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Synthesis and Crystal Structure of the Porous Metal–Organic Coordination Polymer $[Zn_4(Ndc)_4(Oxdz)_2] \cdot 2H_2O$

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Abstract—New metal–organic coordination polymer $[Zn_4(Ndc)_4(Oxdz)_2] \cdot 2H_2O$ (H2Ndc = 2,6-naphthalenedicarboxylic acid, Oxdz = 1,3,4-oxadiazole) was prepared by heating a solution of zinc nitrate, naphthalenedicarboxylic acid, and 4-aminotriazole in DMF. Of particular interest is the in situ transformation of 4-aminotriazole into 1,3,4-oxadiazole. The structure and the composition of the obtained compounds were established by X-ray diffraction, IR spectroscopy, and elemental analysis. The metal–organic framework is electrically neutral and forms a channel structure with the pore diameter of 9 Å.

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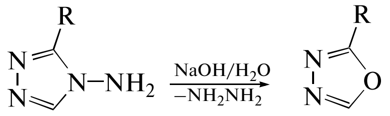
Metal–organic coordination polymers (MOCP) are compounds with metal–ligand coordination bonds in which atoms or polynuclear metal clusters are connected by bridging organic ligands thus forming a regular structure [1–3]. Of particular interest are porous coordination polymers. The interest in the porous MOCP is caused by the possibility of using them as sorbents of gases (acetylene, carbon dioxide, hydrogen, and methane) [4–6], for substance separation and purification [7, 8], and as catalytic nanoreactors [9–11]. A number of MOCP based on 1,3,4-oxadiazole derivatives have been reported [12–14]; however, there are no examples of MOCP based on the unsubstituted oxadiazole, apparently, due to poor accessibility of this compound.

The transformation of 4-aminotriazole into 1,3,4-oxadiazole (Oxdz) occurs in an alkaline medium, the hydrazine part of the substrate being replaced by a hydroxy group:



This reaction has found extensive use in the syntheses of compounds with potential biological activity [15, 16].

Here we report a new method for the formation of unsubstituted coordinated 1,3,4-oxadiazole from 4-amino-1,2,4-triazole, which occurs in the synthesis of a new microporous MOCP, $[Zn_4(Ndc)_4(Oxdz)_2] \cdot 2H_2O$ (**I** $\cdot$ $2H_2O$), in situ by the reaction of zinc nitrate, 2,6-naphthalenedicarboxylic acid (H_2Ndc), and 4-aminotriazole in N,N'-dimethylformamide (DMF) solution.

EXPERIMENTAL

Commercial H_2Ndc, 4-aminotriazole, DMF, and $Zn(NO_3)_2 \cdot 6H_2O$ of at least reagent grade were used as received. The elemental analysis for C, H, and N was performed at the analytical laboratory of the Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, using a Euro EA 3000 instrument. The IR spectra were measured on a Scimitar FTS 2000 spectrophotometer for KBr pellets.

Synthesis of I $\cdot$ $1.4(C_2H_5)_2O \cdot 1.1(CH_3)_2NCHO \cdot H_2O$. Dimethylformamide (25.0 mL) was added to a mixture of naphthalenedicarboxylic acid (0.216 g, 1 mmol), 4-aminotriazole (0.042 g, 0.5 mmol), and $Zn(NO_3)_2 \cdot 6H_2O$ (0.297 g, 1 mmol). The mixture was sonicated for 5 min. The resulting colorless solution in a screw cap glass vial was maintained at a constant temperature (80°C) for 48 h and left at room temperature. After 2 months, coarse colorless cubic crystals precipitated. A single crystal suitable for X-ray diffraction was collected from the mother liquor. The other crystals were separated from the mother liquor, washed with DMF and diethyl ether, and dried in air at room temperature. Yield 0.10 g (28%).

For $C_{60.9}H_{51.7}N_{5.1}O_{21.5}Zn_4$ (in relation to **I** $\cdot 1.4(C_2H_5)_2O \cdot 1.1(CH_3)_2NCHO \cdot H_2O$)

anal. calcd. (%):	C, 50.3;	H, 3.6;	N, 4.9.
Found (%):	C, 50.2;	H, 4.0;	N, 4.8.

