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Synthesis and Structure of New Zn(II) and Co(II) Coordination Polymers with 1,3,5-Benzenetricarboxylic Acid

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Abstract—Two new Zn(II) and Co(II) compounds obtained by reactions of tetrafluoroborates of these metals with 1,3,5-benzenetricarboxylic (trimesic) acid (H_3Btc) and 1,3-bis(pyridyl)propane (Bpp) as an additional ligand were studied by X-ray diffraction. The formation of coordination polymers of various dimensionality, $\{[Zn_4(Bpp)_4(HBtc)_3((Me)Btc)]\{(Me)_2HBtc\} \cdot 2H_2O\}_n$ (**I**), 1D, and $\{[Co_4(\mu_3\text{-}OH)_2(Btc)_2(H_2O)_8] \cdot 4(H_2O)\}_n$ (**II**), 2D (CIF files CCDC no. 1552167 (**I**), 1552168 (**II**)) was demonstrated. Since H_3Btc is partially methylated during the reaction, in **I**, this acid is stabilized in three forms: $HBtc^{2-}$, $(Me)Btc^{2-}$, and $(Me)_2HBtc$. The tetrahedral Zn(II) coordination polyhedron is formed by the N_2O_2 set of donor atoms: the O atoms belong to two different carboxylate ligands, $HBtc^{2-}$ and $(Me)Btc^{2-}$, while the N atoms belong to two Bpp ligands. In **II**, the Bpp ligand is not incorporated in the complex and H_3Btc is coordinated to five metal atoms as a triply deprotonated ligand. Two carboxyl groups are coordinated to Co atoms as bidentate bridging ligands, while the third group is monodentate. The octahedral coordination polyhedra of Co(II) atoms in **II** are supplemented by terminal water molecules and μ_3-bridging OH^- groups.

Keywords: coordination polymers, benzenetricarboxylic acid, bridging ligands, X-ray diffraction

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INTRODUCTION

In recent years, particular attention of researchers has been attracted by coordination polymers, i.e., metal-organic networks formed by metallic or metal-organic units connected in the crystals via bridging ligands [1–4]. The enhanced interest in these entities is apparently caused by the fact that crystals of this type can form pores with a large surface area and assumed topology, which may result in various structural architectures and promising applications. New compounds of this class can be used in ion exchange and adsorption, including dehydrogenation and gas storage [1, 5–10], drug delivery [11, 12], sensing equipment [13], luminescence, magnetism [1, 14–17], and other fields. Analysis of the Cambridge Crystallographic Data Centre (CCDC) [18] demonstrated that aromatic polyacids and bipyridine ligands have good prospects for the preparation of transition metal-based coordination polymers. Although CCDC has ~1485 examples of metal compounds with 1,3,5-benzenetricarboxylic acid (H_3Btc), of which 23 compounds contain doubly or triply deprotonated H_3Btc and bis(pyridyl)propane (Bpp), these are mainly polymeric complexes of Cd(II) [19–21] and Zn(II) [22, 23] and one Ni(II) polymer [24]. However, whereas in Cd(II) and Ni(II) complexes, Bpp is coordinated to metal atoms (M) as a bidentate bridging ligand, in the above-mentioned Zn(II) complexes, the Bpp is only monodentate and occurs in the singly protonated state ($HBpp^+$). The search through the CCDC for this type of metal complexes with H_3Btc and bis(pyridyl)ethane (Bpe) revealed eight examples of mainly polymeric complexes of Cd(II) [25, 26], Co(II) [27, 28], and Zn(II) (one polymer) [29]. The use of Bpe markedly extends the number of compounds (33) and the diversity of metals. Attempts have been made to synthesize new compounds also by blocking carboxyl groups via methylation in the reactions of various metal salts ($Zn(BF_4)_2$, $Cu(BF_4)_2$, $Cd(NO_3)_2$, $CoCl_2$, $Co(NO_3)_2$, and $Co(BF_4)_2$) with H_3Btc and Bpp or Bpe using the hydrothermal method of synthesis. Out of the 19 metal compounds with one methylated carboxyl group present in the CCDC, 16 compounds are Cu(II) trinuclear complexes and coordination polymers [30]. X-ray diffraction crystal structure determination has proven the formation of two new coordination polymers of various dimensionality: $\{[Zn_4(Bpp)_4(HBtc)_3((Me)Btc)]\{(Me)_2HBtc\} \cdot 2H_2O\}_n$ (**I**), 1D, and $\{[Co_4(\mu_3\text{-}OH)_2(Btc)_2(H_2O)_8] \cdot 4(H_2O)\}_n$ (**II**), 2D; the other compounds are known coordination polymers of these metals [25, 27, 31–33].

