysis are obtained. This situation may be attributed to the complexity of the hydrothermal reaction.

**Crystal Structures.** A crystallographic analysis of **1** exhibited a 3D structure constructed from the Gd$_2$Zn(pzdc)$_4$(H$_2$O)$_6$ basic unit, as shown in Fig. 1. Each Zn center is coordinated by two nitrogen and two oxygen atoms from two pzdc ligands to form a five-membered chelating ring, and further coordinated by two apical oxygen atoms from the carboxylate group of two different pzdc ligands to form an octahedral geometry. The Zn–N bond length is 2.062(9) Å, whereas the Zn–O22 and Zn–O24 bond distances are 2.220(8) and 2.080(8) Å, respectively. The bond angles of O22B–Zn–O22C, O24–Zn–O24A and N4–Zn–N4A are 180°. The bond angles of O(O22,O24)–Zn–N4 and O22–Zn–O24 are in the range of 83.4(3)–100.2(3)° and 78.7(3)–101.3(3)°, respectively. Each gadolinium(III) atom is coordinated by two nitrogen and four oxygen atoms from four pzdc ligands and three oxygen atoms from coordinated water molecules. The Gd–O bonds range from 2.328(8) to 2.556(8) Å, while the Gd–N1 and Gd–N2 bond lengths are 2.714(9) and 2.801(9) Å, respectively. The ranges of the O–Gd–O and O–Gd–N angles are from 64.9(3) to 140.9(3)° and from 60.9(3) to 146.9(3)°, respectively. In this complex, the carboxylate group and the pyrazine ring of the pzdc ligand are not coplanar. The dihedral angles between plane I (pyrazine ring containing N1 and N2) or the carboxylate plane containing O13 and O14, and the carboxylate plane containing O11 and O12 is 41.2° and 20.0°, respectively. The dihedral angles between the carboxylate plane containing O21 and O22 and plane II (pyrazine ring containing N3 and N4), and the carboxylate plane containing O23 and O24) and plane II are 97.4° and 13.4°, respectively. The N3 atom of pzdc ligand was not bonded to metal ion. Two coordination modes of pzdc ligands are present in 1, as shown in Scheme 1.



Scheme 1. The coordination modes of pzdc ligands in **1**, **2** and **3** (Ln = Gd, Nd, Sm).

The above-mentioned basic units were extended further through a multifunctional group of the pzdc ligand to entrain a zigzag-type Gd$_4$Zn$_2$(pzdc)$_8$(H$_2$O)$_{12}$ chain, and the adjacent Gd(III) were linked through the pzdc ligand by choosing the Scheme 1a coordination mode. Gd(III) has two different types of pzdc ligands in the coordination mode. One is the chelated coordination mode, using the nitrogen (N1, N2) and oxygen (O11, O13) atoms of pzdc ligand. This mode makes the basic units linking into a 2D structure, as shown in Fig. 2. Another involves a mono-dentated oxygen (O14) atom from the pzdc ligand, that makes a 2D structure extending further into a 3D brick-like structure (Fig. 3). In Fig. 3, each brick-like framework with a size of 16.37×6.12 Å (the distances between the metal centers) accommodates two water molecules as guest. The 3D structure can also be viewed as two building-block [Gd$_2$(pzdc)$_4$(H$_2$O)] and [Zn(pzdc)$_2$] units, connected by an oxygen atom of the carboxylate group of the pzdc ligand. The former is connected with each other to form a zigzag Gd(III) chain (see Fig. 3) through sharing a pzdc ligand which adopts the chelated coordination mode of Scheme 1a, and further extended to a 2D structure by a Gd–O14 bond linkage. Each gadolinium(III) acts as a turning point that is connected a neighboring building block by a pzdc ligand. The adjacent Gd(III) chain was linked together through a [Zn(pzdc)$_2$] unit to form an extended brick-like packing structure. In the [{Gd$_2$Zn(pzdc)$_4$(H$_2$O)$_6$}·2H$_2$O]$_n$ complex, each gadolinium(III) atom is connected to three gadolinium atoms and one zinc(II) atoms, while each zinc(II) is connected to two Gd(III) atoms both via a pzdc ligand with Gd···Gd distances in the range of 6.120–6.867 Å and Gd···Zn distances of 6.706 Å, respectively.