Table 1. Crystallographic data and X-ray experiment details for **I** · $2H_2O$

Parameter	Value
Molecular formula	$C_{26}H_{18}N_2O_{11}Zn_2$
M	665.16
System	Orthorhombic
Space group	*Immm*
a, Å	14.2725(11)
b, Å	19.5898(14)
c, Å	20.7591(14)
V, Å^3	5804.1(7)
Z	4
μ, mm^{-1}	0.856
Crystal size, mm	0.20 × 0.18 × 0.10
T_{min}/T_{max}	0.847/0.919
The number of measured/ independent reflections	22407/3659
R_{int}	0.049
The number of reflections with $F > 4\sigma(F)$	2925
Scanning range over θ, deg	2.08–27.49
Range of indices h, k, l	$-19 < h < 19$, $-26 < k < 22$, $-21 < l < 27$
R-factors ($F > 4\sigma(F)$)	$R_1 = 0.0849$, $wR_2 = 0.3228$
R-factors (for all reflections)	$R_1 = 0.0994$, $wR_2 = 0.3277$
Goodness on F^2	1.217
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.70/–1.18

IR (KBr; ν, cm^{-1}): 1670 s, 1606 s, 1581 s, 1492 m, 1400 s, 1354 s, 1253 w, 1193 s, 1161 w, 1138 w, 1097 m, 1078 m, 1047 m, 1005 m, 924 m, 870 w, 841 m, 789 s, 663 m, 646 w, 619 m, 578 w, 482 m.

X-Ray diffraction data were collected at 295 K on a Bruker X8Apex CCD four-circle automated diffractometer equipped with a two-dimensional detector (φ scan mode, $\lambda(MoK_\alpha) = 0.71073$ Å, graphite monochromator). The crystallographic data and X-ray experiment details are summarized in Table 1. The absorption corrections were applied by measuring the divergence of equivalent reflections using the SADABS program [17]. The structure was solved by the direct method and refined by full-matrix least-square calculations in the anisotropic (except for hydrogen atoms) approximation (SHELX-97) [18]. The hydrogen positions for organic ligands were calculated geometrically and refined by the riding model. The hydrogen positions for water molecules were not localized. Selected interatomic distances and bond angles are summarized in Table 2. The full tables of interatomic distances and bond angles, atom coordinates, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (no. 874013; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

The metal–organic coordination polymer **I** · $2H_2O$ was obtained by heating at 80°C of a mixture of zinc nitrate crystal hydrate, 2,6-naphthalenedicarboxylic acid, and 4-aminotriazole in DMF. Upon hydrolysis, 4-aminotriazole was converted to coordinated 1,3,4-oxadiazole in the absence of strong bases in the aprotic polar DMF solvent and served as a linker in the formation of MOCP **I** · $2H_2O$. This formation of the poorly

Table 2. Selected bond lengths and bond angles in **I** · $2H_2O$ complex*

Bond	d, Å	Bond	d, Å
Zn(1)–O(11)	2.034(5)	Zn(2)–O(12)	1.964(8)
Zn(1)–O(1)	2.000(10)	Zn(2)–N(1)^{ii}	2.024(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(11)Zn(1)O(11)^{i}	88.0(5)	O(12)Zn(2)O(12)^{v}	124.7(6)
O(11)^{iii}Zn(1)O(11)	88.5(5)	O(12)Zn(2)N(1)^{ii}	106.80(18)
O(11)^{iv}Zn(1)O11	159.9(4)	N(1)^{vi}Zn(2)N(1)^{ii}	102.9(4)
O(1)Zn(1)O(11)	100.06(17)		

* The coordinates of dependent atoms are related by the following symmetry codes: $^{i}x, y, -z$; $^{ii}-x + 1/2, -y + 1/2, -z + 1/2$; $^{iii}x, -y + 1, z$; $^{iv}x, -y + 1, -z$; $^{v}x, y, -z + 1$; $^{vi}x + 1/2, -y + 1/2, z + 1/2$.

