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Cadmium(II) Metal-Organic Frameworks Based on Iodine-Substituted Terephthalic Acid Derivatives and 1,1'-(1,4-Butanediyl)-bis-imidazole

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Abstract—Two metal-organic frameworks based on Cd(II) and 2-iodo-(2-I-Bdc) and 2,5-diodo-(2,5-I-Bdc)terephthalate were obtained: {[Cd(2-I-Bdc)(Bbi)]} (**I**) and {[Cd2(2,5-I-Bdc)2(DMF)2(Bbi)]} (**II**) (Bbi = 1,1'-(1,4-butanediyl)bis(imidazole)). The structures of both complexes were established by X-ray diffraction (CCDC no. 2258217 (**I**) and 2257566 (**II**)).

Keywords: cadmium, metal-organic frameworks, carboxylates, X-ray diffraction analysis

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INTRODUCTION

Metal-organic frameworks (MOFs) have been actively studied during the last decades [1–7]. This is due to the broad scope of their applicability in various fields of both chemistry and materials science, including, to mention only some of them, selective separation of gases [8–10] and other substrates, most often, organic compounds [11–13], luminescence sensors [14–16], etc. A greater part of MOFs are metal carboxylates (most often, aromatic) [17–19]. A key factor is the design of linker ligands, as they are largely responsible for various types of non-covalent interactions with guest molecules located in the pores and, hence, for the selectivity (of sorption, recognition, etc.). Hydrogen bonds play the most important role in these processes [20]. Nevertheless, there are recent studies describing MOFs that contain building blocks capable of forming also other types of supramolecular contacts. An example of these contacts is halogen bond (HalB) [21–29]. Although the number of papers devoted to HalBs in MOFs is still moderate [30, 31], we believe that this area has great potential for development.

Here we prepared two MOFs based on Cd(II) and iodo-substituted terephthalic acid derivatives, {[Cd(2-I-Bdc)(Bbi)]} (**I**) and {[Cd2(2,5-I-Bdc)2-(DMF)2(Bbi)]} (**II**) (2-I-Bdc = 2-iodoterephthalate, 2,5-I-Bdc = 2,5-diodoterephthalate, Bbi = 1,1'-(1,4-butanediyl)bis(imidazole)), and studied them by X-ray diffraction.

EXPERIMENTAL

The starting reagents were received from commercial sources. 2-Iodo- [32] and 2,5-diiodoterephthalic [33] acids and 1,1'-(1,4-Butanediyl)-bis(imidazole) [34] were prepared by published procedures.

Synthesis of {[Cd(2-I-Bdc)(Bbi)]} (I). $Cd(NO_3)_2 \cdot 4H_2O$ (31 mg), 2-iodoterephthalic acid (H2(2-I-Bdc)) (29 mg), Bbi (19 mg), and DMF (7.5 mL) were placed into a tube, which was sealed, treated with ultrasound (10 min), kept at 125°C for 48 h, and slowly cooled down. Colorless crystals of **I** were deposited on the tube wall. The yield was 85%.

Synthesis of {[Cd2(2,5-I-Bdc)2(DMF)2(Bbi)]} (II) was performed similarly to **I** using 2,5-diiodoterephthalic acid (42 mg). Compound **II** was formed as colorless crystals.

X-ray diffraction study of complexes **I** and **II** was carried out on a Bruker D8 Venture diffractometer (MoK_α-radiation, $\lambda = 0.71073$ Å) at 150 K. The reflection intensities were measured by ω- and φ-scanning of narrow (0.5°) frames. The absorption corrections were applied empirically using SADABS software. The structures were solved by the direct method using the SHELXT program [35] and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms using the SHELXL 2017\1 algorithm [36] in the ShelXle program [37]. The crystal data and structure refinement details are summarized in Table 1.

