Design of scaffold-like metal-organic coordination polymers based on dinuclear zinc(II) carboxylate complexes

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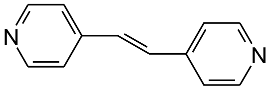
Two new scaffold-like metal-organic coordination polymers, $[Zn_2ndc_2bpe]\cdot DMF$ and $[Zn_2ndc_2dedpbp]\cdot 4DMF$ (ndc is 2,6-naphthalenedicarboxylate, bpe is *trans*-bis(4-pyridyl)ethylene, and dedpbp is 4,4´-diethynyl-4″,4‴-dipyridylbiphenyl), were synthesized by heating stoichiometric amounts of zinc(II) nitrate, H_2ndc, and bpe or dedpbp in DMF. The structures of the polymers were established by X-ray diffraction. Coordination of linear dicarboxylate ligands to zinc cations gives rise to planar square-grid networks, and additional coordination of the bifunctional nitrogen-containing ligands results in the formation of scaffold-like triply interpenetrating structures with a primitive cubic topology.

Key words: coordination polymers, zinc complexes, synthesis, crystal structure.

Porous hybrid metal-organic coordination polymers have been extensively studied in recent years[1,2] in view of the fact that new materials based on these polymers hold considerable promise for sorption of gases and other guests,[3—5] separation of organic molecules,[6—8] and heterogeneous catalysis.[9—11] Hybrid porous materials are of most interest for the synthesis of three-dimensional scaffold-like structures, because they provide a regular arrangement of cavities in structures and high stability of polymer frameworks after removal of guest molecules. One of possible approaches to the design of scaffold-like coordination polymers is based on formation of three-dimensional frameworks from two-dimensional layered network structures by their linking *via* bifunctional bridging ligands.[12,13] Recently,[14—17] a series of isotypic scaffold-like porous metal-organic structures based on the dinuclear carboxylate building fragment $\{M_2(OOC—R)_4L_2\}$ with a distorted octahedral geometry have been described. Coordination of metal atoms by dicarboxylate ligands gives rise to planar square-grid networks, and these networks are linked to each other through additional coordination of metal atoms by bifunctional nitrogen-containing ligands L (spacers) to form scaffold-like porous structures with a primitive cubic topology. Variations in the length of organic ligands and the introduction of substituents into these ligands allow changes in both the geometric parameters of the polymer network and the internal functional environment of the resulting cavities, which is reflected in the sorption properties of porous coordination polymers.[14,15] In this case, both the octahedral building block $\{M_2(OOC—R)_4L_2\}$ and the general topology of the polymer framework remain unchanged.

In the present study, we applied this approach to the synthesis of two new isotypic scaffold-like metal-organic coordination polymers, $[Zn_2ndc_2bpe]\cdot DMF$ (**1**) and $[Zn_2ndc_2dedpbp]\cdot 4DMF$ (**2**) (ndc is 2,6-naphthalenedicarboxylate, bpe is *trans*-bis(4-pyridyl)ethylene, and dedpbp is 4,4´-diethynyl-4″,4‴-dipyridylbiphenyl), and investigated their structures. In these compounds, the Zn_2 dimers are linked to each other *via* the carboxylate groups to form planar networks, and the networks are linked by spacers of different lengths (bpe for **1** and dedpbp for **2**) to form three-dimensional frameworks. The structures of **1** and **2** can be described as three-dimensional triply interpenetrating networks with a primitive cubic topology. In spite of the triple interpenetration of the networks, there is a sufficient interframework void space occupied by solvent molecules (one and four DMF mol-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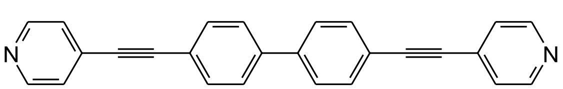
dedpbp

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ecules per formula unit in compounds **1** and **2**, respectively).