EXPERIMENTAL

Compounds **I** and **II** were synthesized by the hydrothermal method.

Synthesis of I. A mixture of H_3Btc (0.21 g, 1 mmol), $Zn(BF_4)_2 \cdot nH_2O$ (0.24 g, 1 mmol), Bpp (0.15 g, 1 mmol), water (3 mL), methanol (3 mL), and DMF (10 drops) was sealed in a Teflon-lined 8-mL reactor and heated in an autoclave at 120°C for 72 h. Then the autoclave was slowly cooled to room temperature. The colorless crystals suitable for X-ray diffraction were isolated from the solution by filtration. The crystals were soluble in methanol, ethanol, and DMF and were insoluble in diethyl ether. Yield 21%.

For $C_{25}H_{20.75}N_2O_8Zn$

Anal. calcd., %:	C, 54.97;	H, 3.72;	N, 4.89.
Found, %:	C, 55.34;	H, 3.85;	N, 5.17.

IR (ν, cm^{-1}): 3116 w, 2924 m, 1602 s, 1568 vs, 1436 m, 1396 vs, 1288 s, 1231 s, 1109 w, 757 m, 714 w.

Synthesis of II. A mixture of H_3Dtc (0.21 g, 1 mmol), $Co(BF_4)_2 \cdot 6H_2O$ (0.34 g, 1 mmol), Dpp (0.15 g, 1 mmol), water (3 mL), methanol (3 mL), and DMF (10 drops) was sealed in a Teflon-lined 8-mL reactor and heated in an autoclave at 120°C for 48 h. Then the autoclave was slowly cooled to room temperature. The red crystals suitable for X-ray diffraction that formed on cooling were isolated by filtration. The crystals were soluble in methanol, ethanol, and DMF and were insoluble in diethyl ether. Yield 19%.

For $C_9H_{16}O_{13}Co_2$

Anal. calcd., %:	C, 23.76;	H, 3.42.
Found, %:	C, 24.02;	H, 3.58.

IR (ν, cm^{-1}): 3195 m, 2952 m, 1609 s, 1556 s, 1371 vs, 1105 w, 932 vw, 815 vw, 712 s.

All chemicals and solvents (Aldrich) were used as received. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer in the 4000–400 cm^{-1} range.

X-ray diffraction study of I and II. The X-ray diffraction data were collected on a Xcalibur E diffractometer (graphite monochromator, MoK_α radiation) at room temperature. The unit cell parameters were determined and experimental data were processed using a CrysAlis Oxford Diffraction Ltd. program [34]. The structures of compounds **I** and **II** were solved by direct methods and refined by least squares in the anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [35]. One acid residue in **I** was found to exist as two forms (HBtc^{2-} and (Me)Btc^{2-}) in 1 : 1 ratio. The positions of O atoms of the water molecules of crystallization and the C atom of the CH_3 group in **I** as well as water O atoms in **II** with a site occupancy factor of <0.4 were refined isotropically. The positions of hydrogen atoms bound to oxygen atoms were obtained from difference Fourier maps and the positions of other hydrogen atoms were calculated geometrically. The X-ray experiment and structure refinement details for **I** and **II** are summarized in Table 1, interatomic distances and bond angles in the coordination units are in Table 2, and the geometric parameters of the hydrogen bonds are given in Table 3. The atom positions and thermal parameters are deposited with the CCDC (CIF files CCDC no. 1552167 (**I**), 1552168 (**II**); www.ccdc.cam.ac.uk/conts/retrieving.html or deposit@ccdc.ca.ac.uk).

