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Two Novel Four-Coordinated Zinc(II) Polymers: Synthesis, Structures, and Properties[1]

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Abstract—The synthsis, crystal structure, thermal analysis and spectroscopic studies of two novel zinc(II) coordination polymers $Zn_4(NA)_4Dpa_2$ (**I**) and $Zn(Inic)(Bpdc)_{0.5}$ (**II**) (NA = niacin, Inic = isonictinic acid, Dpa = 2,2'-biphenyldicarboxlate, Bpdc = 4,4'-biphenyldicarboxylate) are presented here. The crystal structure of **I** is a two-dimensional network whose tetranuclear unit is a slightly distorted square. Two kinds of ligand connect adjacent zinc(II) ions, respectively, in a coordinate direction. The structure of **II** is a three-dimensional and it consist of corrugated square layers of isonictinic acid–bridged zinc(II) ions which are pillared by 4,4'-biphenyldicarboxylate. The rod-ligands in **II** appear as useful tools to control the interlayer metal–metal separation. Each zinc(II) ion in **I** and **II** is four-coordinated with three oxygen atoms and one nitrogen atom building distorted tetrahedron environments.

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INTRODUCTION

The construction of coordination polymers has attracted remarkable interest. These polymers become a quite active research field in recent years, not only due to their fascinating structural diversities such as molecular cage, honeycomb, grid, ladder, polyrotaxanes, and multidimensional frameworks [1, 2], but also because of their interesting properties and potential applications as functional materials in optical, electronic, magnetic fields, gas storage, catalysis, ionic/molecular recognition and drug delivery [3, 4].

Up to now, a great number of inorganic-organic hybrid coordination polymers have been synthesized based on strong covalent bonds or weak supramolecular connections, such as hydrogen bonds and/or π–π interactions [5]. It has been documented that the geometries of the organic ligands have a great effect on the structural framework of such coordination polymers; thus, much effort has been devoted to modifying the building blocks and to controlling the assembled motifs for required products through the selection of different organic ligands. Previous studies have shown that rigid bridging ligands to afford moderately robust networks of variable dimensionality and porosity [6, 7].

We report two novel four-coordinated zinc(II) polymers $Zn_4(NA)_4Dpa)_2$ (**I**) and $Zn(Inic)(Bpdc)_{0.5}$ (**II**) (NA = niacin, Inic = isonictinic acid, Dpa = 2,2'-biphenyldicarboxlate, Bpdc = 4,4'-biphenyldicarboxylate) not only due to their infrequent four-coordinated mode, but also because of their fascinating structural motifs and interesting properties. Herein we reported the syntheses, elemental analysis, IR spectrum, TGA, single-crystal X-ray diffraction analysis and powder X-ray diffraction analysis.

EXPERIMENTAL

Materials and instrumentation. All chemicals were commercial materials of analytical grade and used without purification. Elemental analysis for C, H, and N was carried out on a PerkinElmer 2400 II elemental analyzer. Infrared spectrum was recorded in KBr pellets using a PE Spectrum One FT-IR Spectrometer Fourier transform infrared spectroscopy in the 4000–400 cm^{-1} regions. PerkinElmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG curves in the static air atmosphere at a heating rate of 10 K min^{-1} in the temperature range 25–1000°C using platinum crucibles. Powder X-ray diffraction patterns of all samples were recorded on a Rigaku D/M-2200 T automated diffractometer (Ultima+) using CuK_α radiation ($\lambda = 1.5406$ Å). Graphite monochromator was used and the generator power settings are at 40 kV and 40 mA.

Synthesis of complex I. A mixture of $ZnSO_4 \cdot 7H_2O$ (0.1438 g, 0.5 mmol), H_2Dpa (0.1213 g, 0.5 mmol), NA (0.0616 g, 0.5 mmol), Py (0.5 mL), H_2O (10 mL), methanol (5 mL), and DMF (2.5 mL) was stirred for 20 min in the beaker. Then an aqueous solution of

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NaOH was added dropwise in the stirring condition to adjust the pH value of the mixture to 6. After keeping on stirring for another 1 h, the resulting mixture was transferred to a 30 mL Teflon-lined stainless steel reactor, kept under ordinary pressure at 160°C for 72 h in the oven, and then slowly cooled to room temperature at a rate of 10°C per hour. The colourlessblock crystals which were suitable for X-ray diffraction were isolated directly, washed with methanol and dried in the air (the yield was 86.7%).