Results and Discussion

Pale-yellow crystals of compounds **1** and **2** were prepared in high yields by heating stoichiometric amounts of $Zn(NO_3)_2$, H_2ndc, and bpe (dedpbp) in DMF. Their compositions and structures were established by single-crystal X-ray diffraction. Compounds **1** and **2** were demonstrated to be three-dimensional coordination polymers composed of similar building blocks with the same framework topology. The dinuclear Zn_2 carboxylate complex, which contains four carboxylate groups of naphthyldicarboxylate ions in the equatorial plane, serves as the building block in molecules **1** and **2** (Figs 1 and 2). The fifth coordination site at each zinc atom is occupied by the nitrogen atom of the bis(pyridyl)ethylene (in **1**) or 4,4´-diethynyl-4″,4‴-dipyridylbiphenyl (in **2**) ligand. Therefore, each zinc atom is in a tetragonal-pyramidal coordination environment, and the $\{Zn_2(OOC)_4N_2\}$ fragment has a distorted octahedral geometry. Selected bond lengths in molecules **1** and **2** are given in Table 1. The connection of the bimetallic building blocks *via* the rigid linear bridging ndc ligands gives rise to the polymeric square-grid networks $\{Zn_2(ndc)_2\}$, whose structures in both compounds have no substantial difference. In turn, these networks are linked to each other *via* the linear N-donor bpe or dedpbp spacers to form isotypic scaffold-like polymer structures with a six-connected primitive cubic topology (pcu)[18] (Fig. 3). An elongation of the N-donor dedpbp ligand (20.8 Å) compared to the bpe ligand (9.4 Å) leads to an increase in the distance between the $\{Zn_2(ndc)_2\}$ networks (~16 and 28 Å for **1** and **2**, respectively).

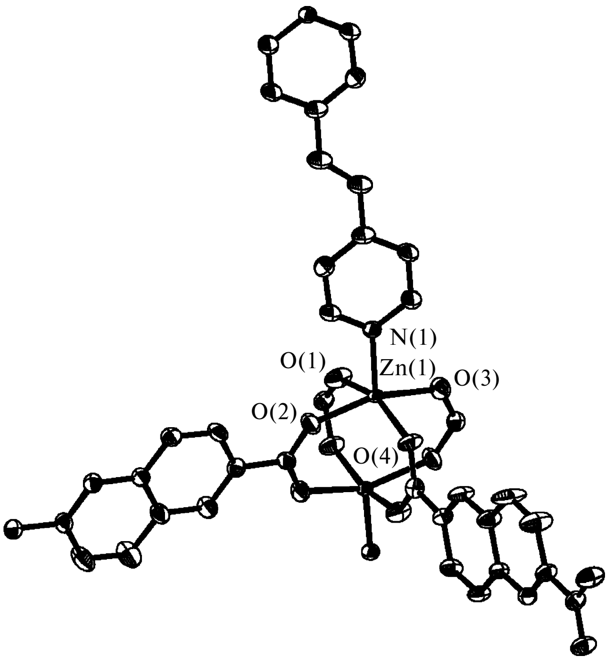

Fig. 1. Fragment of the crystal structure of **1** represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

