ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 2, pp. 81–91. © Pleiades Publishing, Ltd., 2019.
Russian Text © A.A. Vitiu, E.B. Coropceanu, P.N. Bourosh, 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 2, pp. 67–78.

New Zn(II) and Cd(II) Coordination Polymers with 1,2-Benzenedicarboxylic Acid: Synthesis and Structures

A. A. Vitiu[a, b], **E. B. Coropceanu**[b, c], **and P. N. Bourosh**[a, c, *]
[a] *Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, Republic of Moldova*
[b] *Institute of Chemistry, Academy of Sciences of Moldova, Chisinau, Republic of Moldova*
[c] *Tiraspol State University, Chisinau, Republic of Moldova*
**e-mail: bourosh.xray@phys.asm.md*

Received February 20, 2018; Revised May 14, 2018; Accepted June 15, 2018

Abstract—1,2-Benzenedicarboxylic (phthalic) acid (1,2-BdcH_2) and bipyridine ligands are used for the synthesis of the Zn(II) and Cd(II) coordination polymers. As a result, the target assembling of four complexes is carried out. The structures of the synthesized complexes are studied by X-ray diffraction analysis. Three of the obtained compounds are new coordination polymers $[Zn_2(1,2\text{-Bdc})_2(Bpe)_2]_n \cdot 0.25n(Dmf) \cdot 0.25nH_2O$ (**I**), $[Zn_2(1,2\text{-Bdc})_2(Bpp)_2]_n$ (**II**), and $[Cd(1,2\text{-Bdc})(Bpp)(H_2O)]_n$ (**III**) (Bpe is bis(4-pyridyl)ethane, Bpp is 1,2-bis(4-pyridyl)propane, and Dmf is dimethylformamide) (CIF files CCDC nos. 1824264 (**I**), 1824265 (**II**), and 1824266 (**III**)), and the fourth one is the known Cd(II) compound $[Cd(1,2\text{-Bdc})(H_2O)]_n$. The study of the structures of compounds **I–III** reveals the dimensionalities of the polymers: 3D for the Zn(II) polymer and 2D for the Cd(II) polymer. Different shapes of the coordination polyhedra of Zn(II) are found in compounds **I** and **II**, and different coordination modes of the doubly deprotonated ligand $(1,2\text{-Bdc})^{2-}$ to the metals are observed in compounds **I–III**.

Keywords: coordination polymers, benzenedicarboxylic acid, bridging bipyridine ligands, X-ray diffraction analysis

DOI: 10.1134/S1070328419020106

INTRODUCTION

In the recent decades the design and efficient synthesis of coordination polymers based on the self-assembling of metal ions and mixed organic ligands remain to be among the most demanded problems, including studies of the materials with noncentrosymmetric structures [1, 2]. A reasonable choice of organic ligands is one of the foundations in the strategy of designing coordination polymers with intriguing topologies and promising properties. A combination of various carboxylic acids with aromatic N-donor ligands of the bipyridine type, which can function as bridging ligands capable of forming high-dimensional architectures, is widely used in order to change the dimensionality of coordination compounds [3–5]. Among the bipyridine type ligands, flexible ligands such as 1,2-bis(4-pyridyl)ethane (Bpe) and 1,2-bis(4-pyridyl)propane (Bpp) are of special interest. They can take various conformations due to relative orientations of the methylene groups between two pyridine rings [6]. An analysis of the Cambridge Structural database (CSD) [7] shows that 27 compounds of transition metals with the 1,2-dicarboxylic acid residues $(1,2\text{-Bdc})^{2-}$ and bipyridine type ligands (bipyridine (Bipy), Bpe, Bpp, and bis(4-pyridyl)ethene) have been registered to the present time, and 21 of them are compounds with Bipy. These are eight Zn(II) complexes [8–13] and two Cd(II) compounds [14, 15], and only five compounds contain no Bipy [8–10]. Some compounds of this class crystallize in noncentrosymmetric space groups assuming the formation of materials with useful physical properties such as the second harmonic generation and segneto-, piezo-, and pyroelectricity. As a result, these complexes can be used for electronic and nonlinear optical devices, signal processing, and information storage [16, 17].

For the purpose of an efficient synthesis of functional coordination polymers, we focused attention on the Zn(II) and Cd(II) compounds with 1,2-benzenedicarboxylic acid containing Bpe and Bpp. As a result, we synthesized four compounds, three of which are new coordination polymers $[Zn_2(1,2\text{-Bdc})_2(Bpe)_2]_n \cdot 0.25n(Dmf) \cdot 0.25nH_2O$ (**I**), $[Zn_2(1,2\text{-Bdc})_2(Bpp)_2]_n$ (**II**), and $[Cd(1,2\text{-Bdc})(Bpp)(H_2O)]_n$ (**III**) (Dmf is dimethylformamide), and the fourth one is the known Cd(II) compound $[Cd(1,2\text{-Bdc})(H_2O)]_n$ [18]. We failed to obtain a Cd(II) compound with $(1,2\text{-Bdc})^{2-}$ and Bpe but succeeded in preparing the new Zn(II) compound with $(1,2\text{-Bdc})^{2-}$ and Bpp, although the CSD already contains two compounds of this metal with the same ligands [8, 9]. In this work we continue to study transition metal compounds with carboxylic acids and ligands of the bipyridine class [19].

EXPERIMENTAL

Compounds **I–III** were synthesized under hydrothermal conditions.

Synthesis of compound I. A mixture of 1,2-BdcH_2 (0.18 g, 1 mmol), $Zn(BF_4)_2 \cdot nH_2O$ (0.24 g, 1 mmol), Bpe (0.18 g, 1 mmol), water (3 mL), methanol (3 mL), and Dmf (5 droplets) was sealed in a 8-mL reactor with the Teflon lining and heated in an autoclave at 120°C for 48 h. Then the autoclave was slowly cooled to room temperature. Colorless crystals suitable for X-ray diffraction analysis were filtered off from the solutions. The crystals were soluble in methanol, ethanol, and Dmf and insoluble in ether. The yield was 21%.

For $C_{40.75}H_{34.25}N_{4.25}O_{8.50}Zn_2$

Anal. calcd., %	C, 83.57	H, 5.94	N, 8.40
Found, %	C, 84.17	H, 6.00	N, 8.81

Synthesis of compound II. A mixture of 1,2-BdcH_2 (0.18 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 (5 droplets) was sealed in a 8-mL reactor with the Teflon lining and heated in an autoclave at 120°C for 48 h. Then the autoclave was slowly cooled to room temperature. Colorless crystals suitable for X-ray diffraction analysis were filtered off from the solutions. The crystals were soluble in methanol, ethanol, and Dmf and insoluble in ether. The yield was 25%.