For $C_{52}H_{32}N_4O_{16}Zn_4$				
anal. calcd., %:	C, 50.72;	H, 2.60;	O, 20.81;	N, 4.52.
Found, %:	C, 50.68;	H, 2.63;	O, 20.86;	N, 4.46.

IR data (KBr; ν, cm^{-1}): 3071 s, 1608 v.s, 1451 m 1389 v.s, 1219 m, 1147 m, 849 m, 749 s, 697 s.

Synthesis of complex II. A solution of $ZnSO_4 \cdot 7H_2O$ (0.1438 g, 0.5 mmol) and Inic (0.0615 g, 0.5 mmol), which are dissolved in the mixed solvent of 5 mL DMF and 5 mL methanol, was added dropwise with stirring at room temperature to a mixture of H_2Bpdc (0.1213 g, 0.5 mmol) and 10 mL DMF. Then an aqueous solution of sodium hydroxide was dropwise added with stirring to adjust the pH value of the solution being 6. After keeping on stirring for another 1 h, the resulting mixture was transferred to a 30 mL Teflon-lined stainless steel reactor, kept under ordinary pressure at 145°C for 72 h in the oven, and then slowly cooled to room temperature at a rate of 10°C per hour. The purple block crystals which were suitable for X-ray diffraction were isolated directly, washed with methanol and dried in the air (the yield was 81.5%).

For $C_{13}H_8NO_4Zn$				
anal. calcd., %:	C 50.72;	H 2.60;	N 4.55;	O 20.81.
Found, %:	C 50.68;	H 2.68;	N 4.47;	O 20.91.

IR data (KBr; ν, cm^{-1}): 3083 s, 2359 w, 1590 v.s, 1542 s, 1421 s, 1057 m, 1023 m, 769 s, 704 s.

X-ray structure determination. A high-quality crystal of complex was slected and mounted on the top of a glass fiber. The data was measured by a Bruker SMART CCD area detector using graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 296 K. Absorption correction were applied using SADABS program [8]. The crystal structure was solved by the direct method and refined with a full-matrix least-squares technique using SHELXTL program [9]. All non-hydrogen atoms were refined anisotronically. Hydrogen atoms were generated geometrically. The crystal data and structure refinement details for two complexes are shown in Table 1. Selected bond lengths and angles of the complexes are listed in Table 2.

Crystallographic data for the structures **I** and **II** have been deposited with the Cambridge Crystallographic Data Centre (№ 945429 (**I**), 945430 (**II**); deposit @ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The coordination environment around the Zn(II) center in **I** is presented in Fig. 1a with atom numbering scheme. Each Zn(II) atom is tetracoordinated by three oxygen atoms with one coming from μ_1,η^1-carboxylate groups and one coming from μ_2,η^1,η^1-carboxylate groups, which come from the same Dpa ligand. The last oxygen atom and nitrogen come from NA ligand. The coordination polyhedron around Zn(II) atoms are arranged in a 2D network plane composed of $ZnNO_3$ tetrahedra which could be best described as trigonal pyramid. The Zn–N bond distances are in the range from 2.014(5) to 2.054(5) Å while the Zn–O bond distances are in the range from 1.927(4) to 2.008(5) Å (Table 2). The molecular structure of **I** exists as a slightly distorted rectangle cluster (Fig. 2), which contains Zn(II) centres in four different environments. Adjacently nobonding distances of Zn(1)–Zn(4) are 4.5778(15) and 4.7523(15) Å, respectively, while adjacently nobonding distances of Zn(2)–Zn(3) are 4.6030(14) and 4.7068(15) Å, respectively. Adjacently nobonding distances of Zn(1)–Zn(2) and Zn(3)–Zn(4) are constant and are 7.3379(18) and 7.2396(18) Å, respectively (Fig. 3).