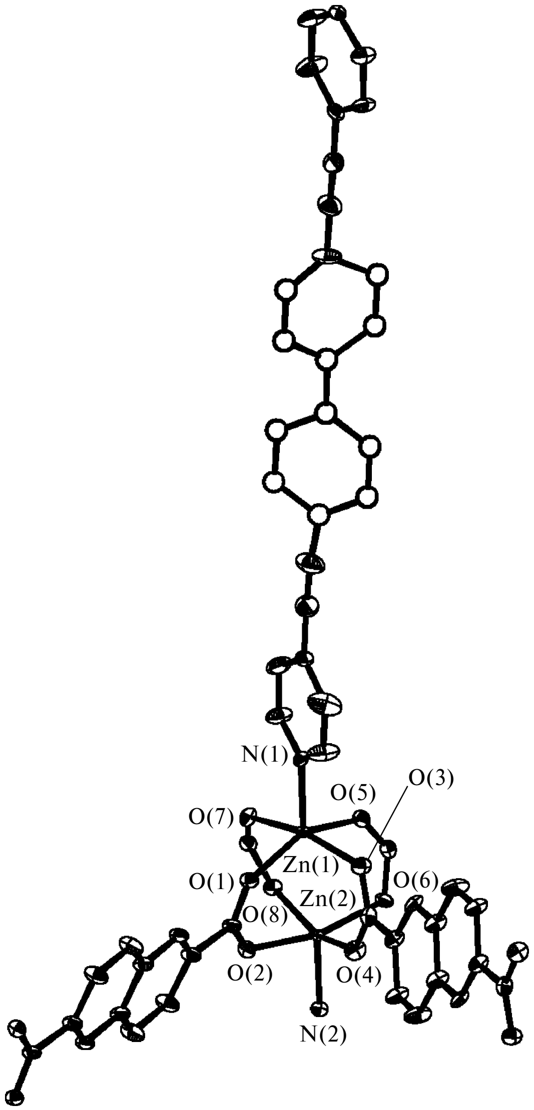

Fig. 2. Fragment of the crystal structure of **2** represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms and selected disordered positions of the carbon atoms in the dedpbp ligand are omitted. The carbon atoms refined isotropically are indicated by open circles.

Interestingly, the X-ray diffraction study demonstrated that the 4,4´-diethynyl-4″,4‴-dipyridylbiphenyl molecule in complex **2**, unlike the bis(pyridyl)ethylene molecule in **1**, is slightly bent rather than being strictly linear. Two possible positions of the biphenyl fragment were located (Fig. 4). The deviation from the line between the zinc atoms is 0.30 and 0.18 Å for two positions of the disordered biphenyl fragment.

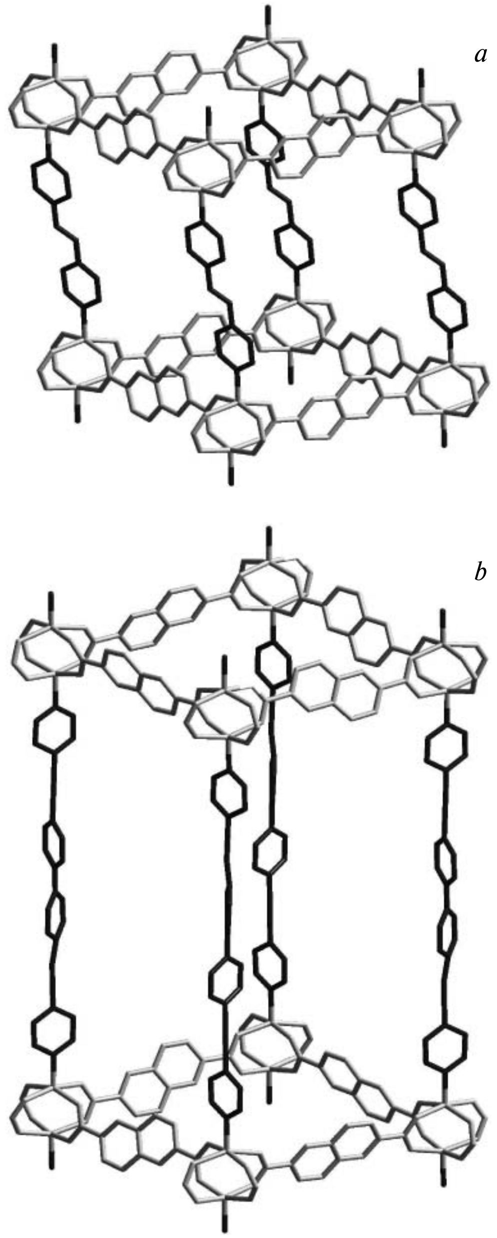

Fig. 3. Fragment of the crystal structure of the polymer framework in compounds **1** (*a*) and **2** (*b*). The {Zn_2ndc_2} networks are in pale-gray, and the N-donor spacers, which link the networks to form a framework, are black. The hydrogen atoms and selected disordered positions of the carbon atoms in the dedpbp ligand (compound **2**) are omitted.