For $C_{42}H_{36}N_4O_8Zn_2$

Anal. calcd., %	C, 68.73	H, 4.94	N, 6.40
Found, %	C, 69.59	H, 5.00	N, 6.63

Synthesis of compound III. A mixture of 1,2-BdcH_2 (0.18 g, 1 mmol), $Cd(BF_4)_2 \cdot nH_2O$ (0.24 g, 1 mmol), Bpp (0.15 g, 1 mmol), water (3 mL), methanol (3 mL), and Dmf (10 droplets) was sealed in a 8-mL reactor with the Teflon lining and heated in an autoclave at 120°C for 24 h. Then the autoclave was slowly cooled to room temperature. Colorless crystals suitable for X-ray diffraction analysis were filtered off from the solutions. The crystals were soluble in methanol, ethanol, and Dmf and insoluble in ether. The yield was 30%.

For $C_{21}H_{20}N_2O_5Cd$

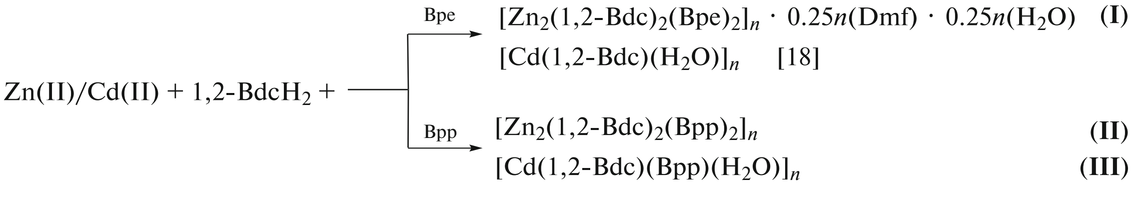
Anal. calcd., %	C, 65.73	H, 4.83	N, 6.92
Found, %	C, 66.12	H, 5.09	N, 7.16

All chemical substances and solvents were purchased from Aldrich and used as received.

X-ray diffraction analysis of compounds I–III. The X-ray diffraction data were obtained on an Xcalibur E diffractometer (graphite monochromator, MoK_α radiation) at room temperature. The unit cell parameters were determined and the experimental data were processed using the CrysAlis Oxford Diffraction Ltd. program [20]. The structures of compounds **I–III** were determined by direct methods and refined by least squares in the anisotropic full-matrix approximation for non-hydrogen atoms (SHELX-97) [21]. The experimental data obtained from a twin crystal were used for the structure determination of compound **II**. The disordering over two positions in a ratio of 1 : 1 was determined in the structure of compound **III** for the propane fragment of the Bpp ligand. The positions of the hydrogen atoms related to the oxygen atoms were obtained from the difference Fourier syntheses, and the positions of all other hydrogen atoms were calculated geometrically. The experimental and structure refinement characteristics for compounds **I–III** are presented in Table 1. The interatomic distances and bond angles in the coordination nodes are given in Table 2. The hydrogen bonding geometry is presented in Table 3. The positions and thermal parameters of atoms of compounds **I–III** were deposited with the CSD in the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1824264 (**I**), 1824265 (**II**), 1824266 (**III**); deposit@ccdc.ca.ac.uk or www.ccdc. cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

The X-ray diffraction data showed that the reactions of the Zn(II) and Cd(II) salts containing BF_4^- anions with 1,2-BdcH_2 and Bpe or Bpp afforded four coordination polymers. Compounds **I–III** (see Scheme 1) are new and contain both organic ligands, whereas the known coordination polymer was formed in the reaction of the Cd(II) salt, 1,2-BdcH_2, and Bpe [18]. All materials obtained are coordination polymers with different compositions, topologies, and dimensionalities.



Scheme 1.

Table 1. Crystallographic data and experimental characteristics for the structures of compounds **I–III**

Parameter	Value		
	I	**II**	**III**
FW	850.21	855.49	492.79
Crystal system	Monoclinic	Hexagonal	Monoclinic
Space group	$P2_1/n$	$P6_1$	$P2_1/n$
a, Å	12.4678(4)	12.1988(6)	10.5046(3)
b, Å	17.8150(10)	12.1988(6)	10.1790(3)
c, Å	20.6837(11)	49.197(4)	18.2972(5)
β, deg	96.237(3)	90	103.166(3)
V, Å^3	4566.9(4)	6340.2(6)	1905.02(9)
Z	4	6	4
ρ_{calcd}, g/cm^3	1.237	1.344	1.718
μ, mm^{-1}	1.101	1.189	1.183
F(000)	1746	2640	992
Crystal sizes, mm	0.4 × 0.15 × 0.1	0.4 × 0.2 × 0.1	0.4 × 0.36 × 0.12
Range over θ, deg	2.93–25.00	3.14–25.00	3.04–25.50
Ranges of reflection indices	$-14 \le h \le 10$, $-13 \le k \le 21$, $-24 \le l \le 22$	$-14 \le h \le 5$, $-10 \le k \le 13$, $-35 \le l \le 57$	$-12 \le h \le 8$, $-12 \le k \le 10$, $-21 \le l \le 22$
Number of measured/independent reflections (R_{int})	15594/8008 (0.0466)	12931/6019 (0.0703)	6426/3532 (0.0216)
Completeness, %	99.5	99.7	99.4
Number of reflections with $I > 2\sigma(I)$	4928	3269	3003
Number of refined parameters	512	459	271
GOOF	1.007	1.009	1.003
R factor ($I > 2\sigma(I)$)	$R_1 = 0.0770$, $wR_2 = 0.2138$	$R_1 = 0.0892$, $wR_2 = 0.2129$	$R_1 = 0.0342$, $wR_2 = 0.0813$
R factor (for all data)	$R_1 = 0.1305$, $wR_2 = 0.2461$	$R_1 = 0.1536$, $wR_2 = 0.2499$	$R_1 = 0.0428$, $wR_2 = 0.0858$
$\Delta\rho_{max}/\rho_{min}$, e Å^{-3}	0.916/–0.430	0.596/–0.356	0.621/–0.940

The independent part of the unit cell of compound **I** contains a fragment of the coordination 3D polymer $[Zn_2(1,2\text{-Bdc})_2(Bpe)_2]_n$ formed by two crystallographically independent atoms Zn(1) and Zn(2), two doubly deprotonated ligands $(1,2\text{-Bdc})^{2-}$, three neutral ligands Bpe (two of which are centrosymmetric), and crystallization molecules Dmf and H_2O in the metal to Dmf to H_2O ratio equal to 2 : 0.25 : 0.25. The coordination polyhedra of both atoms Zn(1) and Zn(2) in compound **I** are tetrahedra formed by the donor set of atoms N_2O_2, whose nitrogen atoms belong to two crystallographically different Bpe ligands and the oxygen atoms belong to two different $(1,2\text{-Bdc})^{2-}$ ligands (Fig. 1). In the coordination polyhedra of the Zn(1) and Zn(2) atoms, the interatomic distances Zn–O (1.945(4)–1.969(5) Å) and Zn–N (2.017(6)–2.036(6) Å) (Table 2) correspond to the values found for the compounds with the tetrahedral environment of the zinc atoms (coordination number 4) [8]. An analysis of the CSD shows that the coordination number of Zn(II) atoms in the Bipy-containing compounds of this class can take different values (both 5 and 6) [11, 12]. In the coordination polymer of compound **I**, two independent ligands $(1,2\text{-Bdc})^{2-}$ coordinate to the metal via the bidentate-bridging mode (Fig. 1), although it is known that this ligand can coordinate via diverse modes: monodentate, bidentate-chelating, and various bridging modes (μ_2, μ_3, μ_4) [22, 23]. As a result, coil chains arranged along the *a* parameter of the unit cell are formed in the crystal of compound **I**, and the interatomic Zn(1)···Zn(2)* dis-

