Synthesis, Crystal Structure, and Thermal Properties of Three Novel Complexes Based on 2,3-Pdc[1]

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Abstract—Three new metal-organic complexes, $[Cd_4(2,3\text{-}Pdc)_4 \cdot 4H_2O]$ (**I**), $[Fe_4(2,3\text{-}Pdc)_4 \cdot 12H_2O]$ (**II**), $[Ba_8(2,3\text{-}Pdc)_4 \cdot 12H_2O]$ (**III**) (2,3-Pdc = 2,3-pyridinedicarboxylic acid), have been synthesized and characteristic by IR spectrum, elemental analysis, single-crystal X-ray diffraction, thermogravimetric analysis. X-ray structure analysis shows that complex **I** is 3D structure, complex **II** and complex **III** are 1D chain structures (CIF files CCDC nos. 1002757 (**I**), 1002888 (**II**) and 1002980 (**III**)). 2,3-Pdc has many kinds of coordination mode, so it can form many different of coordination polymers. Complexes can be packed by the weak C−H···O, N−H···O and π−π interactions.

INTRODUCTION

Crystal engineering of metal complexes, especially coordination polymers have been greatly developing for the past decades [1−10], because of their various structure and potential applications as electronic, magnetic, optical, absorbent and catalytic materials [11−16]. As bridging ligand, carboxylate ligand, particularly pyridine carboxylic acid, forms complicated coordination polymers much easier. So it is necessary to study the syntheses and crystal structure of the complexes formed by pyridine systematically to understand the factors that influence the formation and structures of such complexes. We will study that may lead to functional materials and also provide theoretical foundations for supramolecular chemistry and crystal engineering [17]. The role of hydrogen bonding in metal-coordinated network structures result in a large number of coordination polymers.

2,3-Pyridinedicarboxylic acid (2,3-Pdc) is a representative bridging ligand and carboxylate ligand. It has nitrogen atom and oxygen atom, so 2,3-Pdc can have many kinds of coordination mode. In this paper, we report synthesis the three novel complexes, $[Cd_4(2,3\text{-}Pdc)_4 \cdot 4H_2O]$ (**I**), $[Fe_4(2,3\text{-}Pdc)_4 \cdot 12H_2O]$ (**II**), $[Ba_8(2,3\text{-}Pdc)_4 \cdot 12H_2O]$ (**III**).

EXPERIMENTAL

Materials and methods. All reagents and solvents were used as supplied commercially. Elemental analysis (C, H, and N) were carried out in a PerkinElmer model 240 automatic instrument. Infrared (IR) spectrum on KBr pellets were performed on a BRUKER EQUINOX-55 spectrometer from 4000−400 cm^{-1}. The X-ray powder diffraction (XRPD) was recorded on a XD-3 diffractometer (Beijing, China) at 36 kV, 25 mA for a Cu-target tube, and a graphite monochromator. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the Mercury (Hg) program available free of charge via the Internet at http://www.iucr.org.

Synthesis of complex I. 2,3-Pdc (0.0850 g, 0.5 mmol), nicotinic acid (0.0346 g, 0.5 mmol) and $CdCl_2 \cdot 2H_2O$ (0.0856 g, 0.5 mmol) were added to a mixture of 3 mL DMF (DMF = N,N-Dimethylformamide), 4 mL ethanol, 8 mL H_2O. The resulting mixture was stirred at room temperature until it was homogeneous, and then sealed in a 20 mL Teflon-lined stainless reactor, kept under autogenous pressure in 130°C for 72 h, and then slowly cooled to room temperature at a rate of 5°C/h. Then white crystals suitable for X-ray diffraction were separated and washed with water, which were stable in air and insoluble in water and common white solvents. The yield was 70% based on Cd.

For $C_{28}H_{20}N_4O_{20}Cd_4$

anal. calcd., %: C, 28.45;   H, 1.71;   N, 4.74.
Found, %:   C, 28.38;   H, 1.67;   N, 4.75.

IR data (KBr; ν, cm^{-1}): 3748 m, 3672 m, 3648 m, 3522 m, 1666 m, 1628 s, 1544 v.s, 1458 s, 1400 s, 1378 s, 1269 s, 1233 s, 1102 v.s, 871 s, 841 s, 776 s, 702 s, 542 m, 452 s.

