Journal of Structural Chemistry. Vol. 59, No. 2, pp. 487-493, 2018.
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CRYSTAL STRUCTURE OF COORDINATION POLYMERS BASED ON A HETEROMETALLIC CARBOXYLATE COMPLEX

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Three new metal-organic frameworks $[Zn(Hibdc)_2]\cdot DMF$ (**1**), $(H_2NMe_2)[Li_2Zn_3(H_2O)(dmf)(Hbtc)_3(btc)]\cdot 6DMF\cdot H_2O$ (**2**), and $[Li_2Zn_2(H_2O)_2(bpp)(bpdc)_3]\cdot 7DMF$ (**3**) are obtained in the interaction of heterometallic carboxylate complex $[Li_2Zn_2(piv)_6(py)_2]$ with isophthalic (H_2ibdc) and trimesic (H_3btc) acids and in the presence of both 4,4′-biphenyldicarboxylic acid (H_2bpdc) and 4,4′-bispyridylpropane (bpp). The structure of the obtained compounds is determined by the single crystal X-ray diffraction analysis. In the reactions studied the structure of the initial $\{Li_2Zn_2\}$ fragment is not retained. A complicated fragmentation of this four-nuclear block occurs, including the formation of binuclear heterometallic dimers {LiZn}.

DOI: 10.1134/S0022476618020336

Keywords: lithium, zinc, coordination polymers, metal-organic frameworks, polynuclear complexes, carboxylate complexes, single crystal X-ray diffraction analysis.

INTRODUCTION

Over the last two decades, the preparation of novel metal-organic frameworks (MOFs) has attracted special attention of researchers due to an almost infinite opportunity to vary the polymer structure that, in turn, renders a wide range of possible applications of materials based on these compounds. These are already traditional fields, such as gas storage and separation [1-4], catalysis [5, 6], targeted drug delivery [7], design of sensors [8, 9] and many other functional materials. The traditional approach to the synthesis of novel coordination polymers implies the use of simple salts as the sources of metal centers whereas polynuclear secondary building blocks [10, 11] are often obtained by self-assembly during crystal growth. Examples of the synthesis from pre-synthesized complexes or clusters with the set geometry are rarer, which certainly gives advantages from the standpoint of the rational design of new compounds with the desired structure, and consequently, properties [12].

Four-nuclear heterometallic carboxylate complexes of the composition $[Li_2M_2(piv)_6L_2]$ ($M = Co^{2+}$, Ni^{2+}, Zn^{2+}; $piv^- =$ pivalate anion; L = axial ligand) have recently been obtained, however, they are of special interest as the sources of secondary building blocks for the synthesis of MOFs owing to their magnetic and luminescent properties [13-16]. We have

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previously shown the possibility of substituting both carboxylate and axial ligands to obtain polymer structures based on these complexes [17]. In this work, three novel MOFs were synthsized: [Zn(Hipdc)$_2$]·DMF (**1**), (H$_2$NMe$_2$)[Li$_2$Zn$_3$(H$_2$O)(dmf)(Hbtc)$_3$(btc)]·6DMF·H$_2$O (**2**), and [{LiZn}$_2$ (H$_2$O)$_2$(bpp)(bpdc)$_3$]·7DMF (**3**). The structure of the compounds was determined by the single crystal X-ray diffraction (XRD) analysis.

EXPERIMENTAL

Initial reagents and solvents (acetonitrile (>99%), N,N-dimethylformamide (DMF), isophthalic acid (H$_2$ibdc), trimesic acid (H$_3$btc), 4,4′-biphenyldicarboxylic acid (H$_2$bpdc), and 4,4′-bispyridylpropane (bpp) (Fig. 1) were no worse than chemically pure and were used without additional purification. Pivalate complex [Li$_2$Zn$_2$(piv)$_6$(py)$_2$] was obtained by the known procedure [17].

