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Two- and Three-Dimensional Polymeric Co(II) Terephthalates with 3,3',5,5'-Tetrabromo-4,4'-bipyridine (3,3'5,5'-BrBipy)

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Abstract—The reaction of 3,3',5,5'-tetrabromo-4,4'-bipyridine (BrBipy) with cobalt nitrate and terephthalic acid (H_2Bdc) gave 2D and 3D metal-organic frameworks {[$Co_2(Bdc)_2(BrBipy)_2(H_2O)_4$]·4DMF} (**I**) and {[$Co_2(Ddc)_4(BrDipy)$]·2MeOH} (**II**), respectively. The structure of the complexes was studied by X-ray diffraction (CCDC nos. 2259216 (**I**) and 2259214) (**II**)).

Key words: cobalt, metal-organic frameworks, linker ligands, X-ray diffraction analysis

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INTRODUCTION

Metal-organic frameworks (MOFs) have been a hot topic of modern organic chemistry in recent years [1–8]. These compounds are investigated for applications in a number of fields such as selective separation of organic substrates [9–11], recovery of inorganic ions, including noble metal ions [12–14], isolation of organic and inorganic pollutants from mixtures [15–17], development of sensors [18–21], etc. Most of MOFs are homo- or heterometallic carboxylates (usually aromatic) [4, 22, 23]. An important factor is the design of the appropriate linker, which provides for the diversity of non-covalent interactions with guest molecules in the pores and, hence, determines the selectivity (of sorption, recognition, etc.). As a rule, the crucial role belongs to hydrogen bonds; however, in recent years, enhanced interest has been attracted by MOFs with building blocks capable of forming other types of supramolecular contacts, in particular, halogen bond (HalBs) [24–29]. Although relatively few papers describing such studies are currently available [30, 31], we believe that this area has great potential for development.

Previously, using quantum chemical calculations, we showed [32] that halo-substituted 4,4'-bipyridine derivatives (4,4'-Bipy) can act as HalB donors. Although the syntheses of some compounds of this class have been reported previously [33, 34], the number of MOFs based on them is exceptionally (in our opinion, undeservedly) small. Only a few Ag(I) homo- and hetero-ligand complexes are known for bromo- and iodo-substituted Bipy [35].

In this study, we obtained and structurally characterized 2D and 3D MOFs based on 3,3',5,5'-tetrabromo-4,4'-bipyridine (BrBipy), particularly {[Co_2-$(Bdc)_2(BrBipy)_2(H_2O)_4$]·4DMF} (**I**) and {[$Co_2(Bdc)_4$-(BrBipy)]·2MeOH} (**II**) (Bdc^{2-} = terephthalate anion). The structures of **I** and **II** were studied by X-ray diffraction.

EXPERIMENTAL

The starting reagents were received from commercial sources. 3,3',5,5'-Tetrabromo-4,4'-bipyridine was synthesized by a reported procedure [36].

Synthesis of I. Weighed portions of $Co(NO_3)_2$ (120 mg, 0.65 mmol) and BrBipy (31 mg, 0.63 mmol) were dissolved in a methanol and DMF mixture (25 mL, 1 : 1) in an ultrasonic bath (15 min). Terephthalic acid (110 mg, 0.65 mmol) was added to the solution, the solution was stirred, poured into a Teflon reactor, kept for 48 h at 100°C, and slowly cooled to room temperature for 24 h. Crystals of **I** suitable for X-ray diffraction were formed.

Synthesis of II was performed by a similar procedure using 25 mL of methanol. Crystals of **II** suitable for X-ray diffraction were formed.

