



# A set of new transition metal-based coordination complexes dependent upon Hpztza ligand (Hpztza = 2-(5-(pyrazin-2-yl)-2H-tetrazol-2-yl) acetic acid)

Jie Yang, Lei Shen, Gao-Wen Yang\*, Qiao-Yun Li\*, Wei Shen, Jian-Ning Jin, Jing-Jing Zhao, Jian Dai

Jiangsu Laboratory of Advanced Functional Materials, Department of Chemistry and Materials Engineering, Changshu Institute of Technology, Changshu 215500, Jiangsu, PR China

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## ABSTRACT

Reaction of  $MCl_2 \cdot 4H_2O$  ( $M = Zn, Cd, Mn, Co, Ni$ ) with 2-(5-(pyrazin-2-yl)-2H-tetrazol-2-yl) acetic acid (Hpztza) yielded a set of new  $M(II)/pztza$  complexes,  $[Cd(pztza)_2(H_2O)_6] \cdot 3H_2O \cdot (Hpztza)$  (**1**),  $[M(pztza)_2(H_2O)_2]$  [ $M = Cd$ (**2**),  $Zn$ (**7**),  $Mn$ (**9**)],  $[Cd(pztza)_2] \cdot 2(CH_3OH)$  (**3**),  $[Co(pztza)_2(H_2O)_2] \cdot 6H_2O$  (**4**),  $[Co(pztza)(H_2O)Cl]$  (**6**) and  $[M(pztza)_2(H_2O)_2] \cdot 2H_2O$  [ $M = Co$ (**5**),  $Zn$ (**8**),  $Ni$ (**10**)]. These compounds were structurally characterized by elemental analysis, IR spectroscopy and X-ray single-crystal diffraction. Complex **1** featured a mononuclear structure, complexes **4, 5, 7, 8, 10** showed 1D chains and complexes **2, 3, 6, 9** displayed 2D layer structures. Furthermore, the luminescence properties of **1–10** were investigated at room temperature in the solid state.

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## 1. Introduction

From the view point of crystal engineering, the shapes of the organic ligands are very important in forming the final structures of the coordination frameworks. One of the important characteristics of an organic compound used as a ligand is its diversity coordination modes, molecular rigidity and flexibility, and to determine the orientation of the binding sites [1]. So they can be used as linkers to design and construct varied structural and functional coordination complexes and therefore greatly increase the chances of their potential industrial applications. As versatile building clusters, tetrazoles and its derivatives have been employed extensively as multidentate chelating or bridging linkers because of their diversity of connecting modes [2]. The tetrazole-based ligands cannot only lead to new coordination networks with intriguing topologies, such as dynamic structures [3] and supramolecular isomerism [4], but also develop potential applications in the field of heterogeneous catalysis, optical properties, magnetism and luminescence [5–7]. To the best of our knowledge, 5-(pyrazinyl)tetrazole has been studied and a number of correlative metal–organic coordination complexes have been prepared [8]. However, adducts of another class of carboxylate-5-(pyrazinyl)tetrazole ligands have only been the subject of limited study with metal ions. As is well-known, carboxylate O atoms, pyrazine ring N atoms and tetrazolyl ring N atoms have good

coordination capacities [9], then the 5-(pyrazinyl)tetrazole-carboxylate ligands may inherited these functions and to be excellent and versatile building blocks. Encouraged by these results, we selected 2-(5-(pyrazin-2-yl)-2H-tetrazol-2-yl) acetic acid (Hpztza) as a ligand to construct novel networks. In the Hpztza ligand, the carboxylate group connected to tetrazole ring via the  $-CH_2-$  moiety offers flexible orientations so that their flexibility and conformational freedom may provide more possibilities for the construction of frameworks with new structures. Investigation of their properties can lead to a deeper understanding of the supramolecular assembly processes.

As expected, the reactions of  $MCl_2 \cdot 4H_2O$  and Hpztza produced a set of new  $M(II)/pztza$  complexes,  $[Cd(pztza)_2(H_2O)_6] \cdot 3H_2O \cdot (Hpztza)$  (**1**),  $[M(pztza)_2(H_2O)_2]$  [ $M = Cd$ (**2**),  $Zn$ (**7**),  $Mn$ (**9**)],  $[Cd(pztza)_2] \cdot 2(CH_3OH)$  (**3**),  $[Co(pztza)_2(H_2O)_2] \cdot 6H_2O$  (**4**),  $[Co(pztza)(H_2O)Cl]$  (**6**) and  $[M(pztza)_2(H_2O)_2] \cdot 2H_2O$  [ $M = Co$ (**5**),  $Zn$ (**8**),  $Ni$ (**10**)]. Herein we report their synthesis, crystal structures, and the luminescent properties.

## 2. Experimental

### 2.1. Materials and methods

The ligand Hpztza was prepared according to the literature method [10]. Other chemicals were commercially available reagents of analytical grade and used without further purification. The elemental analysis for C, H and N were performed on a Carlo-Erba EA1110 CHNO-S microanalyzer. The IR spectra were recorded ( $4000-400\text{ cm}^{-1}$ ) on a NICOLET 380 spectrometer with

\* Corresponding authors. Fax: +86 512 52251842.  
E-mail addresses: [ygwswx@126.com](mailto:ygwswx@126.com) (G.-W. Yang),  
[liqiaoyun61@126.com](mailto:liqiaoyun61@126.com) (Q.-Y. Li).

pressed KBr pellets. The photoluminescent spectra were performed on a Hitachi F4600 spectrofluorometer.

## 2.2. Synthesis of $[CD(pztza)_2(H_2O)_6] \cdot 3H_2O \cdot (Hpztza)$ (**1**)

A mixture of  $CdCl_2 \cdot 4H_2O$  (25.54 mg, 0.1 mmol) and  $Hpztza$  (41.23 mg, 0.2 mmol) in mixture of EtOH (1 mL) and water (3 mL) was adjusted to pH=3 with NaOH(1 mol/L) and then stirred for 1 h at room temperature. Evaporation of the solvent at room temperature for four weeks yielded a colorless crystal **1**. For **1**, yield: 61% based on Cd. Anal. Calcd. for  $C_{21}H_{34}CdN_{18}O_{15}$ : C, 28.34; H, 3.74; N, 28.33%. Found: C, 28.29; H, 3.65; N, 28.41%. IR (KBr,  $cm^{-1}$ ): 3450 (br), 1604 (vs), 1430 (m), 1386 (m), 1147 (m), 1069 (m), 821 (m), 668 (m).

## 2.3. Synthesis of $[M(pztza)_2(H_2O)_2]$ ( $M=Cd$ (**2**), $Zn$ (**7**), $Mn$ (**9**)), and $[M(pztza)_2(H_2O)_2] \cdot 2H_2O$ ( $M=Co$ (**5**), $Ni$ (**10**))