The crystal structure of **2** is isomophous to that of **1**. Since the radius of the Nd(III) ion is slightly bigger than that of the Gd(III) ion, all of the metal–ligand bonds and ligand–metal–

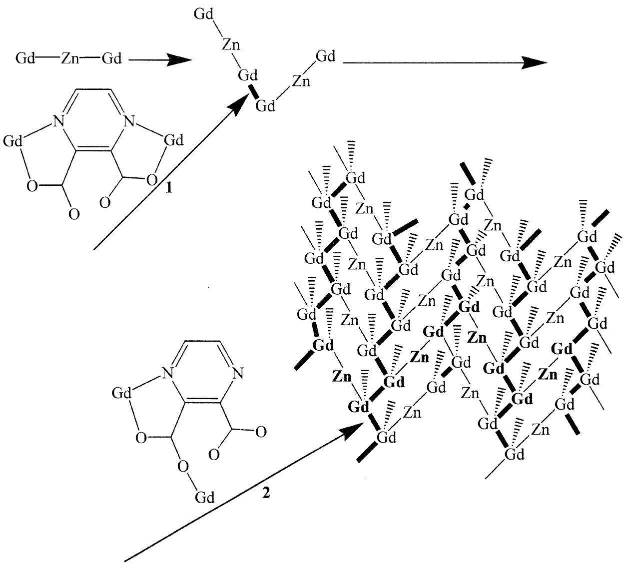


Fig. 2. The schematic diagram of **1** (omitted ligand atoms). Arrowhead **1** represent coordination mode of adjacent Gd atoms (linked by ▬ line in figure); arrowhead **2** represent coordination mode of Gd atom that linked another Gd atom from another layer along vertical paper direction (·ııılll in figure). Gothic atoms represent the arrangement of basic unit in whole 3D structure.

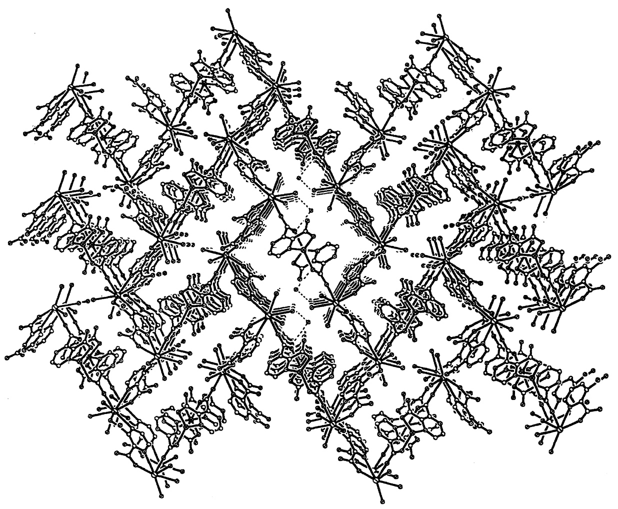


Fig. 3. The 3D packing structure of **1** with 16.37 × 6.12 Å cavity.

ligand angles in **2** are slightly longer and wider, respectively, than the corresponding ones in **1**. For **3**, the unit-cell parameters, elemental analytical data and IR spectra showed that its structure is also isomophous to that of **1**.

**Luminescent Properties for Compounds 1 and 3.** The luminescent properties of solid-state powder sample for **1** and **3** were qualitatively studied at 298 K. Compound **1** exhibits green photoluminescence upon photoexcitation at 362 nm. The excitation spectrum of a solid sample of **1** displays one broad band at 362 nm, that is attributed to the $\pi\pi^*$ state of the ligand. The emission of **1** at $\lambda = 497$ and 524 nm may be assigned as ligand-centred luminescence. This situation is similar to that given in a report.[14] The excitation spectrum of a solid sample of **3** displays one broad and structured band with components at 324 nm, 342 nm, 344 nm, 346 and 375 nm, assigned to the $\pi\pi^*$ state of the pzdc ligand; 403, 418, 441, 453, 464 and 479 nm belong to the characteristic band of the Sm(III) ion. Compound **3** in the solid state displays an intense red photoluminescence with emission at 562, 597 and 644 nm, upon excitation at 345 nm. These emission bands were attributed to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions of the Sm(III)-centred luminescence, respectively.[15] At the same time, the luminescent properties of the ligand center could also be observed at 396, 427 and 494 nm from emission spectra, but its intensity greatly decreased. This is due to the strong luminescent properties of the Sm(III) ion that may cover ligand-centered weak luminescence. Under various excitation conditions, the luminescent behavior of complex **3** can also be observed. However, complex **2** only displays a very weak luminescence behavior, and further it is difficult to observe emission under different conditions. The excitation, and emission spectra of **1** and **3** are shown in Figs. 4(a), (b) and Figs. 5(a), (b), respectively.

