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Heteroligand Zn(II) Metal-Organic Frameworks Based on 4-Substituted 4,2':6',4"-Terpyridine Derivatives and Terephthalates

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Abstract—Metal-organic frameworks based on Zn(II) and 4-substiuted 4,2':6',4"-terpyridine, terephthalate (Bdc), and 2-iodoterephthalate (2-I-Bdc) derivatives, {[Zn_3(FurTerPy)$_2$(Bdc)$_6$]} (**I**), {[Zn(FurTerPy)(2-I-Bdc)}] (**II**), and {[Zn(PyrrTerPy)$_2$(Bdc)} (**III**), were prepared and characterized by X-ray diffraction.

Keywords: zinc, metal-organic frameworks, carboxylates, N-donor ligands, X-ray diffraction
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INTRODUCTION

Metal-organic frameworks (MOFs) represent an extensive class of compounds [1–9] that are used in various fields, in particular catalysis [10–12], separation of gases [13–15] and other substrates [13, 16], design of sensors [17], etc. In recent years, particular attention has been attracted by MOFs that contain ligands able to form non-traditional non-covalent interactions: halogen [18–21], chalcogen [22], and pnictogen [23] bonds, which provide additional opportunities for fine tuning of a number of properties, especially the sorption and sensing selectivity. Currently, the number of such studies is moderate [24, 25], but it steadily and rapidly grows.

Previously, we showed that by using 4'-(thiophen-2-yl)-4,2':6',4"-terpyridine and terephthalic acid (Bdc) derivatives as linker ligands, it is possible to prepare compositionally and structurally different Zn(II) complexes [26]: in the case of Bdc, two-dimensional MOF is formed, while in the case of 2-I-Bdc, three-dimensional MOF is produced; the latter can be used for the selective sorption of some compounds.

In continuation of this work, we obtained complexes based on other 4-substituted 4,2':6',4"-terpyridine derivatives, namely those containing furan (FurTerPy) and pyrrole (PyrrTerPy) substituents: {[Zn_3(FurTerPy)$_2$(Bdc)$_6$]} (**I**), {[Zn(FurTerPy)(2-I-Bdc)}] (**II**), and {[Zn(PyrrTerPy)$_2$(Bdc)} (**III**). The structures of **I**–**III** were established by X-ray diffraction.

EXPERIMENTAL

The synthesis was carried out in air. The starting reactants were received from commercial sources; FurTerPy and PyrrTerPy were prepared according to published procedures [27, 28]; and 2-iodoterephthalic acid was obtained from 2-aminoterephthalic acid according to published procedure [29].

Synthesis of complex I. $Zn(NO_3)_2 \cdot 6H_2O$ (45 mg, 0.15 mmol), terephthalic acid (H_2Bdc) (38 mg, 0.23 mmol), FurTerPy (45 mg, 0.15 mmol), and DMF (7 mL) were placed into a tube, which was sealed, sonicated (10 min), and kept at 120°C for 48 h followed by slow cooling. Colorless crystals of **I** were deposited on the tube wall.

Synthesis of complex II was carried out by a procedure similar to that for **I** using 2-iodoterephthalic acid (0.15 mmol, 44 mg) and FurTerPy (45 mg, 0.15 mmol). This gave colorless crystals of **II**.

Synthesis of complex III was carried out by a procedure similar to that for **I** using terephthalic acid (0.15 mmol, 25 mg) and PyrrTerPy (89 mg, 0.3 mmol). This gave colorless crystals of **III**.

X-ray diffraction study of complexes **I**–**III** was performed by the standard procedure on a Bruker D8

Table 1. Crystallographic data, X-ray diffraction experiment and structure refinement details for structures **I**–**III**

Parameter	Value		
	I	**II**	**III**
Molecular formula	$C_{62}H_{38}N_6O_{14}Zn_3$	$C_{27}H_{16}N_3O_5I_{0.99}Zn$	$C_{46}H_{32}N_8O_4Zn$
M	1287.09	653.43	826.16
System, space group	Monoclinic, $C2/c$	Monoclinic, $C2/c$	Monoclinic, $P2/n$
a, Å	34.4806(15)	14.5949(3)	15.0577(3)
b, Å	11.4593(5)	31.8902(7)	7.4638 (2)
c, Å	14.2614(6)	15.1048(3)	17.9238(4)
β, deg	112.359(1)	102.388(1)	106.942(1)
V, Å^3	5211.4(4)	6866.6(2)	1926.99(8)
Z	4	8	2
μ, mm^{-1}	1.45	1.64	0.70
T_{min}, T_{max}	0.638, 0.746	0.519, 0.744	0.638, 0.746
Number of reflections measured/unique	53971/8689	44275/7027	24480/4993
R_{int}	0.040	0.032	0.037
Number of reflections with $I > 2\sigma(I)$	7842	5658	4408
Data collection range of θ, deg	31.5–1.9	26.4–1.9	28.7–1.6
$(\sin\theta/\lambda)$max, Å^{-1}	0.736	0.625	0.676
Ranges of indices h, k, l	$-50 \le h \le 50$, $-16 \le k \le 16$, $-20 \le l \le 20$	$-18 \le h \le 18$, $-39 \le k \le 39$, $-18 \le l \le 18$	$-20 \le h \le 18$, $-9 \le k \le 10$, $-24 \le l \le 24$
$R(F^2 > 2\sigma(F^2))$, $wR(F^2)$	0.026, 0.075	0.086, 0.280	0.036, 0.102
S	1.08	0.95	1.10
Residual electron density (max/min), e Å^{-3}	0.58/–0.49	1.33/–2.49	0.64/–0.28