Colorless block-shaped crystals of **II** were grown solvothermally. Study by single crystal X-ray diffraction disclosed a 3D framework structure. The Zn shows slightly distorted tetrahedral coordination geometry. It is defined by three oxygen atoms with two (O(3), O(3)') coming from μ_1,η^1-carboxylate groups of two Bpdc ligands and the other two coordinated atoms (O(2), N(1)') coming from two different Inic ligands (Fig. 1b). The overall structure can be viewed as Bpdc ligands pillaring the undulating charge-neutral $[Zn_2(Inic)_4]$ layers. Two bidentate carboxylate groups from two centrosymmetrically related Bpdc ligands coordinate to two zinc(II) centres to form the $[Zn_2(COO)_2]^{2+}$corrugated eight-membered cross-type secondary building unit (SBU, Fig. 4). Two monodentate carboxylates from a pair of centrosymmetrically related Inic ligands coordinate to the two Zn(II) centers, balancing the charges on the SBU. Another pair of nitrogen atoms coming from centrosymmetrically adjacent Inic ligands coordinate to the two Zn(II) centers to form the four-coordinated mode. Thus each SBU becomes a four connecting node, which is linked by Inic ligands to four other SBUs to form the two-dimensional 4^4 (brick-like) net [10] (Fig. 5). The Bpdc ligands coordinate to the Zn(II) centers in two neighboring layers, connecting the layers into the overall 3D structure (Fig. 6). Interestingly, polymer **II** allows three such identical frameworks to interpenetrate each

Table 1. Crystal data and structure refinements for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1230.30	307.57
Temperature, K	293(2)	296(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a, Å	9.235(2)	6.489(4)
b, Å	14.267(3)	18.016(10)
c, Å	18.787(4)	10.704(6)
α, deg	99.729(4)	90
β, deg	97.296(4)	103.744(6)
γ, deg	90.040(3)	90
V, Å^3	2419.2(10)	1215.4(12)
Z	2	4
ρ_{calcd}, g cm^{-3}	1.689	1.681
F(000)	1240	620
θ Rangre, deg	1.11–25.00	2.26–25.00
μ, mm^{-1}	2.038	2.029
Reflections collected/unique	13141/8390	6487/2134
R_{int}	0.0371	0.0276
Data/restraints/parameters	8390/0/685	2134/0/172
Goodness-of-fit on F^2	1.047	1.092
Fianl R indices ($I > 2\sigma(I)$)*	$R_1 = 0.0603$,	$R_1 = 0.0313$,
	$wR_2 = 0.1631$	$wR_2 = 0.0809$
R indices (all data)	$R_1 = 0.1061$,	$R_1 = 0.0408$,
	$wR_2 = 0.1987$	$wR_2 = 0.0862$
Largest diff. peak and hole, e Å^{-3}	1.646 and –0.593	0.935 and –0.273

* $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/Sw(|F_o^2|^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (deg) for **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
Zn(1)–O(16)$^{\#1}$	1.928(4)	Zn(3)–O(8)$^{\#4}$	1.927(5)
Zn(1)–O(2)	1.968(4)	Zn(3)–O(11)	1.961(4)
Zn(1)–O(3)	1.975(5)	Zn(3)–O(10)	1.980(5)
Zn(1)–N(1)	2.014(5)	Zn(3)–N(3)	2.014(5)
Zn(2)–O(6)$^{\#2}$	1.934(5)	Zn(4)–O(14)	1.936(4)
Zn(2)–O(12)$^{\#3}$	1.955(5)	Zn(4)–O(4)	1.963(5)
Zn(2)–O(9)	1.994(5)	Zn(4)–O(1)$^{\#3}$	2.008(5)
Zn(2)–N(4)	2.054(5)	Zn(4)–N(2)	2.021(6)
II			
Zn(1)–O(3)	1.940(2)	Zn(1)–O(4)$^{\#2}$	1.967(2)
Zn(1)–O(2)$^{\#1}$	1.953(2)	Zn(1)–N(1)	2.023(3)
Angle	ω, deg	Angle	ω, deg
I			
O(4)Zn(4)N(2)	118.6(2)	O(9)Zn(2)N(4)	99.0(2)
O(16)$^{\#1}$Zn(1)O(2)	101.43(9)	O(8)$^{\#4}$Zn(3)O(11)	101.5(2)
O(16)$^{\#1}$Zn(1)O(3)	100.1(2)	O(8)$^{\#4}$Zn(3)O(10)	99.7(2)
O(2)Zn(1)O(3)	117.8(2)	O(11)Zn(3)O(10)	119.8(2)
O(16)$^{\#1}$Zn(1)N(1)	133.8(2)	O(8)$^{\#4}$Zn(3)N(3)	136.7(2)
O(2)Zn(1)N(1)	102.8(2)	O(11)Zn(3)N(3)	101.27(9)
O(3)Zn(1)N(1)	102.5(2)	O(10)Zn(3)N(3)	100.2(2)
O(6)$^{\#2}$Zn(2)O(12)$^{\#3}$	99.5(2)	O(14)Zn(4)O(1)$^{\#3}$	129.24(9)
O(6)$^{\#2}$Zn(2)O(9)	128.9(2)	O(4) Zn(4)O(1)$^{\#3}$	95.5(2)
O(12)$^{\#3}$Zn(2)O(9)	94.7(2)	O(14)Zn(4)N(2)	114.1(2)
O(6)$^{\#2}$Zn(2)N(4)	114.7(20	O(1)$^{\#3}$Zn(4)N(2)	98.9(2)
O(12)$^{\#3}$Zn(2)N(4)	120.2(2)		
II			
O(3)Zn(1)O(2)$^{\#1}$	116.52(1)	O(3)Zn(1)N(1)	102.61(1)
O(3)Zn(1)O(4)$^{\#2}$	122.77(1)	O(2)$^{\#1}$Zn(1)N(1)	112.35(1)
O(2)$^{\#1}$Zn(1)O(4)$^{\#2}$	101.68(1)	O(4)$^{\#2}$Zn(1)N(1)	99.85(11)