Table 1. Crystallographic data and structure refinement details for complexes **I** and **II**

Parameter	Value	
	I	**II**
Formula	$C_{36}H_{34}N_8O_8I_2Cd_2$	$C_{32}H_{32}N_6O_{10}I_4Cd_2$
M	1185.31	1393.03
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.1371(2)	9.7866(2)
b, Å	9.8545(2)	10.0262(2)
c, Å	11.9888(3)	12.3614(3)
α, deg	77.148(1)	75.222(1)
β, deg	68.926(1)	67.237(1)
γ, deg	84.510(1)	66.939(1)
V, Å^3	981.91(4)	1021.39(4)
Z	1	1
μ, mm^{-1}	2.72	4.12
$T_{\min}$, $T_{\max}$	0.668, 0.747	0.632, 0.746
Number of reflections measured/unique	12680/3709	9474/3804
Number of reflections with ($I > 2\sigma(I)$)	3617	3540
R_{int}	0.025	0.020
(sin θ/λ)$_{\max}$, Å^{-1}	0.610	0.610
Ranges of indices h, k, l	$-11 \le h \le 11$, $-12 \le k \le 11$, $-14 \le l \le 14$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-15 \le l \le 15$
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.072, 0.186, 1.17	0.050, 0.148, 1.09
Residual electron density (max/min), e Å^{-3}	1.11/–2.51	2.31/–2.88

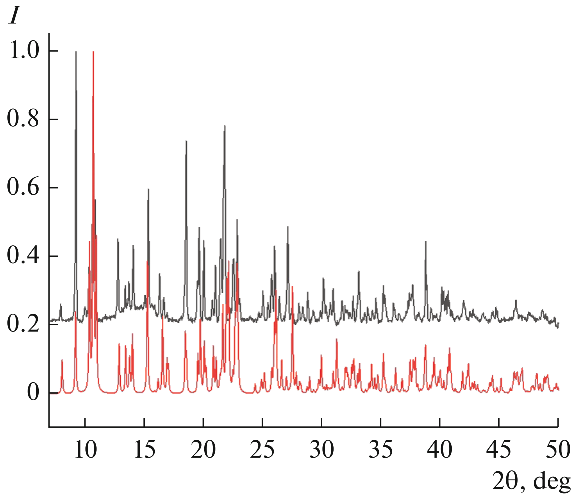

Fig. 1. Powder X-ray diffraction patterns of **I**: (above) experimental and (below) calculated from X-ray diffraction data.

The atom coordinates and other X-ray experiment details were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 2258217 (**I**) and 2257566 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

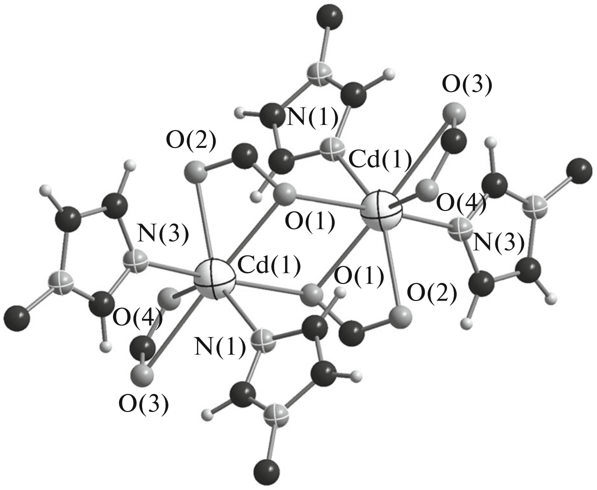

Fig. 2. Structure of the binuclear building blocks in **I**.

RESULTS AND DISCUSSION

Compounds **I** and **II** were prepared by solvothermal synthesis, which is widely used in MOF chemistry [38–42]. According to powder X-ray diffraction data (Fig. 1), complex **I** was formed a single-phase sample,