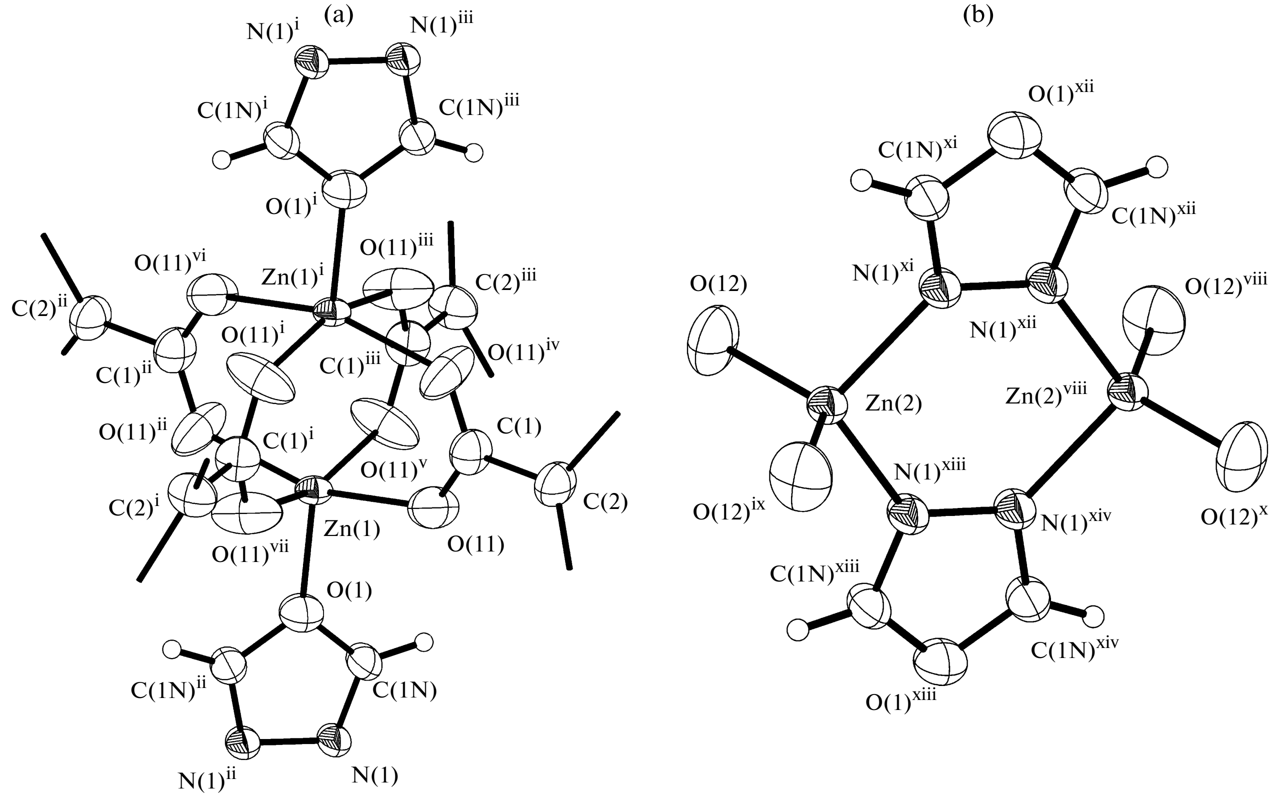


Fig. 1. Coordination environment of (a) Zn(1) and (b) Zn(2) atoms in **I** (40% probability ellipsoids). The coordinates of dependent atoms are related by the following symmetry operations: $^{i}1 - x, 1 - y, z$; $^{ii}x, 1 - y, -z$; $^{iii}1 - x, y, -z$; $^{iv}1 - x, y, z$; $^{v}x, y, -z$; $^{vi}1 - x, 1 - y, -z$; $^{vii}x, 1 - y, z$; $^{viii}1 - x, -y, z$; $^{ix}1 - x, y, 1 - z$; $^{x}x, -y, 1 - z$; $^{xi}1/2 + x, 1/2 - y, 1/2 - z$; $^{xii}1/2 + x, -1/2 + y, 1/2 + z$; $^{xiii}1/2 - x, 1/2 - y, 1/2 + z$; $^{xiv}1/2 - x, -1/2 + y, 1/2 - z$.

accessible compound during the preparation of porous MOCP is a unique example for the supramolecular chemistry and the chemistry of coordination polymers [19].

The structure of **I** · $2H_2O$ was determined by X-ray diffraction. The structure contains two crystallographically independent zinc cations. The Zn(1) coordination environment consists of four carboxyl oxygen atoms of four Ndc ligands and 1,3,4-oxadiazole oxygen (Fig. 1a). The coordination polyhedron is a tetragonal pyramid. The Zn(1) cations are linked by the bridging carboxylate groups of four Ndc ligands to form the binuclear moiety $Zn_2(\mu_2\text{-RCOO-O,O'})_4L_2$, so-called Chinese lantern typical of zinc coordination chemistry. The Zn(1)–O bond lengths are usual for five-coordinate zinc complexes. The tetrahedral environment of Zn(2) is formed by two nitrogen atoms of two Oxdz ligands and two oxygen atoms of two Ndc ligands. The lengths of the Zn(2)–O and Zn(2)–N bridging bonds are typical of tetrahedral zinc complexes. The Oxdz bridging ligands combine the Zn(2) cations into the binuclear moiety $Zn_2(\mu_2\text{-Oxdz-N,N'})_2(RCOO)_2$ (Fig. 1b). These secondary structural blocks are combined by the Ndc bridging ligands to

