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Structural diversity of zinc(II) coordination polymers with octafluorobiphenyl-4,4'-dicarboxylate based on mononuclear, paddle wheel and cuboidal units

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We present a series of six novel Zn(II) complexes containing anions of perfluorinated biphenyl-4,4'-dicarboxylate (oFBPDC^{2–}). Among them are 0D complex [Zn(eg)₃](oFBPDC) (eg = ethylene glycol), 1D [Zn(H₂O)(ur)(oFBPDC)] (ur = urotropine) and [Zn(CH₃OH)₂(CH₃OCH₂CH₂OH)(oFBPDC)] and 2D layered [Zn₂(CH₃CN)₂(oFBPDC)₂]·2C₆H₆·2CH₃CN, [Zn₂(H₂O)₂(oFBPDC)₂]·4(CH₃)₂CO, [{Zn₄(μ_3 -OCH₃)₄}(CH₃OH)₄(oFBPDC)₂]·[{Zn₄(μ_3 -OCH₃)₄}(H₂O)(CH₃OH)₃(oFBPDC)₂]·13CH₃OH. The latter coordination polymer is built up by unique Zn₄(OCH₃)₄ cuboidal units. The complexes are characterized by single-crystal X-ray diffraction, FT-IR, elemental analysis, and TGA. Investigation of CO₂ adsorption at 195 K on [Zn₂(CH₃CN)₂(oFBPDC)₂] and [Zn₂(H₂O)₂(oFBPDC)₂] of layered polymeric structure revealed that they have the BET surface area of 334.8 and 150.6 m²/g, respectively.

Keywords: coordination polymer, zinc(II) complexes, octafluorobiphenyl-4,4'-dicarboxylic acid

Introduction

Coordination polymers or metal-organic frameworks (MOFs) are an enormous class of coordination compounds based on both inorganic building units and organic linkers.^{1,2} The anions of different dicarboxylic and polycarboxylic acids are the most widely used linkers for the design of the diverse framework structures due to different coordination modes of each carboxylic group and their mutual arrangement in the ligand. For instance, the most famous MOFs, like IRMOF,³ MIL^{4–7} and UiO⁸ series, are formed by anions of aromatic carboxylic acids (terephthalic acid, naphthalenedicarboxylic, acid biphenyldicarboxylic acid, *etc.*).

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The replacement of H atoms with F atoms in organic compounds significantly changes their physical and chemical properties, including polarity, polarizability, surface tension, lipophilicity, acidity and the ability to form hydrogen bonds.⁹ As for metal complexes, the presence of F atoms within the structure of organic digand often accounts for enhanced characteristics, *e.g.* the photoluminescence intensity,¹⁰ the adsorption capacity,¹¹⁻¹³ the dimensionality of the coordination polymer in case the metal complex has a polymeric structure.¹⁴ In this regard, fully fluorinated biphenyldicarboxylic acid H₂oFBPDC is a good candidate for the construction of permanently porous coordination polymers. Since H₂oFBPDC²⁻ dianion can become an issue. H₂oFBPDC is a stronger acid than non-fluorinated biphenyldicarboxylic acid, and the synthesis of metal complexes requires mild heating or occurs even at room temperature. On the contrary, the coordination ability of oFBPDC²⁻ is much lower, so that the anion would hardly ever be able to compete with the molecules of strongly coordinating solvents or other species for the binding to the metal cation. Thus, the coordination chemistry of oFBPDC²⁻ dianion and establishing the synthetic conditions of the formation of metal complexes are of significant interest.

The current amount of work on this topic^{15–18} is still very limited in spite of the fact that the pioneering work on oFBPDC^{2–} and Cu(II) complexes was published by Miljanić in 2013 and the complexes obtained did show intriguing properties (Table 1). For instance, activated $[Cu_2(MeOH)_2(oFBPDC)_2]$ (MOFF-1) and $[Cu_2(dabco)(oFBPDC)_2]$ (MOFF-2) with BET surface areas of 580 and 444 m²/g, respectively, showed water contact angles of 108–151°.¹⁵ Permanently porous perfluorinated UiO-66 and UiO-67, Zr₆ MOFs based on dianions of terephthalic and biphenyldicarboxylic acids, were shown to be considerably more Lewis acidic than non-substituted and nitrated counterparts, which is important for catalysis and fine chemical synthesis.¹⁸ Recently we have published the paper describing the synthesis, crystal structures and adsorption properties of six Zn complexes.¹⁷ Among them $[Zn_2(dabco)(oFBPDC)_2]$ is of special interest owing to its permanently porous structure, selective adsorption of CO₂ *vs*. N₂, CO₂ *vs*. CH₄ and benzene *vs*. cyclohexane as well as hydrophobicity (water contact angle of 136°) and the stability in the presence of water vapors.

Herein we present the continuation of our investigation of Zn^{2+} + oFBPDC²⁻ system. Certain modifications of the previously found synthetic conditions allowed us to get six new Zn complexes which crystal structures have been established by single crystal X-ray diffraction technique. The adsorption properties toward CO₂ and N₂ of potentially porous coordination polymers have been investigated.