Table 2. Interatomic distances and bond angles in the coordination polyhedra of Zn(II) and Cd(II) in compounds **I–III***

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
I					
Zn(1)–O(1)	1.969(5)	O(1)Zn(1)O(5)	97.8(2)	O(5)Zn(1)N(1*B*)	117.2(2)
Zn(1)–O(5)	1.932(6)	O(1)Zn(1)N(*A*)	126.3(2)	N(1A)Zn(1)N(1*B*)	105.3(2)
Zn(1)–N(1*A*)	2.029(5)	O(1)Zn(1)N(1*B*)	106.4(2)		
Zn(1)–N(1*B*)	2.036(6)	O(5)Zn(1)N(1*A*)	104.7(2)		
Zn(2)–O(4)$^{\#1}$	1.945(4)	O(4)$^{\#1}$Zn(2)O(7)$^{\#2}$	98.4(2)	O(7)$^{\#2}$Zn(2)N(2*A*)	119.0(2)
Zn(2)–O(7)$^{\#2}$	1.953(4)	O(4)$^{\#1}$Zn(2)N(1*C*)	118.4(2)	N(1*C*)Zn(2)N(2*A*)	108.6(2)
Zn(2)–N(1*C*)	2.017(6)	O(4)$^{\#1}$Zn(2)N(2*A*)	105.8(2)		
Zn(2)–N(2*A*)	2.021(5)	O(7)$^{\#2}$Zn(2)N(1*C*)	107.0(2)		
II					
Zn(1)–O(1)	1.94(1)	O(1)Zn(1)O(5)	103.4(8)	O(5)Zn(1)N(2*A*)$^{\#1}$	97.6(7)
Zn(1)–O(5)	1.89(2)	O(1)Zn(1)N(1*A*)	108.4(5)	N(1*A*)Zn(1)N(2*A*)$^{\#1}$	104.4(4)
Zn(1)–N(1*A*)	2.07(1)	O(1)Zn(1)N(2*A*)$^{\#1}$	120.6(5)		
Zn(1)–N(2*A*)$^{\#1}$	2.03(1)	O(5)Zn(1)N(1*A*)	123.4(7)		
Zn(2)–O(3)	1.95(1)	O(3)Zn(2)O(7)$^{\#3}$	140(1)	N(1*B*)Zn(2)O(7)$^{\#3}$	103(1)
Zn(2)–O(7)$^{\#3}$	2.23(3)	O(3)Zn(2)O(8)$^{\#3}$	92.3(7)	N(2*B*)$^{\#2}$Zn(2)O(7)$^{\#3}$	95(3)
Zn(2)–O(8)$^{\#3}$	2.46(3)	O(3)Zn(2)N(1*B*)	99.6(5)	N(1*B*)Zn(2)O(8)$^{\#3}$	95.2(7)
Zn(2)–N(1*B*)	2.055(8)	O(3)Zn(2)N(2*B*)$^{\#2}$	114(3)	N(2*B*)$^{\#2}$Zn(2)O(8)$^{\#3}$	148(3)
Zn(2)–N(2*B*)$^{\#2}$	2.03(5)	O(7)$^{\#3}$Zn(2)O(8)$^{\#3}$	53.5(4)	N(2*B*)$^{\#2}$Zn(2)N(1*B*)	97(2)
III					
Cd(1)–O(1)	2.349(3)	O(1)Cd(1)O(2)	54.70(9)	O(3)$^{\#1}$Cd(1)O(4)$^{\#1}$	53.83(9)
Cd(1)–O(2)	2.430(3)	O(1)Cd(1)O(3)$^{\#1}$	85.97(9)	O(3)$^{\#1}$Cd(1)O(1*w*)	123.9(1)
Cd(1)–O(3)$^{\#1}$	2.355(3)	O(1)Cd(1)O(4)$^{\#}$1	139.34(9)	O(3)$^{\#1}$Cd(1)N(1)	101.1(1)
Cd(1)–O(4)$^{\#1}$	2.483(3)	O(1)Cd(1)O(1*w*)	150.1(1)	O(3)$^{\#1}$Cd(1)N(2)$^{\#2}$	92.3(1)
Cd(1)–O(1*w*)	2.463(3)	O(1)Cd(1)N(1)	94.8(1)	O(1*w*)Cd(1)O(4)$^{\#1}$	70.5(1)
Cd(1)–N(1)	2.349(3)	O(1)Cd(1)N(2)$^{\#2}$	98.5(1)	N(1)Cd(1)O(4)$^{\#1}$	88.1(1)
Cd(1)–N(2)$^{\#2}$	2.369(3)	O(2)Cd(1)O(3)$^{\#1}$	139.59(9)	N(2)$^{\#2}$Cd(1)O(4)$^{\#1}$	90.0(1)
		O(2)Cd(1)O(4)$^{\#1}$	165.90(9)	N(1)Cd(1)O(1*w*)	82.3(1)
		O(2)Cd(1)O(1*w*)	95.53(9)	N(2)$^{\#2}$Cd(1)O(1*w*)	80.0(1)
		O(2)Cd(1)N(1)	92.0(1)	N(1)Cd(1)N(2)$^{\#2}$	161.8(1)
		O(2)Cd(1)N(2)$^{\#2}$	85.6(1)		

* Symmetry codes: $^{\#1}$ $-x + 3/2, y - 1/2, -z + 1/2$; $^{\#2}$ $-x + 1/2, y - 1/2, -z + 1/2$ (**I**); $^{\#1}$ $x - y, x, z + 1/6$; $^{\#2}$ $x - 1, y - 1, z$; $^{\#3}$ $x - 1, y, z$ (**II**); $^{\#1}$ $-x + 1/2, y + 1/2, -z + 1/2$; $^{\#2}$ $x - 1, y + 1, z$ (**III**).

tances between the atoms linked by the (1,2-Bdc)$^{2-}$ ligands are 6.367 and 6.575 Å (Fig. 2a). In compound **I**, the Bpe ligands coordinate to the metal atoms via the bidentate-bridging mode through the terminal nitrogen atoms (Fig. 2b) linking both Zn(1) with Zn(2) (Fig. 2b), Zn(1) with Zn(1)*, and Zn(2) with Zn(2)*. The interatomic Zn(1)···Zn(2), Zn(1)···Zn(1)*, and Zn(2)···Zn(2)* distances are 13.228, 13.279, and 13.383 Å, respectively. Although the Bpe ligands in the crystal structure of compound **I** differ in symmetry, they are nearly similar. In the noncentrosymmetric ligand, the CCH$_2$CH$_2$C torsion angle containing the ethane fragment is 176° and the dihedral angle between the planes of the aromatic rings is 2.8°. These data do not differ strongly from similar values in the centrosymmetric Bpe ligands. A 2D network involving both the (1,2-Bdc)$^{2-}$ ligands and the noncentrosymmetric Bpe ligand (Fig. 3a) can be distinguished in the crystal of compound **I**. The network is completed to a 3D framework by the cen-