Synthesis of [Zn(Hipdc)$_2$]·DMF (1). Portions of [Li$_2$Zn$_2$(piv)$_6$(py)$_2$] (0.002 g, 0.002 mmol) and isophthalic acid (0.002 g, 0.014 mmol) in 1 ml of DMF were sealed in a glass tube and thermostated at 100 °C for 24 h. The obtained flat rectangular colorless crystals were used for single crystal XRD.

Synthesis of (H$_2$NMe$_2$)[Li$_2$Zn$_3$(H$_2$O)(dmf)(Hbtc)$_3$(btc)]·6DMF·H$_2$O (2). Portions of [Li$_2$Zn$_2$(piv)$_6$(py)$_2$] (0.002 g, 0.002 mmol) and trimesic acid (0.002 g, 0.009 mmol) in 1 ml of DMF were sealed in a glass tube and thermostated at 120 °C for 24 h. The obtained rectangular colorless crystals were used for single crystal XRD.

Synthesis of [{LiZn}$_2$(H$_2$O)$_2$(bpp)(bpdc)$_3$]·7DMF (3). Portions of [Li$_2$Zn$_2$(piv)$_6$(py)$_2$] (0.002 g, 0.002 mmol), 4,4′-bispyridylpropane (0.0014 g, 0.007 mmol), and 4,4′-biphenyldicarboxylic acid (0.002 g, 0.014 mmol) in 1 ml of DMF were sealed in a glass tube and thermostated at 100 °C for 24 h. The obtained flat rectangular colorless crystals were used for single crystal XRD.

Single crystal XRD analysis. XRD data on **1**–**3** single crystals were measured at 130 K on an automated Agilent Xcalibur diffractometer equipped with a two-dimensional AtlasS2detector (graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha) = 0.71073$ Å, ω-scanning). Integration, absorption correction, and determination of unit cell parameters were carried out using the CrysAlisPro program package [18]. The crystal structures of **1**–**3** were solved using the SHELXT program [19] and refined by the full-matrix least squares technique in the anisotropic (except hydrogen atoms) approximation using the SHELXL program [20]. Positions of hydrogen atoms in organic ligands were calculated geometrically and refined in the riding model. In the structure of **1** the isophthalic acid anion is disordered over two orientations with relative weights 0.52(2)/0.48(2). A part of guest molecules in the structures of **1–3** are strongly disordered and cannot be refined as a set of discrete positions. Therefore, the guest subsystem composition in **1**–**3** was determined based on the SQUEEZE/PLATON procedure [21] (152 e^- in 912 Å^3, 1981 e^- in 11396 Å^3, and 1694 e^- in 4969 Å^3 for **1–3** respectively). The crystallographic data and details of XRD experiments are listed in Table 1. Complete tables of interatomic distances and bond angles, atomic coordinates and atomic displacement parameters have been deposited with the Cambridge Crystallography Data Center (CCDC 1573678-1573680) and also can be received from the authors.

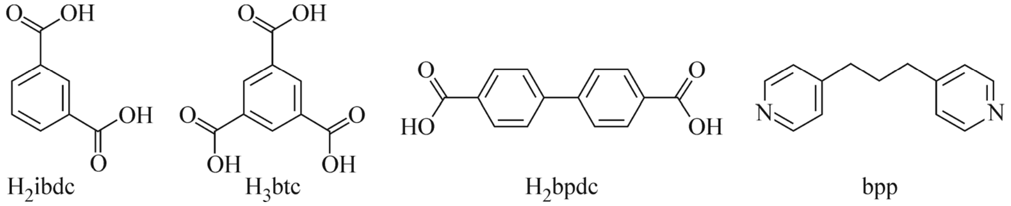

Fig. 1. Organic ligands used for the synthesis of coordination polymers.