RESULTS AND DISCUSSION

The strong IR bands at 1602 (**I**) and 1609 (**II**) cm^{-1} correspond to aromatic ring vibrations. The weak bands at 1109 (**I**), 1105 (**II**), 815 (**II**), 714 (**I**), and 712 (**II**) cm^{-1} can be assigned to in-plane and out-of-plane bending C–H vibrations in the trisubstituted aromatic ring. Strong bands at 1568 (**I**), 1556 (**II**), 1396 (**I**), and 1371 (**II**) cm^{-1} are caused by the $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ modes. The bands at 2924, 1436, and 757 cm^{-1} in **I** can be assigned to CH_2 vibrations of the Bpp ligand.

X-ray diffraction study of the two new compounds, **I** and **II**, showed that the reactions of Zn(II) and Co(II) tetrafluoroborates with H_3Btc and Bpp gave coordination polymers differing both in the composition and topology and in the dimensionality. Compound **I** is formed with participation of both organic ligands and contains H_3Btc as both coordinated doubly deprotonated ligands and neutral molecules of crystallization. Since H_3Btc has been partly methylated during the reaction, it is stabilized in **I** in three forms: HBtc^{2-}, (Me)Btc^{2-}, and $(Me)_2$HBtc. Conversely, in **II**, Bpp is not incorporated in the complex and H_3Btc is coordinated to the metal atoms as the triply deprotonated Btc^{3-} ligand. As a result, a 1D coordination polymer described as $[Zn_4(Bpp)_4(HBtc)_3((Me)Btc)]_n$ is formed in **I** and a 2D polymer described as $[Co_4(\mu_3\text{-}OH)_2(Btc)_2(H_2O)_8]_n$ is formed in **II**. Both compounds contain solvates, that is, molecules of crystallization: $(Me)_2$HBtc and H_2O in **I** and H_2O in **II**. X-ray diffraction data for other crystals of known Cu(II), Cd(II), and Co(II) coordination polymers include, for example, $[Cd_3(Btc)_2(Bpe)_2(H_2O)_4]_n$ [25], $[Co_2(HBtc)_2(Bpe)_2]_n$ [27], $[Co_3(Btc)(HBtc)(OH)(H_2O)_{11}]_n$ [31], $[H_2N(CH_3)_2][Co(HCO_2)_3]_n$ [32], $[Cu_3(Btc)_2(H_2O)_3]_n$ [33], and so on.

The Zn(II)-containing 1D coordination polymer in **I** is formed by coordinated HBtc^{2-}, (Me)Btc^{2-}, and Bpp ligands with *m* symmetry and bridging functions (Fig. 1a). The tetrahedral coordination polyhedron of Zn(II) is composed of the N_2O_2 set of donor atoms. The O atoms belong to two different carboxylate ligands (HBtc^{2-} or (Me)Btc^{2-}), while the N atoms

Table 1. Crystallographic data and X-ray experiment details for **I** and **II**

Parameter	Value	
	I	**II**
M	542.56	450.08
System	Orthorhombic	Triclinic
Space group	*Cmcm*	$P\bar{1}$
a, Å	35.5551(15)	7.7923(8)
b, Å	14.9805(10)	8.7102(7)
s, Å	19.9824(6)	10.7369(11)
α, deg	90	101.043(8)
β, deg	90	92.285(9)
γ, deg	90	95.237(7)
V, Å^3	10643.3(9)	711.04(12)
Z	16	2
ρ(calcd.), g/cm^3	1.354	2.102
μ, mm^{-1}	0.971	2.407
F(000)	4460	456
Crystal size, mm	0.42 × 0.28 × 0.9	0.4 × 0.33 × 0.015
Range of θ, deg	2.99–25.00	3.17–25.04
Ranges of reflection indices	$-29 \le h \le 22$, $-17 \le k \le 17$, $-23 \le l \le 14$	$-9 \le h \le 5$, $-9 \le k \le 10$, $-12 \le l \le 11$
Number of measured/unique reflections (R_{int})	10350/4827 (0.0656)	3812/2507 (0.0389)
Filling, %	98.3	99.4
Number of reflections with $I > 2\sigma(I)$	1958	2036
Number of refined parameters	331	239
GOOF	1.006	1.000
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0838$, $wR_2 = 0.2339$	$R_1 = 0.0705$, $wR_2 = 0.1751$
R factor (for the whole array)	$R_1 = 0.1555$, $wR_2 = 0.2534$	$R_1 = 0.0844$, $wR_2 = 0.1828$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	1.035/–0.831	0.875/–0.724