Synthesis of complex II. 2,3-Pdc (0.0850 g, 0.5 mmol), $FeCl_2 \cdot 4H_2O$ (0.1268 g, 1 mmol) were added to a mixture of 3 mL DMF, 5 mL methanol,

Table 1. Crystallographic data and structural refinement details of complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
Formula weight	1182.08	895.05	2634.74
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pca2_1$	$P2_1/c$
a, Å	6.5512(14)	16.229(3)	6.9035(7)
b, Å	11.0537(2)	6.8269(11)	26.6101(7)
c, Å	10.7444(2)	8.5735(14)	9.0230(6)
α, deg	90	90	90
β, deg	97.655(2)	90	90.295(5)
γ, deg	90	90	90
Volume, Å^3	771.1(3)	949.9(3)	1657.5(2)
Z	4	4	4
ρ_{calc}, g cm^{-3}	2.546	1.923	2.640
Absorption coefficient, mm^{-1}	2.825	1.610	4.794
$F(000)$	568	560	1239
Crystal size, mm	$0.25 \times 0.14 \times 0.15$	$0.28 \times 0.20 \times 0.19$	$0.29 \times 0.22 \times 0.17$
θ Range for data collection, deg	2.66–26.99	2.51–25.45	1.53–27.00
Reflections collected/independent	4775/1675	5055/1757	10133/3593
R_{int}	0.0357	0.0359	0.0949
Reflections ($I > 2\sigma(I)$)	1234	1640	2729
Completeness to $\theta = 28.47°$, %	99.7	100	99.5
Max and min transmission	0.8832 and 0.8355	0.8081 and 0.7104	0.8382 and 0.8196
Data/restraints/parameters	1675/0/127	1757/1/145	3593/636/271
Goodness-of-fit on F^2	1.046	1.065	1.089
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0323$	$R_1 = 0.0393$	$R_1 = 0.0849$
	$wR_2 = 0.0789$	$wR_2 = 0.1013$	$wR_2 = 0.2325$
R indices (all data)	$R_1 = 0.0378$	$R_1 = 0.0427$	$R_1 = 0.0985$
	$wR_2 = 0.0802$	$wR_2 = 0.1040$	$wR_2 = 0.2391$
Largest difference peak and hole, e Å^{-3}	0.902 and −1.641	0.301 and −0.334	0.609 and −1.343

Table 2. Selected bond distances (Å) and angles (deg) for structures **I–III***

Bond	d, Å	Bond	d, Å
		I	
Cd(1)–O(3)$^{\#1}$	2.246(3)	Cd(1)–O(5)$^{\#2}$	2.260(3)
Cd(1)–O(2)	2.309(3)	Cd(1)–N(1)	2.320(4)
Cd(1)–O(4)$^{\#3}$	2.323(3)	Cd(1)–O(1)	2.371(3)
		II	
Fe(1)–O(1)	2.074(3)	Fe(1)–O(7)	2.120(3)
Fe(1)–O(5)	2.120(4)	Fe(1)–O(3)$^{\#1}$	2.131(3)
Fe(1)–N(1)	2.192(4)	Fe(1)–O(6)	2.206(3)

Angle	ω, deg	Angle	ω, deg
		III	
Ba(1)–O(6)	2.713(9)	Ba(1)–O(7)$^{\#1}$	2.727(10)
Ba(1)–O(3)$^{\#2}$	2.744(10)	Ba(1)–O(4)$^{\#3}$	2.786(10)
Ba(1)–O(12)	2.82(2)	Ba(1)–O(8)	2.852(10)
Ba(1)–O(2)	2.890(10)	Ba(1)–N(1)$^{\#3}$	2.914(11)
Ba(1)–O(1)	3.071(10)	Ba(1)–O(4)$^{\#2}$	3.112(10)
Ba(1)–O(5)$^{\#4}$	3.216(10)	Ba(2)–O(3)$^{\#5}$	2.700(10)
Ba(2)–O(2)$^{\#3}$	2.744(10)	Ba(2)–O(6)$^{\#2}$	2.762(10)
Ba(2)–O(5)	2.769(9)	Ba(2)–O(11)	2.828(14)
Ba(2)–O(1)$^{\#5}$	2.864(10)	Ba(2)–O(7)$^{\#3}$	2.873(9)
Ba(2)–N(2)	2.915(11)	Ba(2)–O(8)$^{\#3}$	3.005(10)
Ba(2)–O(5)$^{\#2}$	3.107(10)	Ba(2)–O(4)$^{\#6}$	3.199(10)

