

# Two Novel Coordination Polymers $[\text{Sm}_2(\text{Pzdc})_3(\text{H}_2\text{O})]_x \cdot 2x\text{H}_2\text{O}$ and $[\text{Nd}_2(\text{Pzdc})_3(\text{H}_2\text{O})]_x \cdot 2x\text{H}_2\text{O}$ : Synthesis, Structure, and Photoluminescent Properties<sup>1</sup>

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**Abstract**—Coordination polymers,  $[\text{Sm}_2(\text{Pzdc})_3(\text{H}_2\text{O})]_x \cdot 2x\text{H}_2\text{O}$  (I) and  $[\text{Nd}_2(\text{Pzdc})_3(\text{H}_2\text{O})]_x \cdot 2x\text{H}_2\text{O}$  (II), were obtained by hydrothermal reactions with 2,3-pyrazinedicarboxylic acid ( $\text{H}_2\text{Pzdc}$ ) and the salts nitrates, and characterized by single crystal X-ray structure, thermogravimetric analysis, element analysis and infrared spectroscopy. The X-ray crystal diffraction data indicates that two complexes crystal in a monoclinic system with the space group  $P2_1/c$ , of the three dimensional framework. The Pzdc ligand in the complexes I and II adopts tetradentate, hexadentate, and heptadentate bridging modes. The influences of coordination modes of the Pzdc ligand on the superstructural diversity is discussed. The photoluminescent data suggest that the ligands act as efficient “antennas” sensitizing the luminescence of the  $\text{Sm}^{3+}$  ion. Complex I exhibits strong fluorescent emission bands in the solid state at room temperature.

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## INTRODUCTION

Lanthanide complexes containing carboxylate ligands are the most largely investigated kinds of coordination compounds due to the higher thermal and luminescent stabilities, which make them potential candidates for organic electroluminescent devices applications and as fluoroimmunoassay agents [1, 2]. Since the emission mechanism of trivalent lanthanide ions ( $\text{Ln}^{3+}$ ) is based on “antenna effect”, aromatic carboxylate coordinated ligands act as sensitizers, absorbing, and transferring energy efficiently to the excited levels of the  $\text{Ln}^{3+}$  ion. Additionally, carboxylate group may present various coordination modes, leading to the formation of mononuclear, dinuclear, polymeric or network compounds [3]. The understandings of the structural and chemical factors that control the supramolecular chemistry of the carboxylate compounds are important for several areas, such as optoelectronic, magnetism, and catalysis [4].

Pyrazine is well known to act as a bridging ligand [5–7], especially in the design and construction of coordination polymers. This system is particularly informative, since the use of a relatively simple bridging ligand (pyrazine) permits a study of the mechanism of magnetic coupling over extended distances. It allows electron coupling between the metals to occur via orbital overlap with the ligand orbital. Several linear chain

complexes bridged with pyrazine and its derivatives have been prepared, which exhibit ferromagnetic coupling [8–12], carboxylates have been considered as a good bridging ligand. For example, they form binuclear or polynuclear complexes with transition metal ions, such as  $\text{Cu}(\text{II})$  [13],  $\text{Co}(\text{II})$  [14],  $\text{Ni}(\text{II})$  [15, 16],  $\text{Mn}(\text{II})$  [17], and  $\text{Fe}(\text{II})$  [18], by bonding to two metal ions with each of two oxygen atoms forming a bridge of three atoms or even by pyrazine bonding to two metal ions with a single oxygen atom forming a bridge of a one atom. Generally, in those systems carboxylate groups are coordinated in a monodentate fashion, giving mononuclear compounds with moderately simple structures. However, due to the difference in some properties for  $\text{Ln}^{3+}$  ions, as compared with divalent transition metal ions, such as the higher electrostatic ligand–metal ion interaction and the higher and variable coordination number, a significantly different compound with more complicated features is expected. Therefore, 2,3-pyrazinedicarboxylic acid ( $\text{H}_2\text{Pzdc}$ ) [19] could be a good bridging ligand to build polymeric coordination compounds [20, 21].

In this paper, we report the reaction of  $\text{H}_2\text{Pzdc}$  with samarium(III) and neodymium(III) salts, two new three-dimensional polymeric complexes of novel structure, and the systematic investigation of the structural properties of the compound containing  $\text{H}_2\text{Pzdc}$ .

<sup>1</sup> The article is published in the original.

## EXPERIMENTAL

All reagents and solvents were purchased from commercial sources and were used as received without further purification.