Table 1. Selected Zn—O and Zn—N bond lengths (*d*) in the structures of **1** and **2**

Bond	*d*/Å	Bond	*d*/Å
1			
Zn(1)—O(1)#1	2.048(3)	Zn(1)—O(5)	2.055(4)
Zn(1)—O(2)#2	2.043(3)	Zn(1)—O(7)	2.011(4)
Zn(1)—O(3)#3	2.013(3)	Zn(1)—N(1)	2.026(5)
Zn(1)—O(4)	2.044(3)	Zn(2)—O(2)	2.047(4)
Zn(1)—N(1)	2.019(3)	Zn(2)—O(4)	2.050(4)
2		Zn(2)—O(6)	2.022(4)
Zn(1)—O(1)	2.050(4)	Zn(2)—O(8)	2.053(4)
Zn(1)—O(3)	2.024(4)	Zn(2)—N(2)#4	2.042(5)

Note. Symmetry codes: #1, $-x$, y, $-z + 1/2$; #2, $-x + 1/2$, $y + 1/2$, $-z + 1/2$; #3, $x - 1/2$, $y + 1/2$, z; #4, $x - 1$, $-y + 3/2$, $z - 3/2$.

In the crystal structures of **1** and **2**, the six-connected networks interpenetrate to form a system of three interpenetrating networks (Fig. 5). According to the proposed classification,[19] such structures belong to the interpenetration class I, in which the interpenetrating networks are related to each other only by translational symmetry elements. The structures of **1** and **2** belong to the subclass Ia, which means that there is one crystallographically independent network and the interpenetrating structure is formed as a result of a shift of one network by a total interpenetration vector,[19] which is equal to 1/3 of the body diagonal of the parallelepiped of the pcu network (see Fig. 5).

The interpenetration of networks is rather frequently observed in the design of porous coordination polymers.[19,20] In the case of *n*-fold interpenetration of networks with a pcu topology, each rectangular cell of each network should be penetrated by $n - 1$ linking bridges belonging to the other networks. The maximum degree of interpenetration of the networks is determined by the size of the smallest cell in this network. Earlier,[14] for coordination polymers based on the dinuclear building block {$Zn_2(OOC—R)_4L_2$}, it has been demonstrated that the interpenetration of networks can be completely excluded by using rather short ligands or bulky substituents in spacers, the high degree of porosity of the coordination polymer being retained. In compounds **1** and **2**, the maximum triple interpenetration of

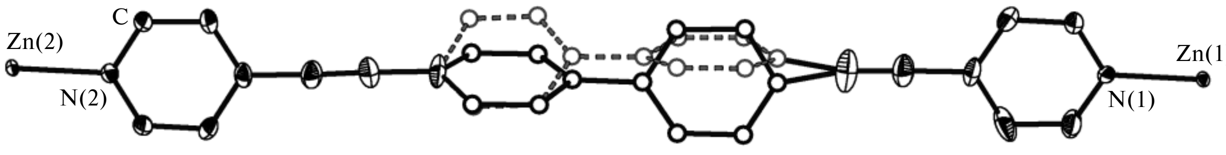

Fig. 4. Scheme of disorder in the biphenyl fragment in the structure of **2** represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The second position of the fragment (50%) is indicated by a dashed line.

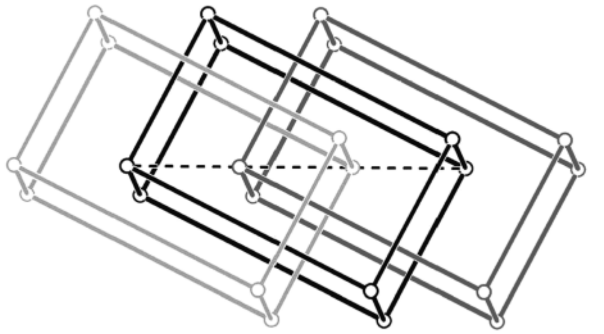

Fig. 5. Schematic representation of the triple interpenetration of the six-connected networks with a primitive cubic topology. The body diagonal of one of the cells in the framework is indicated by a dashed line.