A mixture of  $MCl_2 \cdot 4H_2O$  (25.54 mg ( $M=Cd$ ), 20.84 mg ( $M=Zn$ ), 19.79 mg ( $M=Mn$ ), 20.19 mg ( $M=Co$ ), 20.16 mg ( $M=Ni$ )) 0.1 mmol and  $Hpztza$  (41.23 mg, 0.2 mmol) dissolved in the mixture solution of EtOH (4 mL) and water (1 mL) was adjusted to pH 6 with NaOH(1 mol/L) and stirred for 1 h at room temperature. The colorless block crystals **2**, **7**, **9**, the yellow block crystal **5** and the green crystal **10** were obtained, respectively, through evaporation of the solution at room temperature. For **2**, yield: 52% based on Cd. Anal. Calcd. for  $C_{14}H_{14}CdN_{12}O_6$ : C, 30.09; H, 2.53; N, 30.08%. Found: C, 30.21; H, 2.62; N, 30.19%. IR (KBr,  $cm^{-1}$ ): 3451 (br), 1629 (vs), 1600 (vs), 1429 (m), 1384 (m), 1149 (m), 1072 (m), 829 (m), 676(m). For **5**, yield: 62% based on Co. Anal. Calcd. for  $C_{14}H_{18}N_{12}O_8Co$ : C,31.06; H, 3.35; N, 31.05%. Found: C, 31.15; H, 3.40; N, 31.11%. IR (KBr,  $cm^{-1}$ ): 3452 (br), 1608 (s), 1426 (m), 1396(s), 1153 (m), 1072 (m), 819 (m), 672(m). For **7**, yield: 63% based on Zn. Anal. Calcd. for  $C_{14}H_{14}ZnN_{12}O_6$ : C, 32.86; H, 2.76; N, 32.85%. Found: C, 33.01; H, 2.63; N, 32.76%. IR (KBr,  $cm^{-1}$ ): 3450 (br), 1604 (vs), 1430 (m), 1386 (m), 1147 (m), 1069 (m), 821 (m), 668(m). For **9**, yield: 59% based on Mn. Anal. Calcd. for  $C_{14}H_{14}MnN_{12}O_6$ : C, 33.54; H, 2.82; N, 33.53%. Found: C, 33.74; H, 2.75; N, 33.34%. IR (KBr,  $cm^{-1}$ ): 3450 (br), 1636(s), 1428 (m), 1392 (m), 1154 (m), 1074 (m), 821 (m), 673(m). For **10**, yield: 59% based on Ni. Anal. Calcd. for  $C_{14}H_{18}N_{12}O_8Ni$ : C, 31.08; H, 3.35; N, 31.07%. Found: C, 31.12; H, 3.39; N, 31.15%. IR (KBr,  $cm^{-1}$ ): 3454 (br), 1625 (s), 1424 (m), 1396 (m), 1155 (m), 1076 (m), 818 (m), 680(m).

## 2.4. Synthesis of $[CD(pztza)_2] \cdot 2(CH_3OH)$ (**3**) and $[CO(pztza)(H_2O)Cl]$ (**6**)

A mixture of  $MCl_2 \cdot 4H_2O$  (25.54 mg ( $M=Cd$ ), 20.19 mg ( $M=Co$ ), 0.1 mmol),  $Hpztza$  (41.23 mg, 0.2 mmol) in mixture solution of MeOH (5 mL) and water (1 mL) was adjusted to pH 6 and sealed in a 25 mL teflon-lined stainless steel container, which was heated at 120 °C for 72 h. After the sample was cooled to room temperature at a rate of 5 °C/h, the colorless block crystals **3** and the yellow block crystals **6** were obtained. For **3**, yield: 65% based on Cd. Anal. Calcd. for  $C_{16}H_{18}N_{12}O_6Cd$ : C, 32.75; H, 3.09; N, 28.64%. Found: C, 32.65; H, 3.12; N, 28.70%. IR (KBr,  $cm^{-1}$ ): 3432(br), 1626 (s), 1387 (s), 1151 (m), 1078 (m), 898 (m) and 698 (m). For **6**, yield: 62% based on Co. Anal. Calcd. for  $C_7H_7ClCoN_6O_3$ : C, 26.48; H, 2.22; N, 26.46%. Found: C, 26.39; H, 2.28; N, 26.51%. IR (KBr,  $cm^{-1}$ ): 3452 (br), 1617 (s), 1427 (m), 1392 (s), 1070 (m), 817 (m) and 669(m).

## 2.5. Synthesis of $[CO(pztza)_2(H_2O)_2] \cdot 6H_2O$ (**4**) and $[Zn(pztza)_2(H_2O)_2] \cdot 2H_2O$ (**8**)

A mixture of  $MCl_2 \cdot 4H_2O$  (20.16 mg ( $M=Ni$ ), 20.89 mg ( $M=Zn$ ), 20.19 mg ( $M=Co$ ), 0.1 mmol) and  $Hpztza$  (41.23 mg, 0.2 mmol) in mixture of EtOH (5 mL) and water (1 mL) was adjusted to pH=6 with NaOH(1 mol/L) solution and then sealed in a 25 mL teflon-lined stainless steel container heated at 90 °C for 3 day. After the sample was cooled to room temperature at a rate of 5 °C/h, the green crystal **5**, colorless block crystal **6**, and yellow block crystal **7** were obtained. For **4**, yield: 62% based on Co. Anal. Calcd. for  $C_{14}H_{26}CoN_{12}O_{12}$ : C, 27.41; H, 4.27; N, 27.40%. Found: C, 27.51; H, 4.19; N, 27.35%. IR (KBr,  $cm^{-1}$ ): 3455 (br), 1620(s), 1426 (m), 1396 (m), 1155 (m), 1073 (m), 819 (m), 672(m). For **6**, yield: 40% based on Zn. Anal. Calcd. for  $C_{14}H_{18}N_{12}O_8Zn$ : C, 30.70; H, 3.31; N, 30.68%. Found: C, 30.65; H, 3.40; N, 30.74%. IR (KBr,  $cm^{-1}$ ): 3458 (br), 1615 (s), 1425 (m), 1393 (s), 1152 (m), 1073 (m), 819 (m), 672(m).

## 2.6. X-ray crystallography

Single crystal X-ray crystal data were collected on a Rigaku SCX mini CCD diffractometer equipped with a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.071073$  Å). The intensity data were collected by the  $\omega$  scan technique and were reduced using Crystal-Clear program [11]. An empirical absorption correction based on scans was applied. The structure was solved by the direct methods and refined by full matrix least-squares on  $F^2$  using SHELXTL [12]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the final stage of the refinement on calculated positions bonded to their carrier atoms. Crystallographic data are summarized in Table 1, selected bond lengths and angles are listed in Table 2. Hydrogen-bonding parameters are given in Table S1.

## 3. Results and discussion

### 3.1. Syntheses consideration and general characterizations

Reactions of  $CdCl_2 \cdot 4H_2O$ ,  $Hpztza$  and NaOH with pH=3, pH=6 at room temperature and with pH=6 at 120 °C under the hydrothermal reaction yielded  $[Cd(pztza)_2(H_2O)_6] \cdot 3H_2O \cdot (Hpztza)$  (**1**),  $[Cd(pztza)_2(H_2O)_2]$  (**2**),  $[Cd(pztza)_2] \cdot 2(CH_3OH)$  (**3**). Reactions of  $CoCl_2 \cdot 4H_2O$ ,  $Hpztza$  and NaOH with pH=6 at room temperature, 90 °C and 120 °C yielded  $[Co(pztza)_2(H_2O)_2] \cdot 6H_2O$  (**4**),  $[Co(pztza)_2(H_2O)_2] \cdot 2H_2O$  (**5**) and  $[Co(pztza)(H_2O)Cl]$  (**6**). Reactions of  $ZnCl_2 \cdot 4H_2O$ ,  $Hpztza$  and NaOH with pH=6 at room temperature, 90 °C yielded  $[Zn(pztza)_2(H_2O)_2]$  (**7**),  $[Zn(pztza)_2(H_2O)_2] \cdot 2H_2O$  (**8**). Reactions of  $MnCl_2 \cdot 4H_2O$ ,  $NiCl_2 \cdot 4H_2O$ ,  $Hpztza$  and NaOH with pH=6 at room temperature yielded  $[Mn(pztza)_2(H_2O)_2]$  (**9**),  $[Ni(pztza)_2(H_2O)_2] \cdot 2H_2O$  (**10**) (Scheme 1). These compounds of different structure were formed by Cd, Co and Zn under different reaction temperature at pH=6. And the reaction of  $MCl_2 \cdot 4H_2O$  ( $M=Mn, Ni$ ) with  $Hpztza$  yielded a set of precipitates at pH=6 by varying reaction temperature. Fine powders were formed in all of these reaction systems when the pH value was higher than 6. In addition varying the reaction parameters such as the ligand-to-metal ratio, the cooling speed, and the solvent system have not succeeded in formation of products suitable for single crystal X-ray diffraction analysis. It is worthwhile to point out that the use of  $MSO_4 \cdot 7H_2O$  or  $M(NO_3)_2 \cdot 6H_2O$  instead of  $MCl_2 \cdot 6H_2O$  ( $M=Zn, Mn, Ni$ ), employing the identical technique as for preparation of **7**, **8**, **9** and **10** also results in the same crystallographic cell data compounds, respectively. The results indicate that the product structure weakly depends on the nature of the metal counteranion.