TABLE 1. Crystallographic Characteristics and Parameters of the Diffraction Experiment

Parameter	**1**	**2**	**3**
Chemical formula	$C_{19}H_{17}NO_9Zn$	$C_{59}H_{76}Li_2N_8O_{33}Zn_3$	$C_{76}H_{91}Li_2N_9O_{21}Zn_2$
M, g/mol	468.70	1635.26	1611.19
Crystal symmetry	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$C222_1$	$Pbca$	$P2_12_12_1$
a, Å	11.9960(9)	15.8408(4)	17.7770(5)
b, Å	15.0790(7)	25.2295(6)	17.7867(6)
c, Å	12.9261(6)	47.9827(12)	50.5141(11)
V, Å^3	2338.2(2)	19176.6(8)	15972.3(8)
Z	4	8	8
D_{calc}, g/cm^3	1.331	1.133	1.340
μ, mm^{-1}	1.095	0.815	0.677
$F(000)$	960	6768	6752
Crystal size, mm	0.48×0.22×0.06	0.29×0.18×0.14	0.29×0.29×0.22
θ scanning range, deg	3.40-29.49	3.29-25.35	3.26-25.35
hkl index range	$-16 \le h \le 16$, $-17 \le k \le 20$, $-17 \le l \le 17$	$-14 \le h \le 19$, $-30 \le k \le 30$, $-57 \le l \le 44$	$-21 \le h \le 14$, $-21 \le k \le 20$, $-60 \le l \le 40$
N_{hkl} measured / independent	9088 / 2858	61394 / 17492	39250/ 26179
R_{int}	0.0246	0.0456	0.0442
N_{hkl} with $I > 2\sigma(I)$	2814	11293	21770
Goodness-of-fit on F^2	1.092	1.065	1.045
R factors $[I > 2\sigma(I)]$	$R_1 = 0.0381$, $wR_2 = 0.1036$	$R_1 = 0.0724$, $wR_2 = 0.2070$	$R_1 = 0.0911$, $wR_2 = 0.2285$
R factors (over all reflections)	$R_1 = 0.0388$, $wR_2 = 0.1044$	$R_1 = 0.1047$, $wR_2 = 0.2243$	$R_1 = 0.1055$, $wR_2 = 0.2529$
Residual electron density (max / min), e/Å^3	1.117 / −0.488	1.349 / −0.390	1.304 / −0.665

RESULTS AND DISCUSSION

Crystals of compounds **1**–**3** were obtained by heating a mixture of polynuclear complex $[Li_2Zn_2(piv)_6(py)_2]$ and the respective organic ligands in DMF. The composition and structure of the coordination polymers were determined by single crystal XRD.

The crystal structure of $[Zn(Hipdc)_2]\cdot DMF$ (**1**) represents a metal-organic framework containing a zinc(II) cation in the tetrahedral environment of four oxygen atoms of the carboxylic groups of four different isophthalate anions (Fig. 2). The Zn–O distances are in the range 1.948(3)-1.954(3) Å. Each acid residue coordinates two zinc cations while the layers formed have the sql topology. The layer packing contains one-dimensional rhombic channels with a cross-section of 6×8 Å, which are parallel to the c axis. The free space inside the channels is 39% of the total unit cell volume (calculated by the PLATON software [22]) and is filled with disordered solvent molecules corresponding to one DMF molecule per framework formula unit (Fig. 3).

The structure of polymer $(H_2NMe_2)[Li_2Zn_3(H_2O)(dmf)(Hbtc)_3(btc)]\cdot 6DMF\cdot H_2O$ (**2**) contains three types of secondary building blocks, among which the simplest is the zinc(II) cation in the tetrahedral environment of four oxygen atoms of the carboxyl groups of four benzenetricarboxylate anions. The Zn–O distances are within 1.918(4)-1.948(3) Å. The two remained secondary building blocks are the derivatives of the initial heterometallic complex; two lithium–oxygen bonds