### Synthesis of Complex **I**

$\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (0.082 g, 0.2 mmol),  $\text{H}_2\text{Pzdc}$  (0.067 g, 0.4 mmol) and  $\text{H}_2\text{O}$  (15 ml) in a molar ratio of 1 : 2 were loaded into a 25 cm<sup>3</sup> teflon-lined stainless-steel vessel, which was then sealed and placed in a programmable furnace. The resulting mixture was heated at 160°C for 4 days, followed by slow cooling at the speed 10°C/h to room temperature. Brilliant- yellow prisms single crystal of title complex was obtained.

For  $\text{C}_{18}\text{H}_{12}\text{N}_6\text{O}_{15}\text{Sm}_2$

anal. calcd, %: C, 25.34; H, 1.42; N, 9.85.

Found, %: C, 25.30; H, 1.46; N, 9.82.

IR spectrum (KBr;  $\nu$ , cm<sup>-1</sup>): 3486 m, 1627 s, 1561 s, 1449 s, 1368 s, 1122 s, 898 m, 845 m, 838 m, 449 m.

### Synthesis of Complex **II**

The synthetic procedure is similar to that for compound **I**, using  $\text{NdCl}_3 \cdot \text{H}_2\text{O}$  instead of  $\text{Sm}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ . Purple prisms single crystal of **2** was obtained.

For  $\text{C}_{18}\text{H}_{12}\text{N}_6\text{O}_{15}\text{Nd}_2$

anal. calcd, %: C, 25.71; H, 1.44; N, 10.00.

Found, %: C, 25.67; H, 1.48; N, 9.96.

IR spectrum (KBr;  $\nu$ , cm<sup>-1</sup>): 3492 m, 1621 s, 1558 s, 1448 s, 1366 s, 1120 s, 891 m, 837 m, 445 m.

### Physical Measurements

The C, H, and N analyses were taken with a Perkin Elmer model 2400 element analyzer. Fluorescence

measurements were made on a Hitachi F-4500 spectrophotometer. IR spectra were recorded on an EQUINOX 55 IR spectrophotometer by using KBr pellets. The thermal stability of **I** and **II** was measured by TG-DTG under a N<sub>2</sub> atmosphere and using heating rate of 10°C/min.

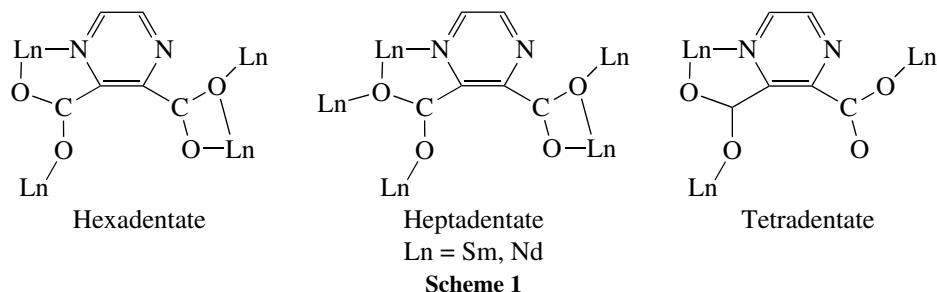
The fluorescence properties of the free ligand  $\text{H}_2\text{Pzdc}$  and complex **I** (the solid state) were investigated on a Fluorescence spectrophotometer F-4500 at room temperature. The excitation wavelength is 300 nm.

### Structure X-ray Determination

Crystal of the title compound of a suitable size were mounted on glass fibers. Intensity data were collected on a Bruker Smart-1000 CCD X-ray single crystal diffractometer with graphite-monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073$  Å) and in the  $\omega$  scan mode. The structure was solved by direct methods with SHELXS-97 and refined by full-matrix least-squares method on  $F^2$  values calculations with SHELXL-97 [22, 23]. All the non-hydrogen atoms in complexes **I** and **II** were refined anisotropically. Most of the hydrogen atoms in complexes were located in calculated positions or found from difference fourier maps. Crystallographic data for two complexes is listed in Table 1. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 661646, 661645; deposit@ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

The two coordination polymers **I** and **II** are isomorphous. Only the structure of **I** will be described in detail. The X-ray study reveals that the crystal of **I** is in the monoclinic system with space group  $P2_1/c$ . The asymmetric unit of complex consists of two  $\text{Sm}^{3+}$  ions, three Pzdc groups, one coordinated water and two lattice water molecules (Fig. 1). The most important feature of this complex is that the  $\text{Pzdc}^{2-}$  ions are coordinated to the  $\text{Sm}^{3+}$  ion by three different ways:



The carboxylate groups belonging to  $\text{Pzdc}^{2-}$  are coordinated to the  $\text{Sm}^{3+}$  ion in the bidentate bridging,  $\mu_2$ -bridging, and chelating fashion. The three pyrazine rings are orientated differently in the crystal. The dihe-

dral angles between the pyrazine rings are 70.8°, 76.3°, and 14.4°, owing to the steric effects in the formation of samarium coordination polymers. Although Sm(1) and Sm(2) are both nine-coordinated, the coordination

environments around them are different. The hexadentate Pzdc ligand coordinates to Sm(2) in a bidentate chelating mode through the nitrogen atom N(3) of the pyrazinyl group and the oxygen atom O(6) of the adjacent carboxylate group, and the tetradentate Pzdc ligand coordinates to Sm(2) in a bidentate chelating mode through N(5) of the pyrazinyl group and the oxygen atom O(10) of an adjacent carboxylate group.

In addition, Sm(2) is coordinated by two oxygen atoms (O(12E) and O(13D)) from the  $\mu_2, \eta^3$ -carboxylate group of the hexadentate Pzdc ligand, one oxygen atom (O(9C)) from the carboxylate group of the tetradentate ligand, one oxygen atom (O(2A)) from the  $\mu_2, \eta^2$ -carboxylate group of the heptadentate Pzdc ligand, and one oxygen atom (O(4B)) from the  $\mu_2, \eta^3$ -carboxylate group of another heptadentate Pzdc ligand. Compared with Sm(2), there is only one heptadentate Pzdc ligand that is coordinated to Sm(1) through one nitrogen (N(2)) of pyrazinyl group and one carboxylate oxygen atom (O(1)). Sm(1) is also coordinated by two oxygen atoms (O(3B) and O(4B)) of the carboxylate group from the heptadentate Pzdc ligand, four oxygen atoms (O(1A), O(7C), O(11D), and O(12E)) from the carboxylate groups of two hexadentate, one tetradentate, and another heptadentate Pzdc ligands. The oxygen atom (O(5)) from a water molecule coordinates to Sm(1) to complete a coordination number of nine. Altogether, there are six Pzdc ligands bound to each  $\text{Sm}^{3+}$  ion. Sm(2) is coordinated to two tetradentate, two hexadentate, and two heptadentate Pzdc ligands, while Sm(1) is coordinated to two hexadentate, one tetradentate, and three heptadentate Pzdc ligands, as well as a water molecule. However, their modes of coordination differ as mentioned above. Thus, two central ions are connected by two bidentate bridging carboxyl oxygens and two  $\mu_2, \eta^3$ -bridging carboxyl oxygens. The coordination polyhedron of Sm(III) can be described as a distorted monocapped square antiprism. These polyhedra are connected to each other through the O(4B) and O(12E) atoms belonging to the Pzdc ligand. Selected bond lengths and angles are given in Tables 2 and 3 (the mean bond length of Sm–O and Sm–N 2.630 Å can be seen). Due to the oxophilic character of lanthanide, the bond length of Sm–O is shorter than that of Sm–N.