**Table 1**  
Crystallographic data for **1–10**.

Compound	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Molecular formula	C <sub>21</sub> H <sub>34</sub> CdN <sub>18</sub> O <sub>15</sub>	C <sub>14</sub> H <sub>14</sub> CdN <sub>12</sub> O <sub>6</sub>	C <sub>14</sub> H <sub>10</sub> CdN <sub>12</sub> O <sub>4</sub> ·C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	C <sub>14</sub> H <sub>14</sub> CoN <sub>12</sub> O <sub>6</sub> ·6(H <sub>2</sub> O)	C <sub>14</sub> H <sub>18</sub> CoN <sub>12</sub> O <sub>8</sub>	C <sub>7</sub> H <sub>7</sub> ClCoN <sub>6</sub> O <sub>3</sub>
Formula weight	889.05	558.76	586.83	613.40	541.33	317.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	10.562 (2)	7.2006(14)	13.418 (3)	10.507(2)	7.2524(15)	7.7833(16)
<i>b</i> (Å)	23.497 (5)	9.810(2)	9.872 (2)	18.953(7)	8.7822(18)	12.865(3)
<i>c</i> (Å)	14.431 (3)	13.937(3)	15.608 (3)	13.699(3)	9.2384(18)	12.192(2)
$\gamma$ (deg.)	90	90.00	90.00	90.00	86.36(3)	90.00
<i>V</i> (Å <sup>3</sup> )	3444.4 (12)	966.4(3)	2067.0 (7)	2563.8(12)	555.21(19)	1220.3(4)
<i>Z</i>	4	2	4	4	1	4
<i>T</i> /K	291 (2)	291(2)	291(2)	291(2)	291(2)	291(2)
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.714	1.913	1.886	1.589	1.619	1.729
$\mu$ (mm <sup>-1</sup> )	0.73	1.196	1.12	0.751	0.842	1.635
<i>q</i> (deg.)	3.1–27.5	3.6–27.5	3.0–25.0	3.2–23.3	3.5–24.2	3.1–24.3
Unique reflections ( <i>R</i> <sub>int</sub> )	5552(0.074)	2220 (0.0478)	1806(0.020)	1807 (0.1519)	1793 (0.0621)	1968 (0.069)
No. observations	4487	1731	1761	1388	1422	1602
<i>R</i> <sup>a</sup>	0.0718	0.0304	0.0320	0.0851	0.0548	0.0486
<i>wR</i> <sup>b</sup>	0.2098	0.106	0.0928	0.2216	0.1441	0.142
GOF <sup>c</sup>	1.043	0.761	1.177	1.065	0.887	0.959
$\Delta/\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	1.167	0.617	0.917	0.612	0.240	0.333
$\Delta/\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.716	–0.487	–0.994	–0.574	–0.333	–0.433
Compound	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>		
Molecular formula	C <sub>14</sub> H <sub>14</sub> N <sub>12</sub> O <sub>6</sub> Zn	C <sub>14</sub> H <sub>14</sub> N <sub>12</sub> O <sub>6</sub> Zn·2(H <sub>2</sub> O)	C <sub>14</sub> H <sub>14</sub> MnN <sub>12</sub> O <sub>6</sub>	C <sub>14</sub> H <sub>18</sub> N <sub>12</sub> NiO <sub>8</sub>		
Formula weight	511.76	547.79	501.31	541.09		
Crystal system	triclinic	triclinic	monoclinic	triclinic		
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$		
<i>a</i> (Å)	7.3993(15)	7.3403(15)	7.1801(14)	7.3092(15)		
<i>b</i> (Å)	7.9352(16)	8.7531(18)	9.6579(19)	8.6745(17)		
<i>c</i> (Å)	9.1366(18)	9.1213(18)	13.937(3)	9.1315(18)		
$\gamma$ (deg.)	114.13(3)	86.40(3)	90.00	86.47(3)		
<i>V</i> (Å <sup>3</sup> )	481.19(21)	555.35(19)	950.6(3)	546.97 (19)		
<i>Z</i>	1	1	2	1		
<i>T</i> /K	291(2)	291(2)	291(2)	291(2)		
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	1.766	1.638	1.751	1.643		
$\mu$ (mm <sup>-1</sup> )	1.342	1.175	0.762	0.958		
<i>q</i> (deg.)		3.5–27.5	3.6–24.1	3.5–27.5		
Unique reflections ( <i>R</i> <sub>int</sub> )	2198 (0.0361)	2545 (0.0438)	1507 (0.0661)	1741 (0.0734)		
No. observations	1904	2133	1248	1335		
<i>R</i> <sup>a</sup>	0.0452	0.0474	0.0612	0.0674		
<i>wR</i> <sup>b</sup>	0.1235	0.1454	0.1624	0.1742		
GOF <sup>c</sup>	0.941	0.992	1.131	1.032		
$\Delta/\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.602	0.383	0.254	0.433		
$\Delta/\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.493	–0.436	–0.244	–0.449		

(a)  $R = \sum ||F_o| - |F_c|/ \sum |F_o|$ . (b)  $R_w = \{ \sum w(F_o^2 - F_c^2)^2 / \sum w(F_c^2)^2 \}^{1/2}$ . (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.

As depicted in Scheme 1, complexes **1–10** are described as mononuclear structure, 1D and 2D frameworks with diverse architectures. Complex **1** features mononuclear structure. Complexes **2, 3, 6, 9** display different topologies of 2D layer structures. Complexes **4, 5, 7, 8** and **10** are complicated 1D chains. The structure variation from the 2D framework to the 1D chain and mononuclear structure may be attributed to different coordination modes of the pztza ligands (Scheme 2(I–V)) under different conditions. The pztza ligand adopt coordination modes (Scheme 2(I and II)) via carboxylate group O at pH=3 condition in complex **1**. At pH=6 and room temperature, the bidentate bridging coordination mode [Scheme 2(III)] are found via pyrazinyl N and the carboxylate group O in complexes **2, 4, 5, 7, 8, 9** and **10**. Under the hydrothermal reaction and pH=6, the pztza ligand exhibits two quadridentate coordination modes [Scheme 2(IV and V)] via pyrazinyl N and tetrazolate N and carboxylate group O in complexes **3** and **6**. The information about the dimensionality of the metal compounds and the coordination modes of the ligand observed in the various compounds under different reaction condition are shown in Table 3.

Complexes **1–10** were all air stable. All general characterizations were carried out with crystal samples. The elemental analysis showed that the components of these complexes were well in accordance with the results of the structural analysis. For **1–10**, the characteristic bands of carboxylate groups appeared in the usual region at 1600–1636 cm<sup>-1</sup> for the antisymmetric stretching vibrations and at 1384–1430 cm<sup>-1</sup> for the symmetric stretching vibrations [13]. The absence of any strong absorption bands around 1720 cm<sup>-1</sup> confirm complete deprotonation of the carboxyl groups of the pztza ligand during the reactions. In addition, the strong and broad band centered at 3450 cm<sup>-1</sup> for the compounds are attributable to the O–H stretching vibration of the free or bonded water molecule in the compounds. These are in accordance with the results of the X-ray diffraction analysis.