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

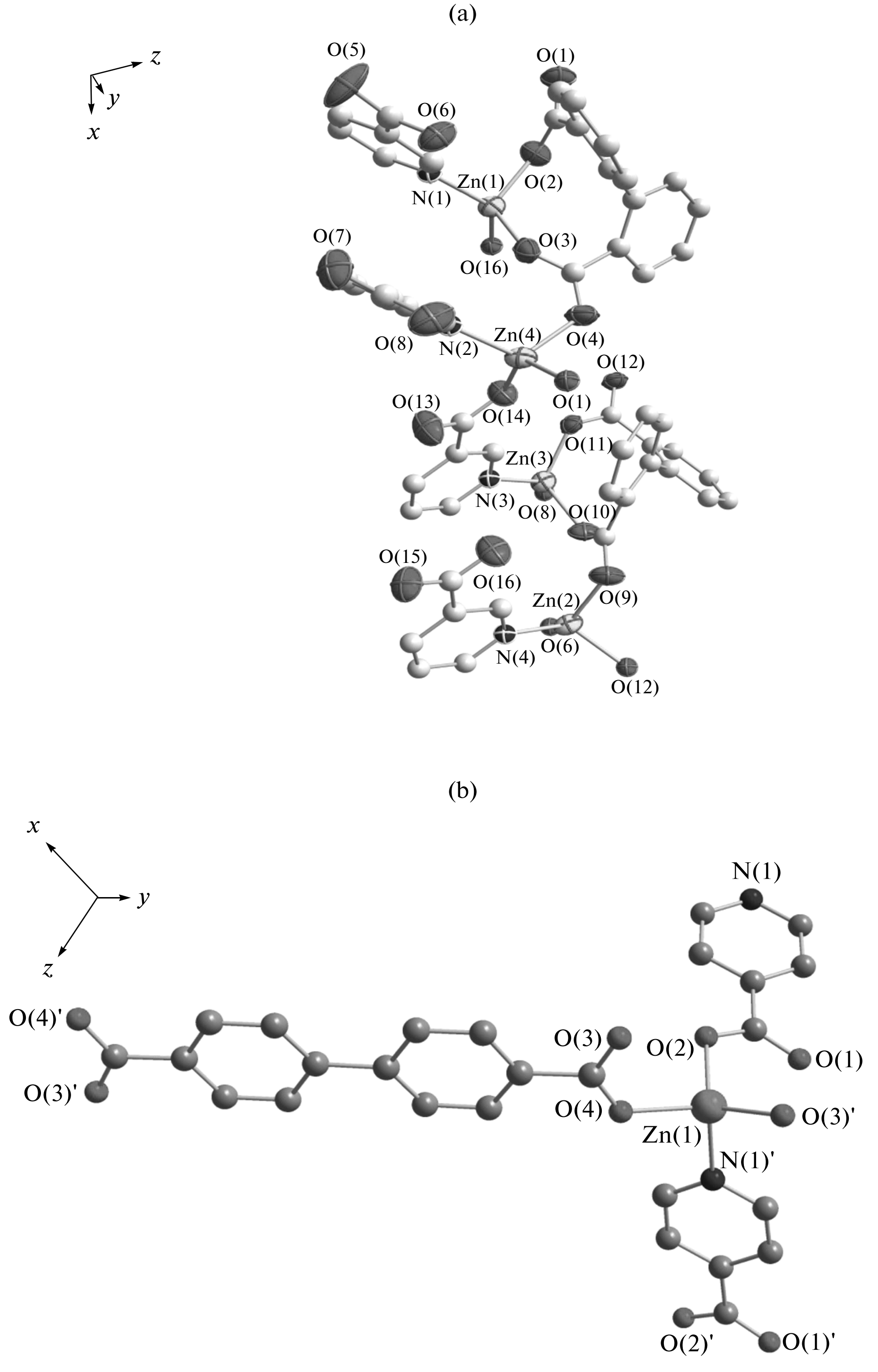

Fig. 1. The coordination environment arround Zn^{2+} ion of complexes **I** (a) and **II** (b). All the hydrogen atoms are omitted for clarity.

other. The total volume of void space estimated by Platon is 104.9 Å^3, equal to 8.6% of the unit-cell volume (1215.4 Å^3).

The TGA curve of **I** (Fig. 7a) shows that the first weight loss of 34.98% between 75 and 