the networks is determined by the size of the square cells in the carboxylate networks {$Zn_2(ndc)_2$}. The simultaneous presence of longer N-donor ligands (spacers) between these networks cannot further increase the degree of interpenetration but leads to an increase in the free space between the polymer networks. This space is occupied by uncoordinated solvent (DMF) molecules, their maximum specific number (one and four molecules per formula unit) correlating well with an elongation of the N-donor spacers in polymer structures **1** and **2**. According to calculations with the use of the PLATON program,[21] the accessible free volume for the metal-organic [Zn_2ndc_2bpe] and [$Zn_2ndc_2dedpbp$] frameworks (without consideration for the DMF solvate molecules) is 23 and 43%, respectively. These are rather high values taking into account the triple interpenetration of the networks in the structures under consideration. The related [Zn_2ndc_2bipy] compound (bipy is 4,4´-bipyridyl) prepared earlier also has a similar triply interpenetrating framework structure. However, due to the use of the shorter bridging bipy ligand, a dence structure without interframework cavities and, consequently, without solvate molecules, is formed.[14]

Therefore, the bimetallic building block {$Zn_2(OOC)_4L_2$} with a distorted octahedral geometry combined with bridging ligands of different lengths provides wide possibilities for the design of porous coordination polymers with a primitive cubic topology of the framework, thus allowing the independent control of both the degree of interpenetration of networks and the free volume of cavities in the structure. In this approach, short or sterically substituted bridging ligands control the minimum size of cells in the framework and, consequently, the maximum degree of interpenetration of the networks. The presence of longer ligands allows the control of the free volume between the interpenetrating networks and, consequently, the inclusion of guest molecules into such porous materials.

Experimental

The starting compounds, *viz*., zinc nitrate (analytical grade), 2,6-naphthalenedicarboxylic acid (Aldrich), and *trans*-bis(4-pyridyl)ethylene (Aldrich), were used without additional purification. The other reagents were of reagent grade. 4,4´-Diethynyl-4″,4‴-dipyridylbiphenyl was synthesized according to a modified procedure.[22] All solvents were purified according to standard procedures. The elemental microanalysis was carried out in the Laboratory of Microanalysis of the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The ^{1}H NMR spectra were recorded on a Bruker DPX-200 instrument (200 MHz) in $CDCl_3$.

4,4´-Diethynyl-4″,4‴-dipyridylbiphenyl (dedpbp). The compound was synthesized by condensation of 4,4´-diethynylbiphenyl (6.0 g, 30 mmol) with 4-bromopyridine (12.0 g, 75 mmol) in the presence of bis(triphenylphosphine)palladium chloride (30 mg, 4.2 mmol) and CuI (15 mg, 8 mmol) in diethylamine (150 mL) and toluene (150 mL) under argon at 50—60 °C. Under these conditions, the reaction was completed in 3 h (TLC monitoring on Silufol-254 plates). The reaction mixture was filtered and washed with water to neutral pH. The resulting solution was dried over $MgSO_4$, and the solvent was distilled off. After recrystallization from toluene, the product was obtained in a yield of 6.0 g (57%), m.p. 231—233 °C (*cf.* lit. data[22]: the yield was at most 20%, m.p. 205—275 °C). Found (%): C, 87.55; H, 4.28; N, 7.78. $C_{26}H_{16}N_2$. Calculated (%): C, 87.62; H, 4.52; N, 7.86. ^{1}H NMR ($CDCl_3$, 20 °C), δ: 8.61 (s, 4 H); 7.63 (s, 8 H); 7.40 (d, 8 H, $J = 4.2$ Hz).

Catena{bis(μ_4-2,6-naphthalenedicarboxylato)[μ_2-*trans*-bis(4-pyridyl)ethylene]dizinc(II)}, solvate with DMF (1). Crystals of compound **1** were prepared by heating $Zn(NO_3)_2 \cdot 6H_2O$ (30 mg, 0.1 mmol), H_2ndc (21.6 mg, 0.1 mmol), and bpe (9.1 mg, 0.05 mmol) in DMF (3 mL) in a sealed tube at 110 °C for 2 days. Pale-yellow crystals were filtered off, washed with a small amount of diethyl ether, and dried in air. The yield was 37 mg (90%). Found (%): C, 57.34; H, 3.61; N, 5.28. $C_{39}H_{29}N_3O_9Zn_2$. Calculated (%): C, 57.52; H, 3.59; N, 5.16.