belong to two Bpp ligand. The interatomic distances in the coordination polyhedron are as follows: Zn(1)–O(1), 1.932(4); Zn(1)–O(4), 1.932(6); Zn(1)–N(1*A*), 2.043(6); Zn(1)–N(1*B*), 2.066(6) Å (Table 2). Furthermore, four metal atoms are linked by four carboxylate ligands, thus giving rise to a symmetrical 32-membered ring in which the Zn···Zn interatomic distances are 8.305 and 10.584 Å. These rings are connected into a chain through four neutral bridging Bpp ligands; the Zn···Zn distance is 11.674 Å (Fig. 1b). This type of metal atom binding has also been found in the Ni(II) coordination polymer with HBtc^{2-} and Bpp [24]. The arrangement of the coordinated ligands in the chain of **I** is stabilized by weak intramolecular hydrogen bonds: C(1*A*)–H···O(5) (C(1*A*)···O(5), 3.374; H···O(5), 2.62 Å, CHO angle, 138°), C(5*A*)–H···O(2) (C(5*A*)···O(2), 3.208; H···O(2), 2.45 Å; CHO angle 139°), and C(1*B*)–H···O(2) (C(1*B*)···O(2), 3.181; H···O(2), 2.42 Å; CHO angle, 139°). In the crystal, the chains are connected only by weak intermolecular hydrogen bonds, C(1*B*)–H···O(2) ($-x + 1/2$, $-y + 1/2$, $-z + 1$) (C(1*B*)···O(2), 3.336; H···O(2), 2.64 Å; CHO angle 132°).

Table 2. Interatomic distances and bond angles in the Zn(II) (**I**) and Co(II) (**II**)* coordination polyhedra

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
		I			
Zn(1)–O(1)	1.932(4)	O(1)Zn(1)O(4)	105.3(2)	O(4)Zn(1)N(1*A*)	119.1(3)
Zn(1)–O(4)	1.932(6)	O(1)Zn(1)N(1*A*)	115.9(2)	O(4)Zn(1)N(1*B*)	94.5(3)
Zn(1)–N(1*A*)	2.043(6)	O(1)Zn(1)N(1*B*)	119.5(2)	N(1*A*)Zn(1)N(*1B*)	101.3(2)
Zn(1)–N(1*B*)	2.066(6)				
		II			
Co(1)–O(1)	2.083(5)	O(1)Co(1)O(1)$^{\#1}$	77.9(2)	O(1)Co(2)O(2)	91.0(2)
Co(1)–O(1)$^{\#1}$	2.084(5)	O(1)Co(1)O(3)$^{\#1}$	171.6(2)	O(1)Co(2)O(4)$^{\#2}$	175.5(2)
Co(1)–O(3)$^{\#1}$	2.047(6)	O(1)Co(1)O(5)$^{\#2}$	97.3(2)	O(1)Co(2)O(6)$^{\#3}$	95.1(2)
Co(1)–O(5)$^{\#2}$	2.035(6)	O(1)Co(1)O(1*w*)	85.4(2)	O(1)Co(2)O(3*w*)	87.6(2)
Co(1)–O(1*w*)	2.072(7)	O(1)Co(1)O(2*w*)	88.8(2)	O(1)Co(2)O(4*w*)	173.5(2)
Co(1)–O(2*w*)	2.151(7)	O(1)$^{\#1}$Co(1)O(3)$^{\#1}$	96.5(2)	O(2)Co(2)O(4)$^{\#2}$	175.5(2)
Co(2)–O(1)	2.035(5)	O(1)$^{\#1}$Co(1)O(5)$^{\#2}$	173.8(2)	O(2)Co(2)O(6)$^{\#3}$	90.1(3)
Co(2)–O(2)	2.033(6)	O(1)$^{\#1}$Co(1)O(1*w*)	94.2(2)	O(2)Co(2)O(3*w*)	93.6(3)
Co(2)–O(4)$^{\#2}$	2.054(6)	O(1)$^{\#1}$Co(1)O(2*w*)	86.8(2)	O(2)Co(2)O(4*w*)	87.0(2)
Co(2)–O(6)$^{\#3}$	2.133(6)	O(3)$^{\#1}$Co(1)O(5)$^{\#2}$	88.7(3)	O(4)$^{\#2}$Co(2)O(6)$^{\#3}$	89.8(2)
Co(2)–O(3*w*)	2.145(7)	O(3)$^{\#1}$Co(1)O(1*w*)	88.8(3)	O(4)$^{\#2}$Co(2)O(3*w*)	86.2(2)
Co(2)–O(4*w*)	2.099(6)	O(3)$^{\#1}$Co(1)O(2*w*)	97.2(3)	O(4)$^{\#2}$Co(2)O(4*w*)	88.5(2)
		O(5)$^{\#2}$Co(1)O(1*w*)	89.2(3)	O(6)$^{\#3}$Co(2)O(3*w*)	175.3(2)
		O(5)$^{\#2}$Co(1)O(2*w*)	89.3(3)	O(6)$^{\#3}$Co(2)O(4*w*)	91.1(2)
		O(1*w*)Co(1)O(2*w*)	173.7(3)	O(3*w*)Co(2)O(4*w*)	86.3(2)