Table 3. Hydrogen bonding geometry in compounds **I–III**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transforms for atoms A
	D–H	H···A	D···A		
			I		
O(1*w*)–H(1)···O(2)	0.83	2.07	2.87(3)	162	x, y, z
O(1*w*)–H(2)···O(8)	0.85	2.15	3.00(3)	178	$-x + 3/2, y - 1/2, -z + 1/2$
C(1)–H···O(8)	0.93	2.47	3.199(9)	136	$-x + 3/2, y - 1/2, -z + 1/2$
C(4)–H···O(4)	0.93	2.61	3.523(8)	166	$x - 1, y, z$
C(9)–H···O(5)	0.93	2.59	3.493(8)	163	$-x + 3/2, y - 1/2, -z + 1/2$
C(10)–H···O(3)	0.93	2.63	3.335(9)	134	$-x + 3/2, y - 1/2, -z + 1/2$
C(11)–H···O(8)	0.93	2.30	3.091(8)	143	$-x + 1/2, y - 1/2, -z + 1/2$
C(12)–H···O(3)	0.93	2.48	3.369(9)	161	$x - 1, y, z$
C(2*A*)–H···O(1*D*)	0.93	2.69	3.560(9)	156	$x + 1, y, z$
C(5*A*)–H···O(6)	0.93	2.35	3.181(10)	148	x, y, z
C(1*B*)–H···O(6)	0.93	2.41	3.32(1)	165	$-x + 1/2, y - 1/2, -z + 1/2$
C(4*B*)–H···O(1*D*)	0.93	2.77	3.616(9)	152	$-x + 1/2, y - 1/2, -z + 1/2$
			II		
C(5*A*)–H···O(2)	0.93	2.47	3.28(2)	147	x, y, z
C(11*A*)–H···O(2)	0.93	2.21	2.99(2)	140	$y, -x + y, z - 1/6$
C(1*B*)–H···O(3)	0.93	2.52	3.10(2)	120	x, y, z
C(11*B*)–H···O(7)	0.93	2.59	3.18(2)	121	$x, y + 1, z$
			III		
O(1*w*)–H(1)···O(4)	0.84	2.31	2.855(4)	123	$-x + 1/2, y + 1/2, -z + 1/2$
O(1*w*)–H(2)···O(2)	0.87	1.81	2.672(4)	173	$-x, -y + 2, -z$
C(10)–H···O(4)	0.93	2.55	3.461(5)	165	$x + 1/2, -y + 3/2, z - 1/2$
C(12)–H···O(1)	0.93	2.51	3.337(5)	149	$-x + 1/2, y - 1/2, -z + 1/2$
C(18)–H···O(3)	0.93	2.50	3.354(5)	152	$x + 1, y, z$
C(19)–H···O(1)	0.93	2.42	3.296(5)	157	$-x + 3/2, y - 1/2, -z + 1/2$

trosymmetric Bpe ligands (Fig. 3b). The same structure was observed in the coordination 3D polymer $[Zn_2(1,2\text{-}Bdc)_2(Bpp)_2]_n$ (**IV**) [8] in which both ligands $(1,2\text{-}Bdc)^{2-}$ and Bpp are involved in coordination similarly to compound **I** to form a tetrahedral environment of two crystallographically independent metal atoms. However, these results differ strongly from those found for the coordination 1D polymer with the same ligands $[Zn_2(1,2\text{-}Bdc)_2(Bpp)]_n$ [9] in which Bpp joins two Zn^{2+} ions into dimers by the dicarboxylate ligands bound into chains. In the 1D polymer [9], the type of the coordination polyhedron of the metal atom differs from those observed in compounds **I** and **IV** and the $(1,2\text{-}Bdc)^{2-}$ ligands coordinate to the Zn(II) atoms via different modes.

The coordination polymer in the crystal structure of compound **I** is stabilized by weak hydrogen bonds of the C–H···O type. The residues of Dmf and H_2O crystallization molecules linked by hydrogen bonds are incorporated into free cavities of the coordination 3D polymer (Table 3, Fig. 4a). After the removal of crystallization molecules, the volume of the free cavities in compound **I** is 1265.1 Å^3 (of 27.7% of the unit cell volume) (Fig. 4b).

The independent part of the unit cell of compound **II** contains the fragment of the coordination 3D polymer $[Zn_2(1,2\text{-}Bdc)_2(Bpp)_2]_n$ including two crystallographically independent Zn(1) and Zn(2) atoms, two doubly deprotonated $(1,2\text{-}Bdc)^{2-}$ ligands, and two neutral Bpp ligands. The coordination polyhedra of the Zn(1) and Zn(2) metal atoms in compound **II** differ: a tetrahedron formed by the donor set of atoms N_2O_2 (nitrogen atoms of two crystallographically different Bpp ligands and oxygen atoms of two different $(1,2\text{-}Bdc)^{2-}$) is observed for Zn(1), and a strongly distorted tetragonal pyramid with the donor set of atoms N_2O_3 is observed for Zn(2), since the τ index of the tetragonal pyramid polyhedron calculated by the equation $\tau = \beta - \alpha/60$ [24, 25] is equal to 0.135; i.e., its value is closer to 0 than to 1. In the coordination polyhedron of Zn(2), two nitrogen atoms belong to two crystallographically different Bpp ligands and