Angle	ω, deg	Angle	ω, deg
		I	
O(3)$^{\#1}$Cd(1)O(5)$^{\#2}$	91.64(11)	O(3)$^{\#1}$Cd(1)O(2)	171.29(10)
O(5)$^{\#2}$Cd(1)O(2)	97.07(11)	O(3)$^{\#1}$Cd(1)N(1)	105.18(11)
O(5)$^{\#2}$Cd(1)N(1)	105.27(12)	O(2)Cd(1)N(1)	72.22(10)
O(3)$^{\#1}$Cd(1)O(4)$^{\#3}$	88.92(12)	O(5)$^{\#2}$Cd(1)O(4)$^{\#3}$	163.47(11)
O(2)Cd(1)O(4)$^{\#3}$	82.83(12)	N(1)Cd(1)O(4)$^{\#3}$	90.49(11)
O(3)$^{\#1}$Cd(1)O(1)	80.88(11)	O(5)$^{\#2}$Cd(1)O(1)	84.32(11)
O(2)Cd(1)O(1)	100.26(11)	N(1)Cd(1)O(1)	168.26(12)
O(4)$^{\#3}$Cd(1)O(1)	79.46(11)		
		II	
O(1)Fe(1)O(7)	92.90(13)	O(1)Fe(1)O(5)	94.68(14)
O(7)Fe(1)O(5)	83.80(14)	O(1)Fe(1)O(3)$^{\#1}$	100.30(14)
O(7)Fe(1)O(3)$^{\#1}$	85.92(14)	O(5)Fe(1)O(3)$^{\#1}$	162.23(13)
O(1)Fe(1)N(1)	76.98(13)	O(7)Fe(1)N(1)	166.26(14)
O(5)Fe(1)N(1)	87.74(14)	O(3)$^{\#1}$Fe(1)N(1)	104.85(14)
O(1)Fe(1)O(6)	172.73(13)	O(7)Fe(1)O(6)	93.88(13)
O(5)Fe(1)O(6)	83.45(13)	O(3)$^{\#1}$Fe(1)O(6)	82.82(12)
N(1)Fe(1)O(6)	95.89(13)		
		III	
O(6)Ba(1)O(7)$^{\#1}$	140.2(3)	O(6)Ba(1)O(3)$^{\#2}$	103.0(3)
O(7)$^{\#1}$Ba(1)O(3)$^{\#2}$	73.3(3)	O(6)Ba(1)O(4)$^{\#3}$	71.5(3)
O(7)$^{\#1}$Ba(1)O(4)$^{\#3}$	72.0(3)	O(3)$^{\#2}$Ba(1)O(4)$^{\#3}$	62.8(3)
O(6)Ba(1)O(12)	87.5(5)	O(7)$^{\#1}$Ba(1)O(12)	105.5(4)
O(3)$^{\#2}$Ba(1)O(12)	35.4(4)	O(4)$^{\#3}$Ba(1)O(12)	86.6(6)
O(4)$^{\#2}$Ba(1)O(5)$^{\#4}$	73.2(2)	O(3)$^{\#5}$Ba(2)O(2)$^{\#3}$	140.1(3)
O(3)$^{\#5}$Ba(2)O(6)$^{\#2}$	103.4(3)	O(2)$^{\#3}$Ba(2)O(6)$^{\#2}$	73.5(3)
O(3)$^{\#5}$Ba(2)O(5)	71.8(3)	O(2)$^{\#3}$Ba(2)O(5)	71.8(3)
O(6)$^{\#2}$Ba(2)O(5)	63.2(3)	O(3)$^{\#5}$Ba(2)O(11)	72.0(4)
O(2)$^{\#3}$Ba(2)O(11)	105.4(3)	O(6)$^{\#2}$Ba(2)O(11)	33.7(3)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ x, $-y + 1/2$, $z - 1/2$; $^{\#2}$ $-x + 2$, $y + 1/2$, $-z + 3/2$; $^{\#3}$ $-x + 1$, $y + 1/2$, $-z + 3/2$ (for **I**); $^{\#1}$ $-x + 1/2$, y, $z - 1/2$ (for **II**); $^{\#1}$ $x - 1$, y, z; $^{\#2}$ x, $-y + 3/2$, $z - 1/2$; $^{\#3}$ x, y, $z - 1$; $^{\#4}$ x, $-y + 3/2$, $z + 1/2$; $^{\#5}$ $x + 1$, y, $z - 1$; $^{\#6}$ $x + 1$, $-y + 3/2$, $z - 3/2$ (for **III**).

Table 3. Geometric parametes of hydrogen bonds of complexes **I–III**

D–H⋯A	Distance, Å				Symmetry codes
	D–H	H⋯A	D⋯A	D–H⋯A	
I					
O(1)–H(1*A*)⋯O(3)	0.85	2.09	2.934(4)	173	$-x + 1, y - 1/2, -z + 1/2$
O(1)–H(1*B*)⋯O(4)	0.85	2.03	2.879(5)	173	$x, -y + 3/2, z + 1/2$
II					
O(5)–H(5*A*)⋯O(2)	0.85	1.88	2.732(6)	176	$-x + 1/2, y, z + 1/2$
O(5)–H(5*B*)⋯O(3)	0.85	1.90	2.751(5)	176	$x + 1/2, -y + 1, z$
O(6)–H(6*A*)⋯O(2)	0.85	1.87	2.721(4)	174	$x + 1/2, -y + 1, z$
O(6)–H(6B)⋯O(4)	0.85	1.86	2.705(5)	174	$x + 1/2, -y, z$
O(7)–H(7*A*)⋯O(4)	0.85	1.88	2.724(5)	174	$x + 1/2, -y + 1, z$
O(7)–H(7*B*)⋯O(6)	0.85	2.00	2.847(5)	174	$-x + 1, -y + 1, z - 1/2$
III					
O(10)–H(10*A*)⋯O(1)	0.85	2.11	2.894(19)	171	$-x + 1, -y + 1, -z + 1$
O(10)–H(10*B*)⋯O(9)	0.85	2.03	2.820(19)	171	$x, y, z + 1$
O(11)–H(11*A*)⋯O(7)	0.85	2.13	2.925(17)	172	
O(11)–H(11*B*)⋯O(5)	0.85	2.14	2.978(17)	171	$x, -y + 3/2, z - 1/2$
O(12)–H(12*A*)⋯O(3)	0.85	2.06	2.899(2)	174	$x, -y + 3/2, z - 1/2$
O(12)–H(12*B*)⋯N(1)	0.85	2.08	2.912(4)	178	$x, -y + 3/2, z - 1/2$