* Symmetry codes: $^{\#1}$ $-x + 1, y, -z + 1$, $^{\#2}$ $x - 1, y - 1, z$, $^{\#3}$ $-x + 1, -y + 1, -z + 2$ (**II**).

The crystal of **I** is a predictable porous coordination polymer with a relatively large voids accessible for the molecules of crystallization; the volume of the voids is 3093.0 Å^3 per unit cell (29.1%) (Fig. 2). The O(1*w*) water molecules of crystallization are joined with the coordination polymer by intermolecular hydrogen bonds, O(1*w*)–H···O(5), and O(2*w*) are joined with O(1*w*) (Table 3). The uncoordinated $(Me)_2HBtc$ molecules are connected to the polymer by only weak intermolecular C–H···O hydrogen bonds.

Compound **II** contains, in the independent part of the structure, two metal atoms, Co(1) and Co(2), the O(1) hydroxyl group, four coordinated water molecules (O(1*w*)–O(4*w*)), the triply deprotonated Btc^{3-} ligand, and two disordered water molecules of crystallization. In the 2D coordination polymer **II**, it is possible to distinguish a tetranuclear symmetric cluster (Fig. 3a), in which four metal atoms are linked by two μ_3-bridging OH^- groups. The Co(1)···Co(1)$^{\#}$, Co(1)···Co(2), and Co(1)···Co(2)$^{\#}$ interatomic distances in the cluster are 3.235, 3.645, and 3.674 Å, respectively; the Co(2)···Co(2)$^{\#}$ distances are 6.565 Å. As a result, the octahedral coordination polyhedron of each Co(II) atom in **II** is formed by two water molecules coordinated in the monodentate fashion and completed in different ways for Co(1) and Co(2). Whereas Co(1) is linked to two OH^- groups and two O atoms of two different Btc^{3-} ligands, Co(2) is bound to one OH^- group and three Btc^{3-} ligands (Fig. 3b). The interatomic distances in the coordination polyhedra are as follows: Co(1)–O(1*w*), 2.072(7); Co(1)–O(2*w*), 2.151(7); Co(1)–O(1), 2.083(5); Co(1)–O(1)$^{\#}$, 2.084(5); Co(1)–O(3)$^{\#}$, 2.047(6); Co(1)–O(5)$^{\#}$, 2.035(6) Å; Co(2)–O(3*w*), 2.145(7); Co(2)–O(4*w*), 2.099(6); Co(2)–O(1), 2.035(5); Co(2)–O(2), 2.033(6); Co(2)–