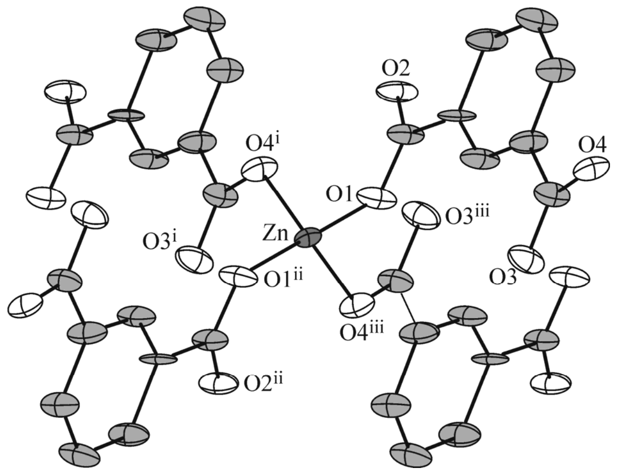

Fig. 2. Coordination environment of the zinc cation in **1**. 50% probability ellipsoids. Hydrogen atoms are omitted. Equivalent atomic coordinates are obtained by the following symmetry operations: ^{i} $-1/2+x$, $-1/2+y$, z; ^{ii} $1-x$, y, $3/2-z$; ^{iii} $3/2-x$, $-1/2+y$, $3/2-z$.

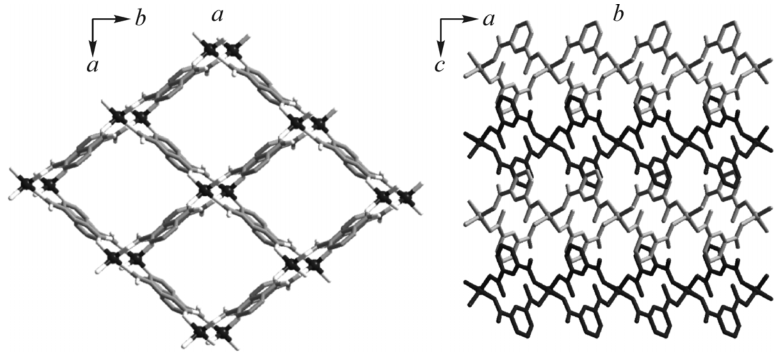

Fig. 3. Structure of the polymer layer in **1** (projection on the *ab* plane) (*a*); layer packing (projection on the *ac* plane) (*b*). Metal atoms are designated as dark gray balls; hydrogen atoms are not shown.

break in them, and in the heterometallic tricarboxylate fragment formed the pivalic acid anions are replaced by benzenetricarboxylate anions. In the first of these $\{LiZn(\mu\text{-}RCOO)_3(dmf)(RCOO)\}$ blocks the lithium cation completes its tetrahedral environment with a coordinated DMF molecule and the zinc cation completes its tetrahedral environment with an oxygen atom of the carboxylic group of the benzenetricarboxylate anion, forming a four-connected node in the polymer structure. Another secondary building block $\{LiZn(\mu\text{-}RCOO)_3(H_2O)(RCOO)\}$ is also a four-connected node, however, the lithium cation coordinates the aqua ligand oxygen atom while zinc cation c.n. changes to 5 due to coordination of both carboxyl oxygen atoms of the benzenetricarboxylate anion (Fig. 4). The Zn–O distances are within 1.918(4)-1.947(4) Å and 1.970(3)-2.060(4) Å, and Li–O are within 1.875(9)-1.939(11) Å, 1.872(10)-2.053(11) Å for the second and third blocks respectively. Three types of the secondary building blocks form a complex three-dimensional topology with a system of intersecting channels whose diameter varies within 4-8 Å (Fig. 5). The total volume of cavities amounts to 59% of the unit cell volume and is occupied by disordered solvent molecules and dimethylammonia cations because the framework itself carries a negative charge.