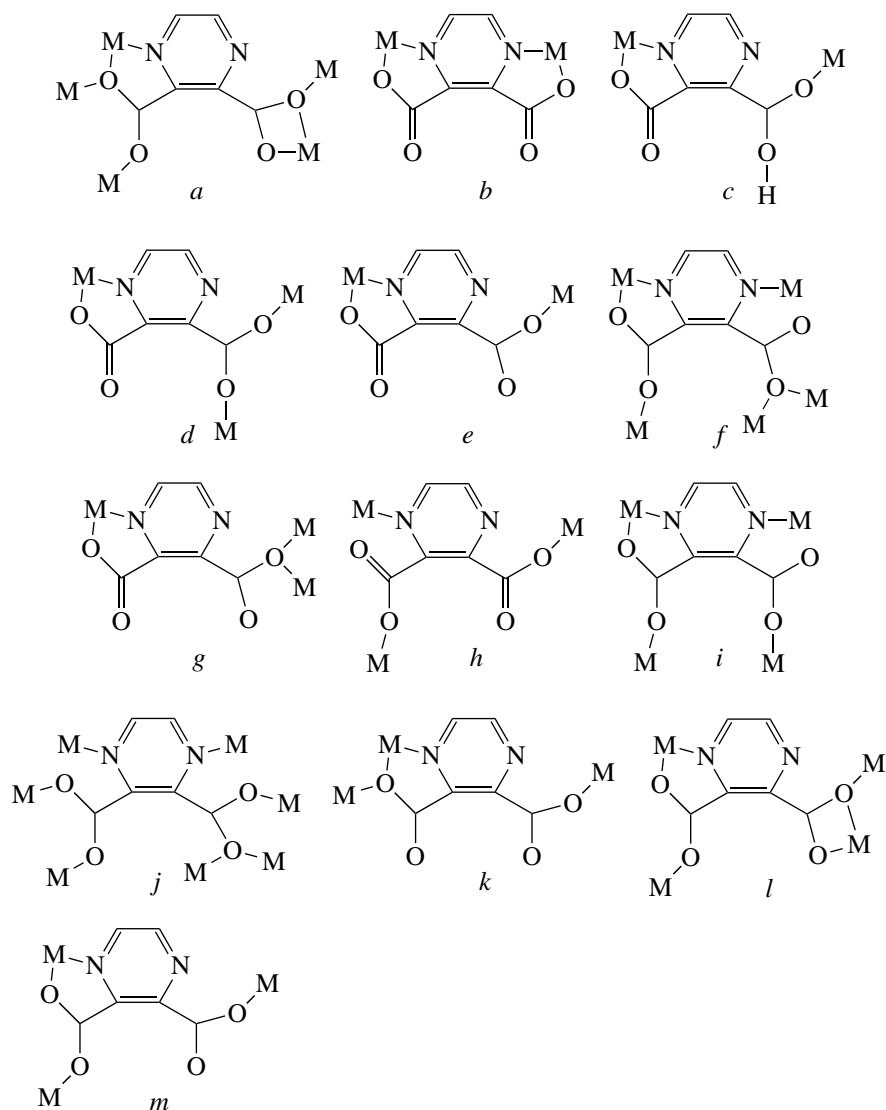
The framework structure of title complex **I** constructs from the  $[\text{Sm}_2(\text{Pzdc})_3\text{H}_2\text{O}]$  unit. Firstly, two hexadentate and two heptadentate Pzdc ligands link two disamarium building units to form a parallelogram, the four vertices of which are occupied by four  $\text{Sm}^{3+}$  ions (Fig. 2). The two heptadentate Pzdc ligands are located above and below the plane of the parallelogram and link the four  $\text{Sm}^{3+}$  ions, resulting in a “cage-like” motif. The distances between Sm(1) and Sm(2), and Sm(1) and Sm(2B) are 4.08 and 6.04 Å, respectively, and that between Sm(2) and Sm(2B) is 4.22 Å. Four tetradentate Pzdc ligands then link each parallelogram with four adjacent parallelograms, which are orientated in a different manner.

**Table 1.** Crystallographic data and details of the experiment and refinement of structures **I**

Parameter	Value	
	I	II
Formula weight	853.039	835.8515
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
$a$ , Å	8.8538(13)	8.8893(14)
$b$ , Å	16.802(2)	16.853(3)
$c$ , Å	15.328(2)	15.393(2)
$\alpha$ , deg	90.00	90.00
$\beta$ , deg	100.877(2)	101.108(3)
$\gamma$ , deg	90.00	90.00
$V$	2239.3(6)	2262.9(6)
$Z$	4	4
$\rho_{\text{calcd}}$ , g cm $^{-3}$	2.512	2.554
$T$ , K	296(2)	296(2)
Dimension, mm	$0.38 \times 0.21 \times 0.13$	$0.30 \times 0.20 \times 0.13$
$\mu$ , mm $^{-1}$	5.290	4.754
$F(000)$	1600	1652
$\theta$ scan range for collection, deg	2.42–27.57	1.81–25.10
Index ranges	$-10 \leq h \leq 10$ , $-18 \leq k \leq 20$ , $-18 \leq l \leq 18$	$-10 \leq h \leq 10$ , $-20 \leq k \leq 19$ , $-14 \leq l \leq 18$
$R_{\text{int}}$	0.0282	0.0401
Number of unique data	3980	4032
Number of observed data	3419	3320
Number of variable parameters	370	370
$R^*$	0.0216	0.0268
$wR$	0.0539	0.0637
Goodness-of-fit on $F^2$	1.096	1.038
Residual electronic density (max/min), e Å $^{-3}$	1.093/–0.840	0.997/–1.165

$$* R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma (F_o^2)^2]^{1/2}.$$

The observed coordination modes of the six donor atoms of the Pzdc ligand (**a–m**) are schematically represented in below:



Scheme 2

Usually, there are 13 kinds of coordination mode of the six donor atoms of the Pzdc ligand in the known complexes. In  $[\text{MPzdc}(\text{H}_2\text{O})_2]_x \cdot 2x\text{H}_2\text{O}$  ( $\text{M} = \text{Fe}$  [24],  $\text{Mn}$  [25]) and  $[\text{Zn}(\text{Pzdc}) \cdot 3\text{H}_2\text{O}]_x$  [18], the Pzdc ligands chelate to a metal ion in one chain and bridge two metal ions in the second chain by O–C–O links of a second carboxylate group of the same Pzdc ligand, as shown in Scheme 2 (b). While in  $[\text{M}(\text{Pzdc})(\text{H}_2\text{O})_3]_x \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Zn}$  [26],  $\text{Cd}$  [27]), the Pzdc ligand links one metal ion forming a chelate and bridges of another metal ion with the second carboxylate group in a monodentate fashion, as depicted in Scheme 2 (c). In  $[\text{NH}_4]_x[\text{Ag}(\text{Pzdc})]_x$  [28], besides one  $\text{Ag}^+$  ion coordinated by one nitrogen atom of 1,4-diazine, two carboxylate groups of Pzdc coordinate to one  $\text{Ag}^+$  ion in a monodentate fashion. Generally speaking, in the above reported d-block transition metal complexes, the Pzdc ligand adopts only one bridging mode in each complex. While in the title complex **I**, Pzdc adopts three bridging modes, and its bridging

mode is much more complicated than those in the d-block transition metal complexes (Scheme 1). This can be attributed to the larger radii and greater positive charge of the  $\text{Ln}^{3+}$  ions and hence the large coordination number and different coordination modes required by the samarium ions. The type of crystal structure and the coordination model in 2,3-Pzdc complexes are schematically represented in Table 4.

In addition, there are abundant hydrogen bonds in the molecule. Two types of hydrogen bonds exist in the crystal: intramolecular and intermolecular. A hydrogen bond forms between the lattice water molecules, and another one forms between the coordinated water molecule and the lattice water molecule. The structure also shows that all coordinated and noncoordinated water molecules have extensive hydrogen bonds. The donor–acceptor bond angles and distances are listed in Table 5. These hydrogen bonds stabilize the crystal. The shortest interatomic distance in the coordination polyhedra