340°C corresponds to the loss of four NA molecules per formula unit (calcd. 39.17%), then it stable up to 350°C. The framework collapsed in the temperature range 350 to 430°C before the final formation of a metal oxide, whose remainder weight is 25.22% (calcd. 26.34%).

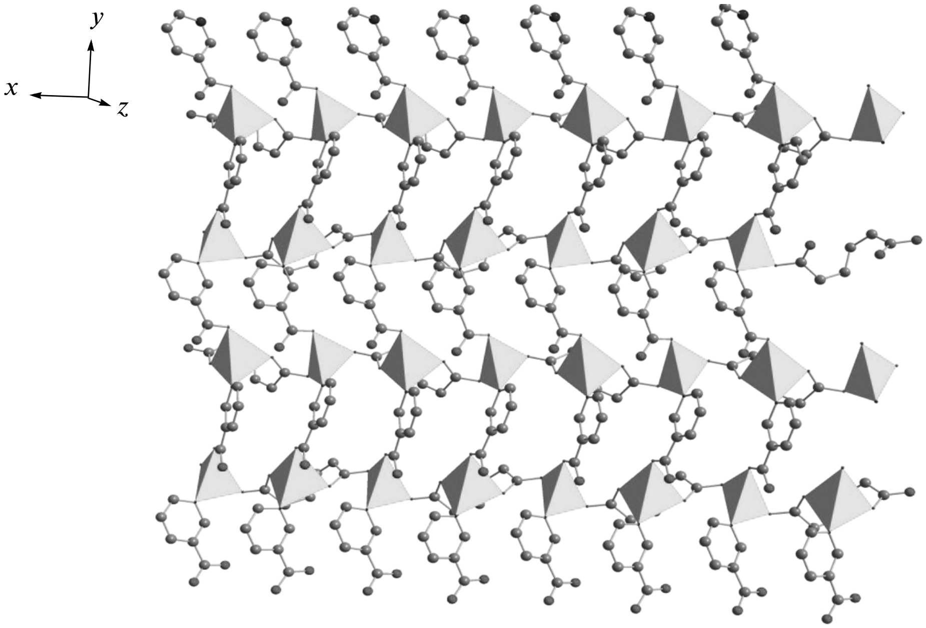

Fig. 2. The 2D net work plane and the coordination polyhedron of the Zn^{2+} ion of complex **I**. Unnecessary atoms are omitted for clarity.