8 mL H_2O. The resulting mixture was stirred at room temperature until it was homogeneous, and then sealed in a 20 mL Teflon-lined stainless reactor, kept under autogenous pressure in 120°C for 72 h, and then slowly cooled to room temperature at a rate of 5°C/h. Then red bulk crystals suitable for X-ray diffraction were separated and washed with water, which were stable in air and insoluble in water and common red solvents. The yield was 67% based on Fe.

For $C_{28}H_{36}N_4O_{28}Fe_4$

anal. calcd., %: C, 30.57; H, 3.30; N, 5.09.
Found, %: C, 30.54; H, 3.32; N, 5.06.

IR data (KBr; ν, cm^{-1}): 3460 m, 3197 m, 1657 m, 1618 s, 1585 s, 1461 s, 1381 v.s, 1272 s, 1233 s, 1155 s, 1105 v.s, 1064 s, 880 s, 824 m, 772 m, 708 s, 543 s.

Synthesis of complex III was similar to that of **II** except that $BaCl_2$ (0.105 g, 0.5 mmol) was used instead of $FeCl_2 \cdot 4H_2O$ (0.1268 g, 1 mmol). The pH was adjusted into 6, the mixture keep under autogenous pressure in 120°C for 78 h, and then slowly cooled to room temperature at a rate of 5°C/h. Then white crystals suitable for X-ray diffraction were separated and washed with water, which were stable in air and insol-

uble in water and common white solvents. The yield was 58% based on Ba.

For $C_{56}H_{48}N_8O_{44}Ba_8$

|			
anal. calcd., %:	C, 25.53;	H, 1.84;	N, 4.25.
Found, %:	C, 25.49;	H, 1.86;	N, 4.28.

IR data (KBr; ν, cm^{-1}): 3853 m, 3748 m, 3673 m, 3648 m, 3420 m, 3049 m, 599 v.s, 1559 v.s, 1453 v.s, 1394 v.s, 1232 s, 1180 m, 1152 m, 1092 s, 1057 m, 869 v.s, 833 v.s, 811 s, 781 s, 712 v.s, 536 s, 410 s.

X-ray structure determination. Crystallographic data of complex was collected on a Bruker SMART CCD diffractometer with graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 296(2) K. Absorption corrections were applied by using the multi-scan program [18]. The structure was solved by direct methods and successive Fourier difference syntheses (SHELXS-97), and anisotropic thermal parameters for all nonhydrogen atoms were refined by full-matrix least-squares procedure against F^2 (SHELXL-97) [19]. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode with a common thermal parameter. H atoms for H_2O molecules were located in different synthesis and refined isotropically. The crystallographic data and experimental details for the structure analysis are summarized in Table 1, the selected bond lengths and angles are listed in Table 2, meanwhile, the hydrogen-bonds of the complexes are listed in Table 3.