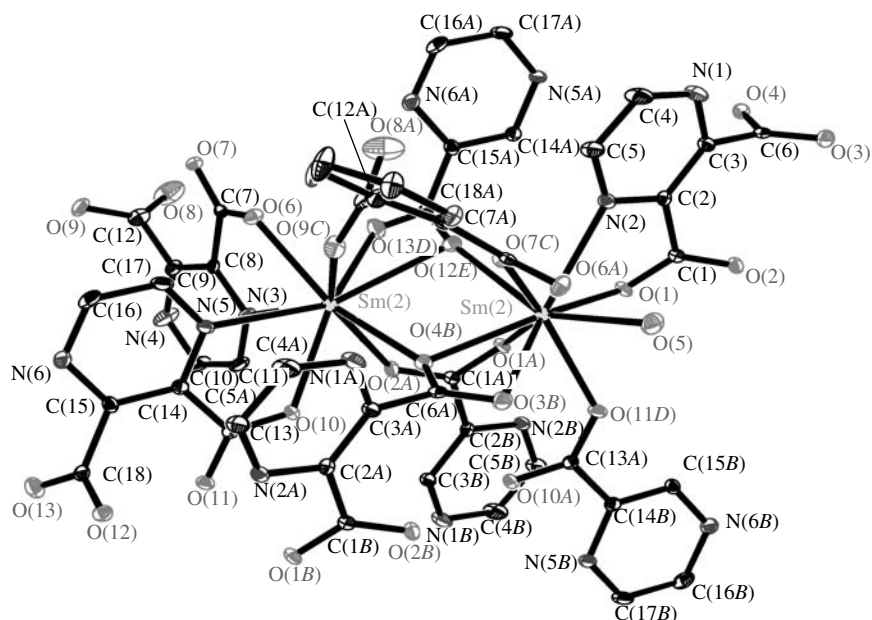


Fig. 1. The coordination environment of the samarium atom

Table 2. Selected bond lengths for I\*

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Sm(1)–O(7) <sup>#1</sup>	2.366(3)	Sm(1)–O(11) <sup>#2</sup>	2.408(3)	Sm(1)–O(5)	2.429(3)
Sm(1)–O(12) <sup>#3</sup>	2.446(3)	Sm(1)–O(1)	2.472(3)	Sm(1)–O(4) <sup>#4</sup>	2.479(3)
Sm(1)–O(1) <sup>#5</sup>	2.573(3)	Sm(1)–N(2)	2.669(4)	Sm(1)–O(3) <sup>#4</sup>	2.679(3)
Sm(2)–O(9) <sup>#1</sup>	2.307(3)	Sm(2)–O(4) <sup>#4</sup>	2.427(3)	Sm(2)–O(10)	2.427(3)
Sm(2)–O(6)	2.438(3)	Sm(2)–O(2) <sup>#5</sup>	2.472(3)	Sm(2)–O(13) <sup>#3</sup>	2.547(3)
Sm(2)–N(3)	2.601(4)	Sm(2)–N(5)	2.644(4)	Sm(2)–O(12) <sup>#3</sup>	2.661(3)
O(1)–C(1)	1.272(5)	O(2)–C(1)	1.239(5)	O(3)–C(6)	1.234(5)
O(4)–C(6)	1.296(5)	O(7)–C(7)	1.256(5)		

\* Symmetry operation: <sup>#1</sup>  $x, -y + 3/2, z - 1/2$ ; <sup>#2</sup>  $-x, -y + 2, -z + 1$ ; <sup>#3</sup>  $x + 1, y, z$ ; <sup>#4</sup>  $x - 1, y, z$ ; <sup>#5</sup>  $-x + 1, -y + 2, -z + 1$ .

Table 3. Selected bond lengths for II\*

Bond	<i>d</i> , Å	Bond	<i>d</i> , Å	Bond	<i>d</i> , Å
Nd(1)–O(2) <sup>#1</sup>	2.390(3)	Nd(1)–O(6) <sup>#2</sup>	2.432(3)	Nd(1)–O(13)	2.457(4)
Nd(1)–O(7)	2.477(3)	Nd(1)–O(9)	2.503(3)	Nd(1)–O(12) <sup>#3</sup>	2.518(3)
Nd(1)–O(9) <sup>#2</sup>	2.584(3)	Nd(1)–O(11) <sup>#3</sup>	2.684(3)	Nd(1)–N(5)	2.700(4)
Nd(1)–C(18) <sup>#3</sup>	2.944(5)	Nd(2)–O(4) <sup>#4</sup>	2.334(4)	Nd(2)–O(1)	2.450(3)
Nd(2)–O(12)	2.449(3)	Nd(2)–O(5)	2.455(3)	Nd(2)–O(10) <sup>#5</sup>	2.508(3)
Nd(2)–O(8) <sup>#6</sup>	2.562(3)	Nd(2)–N(2)	2.635(4)	Nd(2)–N(3)	2.673(4)
Nd(2)–O(7) <sup>#6</sup>	2.670(3)	O(2)–Nd(1) <sup>#7</sup>	2.390(3)	O(4)–Nd(2) <sup>#8</sup>	2.334(4)
O(7)–Nd(2) <sup>#3</sup>	2.670(3)	O(6)–Nd(1) <sup>#2</sup>	2.432(3)	O(8)–Nd(2) <sup>#3</sup>	2.562(3)
O(9)–Nd(1) <sup>#2</sup>	2.584(3)	O(10)–Nd(2) <sup>#5</sup>	2.508(3)	O(11)–Nd(1) <sup>#6</sup>	2.684(3)
O(12)–Nd(1) <sup>#6</sup>	2.518(3)	N(1)–C(2)	1.343(6)	O(1)–C(4)	1.245(5)

\* Symmetry operation: <sup>#1</sup>  $x - 1, -y + 1/2, z - 1/2$ ; <sup>#2</sup>  $-x, -y, -z$ ; <sup>#3</sup>  $x - 1, y, z$ ; <sup>#4</sup>  $x, -y + 1/2, z - 1/2$ ; <sup>#5</sup>  $-x + 1, -y, -z$ ; <sup>#6</sup>  $x + 1, y, z$ ; <sup>#7</sup>  $x + 1, -y + 1/2, z + 1/2$ ; <sup>#8</sup>  $x, -y + 1/2, z + 1$ .