The structure of compound $[\{LiZn\}_2(H_2O)_2(bpp)(bpdc)_3]\cdot 7DMF$ (**3**) contains the binuclear building block $\{LiZn(\mu\text{-}RCOO)_3(H_2O)(N)\}$ being a bimetallic tricarboxylate derivative of the initial complex. Pivalate anions are substituted by biphenyldicarboxylate anions whereas lithium and zinc cations complete their tetrahedral environment by oxygen atoms of

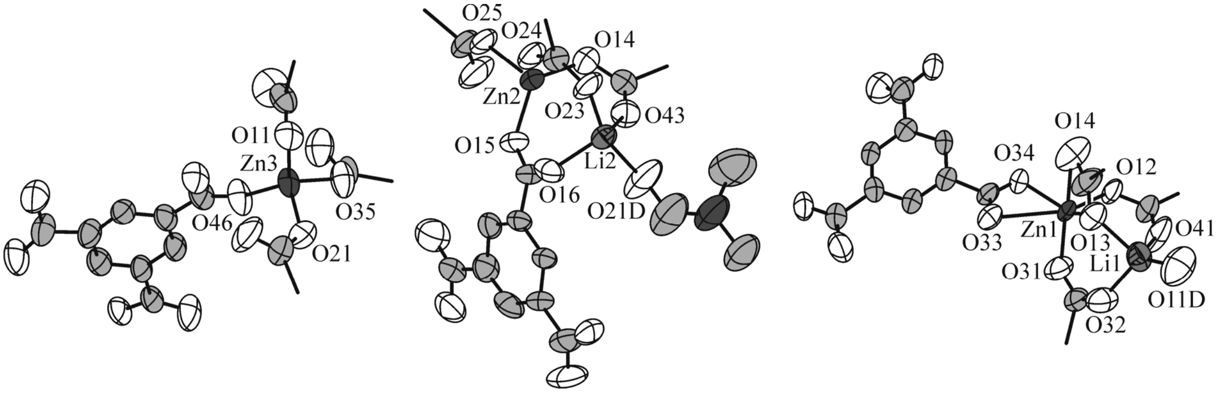

Fig. 4. Coordination environment of Zn^{2+} and Li^+ cations in **2**. 50% probability ellipsoids. Hydrogen atoms are omitted.

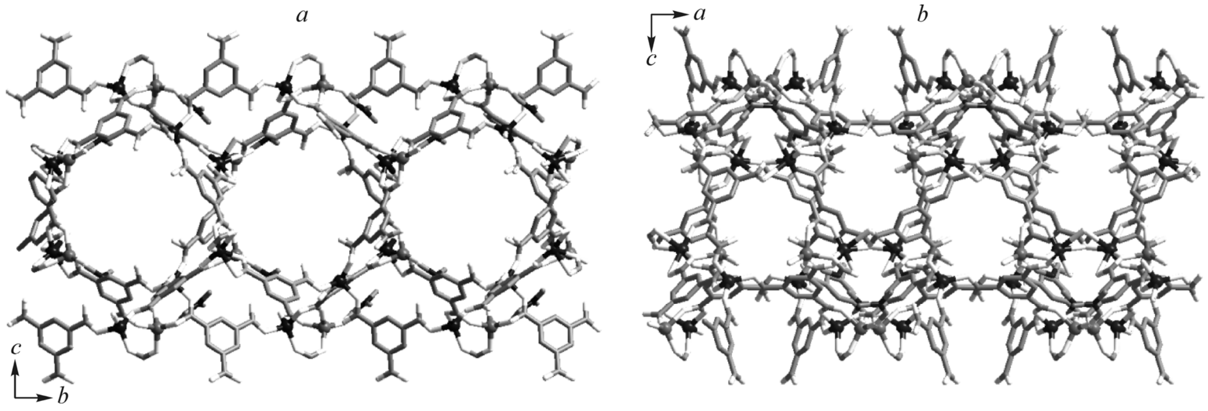

Fig. 5. Structure of the metal-organic framework of **2**: projection on the *bc* plane (*a*), projection on the *ac* plane (*b*). Zinc atoms are designated as dark balls; lithium atoms are designated as light ones; hydrogen atoms are not shown.

the water molecule and nitrogen atoms of the bpp linker correspondingly. The structure contains four independent blocks of this type, two of which differ in the turn angle of the pyridine ring of the bipyridyl linker (Fig. 6) while two others insignificantly differ from the first two by the binding angles between the blocks. The Zn–O distances are within 1.877(11)-1.978(10) Å and Li–O are 1.83(3)-2.01(3) Å. Four-connected nodes are bound with each other by bridging bpp and $bpdc^{2-}$ ligands, forming an interpenetrated metal-organic framework (Fig. 7). The structure contains a system of connected cavities whose volume comprises 31% of the cell volume. The cavities contain guest DMF molecules.