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

Parameter	Value	
	I	**II**
Molecular formula	$C_{36}H_{24}N_4O_{12}Br_8Co_2 \cdot 4(C_3H_7NO)$	$C_{52}H_{24}N_4O_{16}Br_8Co_4 \cdot 4(CH_4O)$
M	1754.11	1963.92
System	Orthorhombic	Monoclinic
Space group	$P2_12_12$	$C2/m$
a, Å	21.6736(3)	16.0645(16)
b, Å	11.7936(2)	14.8872(13)
c, Å	11.4544(2)	13.7455(13)
β, deg	90	92.773 (3)
V, Å^3	2927.86(8)	3283.5(5)
Z	2	2
μ, mm^{-1}	11.46	5.94
$T_{\min}$, $T_{\max}$	0.360, 0.681	0.384, 0.862
Number of reflections measured/unique	15151, 5757	7127, 7127
Number of reflections with ($I > 2\sigma(I)$)	5392	5874
R_{int}	0.053	0.0717
Scan range of θ, deg	75.9–3.9	28.8–1.5
$(\sin\theta/\lambda)_{\max}$, Å^{-1}	0.629	0.677
Ranges of indices h, k, l	$-26 \le h \le 23$, $-14 \le k \le 13$, $-13 \le l \le 14$	$-21 \le h \le 21$, $0 \le k \le 20$, $0 \le l \le 18$
R ($F^2 > 2\sigma(F^2)$), $wR(F^2)$, S	0.062, 0.150, 1.04	0.062, 0.138, 1.06
Residual electron density (max/min), e Å^{-3}	1.29/–1.19	1.96/–1.46

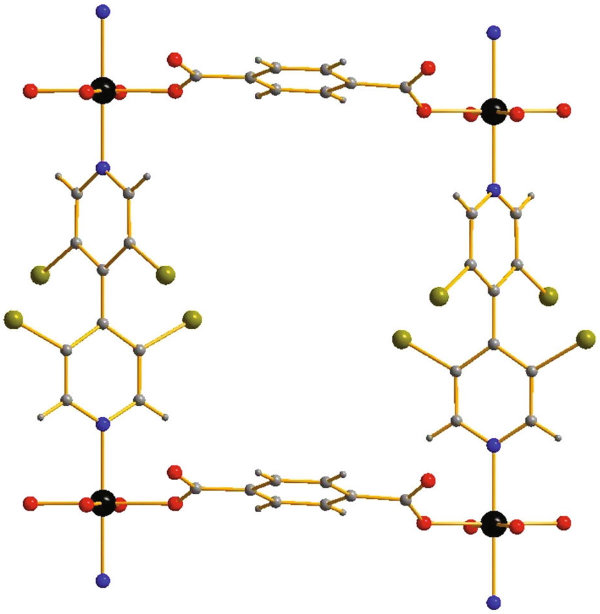

Fig. 1. Fragment of the molecular structure of **I**. Hereinafter Co is black, O is red, Br is olive, C is gray, N is blue. Only donor atoms are shown for some of the ligands

X-ray diffraction study of the crystals of **I** was carried out on a Rigaku XtaLAB Synergy S four-circle diffractometer with an HyPix detector and a PhotonJet microfocus X-ray tube using CuK_α radiation (1.54184 Å) at a temperature of 100 K. The collected data were indexed and integrated using the CrysAlisPro program package. The absorption corrections were applied using the ABSPACK module, including a numerical absorption correction based on Gaussian integration over a polyhedral crystal model and an empirical absorption correction based on spherical harmonics according to crystal symmetry. The GRAL module was used to analyze systemic attenuation and to determine the space group of symmetry. X-ray diffraction analysis of **II** was carried out on a Bruker D8 QUEST automated three-circle diffractometer (graphite monochromator, $\lambda(\mathrm{Mo}K_\alpha)$ = 0.71073 Å, ω- and φ-scan mode with 1° step) at 100(2) K. Data collection and indexing and determination and refinement of unit cell parameters for **II** were carried out using the APEX2 program package. The empirical absorption correction for the crystal of **II** was based on the crystal shape; the additional spherical correction and correction for systematic errors were performed using SADABS.

Both structures were solved by the direct method using the SHELXT software [37] and refined by least-squares method using the SHELXL software [38]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined by the riding model. The crystal data for structures **I** and **II** are summarized in Table 1.