Table 3. Geometric parameters of hydrogen bonds in **I** and **II**

D–H···A	Distance, Å			DHA angle, deg	Symmetry code for A
	D–H	H···A	D···A		
			I		
O(1*w*)–H(1)···O(5)	0.85	1.87	2.73(2)	171	x, y, z
O(1*w*)–H(2)···O(1*w*)	0.85	2.36	3.17(3)	161	$x, y, -z + 3/2$
O(2*w*)–H(1)···O(1*w*)	0.79	2.05	2.83(4)	177	x, y, z
			II		
O(1)–H(1)···O(1*w*)	0.83	2.21	2.817(8)	130	x, y, z
O(1)–H(1)···O(5*w*)	0.83	2.53	3.293(10)	153	x, y, z
O(1*w*)–H(1)···O(7)	0.89	1.88	2.638(9)	143	$x - 1, y - 1, z - 1$
O(1*w*)–H(1)···O(3*w*)	0.89	2.33	3.038(9)	137	$-x + 1, -y, -z + 1$
O(1*w*)–H(2)···O(5*w*)	0.88	1.97	2.778(11)	152	x, y, z
O(1*w*)–H(2)···O(5*wA*)	0.88	2.43	3.19(5)	164	x, y, z
O(2*w*)–H(1)···O(6*w*)	0.89	1.77	2.64(3)	163	$x, y - 1, z$
O(2*w*)–H(1)···O(7*w*)	0.89	2.13	2.94(4)	150	$x, y - 1, z$
O(2*w*)–H(2)···O(5*wA*)	0.85	1.77	2.57(6)	157	$-x + 1, -y, -z + 1$
O(2*w*)–H(2)···O(5*w*)	0.85	2.08	2.926(11)	179	$-x + 1, -y, -z + 1$
O(3*w*)–H(1)···O(7)	0.88	1.89	2.725(9)	157	$-x + 2, -y + 1, -z + 2$
O(3*w*)–H(2)···O(2*w*)	0.88	2.11	2.907(9)	150	x, y, z
O(4*w*)–H(1)···O(4)	0.88	2.26	2.989(9)	141	$-x + 2, -y + 1, -z + 2$
O(4*w*)–H(2)···O(3*w*)	0.88	2.09	2.863(8)	146	$-x + 1, -y, -z + 2$
O(5*w*)–H(1)···O(6)	0.85	2.01	2.769(9)	149	$-x + 1, -y + 1, -z + 2$
O(5*w*)–H(2)···O(3)	0.85	2.41	3.258(11)	175	$x - 1, y, z$
O(6*w*)–H(1)···O(2)	0.85	2.12	2.97(3)	179	x, y, z
O(6*w*)–H(2)···O(2*wA*)	0.85	2.22	2.78(7)	124	$x, y + 1, z$
O(6*w*)–H(2)···O(2*wA*)	0.85	2.47	3.06(7)	127	$-x + 1, -y, -z + 1$
O(7*w*)–H(1)···O(4)	1.04	2.56	3.29(4)	127	$x - 1, y, z$
O(7*w*)–H(2)···O(6)	0.85	2.10	2.95(4)	179	$-x + 1, -y + 1, -z + 2$

O(4)$^{\#}$, 2.054(6); and Co(2)–O(6)$^{\#}$, 2.133(6) Å (Table 2). Since the triply deprotonated Btc^{3-} ligand is coordinated to five metal atoms (with two carboxyl groups functioning as bidentate bridging ligands and one group being monodentate), the 2D coordination polymer contains two types of 16-membered macrocycles, each incorporating two metal atoms connected by two Btc^{3-} groups coordinated in different ways. In the CCDC, this type of topology was found in a Co(II) structure with Btc^{3-} [36]; however, two of the four atoms in this structure are additionally linked by the bridging 1,2,4-triazol-4-ylmethyl)-benzene ligand.

In the crystal of **II**, the 2D coordination polymers are stabilized by intermolecular hydrogen bonds: O(1)–H···O(1*w*), O(1*w*)–H···O(7)$^{\#}$, O(1*w*)–H···O(3*w*), and O(3*w*)–H···O(2*w*). The intermolecular hydrogen bonds, O(3*w*)–H···O(7)$^{\#}$, O(4*w*)–H···O(4)$^{\#}$, and O(4*w*)–H···O(3*w*), combine these layers (Table 3). The water molecules of crystallization in **II** are involved in the system of hydrogen bonds, O(5*w*)–H···O(6)$^{\#}$, O(5*w*)–H···O(3)$^{\#}$, O(6*w*)–H···O(2), O(7*w*)–H···O(4)$^{\#}$, and O(7*w*)–H···O(6)$^{\#}$ (Table 3), which additionally links the coordination polymers to one another. The 2D coordination polymers are packed rather densely, so that the voids accessible for the mol-