Catena[bis(μ_4-2,6-naphthalenedicarboxylato)(μ_2-4,4´-diethynyl-4″,4‴-dipyridylbiphenyl)dizinc(II)], tetrasolvate with DMF (2). Yellowish crystals of compound **2** were obtained under conditions analogous to those used in the synthesis of compound **1** by heating $Zn(NO_3)_2 \cdot 6H_2O$ (15 mg, 0.05 mmol), H_2ndc (10.8 mg, 0.05 mmol), and dedpbp (8.9 mg, 0.025 mmol) in DMF (5 mL) in a sealed tube. The yield was 27 mg (85%). Found (%): C, 59.90; H, 4.66; N, 6.60. $C_{62}H_{56}N_6O_{12}Zn_2$. Calculated (%): C, 60.07; H, 4.55; N, 6.78.

X-ray diffraction study. Single-crystal X-ray diffraction data for [$Zn_2(C_{12}H_6O_4)_2(C_{12}H_{10}N_2)$] $\cdot$ DMF (**1**) and [$Zn_2(C_{12}H_6O_4)_2(C_{26}H_{16}N_2)$] $\cdot$ 4DMF (**2**) were collected on Siemens SMART and Bruker X8APEX diffractometers equipped with CCD area detectors using Mo-Kα radiation ($\lambda = 0.71073$ Å) at 223.0(2) and 90.0(2) K, respectively. The crystallographic data and the X-ray data collection and refinement statistics are given in Table 2. Semiempirical absorption corrections were applied based on the intensities of equivalent reflections with the use of the SADABS program.[23] The structures were solved by direct methods using the SHELXTL[24] (for **1**) and SIR2004[25] (for **2**) program packages and refined by the full-matrix least-

Table 2. Crystallographic data and the X-ray diffraction data collection and refinement statistics for the structures of **1** and **2**

Parameter	**1**	**2**
Molecular formula	$C_{39}H_{29}N_3O_9Zn_2$	$C_{62}H_{56}N_6O_{12}Zn_2$
Molecular weight	814.39	1239.73
T/K	223(2)	90.0(2)
Crystal system	Monoclinic	
Space group	$C2/c$	$P2_1/c$
a/Å	19.717(5)	15.3827(5)
b/Å	17.370(3)	20.9671(7)
c/Å	13.206(2)	19.2300(7)
β/deg	125.30(2)	109.4870(10)
V/Å^3	5847.0(3)	5847.0(3)
Z	4	4
d_{calc}/g cm^{-3}	1.465	1.372
μ/cm^{-3}	1.359	0.888
$2\theta_{max}$/deg	55	50
Number of measured/independent/ observed ($I > 2\sigma(I)$) reflections	10867/4182/2715	22971/10265/6985
R_{int}	0.0665	0.0390
Crystal dimensions/mm	0.5×0.3×0.2	0.50×0.27×0.07
Number of parameters in refinement	257	718
R_1 ($I > 2\sigma(I)$)	0.0534	0.0750
wR_2 (based on all reflections)	0.1382	0.1799
Residual electron density (min/max)/e Å^{-3}	−0.410/0.995	−0.795/2.019

squares method with anisotropic displacement parameters for nonhydrogen atoms with the use of the SHELXTL program package. The carbon atoms of the bipyridyl fragment in the structure of **2** disordered over two positions and the atoms of the strongly disordered DMF solvate molecules were refined isotropically. The occupancies of the carbon atoms in the bipyridyl fragment were refined to nearly 50% and then kept fixed. The hydrogen atoms of the ordered fragments were refined in geometrically calculated positions. Selected bond lengths are given in Table 1. An analysis of the type of interpenetration in the structures of **1** and **2** according to the known classification[19] was performed with the use of the TOPOS4.0 Professional program package.

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