Supplementary material for structures **I**, **II** and **III** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1002757 (**I**), 1002888 (**II**) and 1002980 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single crystal X-ray analysis reveals that complex **I** contain Cd^{2+} ion, four 2,3-Pdc, one water molecule. In complex **I**, the Cd^{2+} ion coordinates with O(3), O(4) and O(5) from three 2,3-Pdc. Then O(2) and N(1) participate in coordination with Cd^{2+} ion, moreover one water molecule takes part in coordination with Cd^{2+} ion, which becomes hexa-coordinated. We can see the environment of Cd in Fig. 1a. In the complex **I**, Cd atoms are bridged by 2,3-Pdc into 3D structure; N(1), O(2), O(3), O(4), O(5) play an important role in construction 3D structure. As shown in Fig. 2a, it seems to exist a big hole. This big hole is irregular hexagon; two Cd atoms, two oxygen atoms and two carbon atoms consist of the hexagon. The hexagons connected to each other to become 3D structure. In addition, there are hydrogen bonds two oxygen atoms, such as O(1)−H(1A)···O(3), O(1)−H(1B)···O(4), each small unit seems to be parallelogram. As shown in
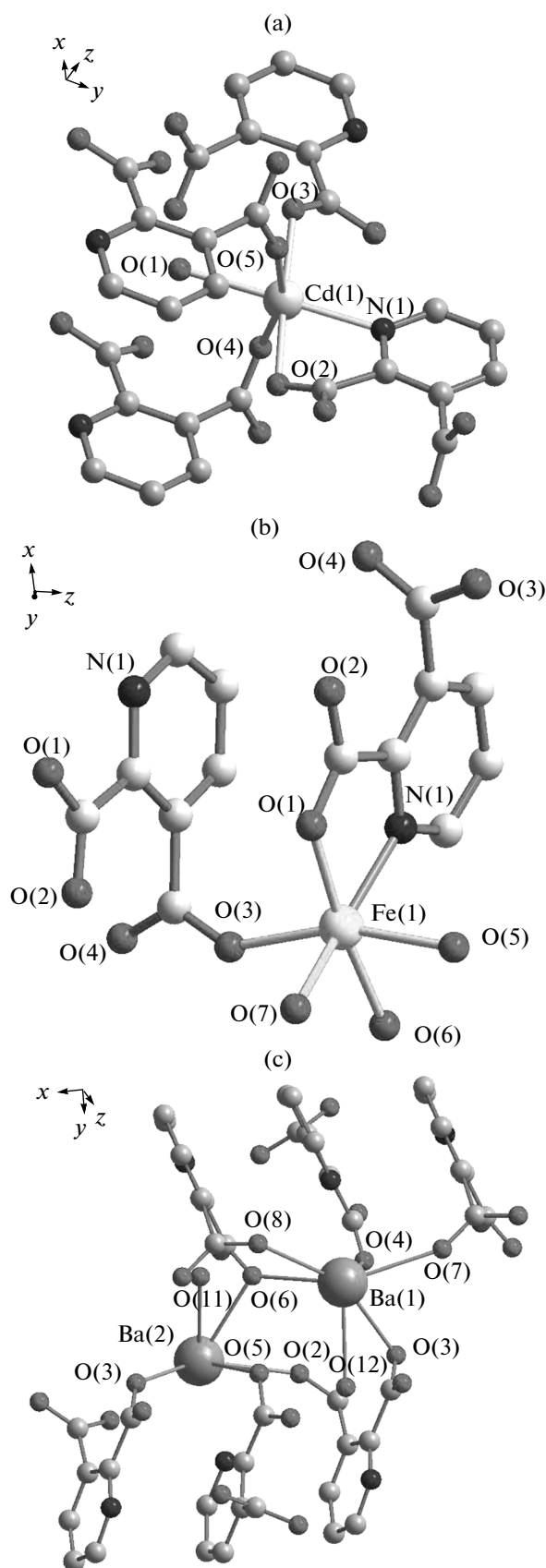
Fig. 1. The coordination environment of **I** (a), **II** (b), **III** (c). Thermal ellipsoids are shown at 30% probability, all H atoms are omitted for clarity.

(a)

(b)
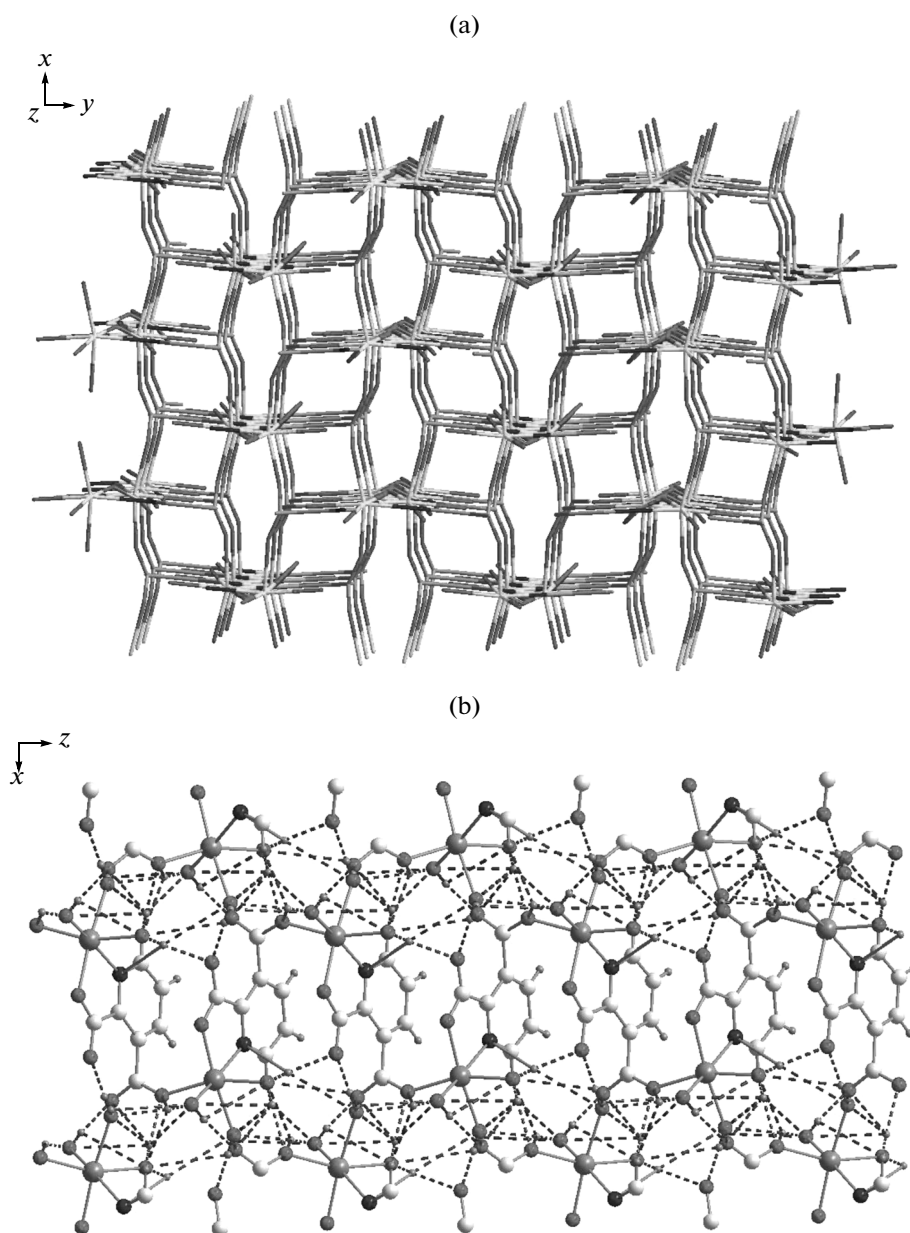
Fig. 2. A view of 3D structure for **I** (a) and **II** (b), **III** (c) via hydrogen bonds. Unnecessary atoms are omitted for clarity.