In conclusion, we have explored the luminescent properties of Ln–Zn (Ln = Gd, Nd, Sm) complexes containing the pzdc ligand. Upon the addition of lanthanide ions, the luminescent

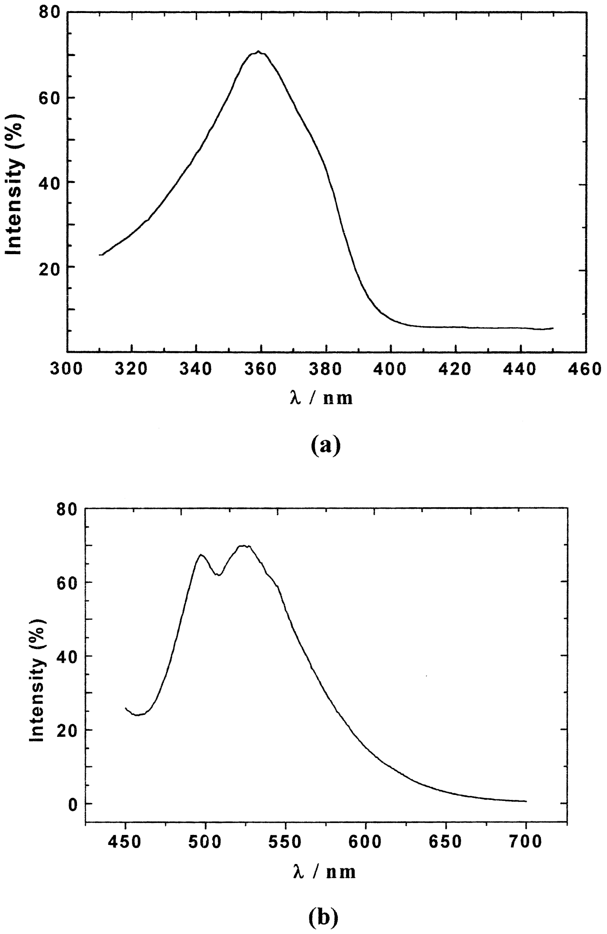


Fig. 4. (a) The excitation spectrum of **1**; (b) The emission spectrum of **1** with 362 nm excitation light

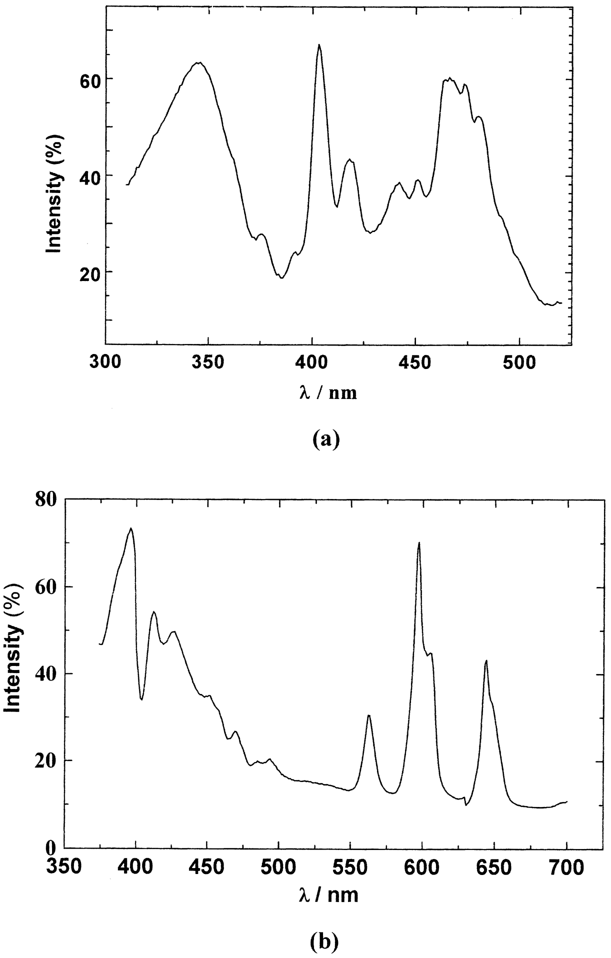


Fig. 5. (a) The excitation spectrum of **3**; (b) The emission spectrum of **3** with 345 nm excitation light.

property of the pzdc ligand is affected. For further work, we plan to study Ln–Zn (Ln = Eu, Tb) complexes containing the pzdc ligand and to discuss their luminescent behavior.

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