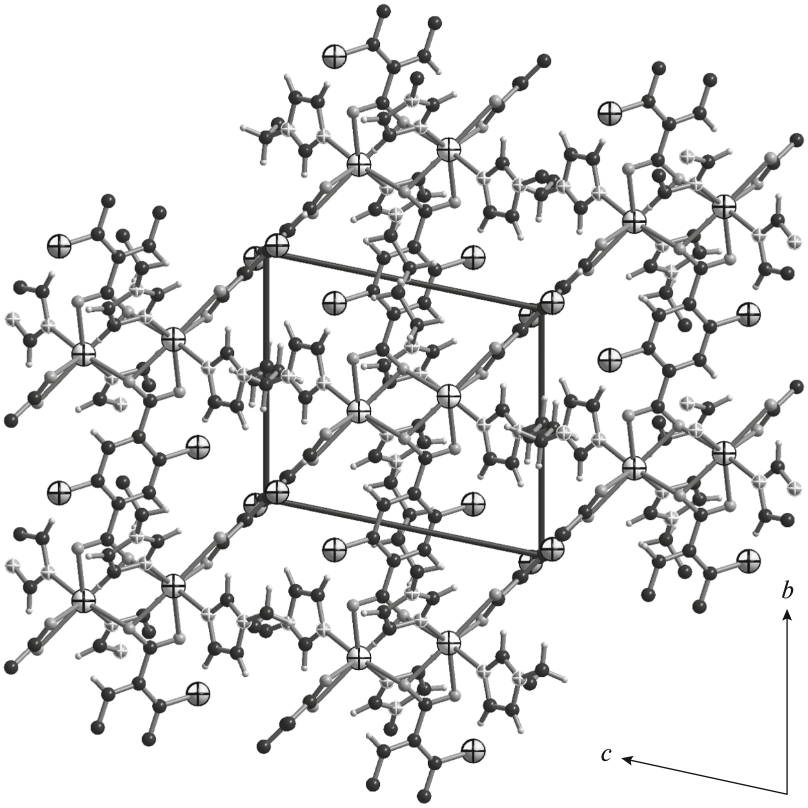

Fig. 3. 3D structure of **I**.

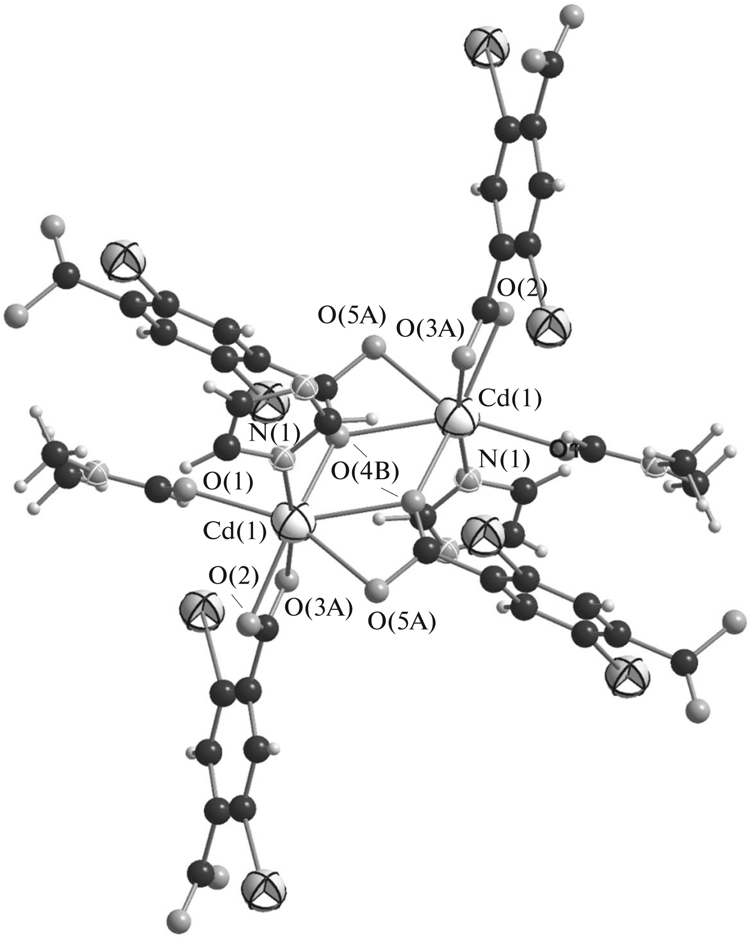

Fig. 4. Binuclear building block $\{Cd_2(2,5\text{-}I\text{-}Bdc)Bbi(DMF)_2\}$ in the crystal structure of **II**.

whereas all attempts to obtain **II** as a single phase failed (additional experiments with variable temperature, solvent volume, etc. were carried out).