### 3.2. Crystal structures

#### 3.2.1. Crystal structures of [CD(pztza)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>]·3(H<sub>2</sub>O)(Hpztza) (**1**)

Single crystal Xray analysis reveals that complex **1** crystallize in monoclinic space group *P*2<sub>1</sub>/*c*. The perspective view of **1**

**Table 2**  
Selected bond distances (Å) and angles (deg.) for **1–10**.

<b>Complex 1</b>					
Cd1–O5	2.379 (7)	Cd1–O8	2.396 (7)	Cd1–O10	2.405 (7)
Cd1–O7	2.424 (7)	Cd1–O11	2.451 (7)	Cd1–O12	2.468 (8)
Cd1–O4	2.480 (7)	Cd1–O9	2.553 (7)	Cd1–O3	2.611 (8)
O5–Cd1–O8	111.1 (3)	O5–Cd1–O10	72.3 (3)	O8–Cd1–O10	68.8 (3)
O5–Cd1–O7	145.4 (3)	O8–Cd1–O7	76.1 (3)	O10–Cd1–O7	137.5 (3)
O5–Cd1–O11	73.3 (3)	O8–Cd1–O11	138.7 (3)	O10–Cd1–O11	142.8 (3)
O7–Cd1–O11	79.8 (3)	O5–Cd1–O12	74.1 (3)	O8–Cd1–O12	71.0 (3)
<b>Complex 2</b>					
Cd1–O2	2.244(2)	Cd1–O3	2.3227	Cd1–N5C	2.384(2)
O2–Cd1–O3	91.31(8)	O2B–Cd1–O3	88.87(8)	O2–Cd1–N5C	99.63(9)
O2B–Cd1–N5C	80.37(9)	O3–Cd1–N5C	86.31(6)	O3B–Cd1–N5C	93.69(7)
<b>Complex 3</b>					
Cd1–O1	2.326 (3)	Cd1–N3B	2.437 (3)	Cd1–N6B	2.554 (3)
Cd1–O2	2.594 (4)	O1A–Cd1–N6B	83.96 (12)	N3C–Cd1–N6B	76.03(11)
O1–Cd1–O1A	104.72(16)	O1–Cd1–N3B	132.24 (11)	O1–Cd1–N3C	84.22(11)
N3B–Cd1–N3C	124.19(15)	O1–Cd1–N6B	159.00 (11)	N3B–Cd1–N6A	66.83(10)
<b>Complex 4</b>					
Co1–O2	2.106(3)	Co1–O3	2.133(3)	Co1–N5C	2.193(5)
O2–Co1–O3	91.06(11)	O2–Co1–O3B	88.94(11)	O2–Co1–N5C	89.93(16)
O3B–Co1–N5C	91.12(16)	O2B–Co1–N5C	90.07(16)	O3–Co1–N5C	88.88(16)
<b>Complex 5</b>					
Co1–O1	2.063(2)	Co1–O3	2.094(2)	Co1–N(5B)	2.189(3)
O1–Co1–O3A	90.30(9)	O1–Co1–O3	89.70(9)	O1–Co1–N5B	90.1(1)
O1A–Co1–N5B	89.9(1)	O3A–Co1–N5B	89.82(9)	O3–Co1–N5B	90.18(9)
<b>Complex 6</b>					
Co1–N6A	2.216(4)	Co1–N1A	2.161(3)	Co1–N5C	2.176(4)
Co1–O1	2.078(3)	Co1–O3	2.1075(13)	Co1–Cl1	2.372(13)
O1–Co1–O3	89.84(9)	O1–Co1–N1A	82.85(13)	O3–Co1–N1A	169.94(10)
O1–Co1–N5C	88.06(13)	O3–Co1–N5C	88.63(10)	N1A–Co1–N5C	97.98(13)
O1–Co1–N6A	83.55(13)	O3–Co1–N6A	95.49(10)	N1A–Co1–N6A	76.88(13)
N5C–Co1–N6A	170.63(14)	O1–Co1–Cl1	174.24(9)	O3–Co1–Cl1	93.84(5)
N1A–Co1–Cl1	92.94(10)	N5C–Co1–Cl1	96.45(10)	N6A–Co1–Cl1	91.68(10)
<b>Complex 7</b>					
Zn1–O1	2.058(2)	Zn1–O3	2.0810(17)	Zn1–N5B	2.277(2)
O1–Zn1–O3	91.46(8)	O1–Zn1–O3A	88.54(8)	O1A–Zn1–N5B	86.84(9)
O1–Zn1–N5B	93.16(9)	O3A–Zn1–N5B	88.15(9)	O3–Zn1–N5B	91.85(9)
O1A–Zn1–O1	180				
<b>Complex 8</b>					
Zn1–O1	2.068(2)	Zn1–O3	2.0903 (15)	Zn1–N5B	2.236(2)
O1–Zn1–O3A	91.08(8)	O1–Zn1–O3	88.92(8)	O1–Zn1–N5B	89.39(10)
O1A–Zn1–N5B	90.61(10)	O3A–Zn1–N5B	90.47(8)	O3–Zn1–N5B	89.53(8)
<b>Complex 9</b>					
Mn1–O1	2.128(3)	Mn1–O3	2.176(3)	Mn1–N5B	2.310(4)
O1–Mn1–O3	90.27(13)	O1–Mn1–O3A	89.73(13)	O3A–Mn1–N5B	92.85(12)
O1A–Mn1–N5B	96.39(13)	O1–Mn1–N5B	83.61(13)	O3–Mn1–N5B	87.15(12)
<b>Complex 10</b>					
Ni1–O1	2.044(4)	Ni1–O3	2.056(3)	Ni1–N5B	2.130(5)
O1A–Ni1–O3	91.59(14)	O1–Ni1–O3	88.41(14)	O1A–Ni1–N5B	89.30(17)
O1–Ni1–N5B	90.70(17)	O3–Ni1–N5B	90.58(15)	O3A–Ni1–N5B	89.42(15)