Venture diffractometer at 150 K using MoK_α radiation (λ = 0.71073 Å). The reflection intensities were measured using ω- and φ-scanning of narrow (0.5°) frames. The absorption corrections were applied empirically by the SADABS software. The structures were solved using the SHELXT program package [30] and refined by full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms according to the SHELXL 2017/1 algorithm [31] with the ShelXle software [32]. The crystallographic data and results of structure refinement are summarized in Table 1. For the structure of **II**, the content of DMF molecules in the framework cavities was estimated by the SQUEEZE software [33]. According to the results, 0.5 solvent molecule per formula unit was present.

The atom coordinates and other X-ray diffraction experiment details were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2211495 (**I**), 2211496 (**II**), 2211497 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The crystals of **I**–**III** were obtained by solvothermal synthesis, which is traditional for MOF chemistry [1, 34–38]. Unfortunately, in all cases, we were unable to find conditions under which **I**–**III** would form as single-phase materials. According to powder X-ray diffraction data, the solid products always contained the target phases, but they were contaminated by non-identified products in all cases. Therefore, it was impossible to determine the product yields in these reactions and to characterize the new complexes by standard physicochemical methods (elemental analysis, infrared spectroscopy, powder X-ray diffraction).

The structure of **I** contains trinuclear $\{Zn_3(Bdc)_6(FurTerPy)_2\}$ moieties (Fig. 1). Contrary to

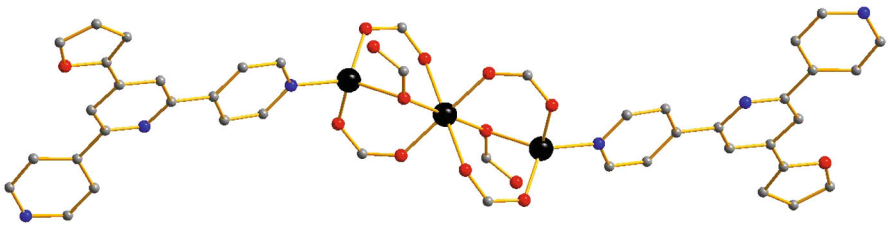

Fig. 1. Structure of the trinuclear $\{Zn_3(Bbdc)_6(FurTerPy)_2\}$ moiety. Here and below, Zn is black, O is red, C is gray, N is blue, and H atoms are omitted. Only the carboxylate groups of the Bdc ligands are shown.