In the structure of **I**, Cd(II) forms binuclear building blocks (Fig. 2). The coordination environment of each Cd atom is composed of two nitrogen atoms of the Bbi linker (Cd–N = 2.245–2.340 Å) and three carboxylate groups of the 2-iodoterephthalate ligands. One ligand is coordinated in the pseudo-bidentate mode: the Cd–O distances are 2.233 and 2.690 Å; most likely, the latter corresponds to seven-coordination. The second and third 2-iodoterephthalate ligands are bridging: one O atom binds to only one Cd atom (Cd–O = 2.369 Å), while the second one occupies a μ_2-bridging position (Cd–O = 2.448–2.523 Å). The iodine atoms of the 2-iodoterephthalate linkers are disordered over two sites with equal occupancy. The three-dimensional structure of **I** is shown in Fig. 3.

The structure of **II** differs considerably from that of **I**. Although the building blocks in **II** are also binuclear (Fig. 4), the coordination sphere of each Cd atom contains only one Bbi ligand (Cd–N = 2.241 Å). Each methylene group of Bbi ligands is disordered over two sites with 0.6 : 0.4 occupancy ratio. The binding motif of carboxylate linkers is identical to that in **I**, but they are partly disordered (Cd–O = 2.265–2.52 Å). In addition, each Cd atom is bound to one DMF molecule (Cd–O = 2.347 Å). The crystal packing of **II** is shown in Fig. 5.

Although both compounds have a three-dimensional structure, according to calculations, there is no free space available for the entry of guest molecules.

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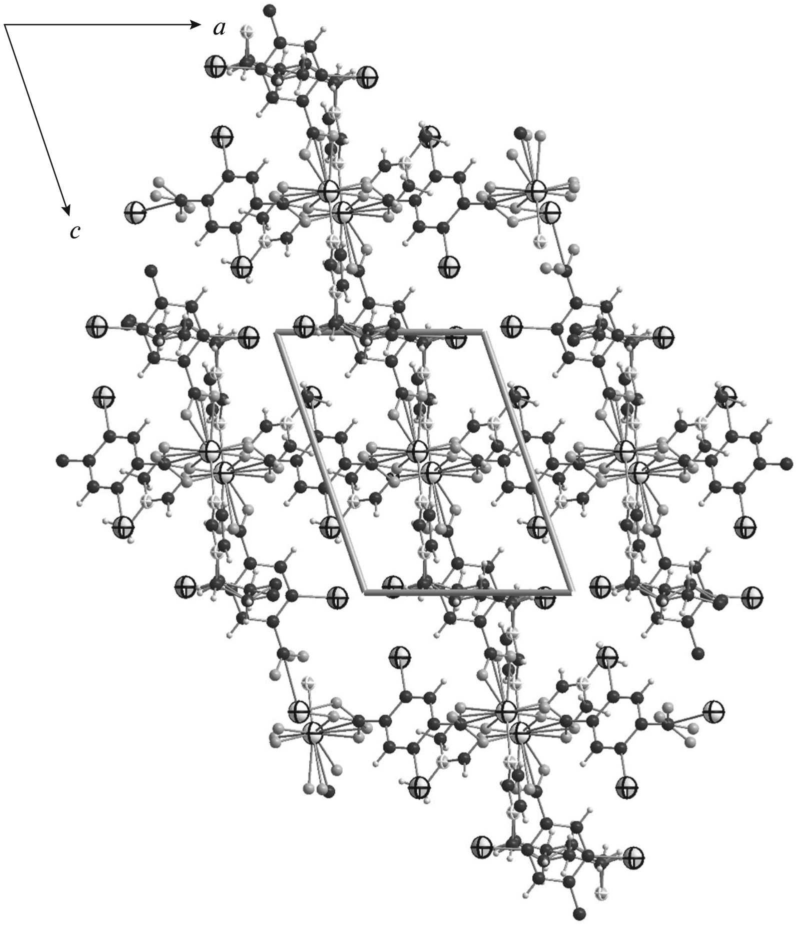

Fig. 5. Crystal packing of complex **II**.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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