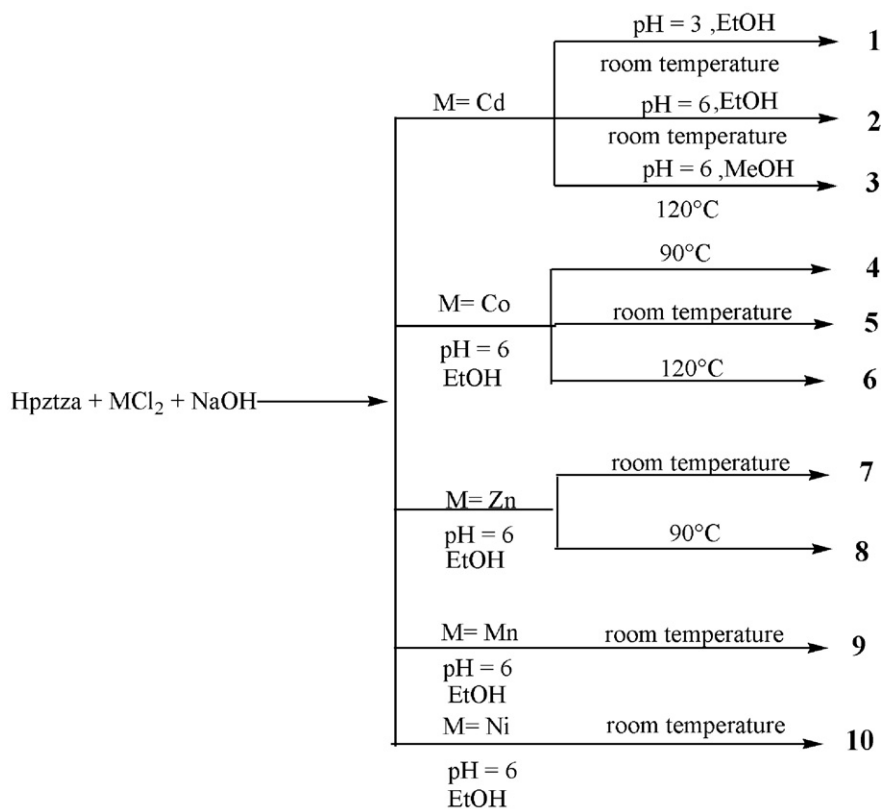
Symmetry codes for **2** (A)  $4-x, -0.5+y, 0.5-z$ ; (B)  $3-x, 4-y, -z$ ; (C)  $x-1, 3.5-y, z-1/2$ ; (D)  $4-x, 0.5+y, 0.5-z$ ; for **3**: (A)  $-1-x, y, 0.5-z$ ; (B)  $-1.5-x, -0.5+y, 0.5-z$ ; (C)  $0.5+x, -0.5+y, z$ ; (D)  $-0.5+x, 1/2+y, z$ ; for **4**: (A)  $-0.5+x, -0.5+y, z$ ; (B)  $-1-x, -y, 2-z$ ; (C)  $0.5+x, 0.5+y, z$ ; (D)  $-1.5-x, -0.5-y, 2-z$ ; for **5**: (A)  $2-x, 2-y, -2-z$ ; (B)  $-1+x, 1+y, z$ ; (C)  $3-x, 1-y, -2-z$ ; (D)  $1+x, -1+y, z$ ; for **6**: (A)  $-x, 2-y, -z$ ; (B)  $-0.5-x, -0.5+y, -0.5-z$ ; (C)  $-0.5-x, 0.5+y, -0.5-z$ ; for **7**: (A)  $-x, 2-y, -z$ ; (B)  $1-x, 2-y, 1-z$ ; (C)  $-1+x, y, -1+z$ ; (D)  $1+x, y, 1+z$ ; for **8**: (A)  $-1-x, 2-y, 1-z$ ; (B)  $-x, 1-y, 1-z$ ; (C)  $-1+x, 1+y, z$ ; (D)  $1+x, -1+y, z$ ; for **9** (A)  $2-x, -y, 2-z$ ; (B)  $1-x, 0.5+y, 1.5-z$ ; (C)  $1+x, -0.5-y, 0.5+z$ ; (D)  $1-x, -0.5+y, 1.5-z$ ; for **10**: (A)  $3-x, -y, -z$ ; (B)  $1+x, -1+y, z$ ; (C)  $2-x, 1-y, -z$ ; (D)  $-1+x, 1+y, z$ .

is shown in Fig. 1, the Cd (II) is connected to three oxygen atoms (O3, O4 and O5) from two different pztza ligands, six oxygen atoms (O7, O8, O9, O10, O11, O12) of six water molecules. The feature of **1** is its unusual nine-coordinate mononuclear tricapped trigonal prism structure ( $\text{CdO}_9$ ) which is very rare for Cd(II) complexes [14]. The Cd–O bond length from 2.379 (7) Å to 2.611 (8) Å are observed in the range of related analogous complexes [15]. In **1**, two kinds of coordination modes of the pztza ligand have been found in the complex (Scheme 2(I–II)): a pztza ligand adopt bidentate chelating coordination mode (Scheme 2(I)), chelating the Cd1 atom via carboxylate group

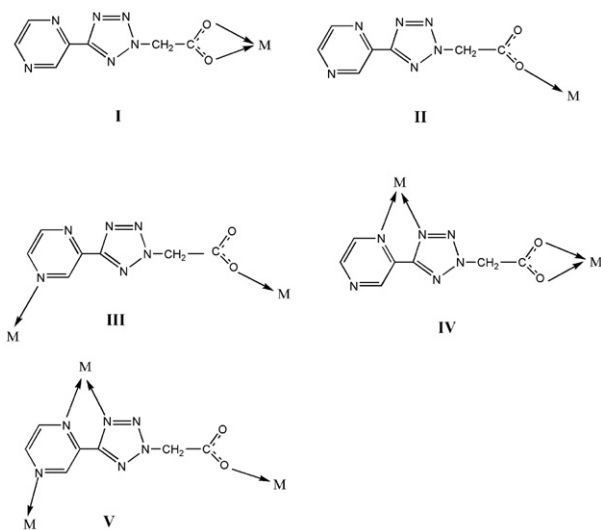
O1 and O3 of pztza; another pztza ligand displays a O3-monodentate mode to link the Cd1 [Scheme 2(II)]. The molecules of **1** are interlinked by intermolecular hydrogen bonds [O–H...O, O–H...N, C–H...O, C–H...N], forming a 3D supermolecular network structure (Fig. S1).

### 3.2.2. Crystal structures of $[M(\text{pttza})_2(\text{H}_2\text{O})_2]$ [ $M=\text{Cd}(\mathbf{2}), \text{Mn}(\mathbf{9})$ ]

The X-ray structure analysis reveals that complex **2** and **9** are isomorphous. Here complex **2** is taken as an example to depict in detail. As shown in Fig. 2, each Cd(II) atom is coordinated by two



Scheme 1. Syntheses of complexes 1–10



Scheme 2. Five coordination modes of the pztza ligand observed in complexes 1–10

nitrogen atoms [Cd–N, 2.384(2) Å] from two pztza ligands, two oxygen atoms [Cd–O, 2.244(2) Å] from two carboxylate groups and two oxygen atoms [Cd–O, 2.3227 Å] from two water molecules. Its coordination geometry can be described as a distorted octahedral geometry. In complex 2, the pztza acts as a bidentate bridging coordination mode (Scheme 2(III)) via the pyrazinyl ring N5 and the carboxylate group O2. Thus, each Cd(II) atom links to four other Cd(II) atoms by four pztza ligands to yield a 2D single-layered network (Fig. 2). The adjacent two single 2D layers in a face-to-face manner are further packed into a 3D supramolecular

Table 3

Dimension and coordination modes of the ligand under different reaction condition

Compound	pH	Temperature	Structure	Coordination modes of the ligand
1	3	Room temperature	Mononuclear	I,II
2		Room temperature	2D	III
3		120 °C	2D	IV
4		90 °C	1D	III
5		Room temperature	1D	III
6	6	120 °C	2D	V
7		Room temperature	1D	III
8		90 °C	1D	III
9		Room temperature	2D	III
10		Room temperature	1D	III

architecture by O–H···O hydrogen bond [O3–H3A···O1 2.6694 Å/151°, –1+x, y, z] and C–H···N hydrogen bond [C2–H2B···N6 3.341(4) Å/154°, –1+x, y, z] (Fig. S2).

### 3.2.3. Crystal structures of [Cd(pztza)<sub>2</sub>]·2(CH<sub>3</sub>OH) (3)

Complex 3 consists of one cadmium atom, two pztza ligands and two methanol molecules in a crystallographically independent asymmetric unit, with monoclinic space group C2/c. Each Cd(II) is coordinated by four nitrogen atoms (N3B, N3C, N6B, N6C) from two pztza ligands and four oxygen atoms (O1, O2, O1A, O2A) from two carboxylate groups (Fig. 3). The interatomic Cd–N bond distances (2.437(3)–2.554(3) Å) are slightly longer than those found in other similar complexes of Cd(II), [CdI<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NCOOMe)<sub>2</sub>] and [CdI<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>NCOOPrn)<sub>2</sub>] (2.346–2.359 Å), whereas the Cd–O bonds (2.594(4) Å) are approximately the same as the ones found