The crystallographic parameters of **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 2259216 (**I**) and 2259214) (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

Samples of **I** and **II** were prepared by solvothermal synthesis, which is widely used in MOF chemistry. Unfortunately, despite numerous experiments, we were unable to find experimental conditions under which **I** and **II** would be formed as single-phase materials (this follows from powder X-ray diffraction data). Therefore, we could not determine the yield or perform complete characterization using additional physicochemical methods. The most likely source of water in **I** is the solvent.

Complex **I** is a 2D MOF (Fig. 1). The Co(II) atom does not form multinuclear groups. The coordination environment of each Co(II) atom is an octahedron, consisting of two BrBipy (Co–N 2.158–2.190 Å) and two terephthalate moieties (Co–O, 2.036–2.056 Å) and two aqua ligands (Co–O, 2.106–2.117 Å). The aqua ligands occupy *trans*-positions, thus preventing further self-assembly to give a 3D framework. Analysis of Br···O distances in comparison with the sum of the corresponding Bondi van der Waals radii (3.35 Å [39, 40]) suggests that Br forms HalB with DMF solvation molecules (Br···O 3.098–3.130 Å).

In the structure of **II**, unlike **I**, Co(II) forms Chinese lantern type binuclear building blocks $\{Co_2Bdc_4\}$

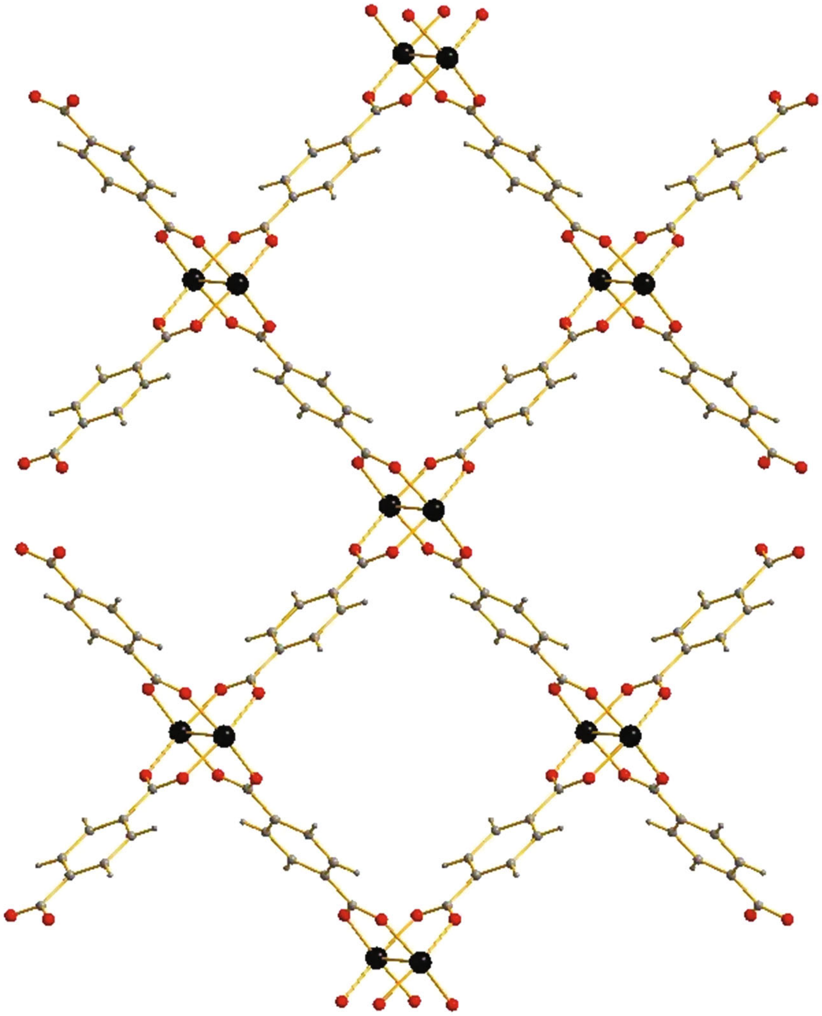

Fig. 2. {[Co_2Bdc_4]} layers in the structure of **II**. Bis-pyridyl ligands are not shown.