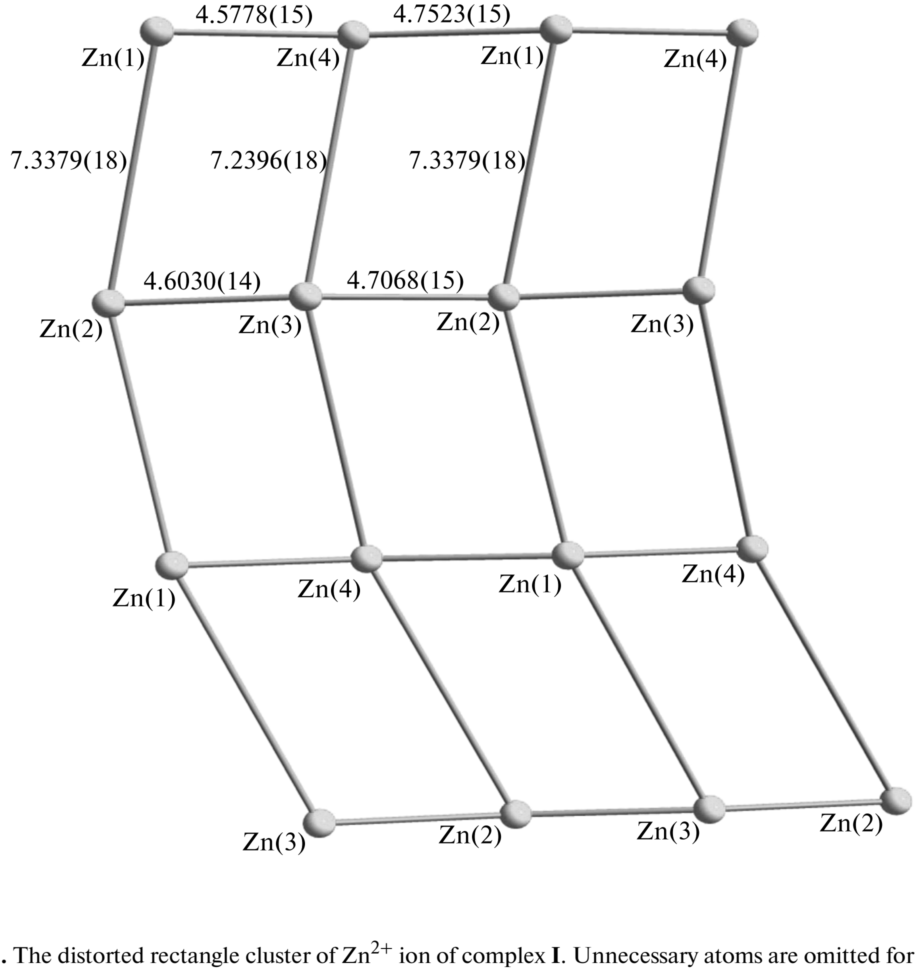

Fig. 3. The distorted rectangle cluster of Zn^{2+} ion of complex **I**. Unnecessary atoms are omitted for clarity.

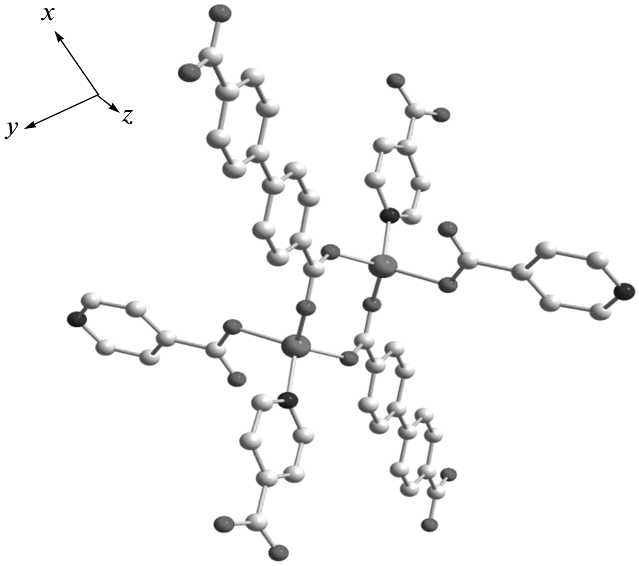

Fig. 4. The eight-membered ring-type SBU of complex **II**. All the hydrogen atoms are omitted for clarity.

For **II** (Fig. 7b), the weight loss begins with decomposition starting at 70°C and ending above 420°C. The remaining weight of 25.16% corresponds to the percentage (calcd. 26.33%) of a metal oxide.

Powder X-ray diffraction patterns were collected between a 2θ of 3° to 50° at a scan speed of 4 deg/min. There is a difference in reflection intensity between the simulated and experimental patterns. That can be explained due to a certain degree of preferred orientation of the powder samples during data collection.