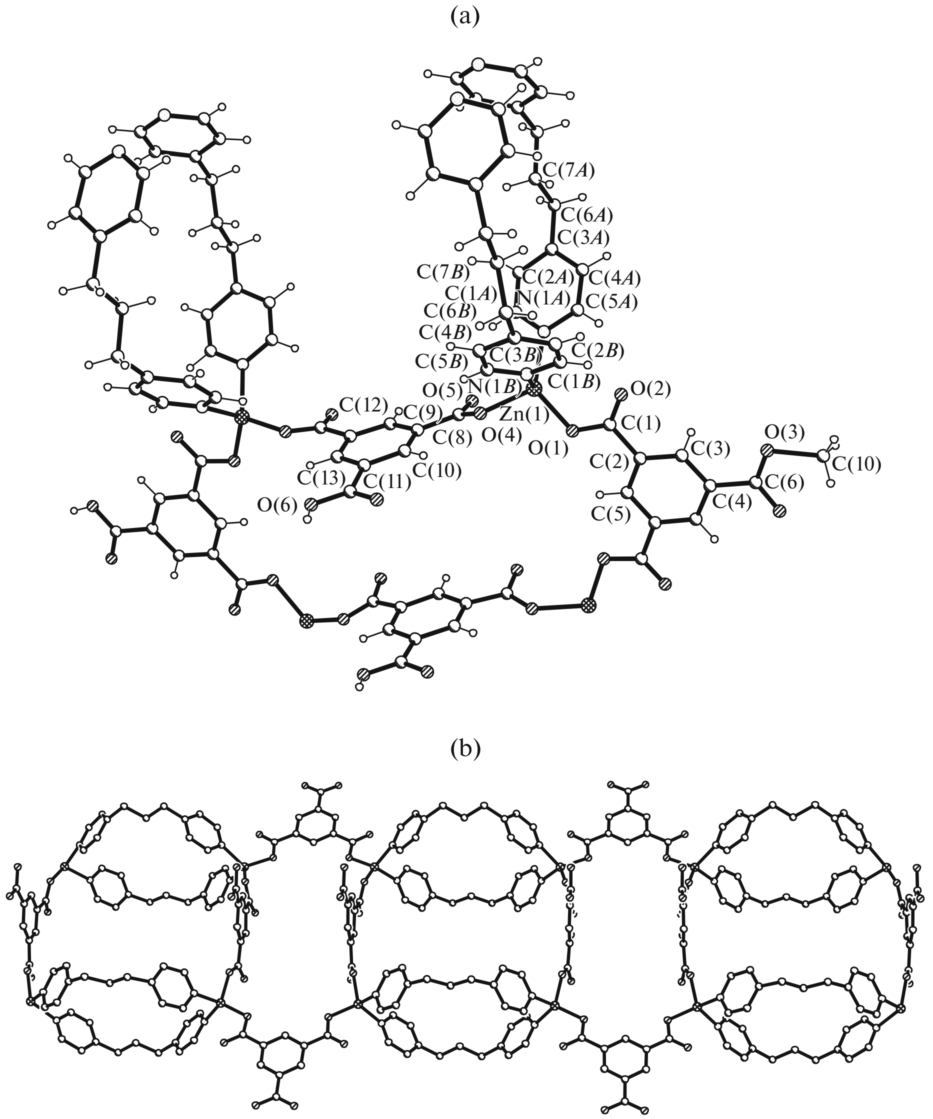

Fig. 1. (a) Fragment of the coordination polymer in **I** with atom numbering in the independent part of the unit cell; (b) structure of 1D coordination polymer in **I**.

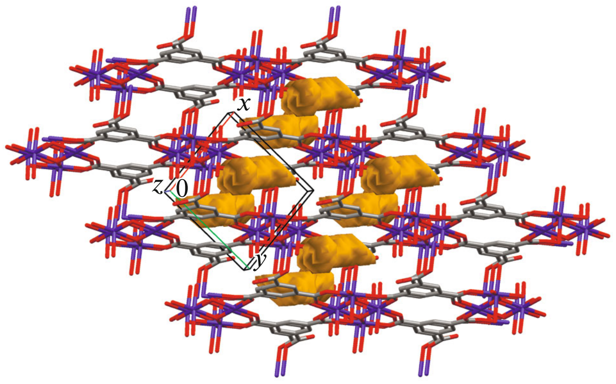

Fig. 2. Packing of coordination polymers in **I** and formation of free channels in the structure upon removal of the molecules of crystallization.