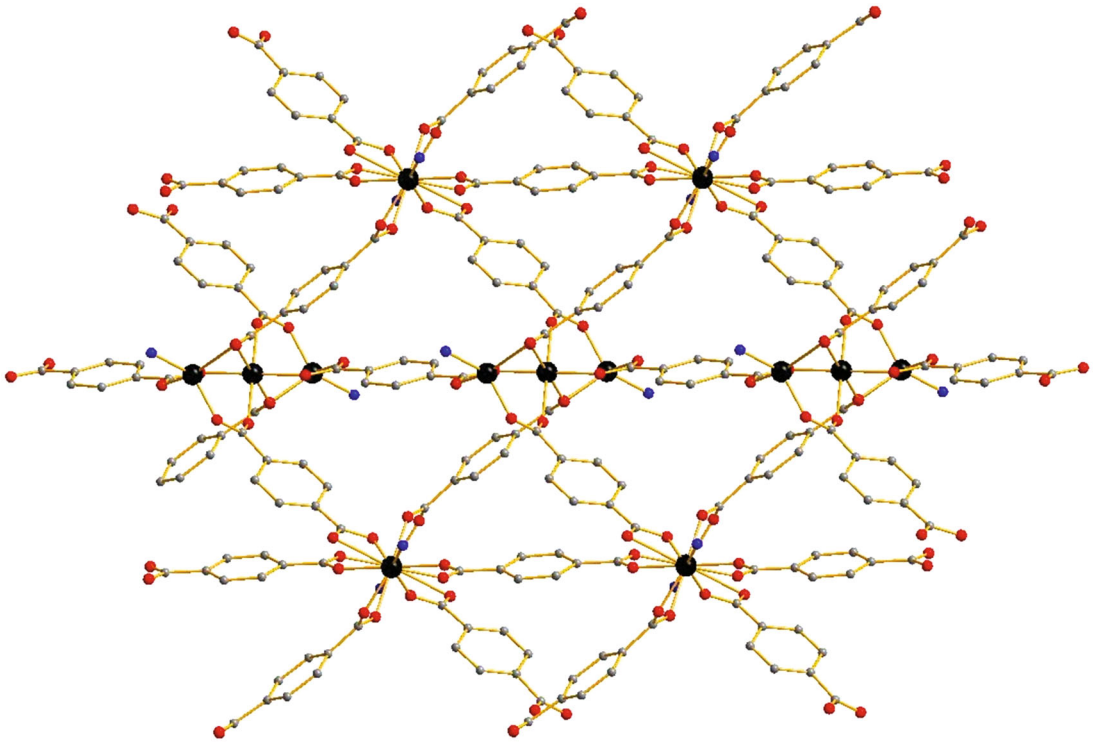

Fig. 2. Structure of layers in **I**. Only the coordinated N atoms of the FurTerPy ligands are shown.

our expectations, the FurTerPy ligands are coordinated in the monodentate fashion (Zn–N, 2.031 Å). The coordination environment of the central Zn atom is octahedral, while the two terminal Zn atoms have a distorted tetrahedral environment. The terephthalate carboxylate groups are coordinated in the 1κO:2κO'-bridging (Zn–O, 1.494–2.059 Å) and μ_2-bridging modes (Zn–O, 2.049–2.119 Å). The Bdc ligands connect the $\{Zn_3(Bdc)_6(FurTerPy)_2\}$ groups to form layers (Fig. 2).

In compound **II**, zinc atoms do not form polynuclear moieties. The structure is three-dimensional (Fig. 3), owing to the fact that FurTerPy molecules act as linkers (4-N atoms are involved in coordination; Zn–N, 2.023–2.026 Å). The Zn–O bond lengths are 1.932–1.956 Å. The iodine atoms and the aromatic rings of the 2-I-Bdc ligands in the structure are highly partially disordered. It is noteworthy that **II** is isostructural to the related {[Zn(ThioTerPy)(2-I-Bdc)}] MOF, which differs only in the heteroatom in the substituent in position 4 (thiophene instead of the furan moiety). The {[Zn(ThioTerPy)(2-I-Bdc)}] complex was described in our previous study [26]; the detailed description of its structural features fully coincides with the published description. It is of interest that {[Zn(ThioTerPy)(2-I-Bdc)}], unlike **II**, was obtained as a single-phase sample.

Complex **III** is a one-dimensional MOF (Fig. 4). By analogy with **I**, the PyrrTerPy molecules are coordinated in the monodentate mode (two ligands per Zn atom; Zn–N, 2.029 Å); the terephthalate anions connect the $\{Zn(PyrrTerPy)_2\}$ moieties into infinite chains (Zn–O, 1.926 Å). Like in **II**, the Zn atoms occur in a tetrahedral environment.