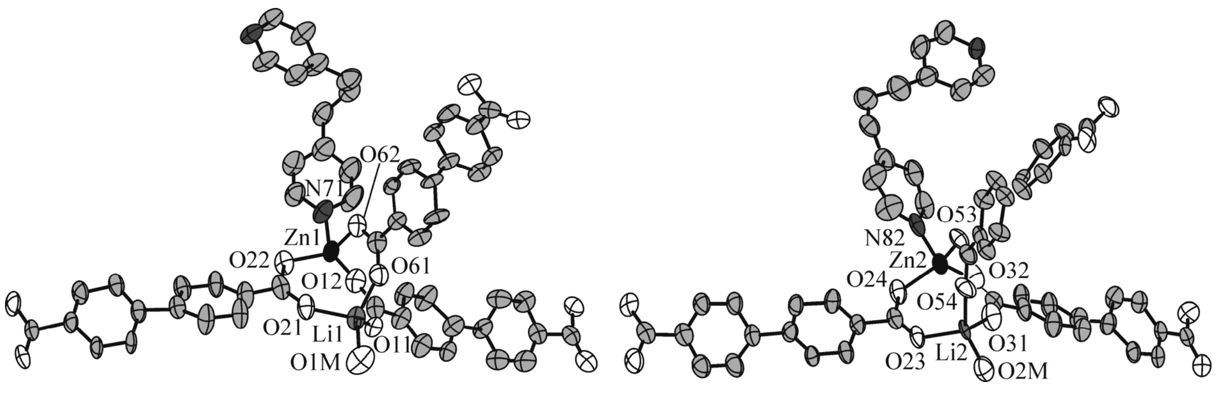

Fig. 6. Structure of binuclear coordination fragments $\{LiZn(H_2O)(bpp)(RCOO)_3\}$ in **3**. 50% probability ellipsoids; hydrogen atoms are omitted.

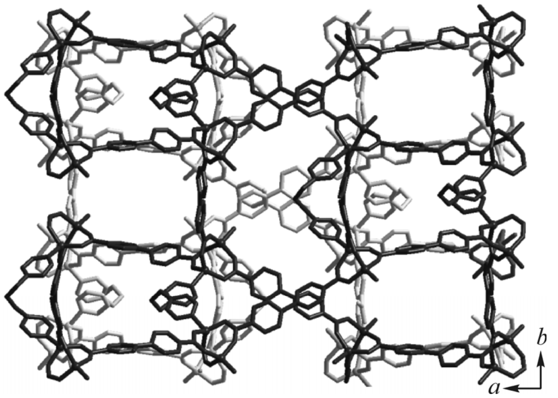

Fig. 7. Packing in the structure of **3** (projection on the *bc* plane). Intergrowth is shown by different shades of gray; hydrogen atoms are omitted.

CONCLUSIONS

We synthesized three new coordination polymers $[Zn(Hibdc)_2]\cdot DMF$, $(H_2NMe_2)[Li_2Zn_3(H_2O)\times\times(dmf)(Hbtc)_3(btc)]\cdot 6DMF\cdot H_2O$, and $[Li_2Zn_2(H_2O)_2(bpp)(bpdc)_3]\cdot 7DMF$, formed in the interaction of pre-synthesized carboxylate heterometallic complex $\{Li_2Zn_2\}$ with various polytopic carboxylate ligands on heating. The composition and structure were determined by single crystal XRD. In the reactions studied the structure of the initial $\{Li_2Zn_2\}$ fragment is not retained. A complicated fragmentation of this four-nuclear block occurs, including the formation of binuclear heterometallic dimers {LiZn}.

The work was supported by RFBR (grant No. 17-53-16015).

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