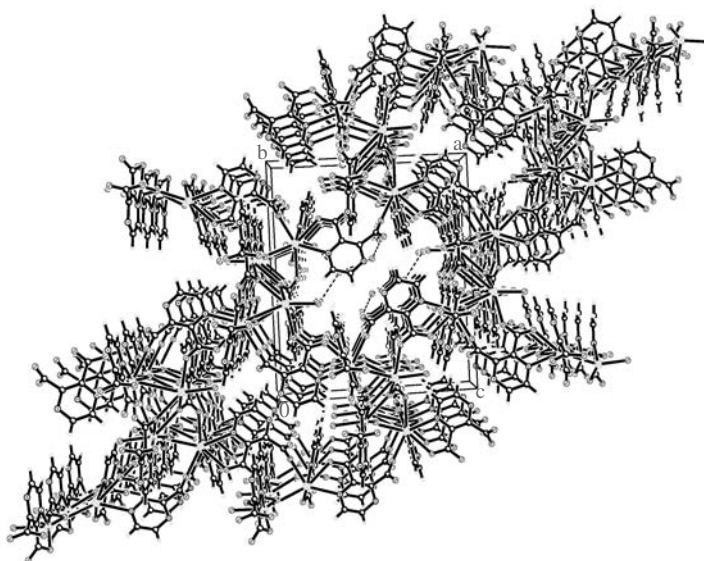


Fig. 2. 3D framework of I viewed along the  $x$  axis

of  $\text{Sm}^{3+}$  is observed for  $\text{O}(9)\text{--}\text{Sm}(2)^{\#6}$  with value of 2.307 Å, while the longest is presented for  $\text{Sm}(1)\text{--}\text{O}(3)^{\#4}$  and  $\text{O}(3)\text{--}\text{Sm}(1)^{\#3}$  with values around 2.605 Å. As it can be seen, one oxygen atom of the bridging carboxylate presents a shorter interatomic distance than those involving the chelate bridging oxygen atoms. This

behavior is similar to that shown in other  $\text{Ln}^{3+}$  complexes that present carboxylate groups coordinated to the metal ion as both chelates through bridging and bridging fashions.

The most important feature of this complex is that the  $\text{Pzdc}^{2-}$  ions are coordinated to the  $\text{Sm}^{3+}$  ion by three

Table 4. The types of crystal structure and the coordination models in 2,3-Pzdc complexes

Complex	Coordination models	Type of structure formed between 2,3-Pzdc and metal atom in crystal	Type of structure in references
$[\text{H}_3\text{O}]_2[\text{Cd}(\text{Pzdc})_2]_x$	$c$	1D	1D [29]
$\text{Cu}(\text{Pzdc}) \cdot \text{HCl}$	$b$	1D	1D [30]
$[\text{Mn}(\text{Pzdc})(\text{H}_2\text{O})_2]_x \cdot 2x\text{H}_2\text{O}$	$d$	1D	1D [30]
$[\{[\text{Cu}_2(\text{Pzdc})_2(\text{Pia})] \cdot x\text{H}_2\text{O}\}_n]$	$d$	2D	2D [31]
$[\text{Co}(\text{Pzdc})(\text{Phen})] \cdot \text{H}_2\text{O}$	$d$	2D	3D [32]
$[\text{Cd}(\text{Pzdc})(\text{Phen})] \cdot \text{H}_2\text{O}$	$d$	2D	2D [19]
$\{\text{Cu}(\text{Pzdc})_2(\text{H}_2\text{O})_3(\text{Idzc})_2\}_n$	$e$	1D	1D [33]
$[\text{Mn}(\text{Pzdc})(\text{H}_2\text{O})_2 \cdot 2\text{HO}]_n$	$e$	1D	1D [34]
$[\{[\text{Cu}_2(\text{Pzdc})_2(\text{Bipy})] \cdot \text{G}\}_n]$	$e$	2D	2D [35]
$[\text{Cu}_4(\text{Pzdc})_4(\text{Phen})_2(\text{H}_2\text{O})_4] \cdot 10\text{H}_2\text{O}$	$e$	1D	1D [19]
$[\{[\text{Cu}_2(\text{Pzdc})_2(\text{Dpyg})] \cdot 8\text{H}_2\text{O}\}_n]$	$g$	2D	3D [36]
$\text{Cd}_2(\text{Pzdc})_2(4,4'\text{-Bipy})(\text{H}_2\text{O})_2$	$g$	1D	2D [19]
$[\{[\text{Cd}(\text{Pzdc})(\text{Azpy})] \cdot 2\text{H}_2\text{O}\}_n]$	$k$	3D	3D [37]
$[\text{Ag}_2(\text{Pzdc})(\text{H}_2\text{O})]$	$f$	3D	3D [38]
$[\text{Ag}_2(\text{Pzdc})]$	$j$	3D	3D [38]
$[\text{Sm}_2(\text{Pzdc})_3] \cdot 3\text{H}_2\text{O}$	$a, l, m$	3D	3D (this work)
$[\text{Nd}_2(\text{Pzdc})_3] \cdot 3\text{H}_2\text{O}$	$a, l, m$	3D	3D (this work)
$[\text{NH}_4][\text{Ag}(\text{Pzdc})]$	$h$	2D	2D [39]
$[\text{Ag}_2(\text{Pzdc})(\text{NH}_3)]_{2n}$	$i$	2D	2D [40]