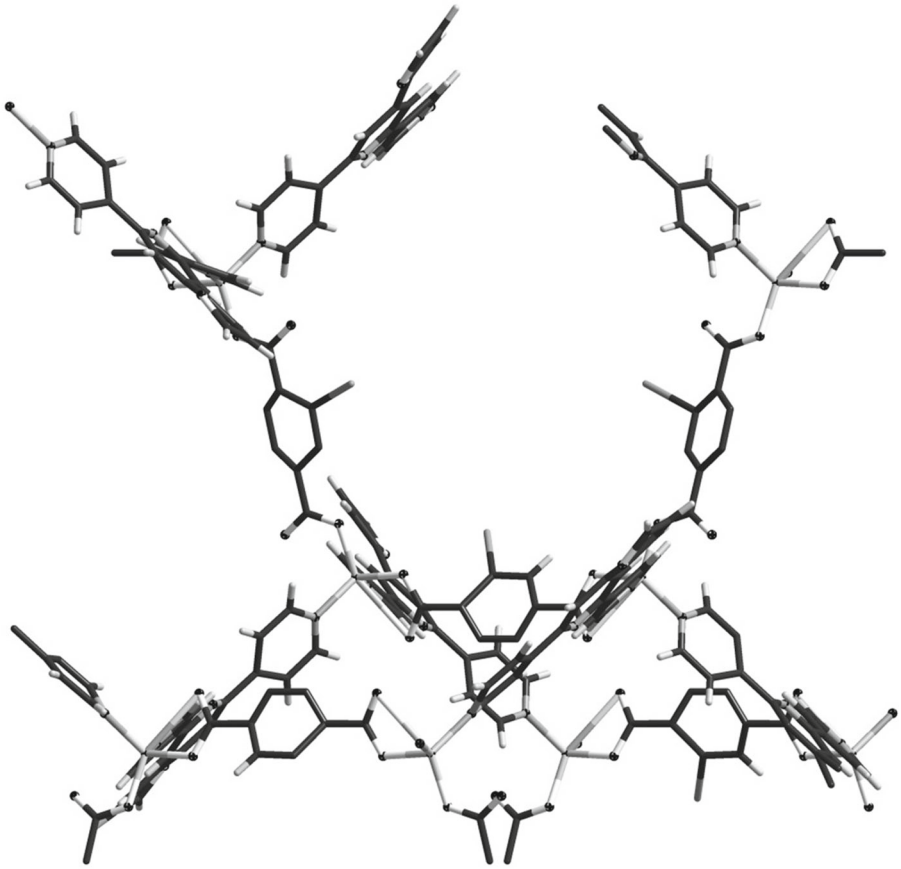

Fig. 3. Structure of metal-organic framework **II**.

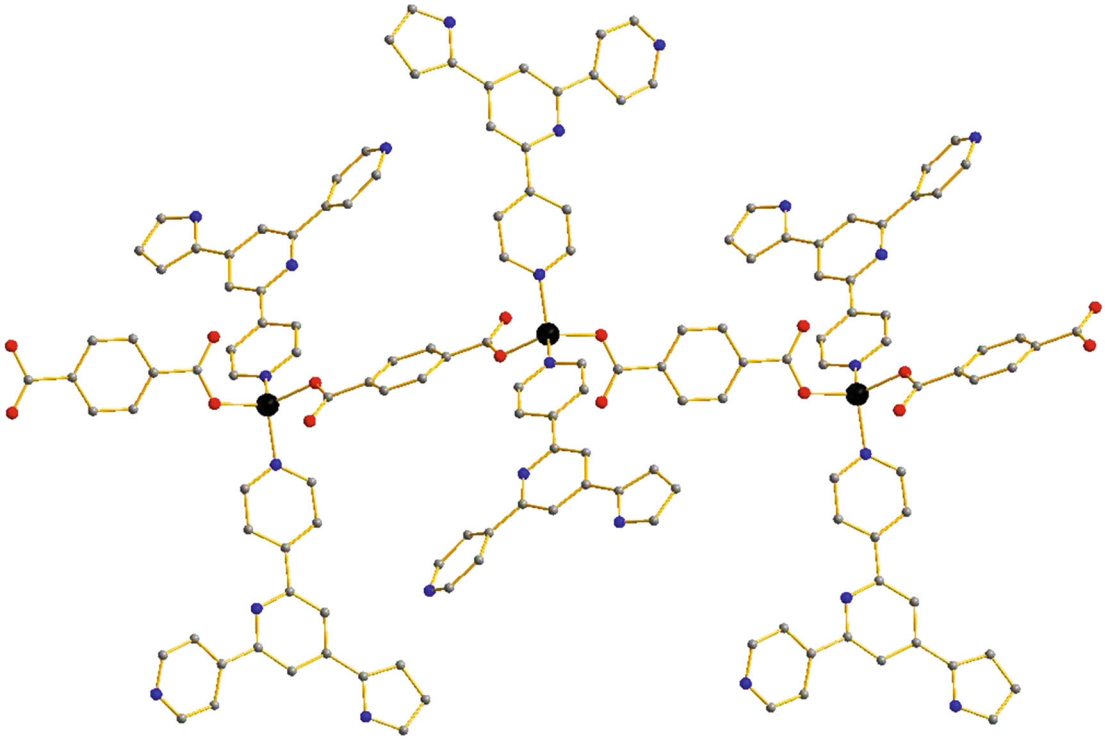

Fig. 4. Structure of chains in the structure of **III**.

Thus, it can be stated that 4-substituted 4,2':6',4"-terpyridine ligands have a potential as linkers for the synthesis of MOFs; however, they do not always perform this (desirable) function. For unknown reasons, only one- and two-dimensional metal-organic frameworks are formed with terephthalic acid, while in the case of 2-iodoterephthalic acid, three-dimensional MOFs are formed.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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