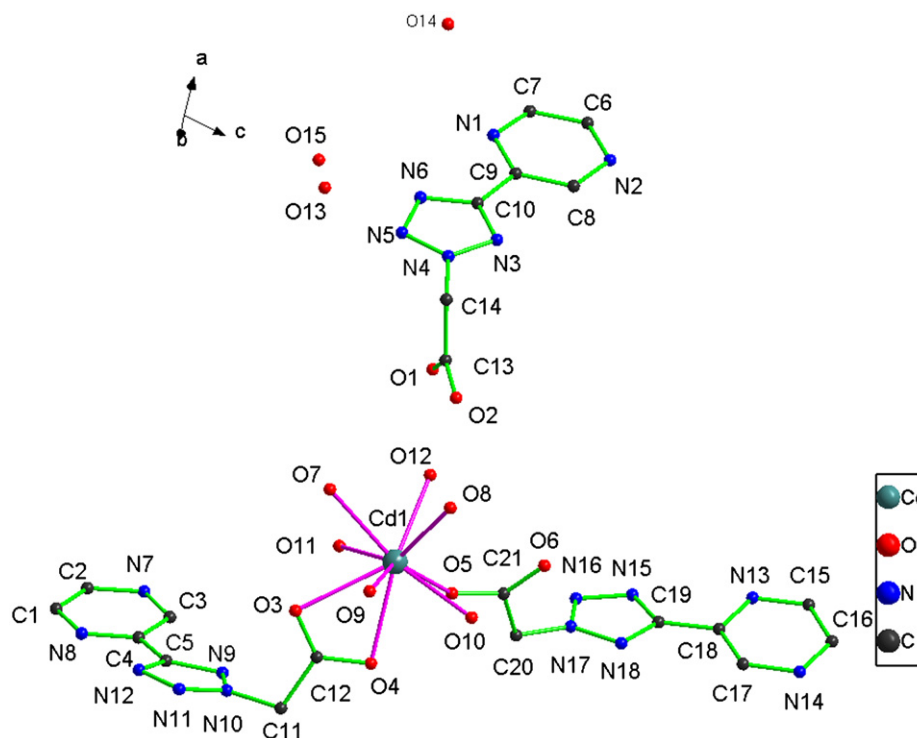


Fig. 1. Coordination environment of Cd(II) atom of complex 1. Hydrogen atoms are omitted for clarity.

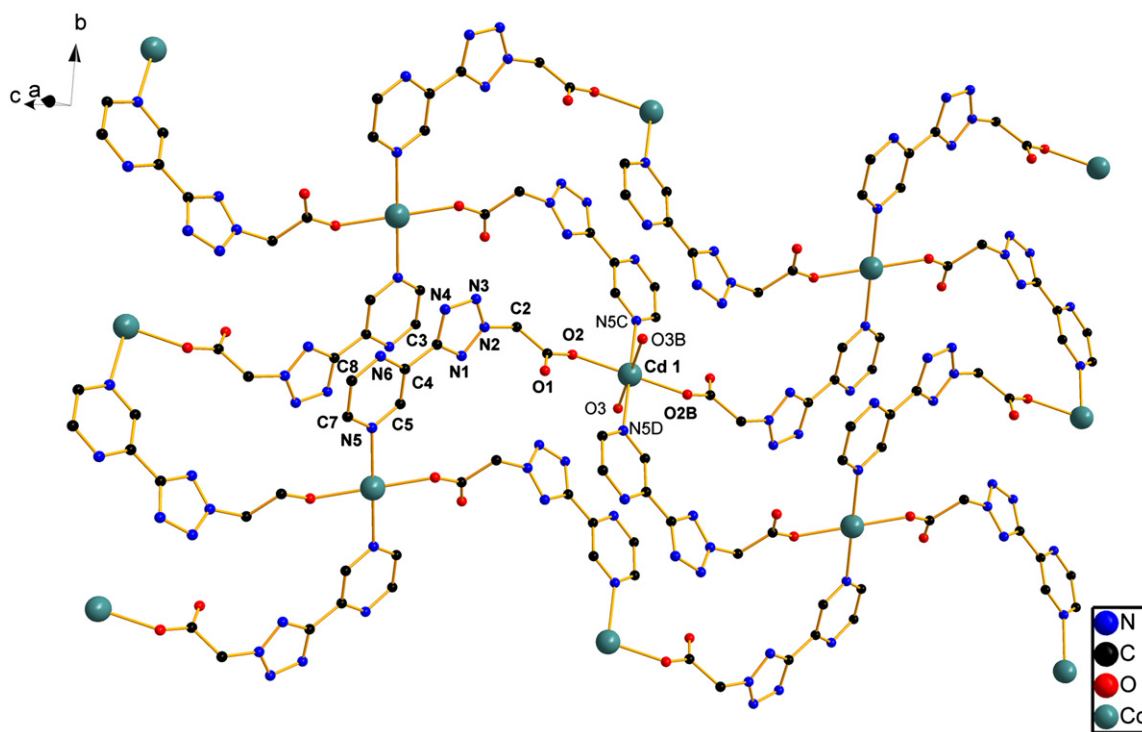


Fig. 2. 2D coordination network of 2 extended along the *bc* planes (hydrogen atoms are omitted for clarity). Showing the coordination environment of Cd(II) atom.

for these complexes (2.503–2.598 Å) [16]. Each pztza ligand exhibits a quadridentate chelating mode (Scheme 2(IV)), chelating the Cd (II) atom via pyrazinyl N3 and tetrazolate N6 with a five-membered chelate ring and chelating the other one Cd (II) atom via carboxylate group O1 and O2 with a four-membered chelate ring, generating a 2D network. Although the single-layered network contains cavities filled by methanol molecules

with the Cd...Cd distance of 13.418(8) Å, the effective cavities in the actual crystal structure of 3 are further reduced due to the significant offset stacking of adjacent two 2D networks. The adjacent 2D layers are further connected through the weak hydrogen bonding interactions between C–H groups and carboxylate groups of the ligands [C5–H5...O1 – 1.5–*x*, 0.5–*y*, 1–*z*. 3.288(6) Å/144°] to construct a 3D framework (Fig. S3).

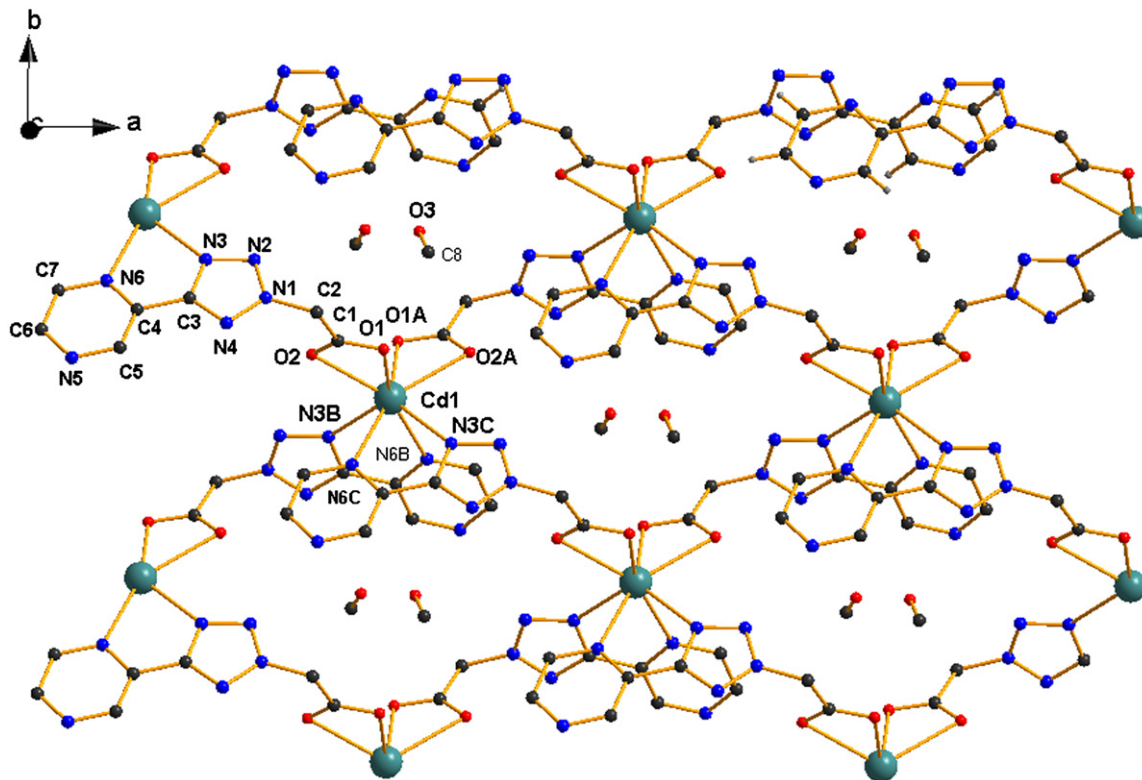


Fig. 3. 2D framework of **3** extended along the *ab* plane (hydrogen atoms are omitted for clarity). Showing the coordination environment of Cd(II) atom.