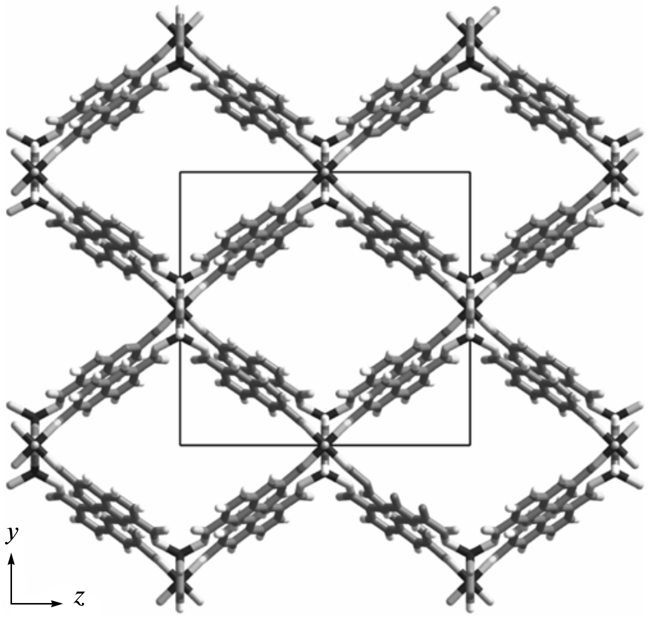


Fig. 2. Fragment of the metal–organic framework of **I**.

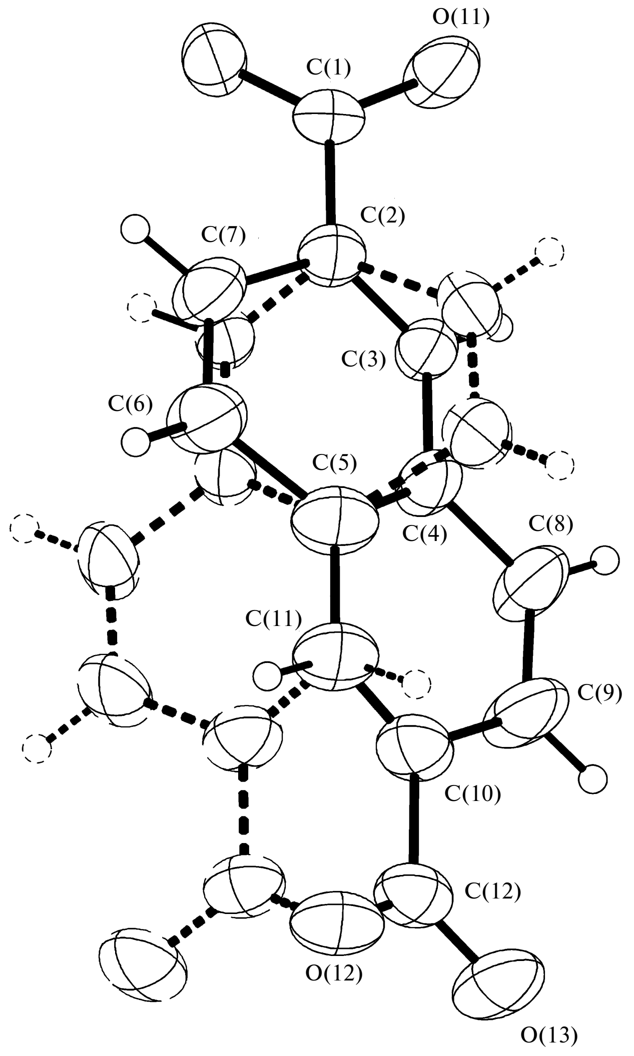


Fig. 3. Disorder of the Ndc^{2-} ligand over two orientations (40% probability ellipsoids). The coordinates of dependent atoms are related by the following symmetry operation: $1 - x, y, z$.

form a porous metal–organic framework having isolated channels with a 9 Å cross-section along the x axis (Fig. 2). The channels accommodate highly disordered water molecules ($2H_2O$ per formula unit of the framework). The Ndc ligand is disordered over two positions related by the mirror plane m (Fig. 3). The free volume of the compound calculated by the PLATON program was 57%. The volume accessible for host molecules is 3332 Å^3.

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