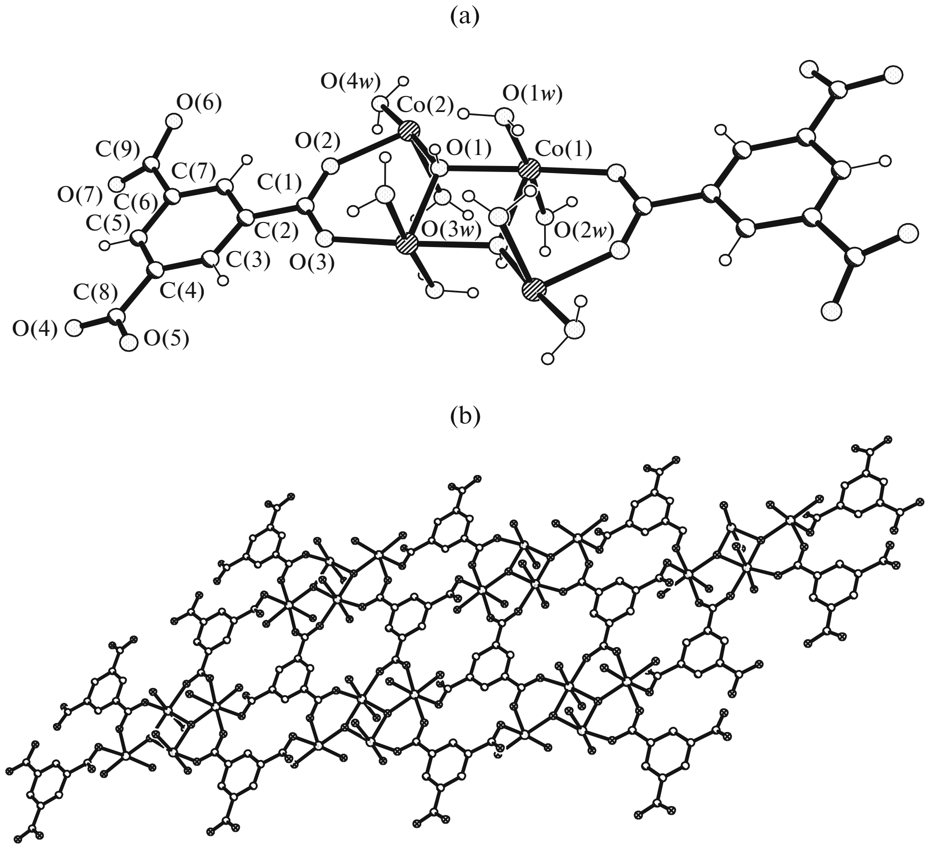

Fig. 3. (a) Fragment of the coordination polymer in **II** with atom numbering in the independent part of the unit cell; (b) structure of 2D coordination polymer in **II**.

ecules of crystallization are 49.9 Å^3 per unit cell (only 7.0%) (Fig. 4).

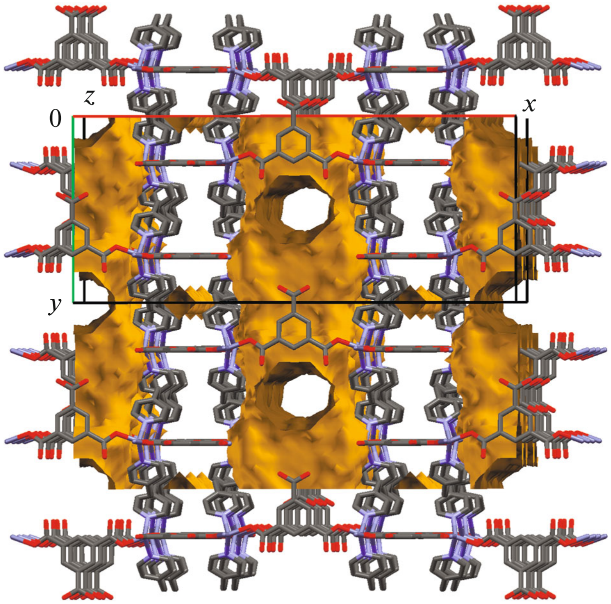

Fig. 4. Packing of the coordination polymers in **II** and formation of voids in the structure upon removal of water molecules.

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