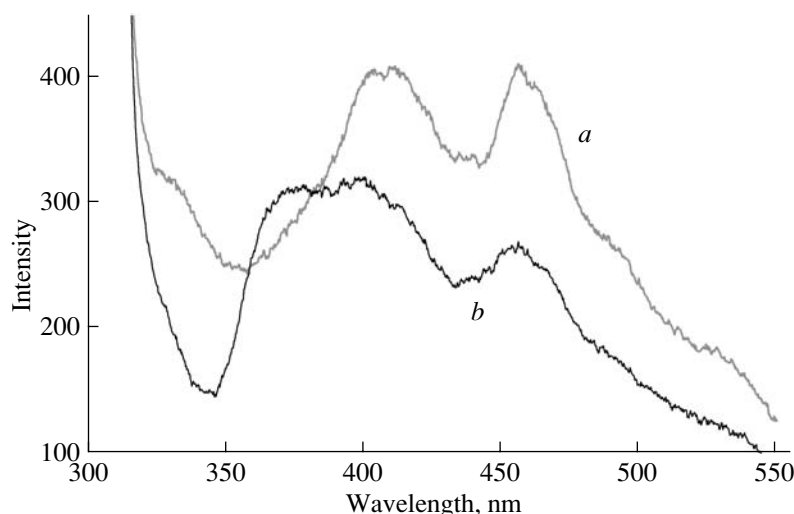


Fig. 3. Solid-state emission spectra of complex **I** (a) and  $\text{H}_2\text{Pzdc}$  (b) at room temperature

different ways, and the carboxylate groups belonging to  $\text{Pzdc}^{2-}$  are coordinated to the  $\text{Sm}^{3+}$  ion in  $\mu_2, \eta^2$ -bridging,  $\mu_2, \eta^3$ -bridging, and chelating fashion.

The TGA curves show that the decomposition process of these two complexes are similar. The dehydration temperature ranges of complexes **I** and **II** are 269.5–289.8 and 265.7–296.5°C, respectively. They begin to decompose beyond 440°C. Taking complex **I** as an example, the TGA curve shows that the first weight loss of 6.5%, which occurs between 269.5 and 289.8°C corresponds to the loss of two uncoordinated water molecules and one coordinated water molecule (calcd: 6.3%). Then the whole crystal collapsed, and a sudden weightlessness process from 335.4 to 893°C (the weightless rate is 27.65%). It indicates that parts of Pzdc groups were lost (if all the Pzdc groups were lost, then the weightless rate is 58%). Finally, the crystal was continually breaking down. Due to the instrument limitation, the complex could not be decomposed completely even at 1000°C, which indicates that title complex is stable.

Table 5. Geometric parameters of hydrogen bonds in structure **I**

Contact D–H...A	Distance, Å			Angle DHA, deg	Coordinates of A atoms
	D–H	H...A	D...A		
O(14)–H(4w)···O(13)	0.85	2.02	152	2.796	$x + 1, y, z$
O(15)–H(2w)···O(8)	0.85	1.89	159	2.703	$-x + 1, y - 1/2, -z + 3/2$
O(5)–H(6w)···O(14)	0.85	1.91	150	2.687	$-x + 1, -y + 2, -z + 1$
O(5)–H(7w)···O(6)	0.85	2.37	142	3.083	$x, -y + 3/2, z - 1/2$

The solid-state emission spectra of the free ligand  $\text{H}_2\text{Pzdc}$  and the complex are given in Fig. 3. The free ligand  $\text{H}_2\text{Pzdc}$  gives two broad emission bands: from 360 to 410 nm with the maximum at 400 nm, and from 450 to 470 nm with the maximum at 460. The complex **I** two intense broad emission bands: from 395 to 420 nm with the maximum at 410 nm, and from 450 to 470 nm with the maximum at 455. The fluorescence enhancement of  $\text{Sm}^{3+}$  reflects the efficient energy transfer from the  $\pi$ -electron conjugated system to the  $\text{Sm}^{3+}$ . The existence of the characteristic emissions of  $\text{Sm}^{3+}$  demonstrates intramolecule energy transfer process by intramolecule resonance coupling effect. The emission may be assigned to the ligand-to-metal charge-transfer bands (LMCT) [41].

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