the Fig. 3, the hydrogen bonds and C, N, O atoms connect to each other, forming supramolecular structure. Then the hydrogen bonds make the 3D structure more stable.

Single crystal X-ray analysis reveals that complex **II** has Fe^{2+} ion, two 2,3-Pdc and three water molecules. The Fe^{2+} ion coordinates with O(3) from one 2,3-Pdc and O(1), N(1) from another 2,3-Pdc, O(5), O(6) and O(7) from three water molecules also take part in coordination with Fe^{2+} ion. So Fe^{2+} becomes hexa-coordinated, as shown in Fig. 1b. We can see the 1D infinite chain in the Fig. 4a. Complex **II** forms 1D chain structure by 2,3-Pdc and Fe atom, which is

the most key component. Besides, O(3), N(1), O(1) also play a role in forming the 1D chain as bridging atoms. We see these hydrogen bonds in Fig. 2b, as O(5)−H(5A)···O(2), O(5)−H(5B)··· O(3), O(6)−H(6A)···O(2), O(6)−H(6B)···O(4), O(7)− H(7A)···O(4), O(7)−H(7B)···O(6). The weak hydrogen bonds lead complex **II** to formation of 3D structure in Fig. 2b. All hydrogen bonds are connected with each other that makes the structure more stable.

Single crystal X-ray analysis reveals that complex **III** contains $Ba(Pdc)_2$, $Ba(OH)_2$ and two water molecules. The O(3), O(4), O(7), O(6), and O(8) atoms from four 2,3-Pdc take part in the coordi-
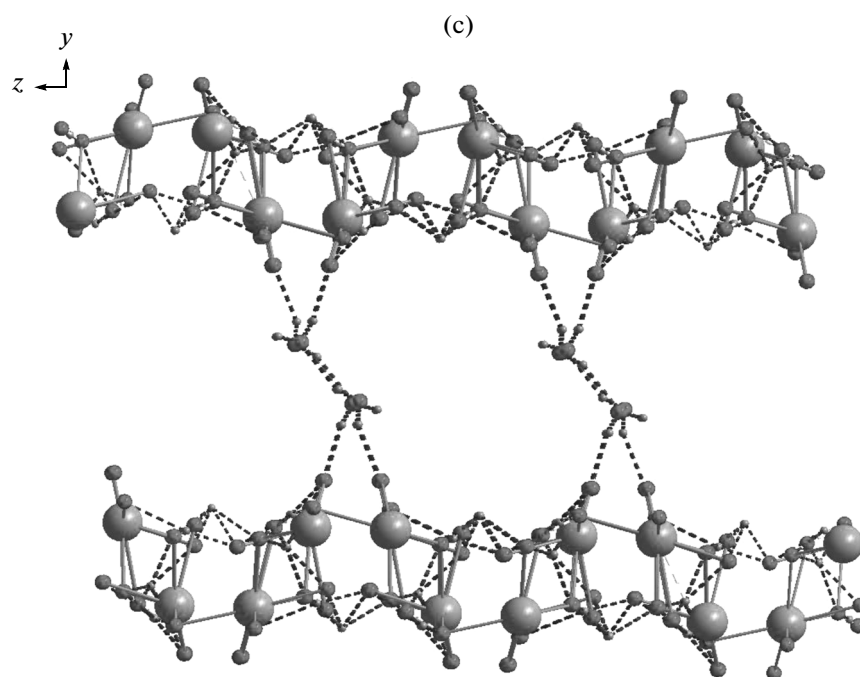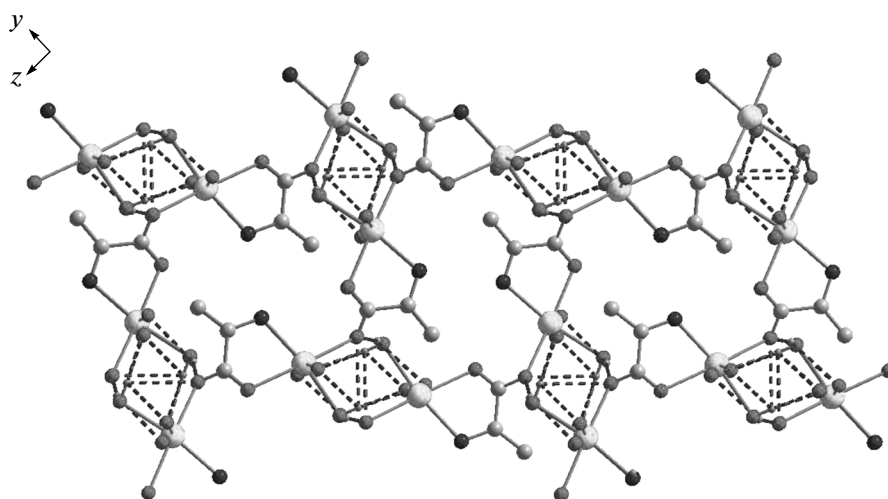
(c)