(Co···Co 2.578 Å). The range of Co–O bond lengths (2.012–2.019 Å) is typical of these groups, i.e., it is in good agreement with published data [41, 42]. The presence of simultaneously four terephthalate ligands gives rise to layers (Fig. 2), which are in turn connected by bis-pyridyl linkers (Co–N, 2.048–2.049 Å) to give a 3D framework (Fig. 3). The angles between the aromatic moieties in BrBipy are 90°. The structure contains highly disordered methanol guest molecules (two molecules per formula unit), which occupy porous framework cavities.

Thus, note that BrBipy can indeed act as a linker ligand and form, in particular, porous MOFs. Moreover, it was confirmed that BrBipy can form HalBs with guest molecules, which attests to the applicability of these compounds for selective separation of organic substrates, provided that the target MOFs have been isolated in a pure state. Studies along this line are being carried out by our team.

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CONFLICT OF INTEREST

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

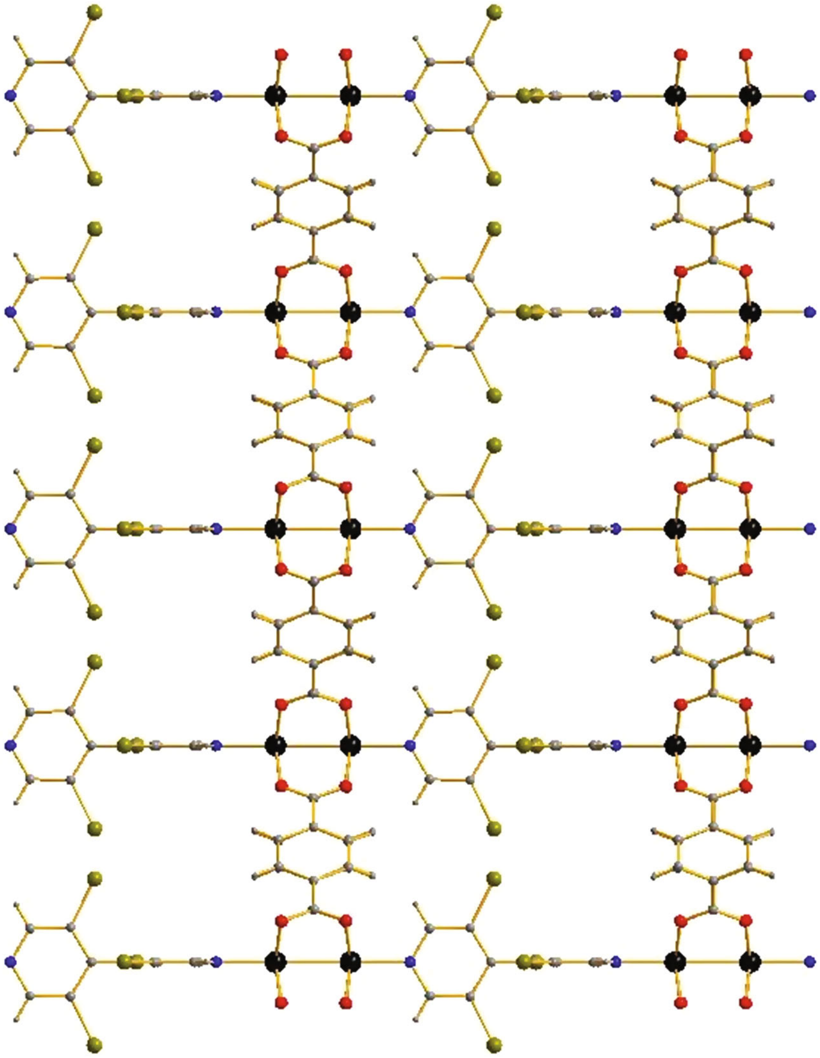

Fig. 3. 3D structure of **II**.

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