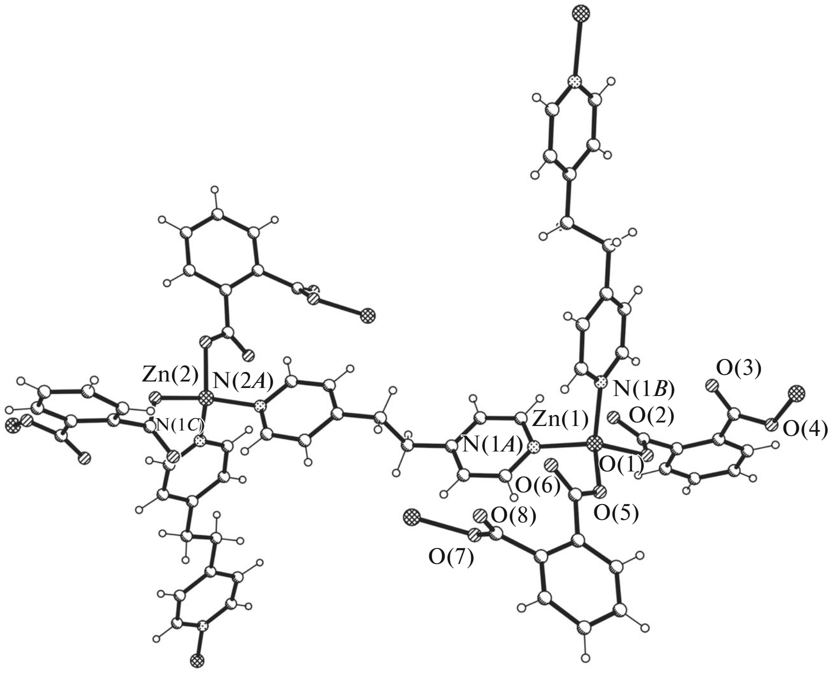
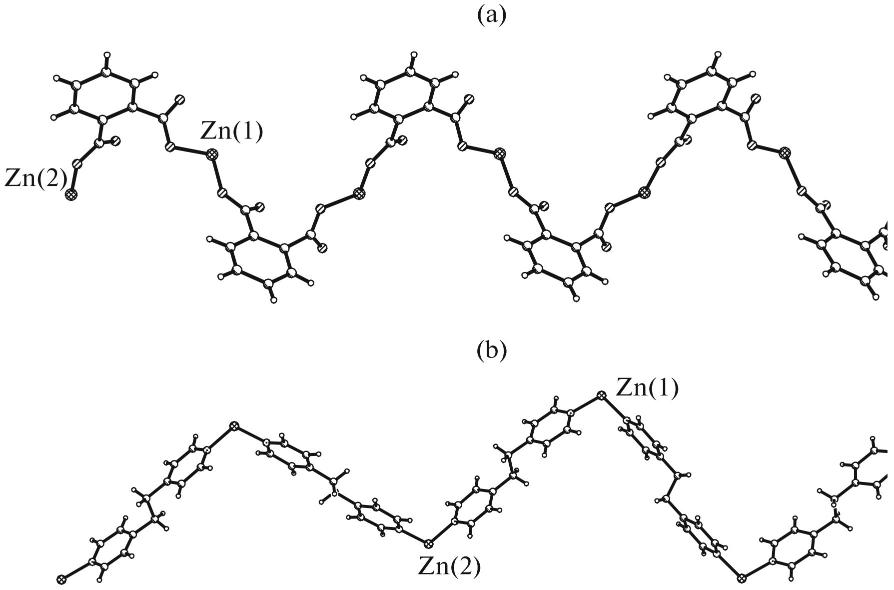


Fig. 1. Fragment of the coordination polymer in compound **I** with the numeration of functional atoms in the independent part of the unit cell.



(a)

(b)

Fig. 2. Structures of the coordination 1D polymer formed by (a) ligands $(1,2\text{-Bdc})^{2-}$ in compound **I** and (b) nonsymmetric ligand Bpe in compound **I**.

three oxygen atoms belong to two different $(1,2\text{-Bdc})^{2-}$ (Fig. 5). In the coordination polyhedron of the Zn(1) atom, the interatomic distances are 1.94(1) and 1.89(2) Å for Zn–O and 2.07(1) and 2.03(1) Å for Zn–N. For the Zn(2) atoms the distances are 1.95(1), 2.23(3), and 2.46(3) Å for Zn–O and 2.055(8) and 2.03(5) Å for Zn–N (Table 2). The type of the coordination polyhedron of the Zn(1) atom is similar to the tetrahedra in compounds **I** and **IV**, whereas the tetragonal pyramid type observed for Zn(2) is similar to that for the metal atom in the Zn(II) complex with $(1,2\text{-BdcH})^{-}$ and Bipy [11].

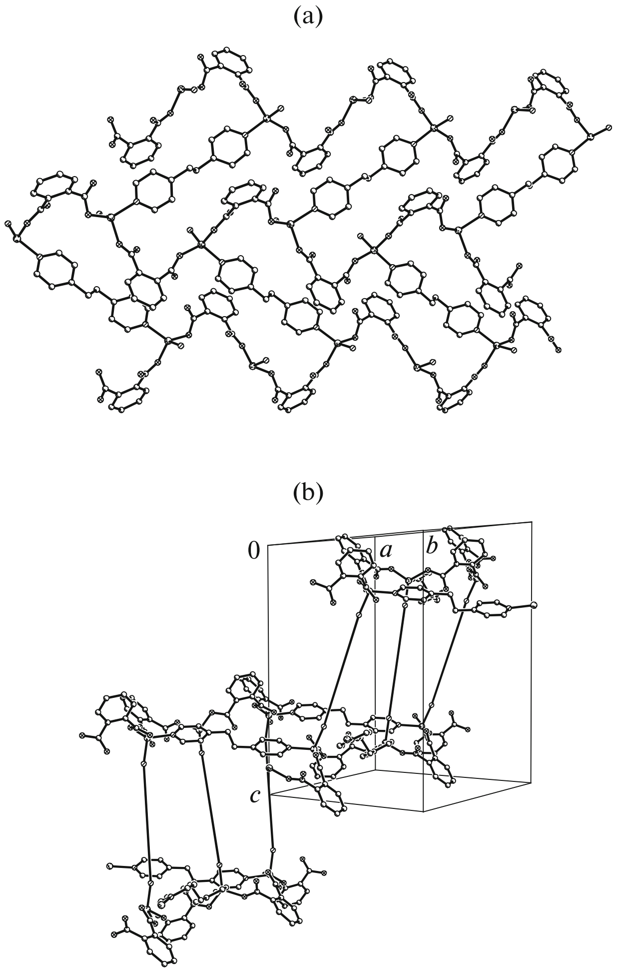


Fig. 3. Structures of the (a) coordination 2D polymer formed by ligands $(1,2\text{-Bdc})^{2-}$ in compound **I** and (b) coordination 3D polymer involving symmetric ligands Bpe (as lines) in compound **I**.

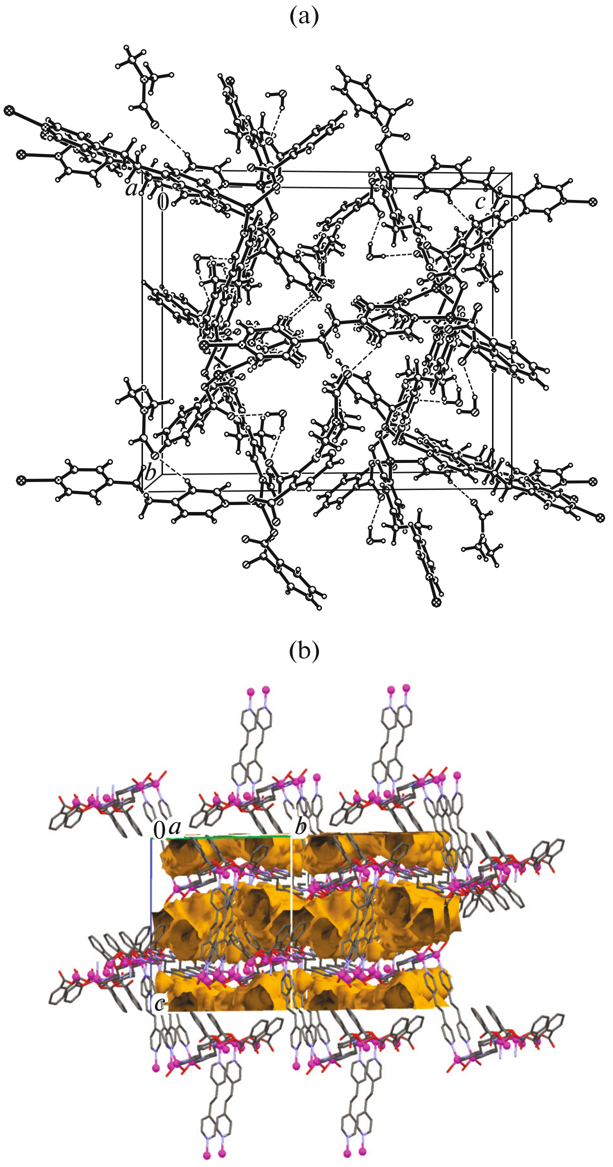


Fig. 4. (a) Coordination 3D polymer and crystallization Dmf and H_2O molecules linked to the 3D polymer in compound **I** and (b) the isolation of free cavities in the structure of compound **I** when the crystallization molecules are removed.