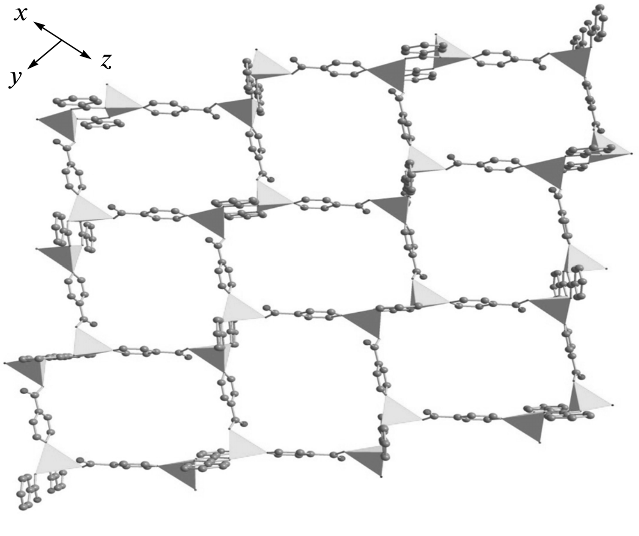

Fig. 5. The 2D 4^4 (brick-like) net and the coordination polyhedron of the Zn^{2+} ion of complex **II**.

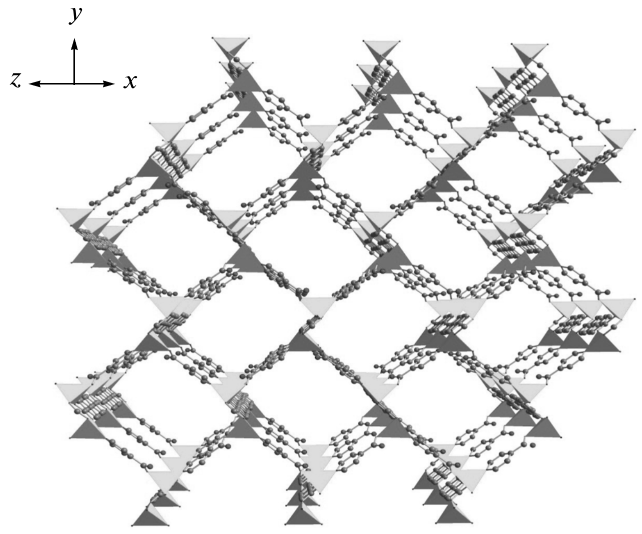

Fig. 6. Perspective view of the 3D structure of complex **II**.

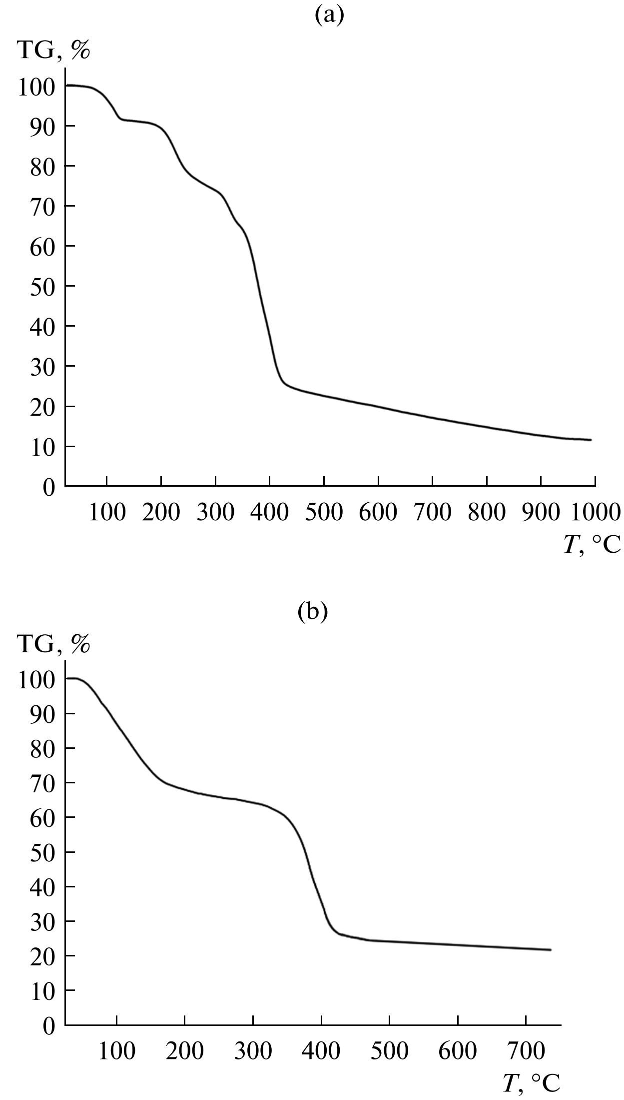

Fig. 7. The TG curves of complexes **I** (a) and **II** (b).

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