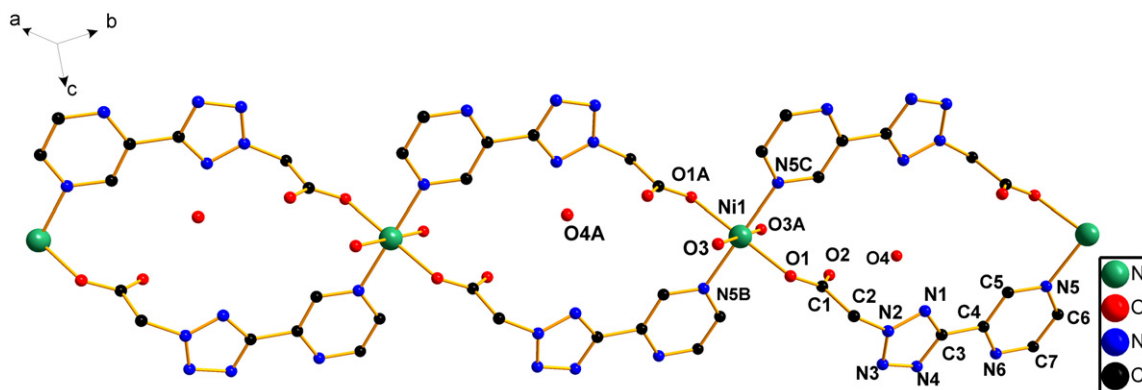


Fig. 4. 1D chain of **10** viewed along *b* axis (hydrogen atoms are omitted for clarity). Showing the coordination environment of Ni(II) atom.

### 3.2.4. Crystal structures of $[M(\text{ptza})_2(\text{H}_2\text{O})_2] \cdot n(\text{H}_2\text{O})$ [ $M = \text{Co}(\mathbf{4})$ ( $n = 6$ ), $\text{Co}(\mathbf{5})$ ( $n = 2$ ), $\text{Zn}(\mathbf{7})$ ( $n = 0$ ), $\text{Zn}(\mathbf{8})$ ( $n = 2$ ), $\text{Ni}(\mathbf{10})$ ( $n = 2$ )]

The X-ray structure analysis reveals that complex **4**, **5**, **7**, **8**, **10** have similar structure and complex **10** with crystallize in triclinic space group *P* was taken as an example for detail. In **10**, the analysis of the asymmetric unit suggest the local coordination geometry around Ni(II) center adopts a slight distorted octahedral coordination mode and contains one nickel atom, two pztza ligands, two coordinated water molecules and two uncoordinated water molecules. The Ni(II) center is coordinated by two nitrogen atoms (N5B, N5C) from two pyrazinyl groups, two carboxylate oxygen atoms (O1, O1A) and two water molecules (O3, O3A) (Fig. 4). The Ni–N bond length is (2.132(5) Å) and Ni–O distance falls in the range of 2.044(4)–2.056(3) Å which was similar to those reported in the related Ni(II) complexes [17]. The ligand–metal–ligand bite angles differ from the ideal value of 90°, varying between 88.4(3)° and 91.6(14)°. It is noticeable that the all bond angles around the Ni(II) center [N5–Ni–N5A, O1–Ni–O1A,

O3–Ni–O3A] are 180°. The linking mode of the pztza ligands is similar to that of **2**. In **10**, the pztza adopts a bidentate bridging coordination mode (Scheme 2 (III)), binding to two Ni(II) atoms by pyrazinyl N5 and carboxylate group O1 atoms, while in complex **2** it is via the N5, O2 sites. Two neighboring Ni ions are bridged by two bidentate bridging pztza ligands to form the holed 1D chain with the Ni···Ni distance of 10.9938(38) Å (Fig. 4). Then the adjacent 1D network is further connected through the hydrogen bonding interactions between uncoordinated water molecules and N atoms of the pztza ligands [O4–H4A···N4 2–*x*, 1–*y*, 1–*z*. 3.1275 Å/124°; O4–H4A···N6 2–*x*, 1–*y*, 1–*z*. 3.2224 Å/167°], coordinated water molecules [O3–H3A···O4 *x*, –1+*y*, *z*. 2.6811 Å/129°] to give a 3D structure (Fig. S4).

### 3.2.5. Crystal structures of $[\text{CO}(\text{ptza})(\text{H}_2\text{O})\text{Cl}]$ (**6**)

Single crystal Xray analysis reveals that **6** crystallize in monoclinic space group  $P2_1/n$ . The perspective view of **6** is shown

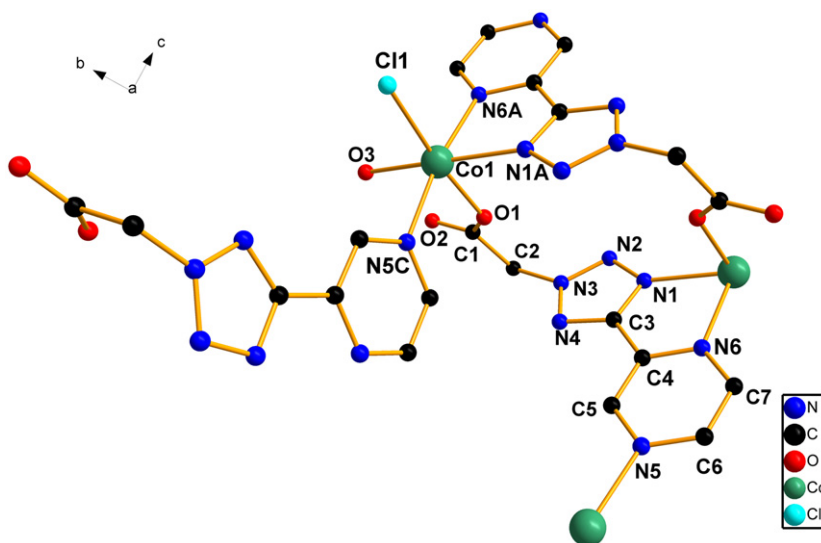


Fig. 5. Perspective view of **6**, showing the coordination environment of Co(II) atom (hydrogen atoms are omitted for clarity).