In the coordination Zn(II) polymer (**II**), two independent $(1,2\text{-Bdc})^{2-}$ ligands coordinate to the metal atoms via different modes. One ligand is bound to two metal atoms via the bidentate-bridging mode involving two oxygen atoms of different carboxyl groups, and the second ligand uses the tridentate chelate-bridging mode and binds the Zn(1) and Zn(2) atoms through one/two oxygen atoms of different carboxyl groups (Fig. 6). The chains along the *b* parameter of the unit cell are formed in the crystal, and the metal atoms and crystallographically independent $(1,2\text{-Bdc})^{2-}$ ligands alternate in the chains. The Zn(1)···Zn(2) and Zn(1)···Zn(2)* interatomic distances are 6.047 and 6.397 Å, respectively. In the crystal of compound **II**, the Bpp ligands coordinate to the metal atom via the bidentate-bridging mode (Fig. 5): one of the ligands binds two Zn(1) atoms, and the second ligand binds two Zn(2) atoms. The Zn(1)···Zn(1)* and Zn(2)···Zn(2)* interatomic distances are 13.287 and 12.199 Å, respectively. Both Bpp ligands in the crystal exist in the general position. The $C{-}CH_2{-}CH_2{-}C$ torsion angles containing the propane fragment are equal to 166° and 171° in one ligand and to 166° and 176° in another ligand. The dihedral angles between the planes of the aromatic rings in these ligands are 109.2° and 98.4°, unlike similar angles in compound **I**. In the crystal of compound **II**, the chains the formation of which involves both $(1,2\text{-Bdc})^{2-}$ ligands are completed by the Bpp ligand to the coordination 3D polymer and are stabilized by weak hydrogen bonds C–H···O (Table 3, Fig. 7a). The volume of the free

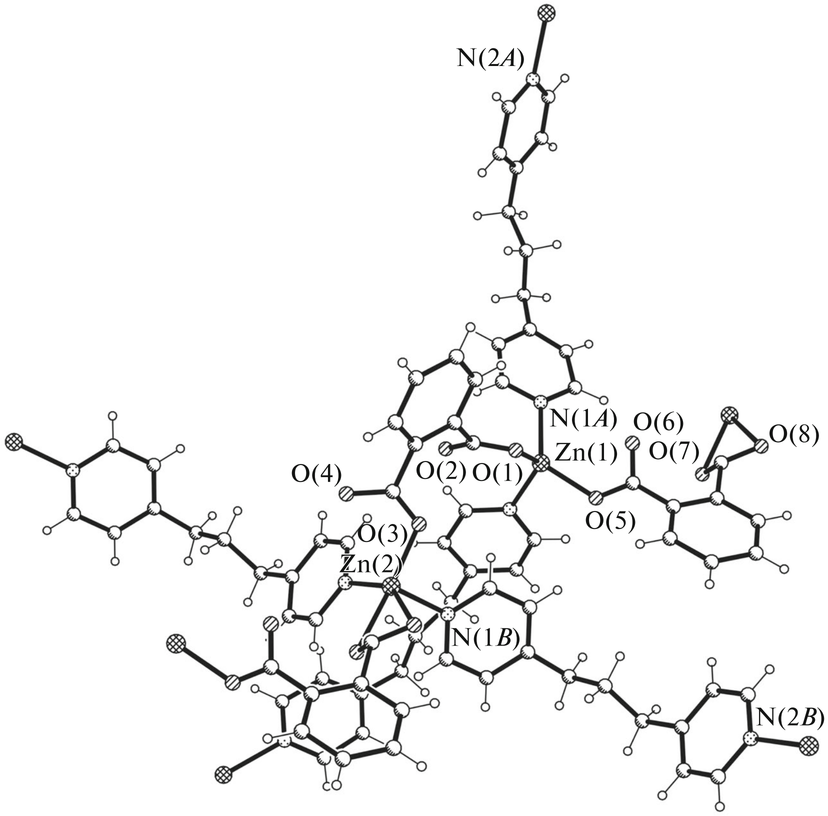


Fig. 5. Fragment of the coordination polymer in compound **II** with the numeration of functional atoms in the independent part of the unit cell.

cavities in compound **II** (763.5 Å^3) is 12.0% of the unit cell volume (Fig. 7b).

The independent part of the unit cell of compound **III** contains the fragment of the coordination 2D polymer [Cd(1,2-Bdc)(Bpp)]$_n$ formed by one crystallographically independent Cd(1) atom, doubly deprotonated (1,2-Bdc)$^{2-}$ ligand, and neutral Bpp ligand. The coordination polyhedron of the Cd(1) atom in compound **III** is a pentagonal bipyramid formed by the donor set of atoms N_2O_5. The nitrogen atoms belong to two Bpp ligands, and the oxygen atoms belong to two (1,2-Bdc)$^{2-}$ ligands and coordinated water molecule (Fig. 8). The Cd–O(Bdc), Cd–N(Bpp), and Cd–O(*w*) interatomic distances are

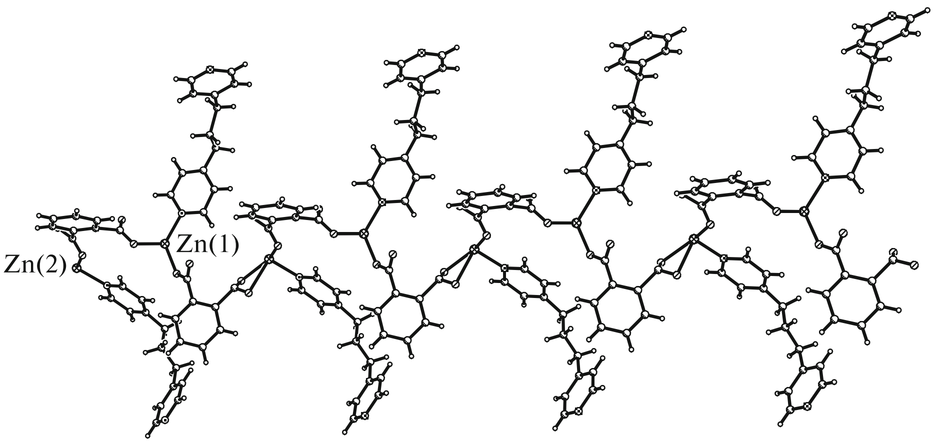


Fig. 6. Structure of the coordination 1D polymer formed by ligands (1,2-Bdc)$^{2-}$ in compound **II** with the beaded Bpp ligands.