Fig. 2. (Contd.)

Fig. 3. A perspective view of C−O−Cd−N frame and weak hydrogen bonds for **I**.

nation with $Ba^{2+}(1)$, as well as O(12) from one water molecule participates in coordination with $Ba^{2+}(1)$. Then $Ba^{2+}(1)$ becomes hexa-coordinated, $Ba^{2+}(2)$ is the same. We can see the environment of Ba in Fig. 1c. As shown in Fig. 4b, 2,3-Pdc, Ba and water molecule lead to formation of 1D chain. The interesting thing is that complex **III** forms 3D structure via hydrogen bonds between oxygen and oxygen, such as O(10)−H(10A)···O(1), O(10)−H(10B)··· O(9), O(11)−H(11A)···O(7), O(11)−H(11B)···O(5), O(12)− H(12A)···O(3), O(12)−H(12B)···N(1) (Fig. 2c). There are π−π stacking interactions between 2,3-Pdc and 2,3-Pdc (Fig. 5). The distance are 3.477− 3.469 and 3.477−3.506 Å, hydrogen bonds and π−π stacking interactions make the coordination polymer fairly stable.

(a)

(b)
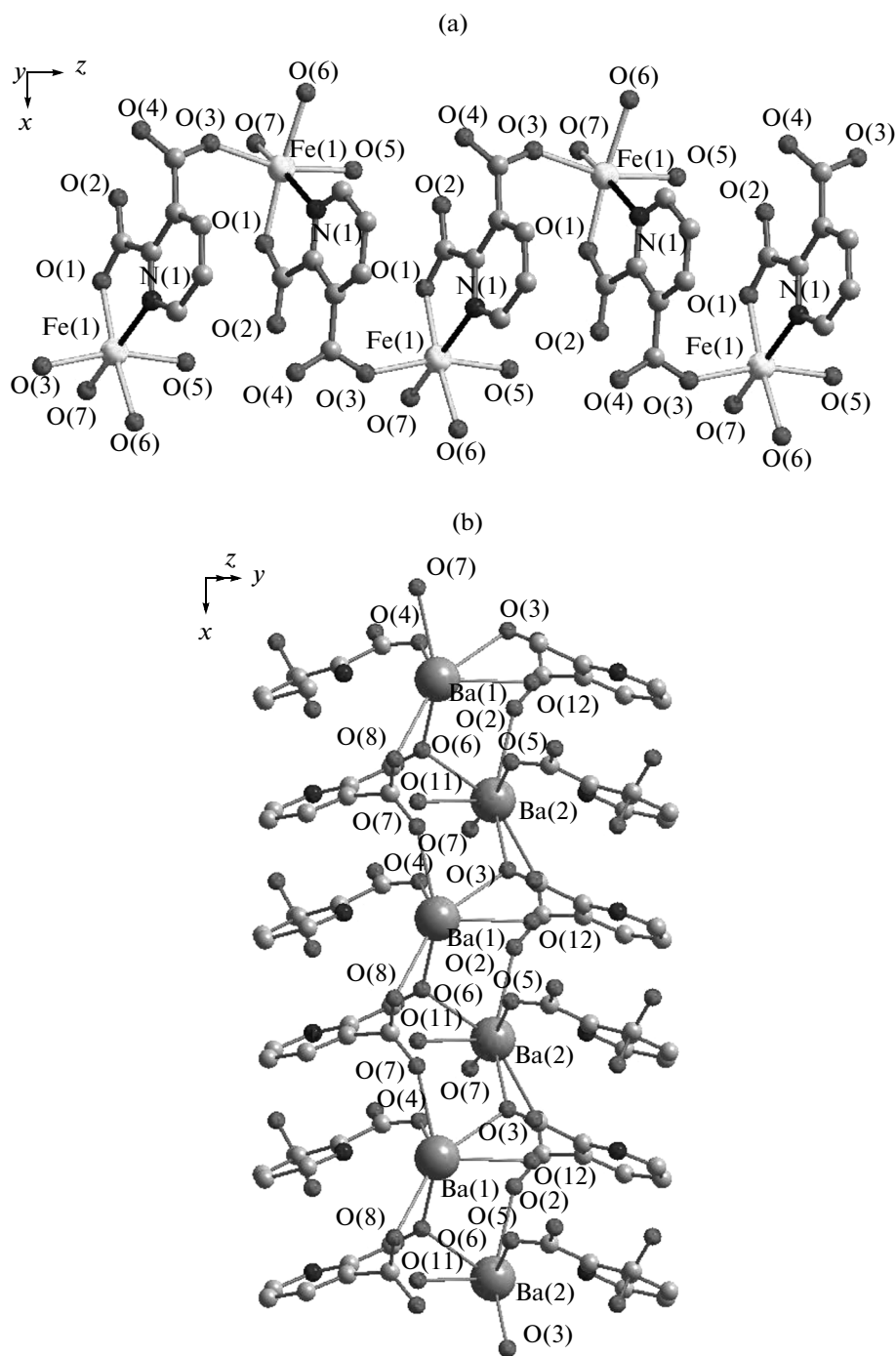
Fig. 4. A view of 1D infinite chain for **II** (a), **III** (b). Unnecessary atoms are omitted for clarity.