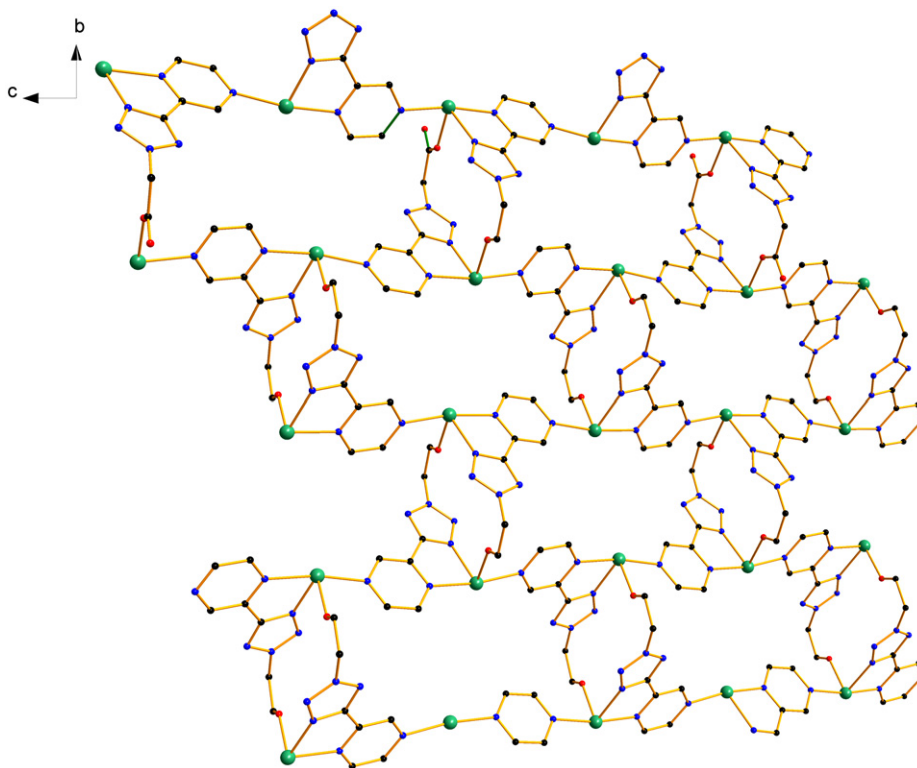


Fig. 6. 2D framework of **6** extended along the *bc* plane (hydrogen atoms are omitted for clarity).

in Fig. 5. The Co (II) center presents a distorted octahedral geometry, defined by three nitrogen atoms (N1A, N6A and N5C) from two different pztza ligands, an oxygen atom (O3) of a water molecule, another oxygen atom (O1) from the carboxylate group and a chlorine atom (Cl1). The Co–N distances from 2.158(4) Å to 2.217(4) Å and the Co–O bond length reach from 2.078(3) Å to 2.108(13) Å are in the range observed in the related analogous complexes [18]. In **6**, the chelating-bridging pztza ligand chelates a Co(II) atom through a tetrazole nitrogen atom (N1) and a pyrazine nitrogen atom (N6) to form a five-membered chelate ring (*M*–N1–C3–C4–N6) and simultaneously links other two Co (II) via

pyrazinyl N5 and carboxylate group O1 (Scheme 2 (V)). Two tetrazole rings and their connected carboxylate groups of the pztza ligands set up a double bridge between neighboring Co(II) atoms to produce a 15-membered bimetallic cycle of  $[\text{Co}_2(\text{ptza})_2]$ , which exhibits the rectangular shape, with the diagonal Co···Co separation being 7.2310 Å (Fig. 6). Each bimetallic cycle is connected to four identical motifs through the pyrazinyl rings from the pztza ligands, and those lead to a 2D sheet viewed along *a* axis. These 2D framework are further stabilized by weak hydrogen bonding interaction O–H···Cl [O3–H3A···Cl1–*x*, 3–*y*, –*z*. 3.1185 Å/127°] to construct a 3D framework (Fig. S5).



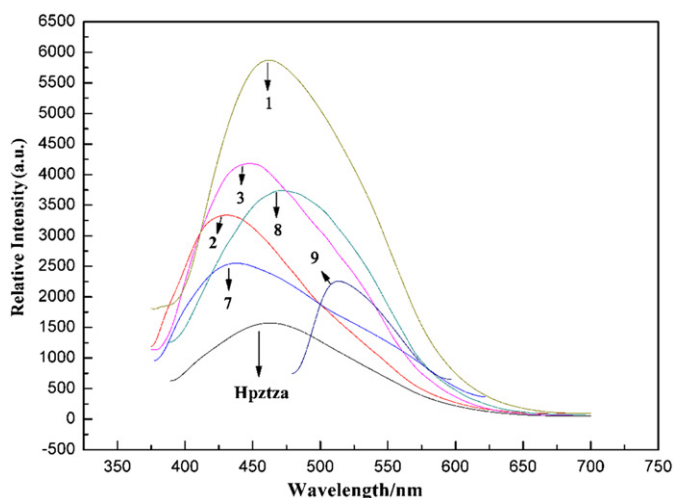


Fig. 7. Solid-state fluorescent spectra for Hpzta, 1–3, 6, 9 and 10.

### 3.3. Luminescent properties

The solid-state emission spectra of **1–10** were measured at room temperature (Fig. 7). In the solid state, complex **1, 2, 3, 7, 8** and **9** exhibit strong fluorescent emission bands at ca. 467, 435, 461, 415, 477, and 505 nm with  $\lambda_{\text{ex}}=377$  nm,  $\lambda_{\text{ex}}=370$  nm,  $\lambda_{\text{ex}}=374$  nm,  $\lambda_{\text{ex}}=351$  nm,  $\lambda_{\text{ex}}=373$  nm and  $\lambda_{\text{ex}}=458$  nm, respectively. The free Hpzta exhibited weak fluorescent emission bands at ca. 468 nm upon excitation at ca. 368 nm. Compared with the emission spectrum of Hpzta, the obvious blue shift of emission length 33 nm in **2** and 53 nm in **7** have been observed, so the emission peaks **2** and **7** can be ascribed to the emission of ligand-to-metal charge-transfer (LMCT) that are in reasonable agreement with literature examples on this class of zinc(II) and cadmium(II) coordination complexes previously reported [19,20]. The emission of **1, 3** and **8** can probably be assigned to intraligand ( $\pi-\pi^*$ ) fluorescent emission since a similar emission ( $\lambda_{\text{max}}=468$  nm) is also observed for free Hpzta. Furthermore, the incorporation of Zn(II)/Cd(II) effectively increased the conformational rigidity of pztza ligand and reduced the loss of energy via vibration motions. Thus, the enhanced fluorescence intensities of **1, 2, 3, 7** and **8** were detected [21]. The emission peaks at 505 nm of **9** can be ascribed to the intraligand transition of Hpzta modified by metal coordination, because photoluminescence behavior is closely associated with the local environment around the metal ion. Complexes **4–6, 10** do not exhibit detectable emission. The reason is complexes **4–6, 10** contain metals (Co, Ni) with low energy  $d-d$  transitions. These transitions quench luminescence. This is extremely rare that such complexes are luminescent.

## 4. Conclusion

To the best of our knowledge, we are the first to investigate coordination complexes containing pztza ligand. Ten new transition metal-based complexes with pztza ligand have been successfully constructed. In the crystals of **1–10**, complex **1** has mononuclear structure, complexes **4, 5, 7, 8, 10** have 1D polymeric chains bearing distinct intermolecular hydrogen-bond interactions to form 3D supramolecular networks, complexes **2, 9** have unusual 2D bilayer networks and form 3D supramolecular networks with their molecular hydrogen-bond interactions and complexes **3, 6** exhibit 2D frameworks. The strong coordinate abilities of flexible carboxylate groups and tetrazole ring endow

Hpzta with abundant coordination modes, and five new coordination modes of the pztza ligand have been observed in **1–10**. Furthermore, the **1, 2, 3, 7, 8** and **9** complexes exhibit strong fluorescent emission. Our research results indicate that, as a promising new type of multifunctional ligand, Hpzta has a great potential in the field of coordination complexes and further endeavors for exploration of Hpzta complexes are underway in our workgroup.

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## Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with Cambridge Crystallographic Data Center, CCDC reference numbers 799961–799970 (**1–10**, respectively). These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## Appendix B. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2011.11.017](https://doi.org/10.1016/j.jssc.2011.11.017).

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