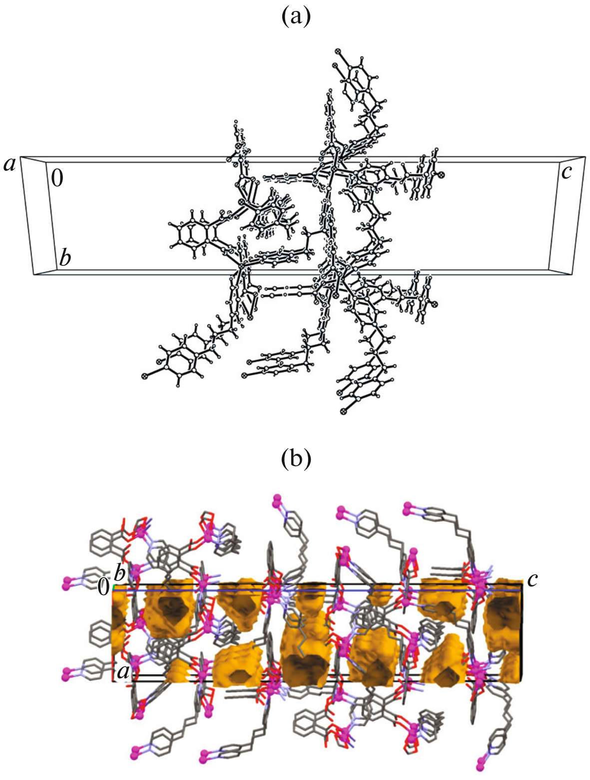

(a)
(b)

Fig. 7. (a) Fragment of the 3D coordination polymer in compound **II** and (b) the isolation of free channels in the structure of compound **II**.

2.349(3)–2.483(3), 2.349(3) and 2.369(3), and 2.463(3) Å, respectively (Table 2). The coordination polyhedron of the Cd(1) atom in compound **III** is similar to that found in the Cd(II) complex without Bpp [18] but differs from polyhedra observed in the complexes of this metal containing $(1,2\text{-Bdc})^{2-}$ or $(1,2\text{-HBdc})^{-}$ and Bipy [14, 15].

In the coordination 2D polymer (**III**), the $(1,2\text{-Bdc})^{2-}$ ligand coordinates to two metal atoms via the tetradentate chelate-bridging mode, i.e., involving both oxygen atoms of the carboxyl groups (Figs. 8, 9). The chains are formed in the crystal along the *b* parameter of the unit cell, the metal atoms in them are linked by the $(1,2\text{-Bdc})^{2-}$ ligands, and the Cd(1)···Cd(1)* interatomic distance is 6.577 Å. The Bpp ligands in the crystal coordinate to the metal atoms in the same way as in compounds **I** and **II**. The Cd(1)···Cd(1)* distance is 14.627 Å (Fig. 8), and the dihedral angle between the planes of the aromatic rings in Bpp (91.5°) differs slightly from the similar angle in compound **II**.

In the crystal of compound **III**, the chains the formation of which involves the $(1,2\text{-Bdc})^{2-}$ ligands are completed by the Bpp ligands to the coordination 2D polymer additionally stabilized by weak hydrogen bonds O(*w*)–H···O and C–H···O involving the atoms of the aromatic fragments of the Bpp ligands as proton donors and the oxygen atoms of the carboxyl groups of the $(1,2\text{-Bdc})^{2-}$ ligands as acceptors (Table 3, Fig. 10a). The 2D layers parallel to the *ab* plane are linked between each other by both O(*w*)–H···O hydrogen bonds and weak C–H···O hydrogen bonds (Table 3, Fig. 10b). The unit cell of compound **III** contains no free volume.

The reactions of the Zn(II) and Cd(II) salts with 1,2-benzenedicarboxylic acid and Bpe and Bpp ligands of the bipyridine type afforded four compounds, three of which are the new coordination polymers $[Zn_2(1,2\text{-Bdc})_2(Bpe)_2]_n \cdot 0.25n(Dmf) \cdot 0.25nH_2O$ (**I**), $[Zn_2(1,2\text{-Bdc})_2(Bpp)_2]_n$ (**II**), and $[Cd(1,2\text{-Bdc})(Bpp)(H_2O)]_n$ (**III**). The fourth synthesized Cd(II) compound containing none of organic ligands has been known earlier [18]. The new Zn(II) compound with $(1,2\text{-Bdc})^{2-}$ and Bpp was obtained by the variation of the reaction conditions and solvents,

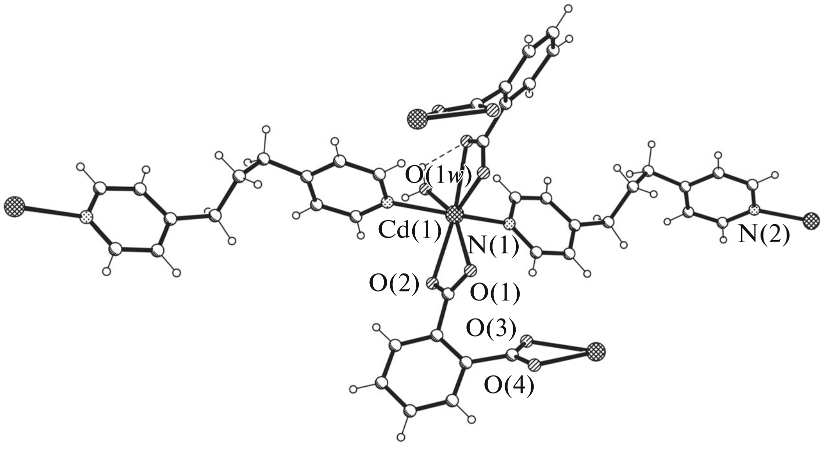


Fig. 8. Fragment of the coordination polymer in compound **III** with the numeration of functional atoms in the independent part of the unit cell.

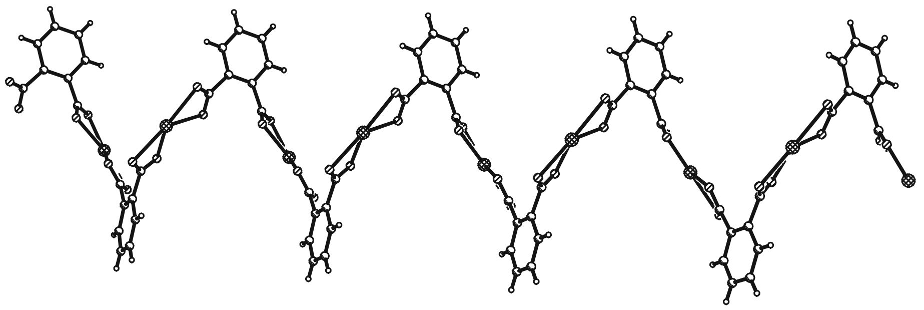


Fig. 9. Structure of the coordination 1D polymer formed by ligands $(1,2\text{-Bdc})^{2-}$ in compound **III**.