Dried samples of **I–III** were characterized by IR spectroscopy. The strong and broad absorptions at 3500–3100 cm^{-1} are attributed to symmetric O−H stretch of lattice and coordinated water molecules in the crystal. The IR spectrum of free ligand shows strong bands of the carboxylate groups at 1628 and 1544 cm^{-1} in complex **I**, 1618 and 1585 cm^{-1} in com-plex **II**, 1599 and 1559 cm^{-1} in complex **III**, which can be assigned as the ν(C=O) antisymmetric stretching vibrations. Besides, the band at around 770 cm^{-1} in all the complexes is attributed to the γ(C−H) of 2,3-Pdc pyridine ring.

For the sake of researching the framework stability of the complex, thermogravimetric analyses. The
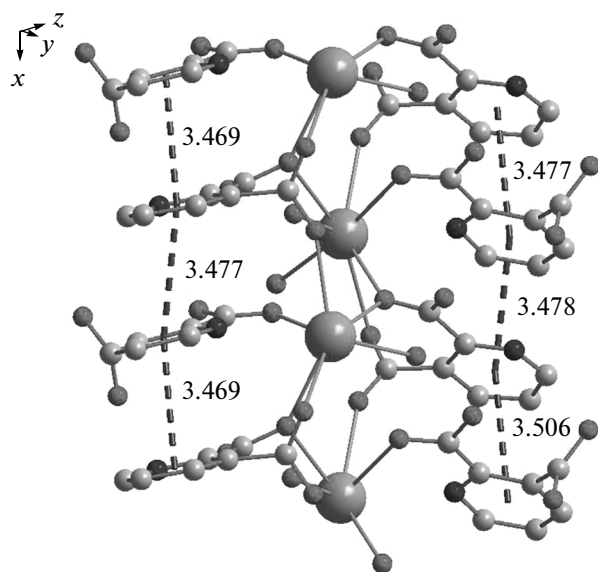
Fig. 5. The 1D layered network of complex **III** via $\pi-\pi$ stacking interactions. Unnecessary atoms are omitted for clarity.

thermal decomposition behaviors of the complex continued to 1000°C in static air atmosphere. The TG shows that the complex **I** and **II** undergoes decomposing in two stages. The first stage happens in the 0−200°C range, conform to decompose about water molecules with weight losses of 9.51% (calcd. 9.47%), 17.92% (calcd. 17.86%) (complex **I** and **II**). The second stage takes place in the 200−700°C range corresponding to loss of 2,3-Pdc with mass loss of 72.65% (calcd. 72.59%), 43.21% (calcd. 43.14%) (complex **I** and **II**). The TG shows that the complex **III** undergoes decomposing in three stages. The first stage happens in the 0−100°C range that conforms to decomposition of water molecules with weight losses of 2.02% (calcd. 1.95%) (complex **III**). The second stage takes place in the 100−350°C range corresponding to loss of Ba(OH)$_2$ with mass loss of 22.52% (calcd. 22.30%). The third stage happens in the 350−800°C range that conforms to decomposition of 2,3-Pdc with weight losses of 21.74% (calcd. 21.61%) (complex **III**). In the end, the decomposition of the complex sustains forming of compounds CdO (expected 17.84%), Fe$_2$O$_3$ (expected 38.87%), and BaO (expected 54.45%).

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