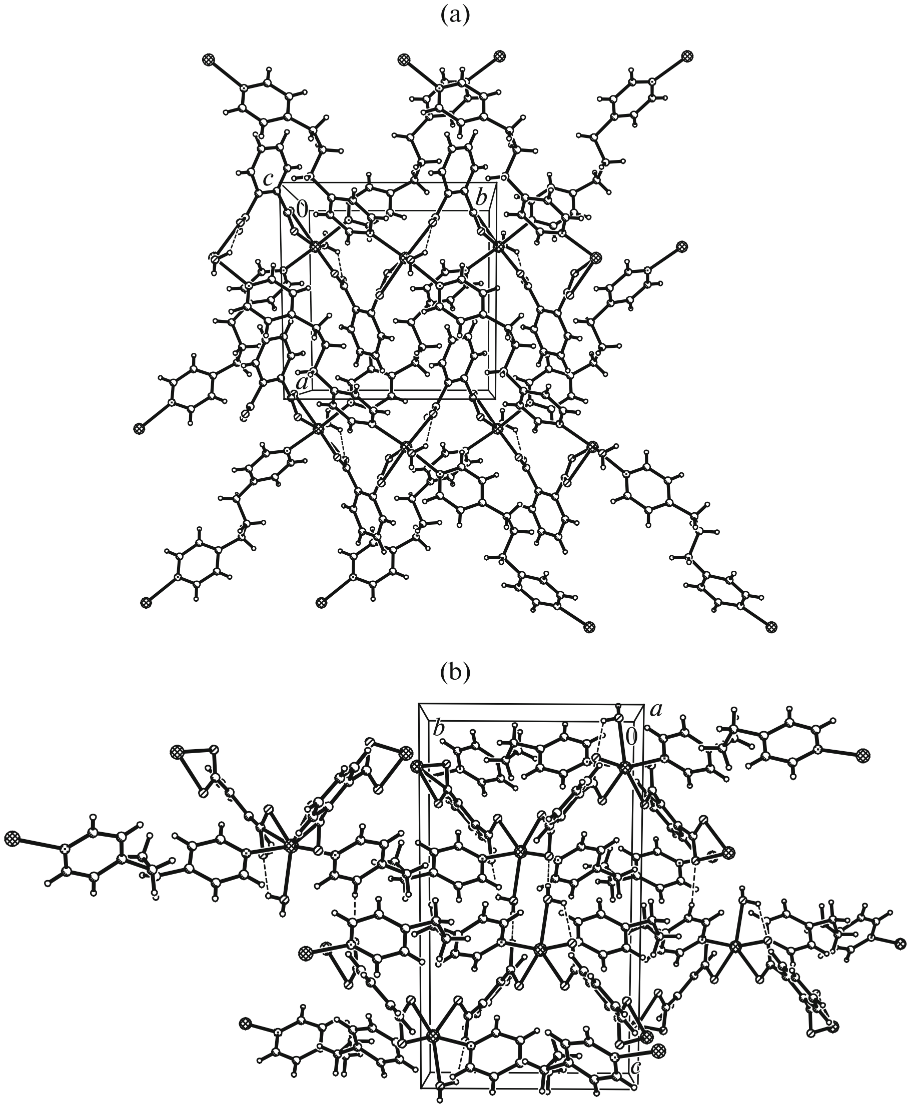


Fig. 10. (a) Structure of the coordination 2D polymer additionally stabilized by weak hydrogen bonds O–H···O and C–H···O and (b) the crystal packing of the layers in compound **III**.

although the compounds of this metal with the same ligands are also known [8, 9].

REFERENCES

1. Gu, Z.-G., Zhou, X.-H., Jin, Y.-B., et al., *Inorg. Chem.*, 2007, vol. 46, p. 5462.
2. Xie, Y.-M., Liu, J.-H., Wu, X.-Y., et al., *Cryst. Growth Des.*, 2008, vol. 8, p. 3914.
3. Biradha, K., Sarkar, M., and Rajput, L., *Chem. Commun.*, 2006, p. 4169.
4. Manna, S.C., Konar, S., Zangrando, E., et al., *Eur. J. Inorg. Chem.*, 2005, p. 4646.
5. Li, Z.-G., Wang, G.-H., Jia, H.-Q., et al., *CrystEngComm*, 2008, vol. 10, p. 983.
6. Carlucci, L., Ciani, G., Proserpio, D.M., and Rizzato, S., *CrystEngComm*, 2002, vol. 4, p. 121.
7. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, nos. 3–1, p. 380.
8. Zheng, Yu.-Q., Zhang, J., and Liu, J.-Yo., *CrystEngComm*, 2010, vol. 12, p. 2740.
9. Chen, Yu-B., Zhang, J., Cheng, J.-K., et al., *Inorg. Chem. Commun.*, 2004, vol. 7, p. 1139.
10. Ou, Y.-C., Liu, W.-T., Li, J.-Y., et al., *Chem. Commun.*, 2011, vol. 47, p. 9384.
11. Tang, En., Dai, Yu-M., and Lin, Sh., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2004, vol. 60, p. m433.
12. Li, X.-M., Wang, Q.-W., Cui, Y.-Ch., et al., *J. Huaxue (Chin.) (Chin. J. Struct. Chem.)*, 2006, vol. 25, p. 621.
13. Wu, Li-li., Rong, He., Zhen, W., Hui-Hua, S, *Chem. Res. Chin. Univ.*, 2011, vol. 27, p. 724.
14. Wang, X., Qin, Ch., Wang, E., and Xu, L., *J. Mol. Struct.*, 2005, vol. 737, p. 49.
15. Suresh, E., Boopalan, K., Jasra, R.V., and Bhadbhade, M.M., *Inorg. Chem.*, 2001, vol. 40, p. 4078.
16. Tobin, J.M. and Mark, A.R., *Angew. Chem., Int. Ed. Engl.*, 1995, vol. 341, p. 155.
17. Paul, A.M., Charlotte, L.S., and Kenneth, R.P., *J. Am. Chem. Soc.*, 2001, p. 7742.
18. Robl, C., *Z. Anorg. Allg. Chem.*, 1988, vol. 566, p. 144.
19. Vitiu, A.A., Coropceanu, Ed.B., and Bourosh, P.N., *Russ. J. Coord. Chem.*, 2017, vol. 43, no. 11, p. 745. doi 10.1134/S1070328417110100
20. *CrysAlis RED. O.D.L. Version 1.171.34.76*, 2003.
21. Sheldrick, G., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
22. Porai-Koshits, M.A. *Zh. Strukt. Khim.*, 1980, vol. 21, no. 3, p. 146.
23. Baca, S.G., Simonov, Yu.A., Gerbeleu, N.V., et al., *Polyhedron*, 2001, vol. 20, p. 831.
24. Reger, D.L., Pascui, A.E., Smith, M.D., et al., *Inorg. Chem.*, 2012, vol. 51, p. 11820.
25. Melnic, E., Coropceanu, E.B., Forni, A., et al., *Cryst. Growth Des.*, 2016, vol. 16, p. 6275.

Translated by E. Yablonskaya