Experimental section

Methods

¹⁹F and ¹H NMR spectra were recorded on a Bruker AV 300 instrument (282.4 and 300 MHz) with $(CD_3)_2CO + CCl_4$ as a solvent. The chemical shifts of the ¹H and ¹⁹F NMR spectra were referenced to internal solvent resonances (2.05 from TMS) and C₆F₆ (-162.9 ppm from CCl₃F). Melting point was determined on

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an Electrothermal IA9100 melting-point apparatus. FT-IR spectra of the samples in KBr pellet were recorded on a SCIMITAR FTS 2000 spectrometer in the range of 4000–400 cm⁻¹. Thermogravimetric analyses were performed on a NETZSCH TG 209 F1 Iris Thermo Microbalance. Approximately 10 mg of each sample was placed in an aluminium crucible and then heated from room temperature up to 400 °C at the rate of 10 °C·min⁻¹ under helium purge flow of 30 mL·min⁻¹. Elemental analysis of fluorine-containing substances was performed in Microanalytical Laboratory of N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry SB RAS. N₂ and CO₂ isotherms of adsorption were measured volumetrically on a Quantachrome Autosorb iQ instrument equipped with cryostat CryoCooler to adjust temperature with ±0.05 K accuracy. The samples were preliminarily degassed in a dynamic vacuum at 150 °C for 2 h. The BET surface areas were calculated using CO₂ adsorption isotherms at 195 K. Pore size distributions were calculated using DFT method.

X-Ray Crystallography. Diffraction data for single-crystals **1**–**6** were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with an area AtlasS2 detector (graphite monochromator, λ (MoK α) = 0.71073 Å, ω -scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package.¹⁹ The structures were solved by dual space algorithm (SHELXT²⁰) and refined by the full-matrix least squares technique (SHELXL²¹) in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. Structure **6** contains a large void volume occupied by highly disordered solvent guest methanol molecules, which could not be refined as a set of discrete atoms. The final composition of compound **6** was defined according to PLATON/SQUEEZE procedure²² (592 e⁻ in 1792 Å³). The crystallographic data and details of the structure refinements are summarized in Table 2. CCDC 1879950-1879955 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center at https://www.ccdc.cam.ac.uk/structures/.

Synthesis of H₂oFBPDC and complexes 1-6

Zn(OH)₂ was obtained in the same way as in our previous paper.¹⁷ Acetone was dried over molecular sieves 3 Å (Sigma Aldrich). All other chemicals and solvents were commercially available and used as received without further purification. Octafluorobiphenyl-4,4'-dicarboxylic acid was synthesized via acid hydrolysis of diethyl octafluorobiphenyl-4,4'-dicarboxylate. The latter was prepared by the reaction of organozinc compound, obtained from ethyl pentafluorobenzoate, with anhydrous CuCl₂ (Scheme S1).¹⁶

Synthesis of octafluorobiphenyl-4,4'-dicarboxylic acid (H₂oFBPDC). Diethyl octafluorobiphenyl-4,4'dicarboxylate (17.29 g, 39.1 mmol), concentrated sulphuric acid (34 ml), glacial acetic acid (100 ml), and water (34 ml) were heated under reflux for 45 h. Then, the reaction mixture was cooled down and evaporated in vacuum. The solid was filtered off, washed with cold water, and dried to a constant weight at 120 °C to give pure octafluorobiphenyl-4,4'-dicarboxylic acid (14.33 g, 37.1 mmol, yield 95%). m.p. 320-322 °C. ¹H NMR spectrum [(CD₃)₂CO + CCl₄], δ , ppm: 10.07 br. s (2H, COOH). ¹⁹F NMR spectrum [(CD₃)₂CO + CCl₄], δ, ppm: -137.4 m (4F), -139.1 m (4F). Found, %: C 43.29; H 0.42; F 39.28; calculated for C₁₄H₂F₈O₄, %: C 43.55; H 0.52; F 39.36.

Synthesis of $[Zn(eg)_3](oFBPDC)$ (1). The mixture of $Zn(OH)_2$ prepared from $Zn(NO_3)_2+6H_2O$ (0.040/g, 0.136 mmol), H₂oFBPDC (0.050 g, 0.128 mmol) was dissolved in 4.0 mL of ethylene glycol (eg) and placed in a 4.5 mL screw cap vial and thoroughly sonicated. Then the vial was heated in the oven at 40 °C for 48 h to obtain a crystalline precipitate. The precipitate was filtered off on the glass frit, washed with eg and dried in air. Yield 0.050 g (60%). TGA profile shows a weight loss of *ca*. 30% by 280 °C which is attributed to the loss of 3 eg molecules per one Zn atom. Found, %: C 37.62, H 2.61, F 23.96; calculated for C₂₀H₁₈F₈O₁₀Zn, %: C 37.79, H 2.85, F 23.91. FT-IR, v/cm⁻¹: 3445 (s, br), 2953 (s), 2884 (m), 1619 (s), 1560 (s), 1469 (s), 1454 (s), 1370 (s), 1263 (m), 1202 (w), 1082 (s), 1040 (s), 1007 (s), 976 (s), 880 (m), 837 (s), 774 (s), 723 (s), 697 (m), 406 (m).

Synthesis of $[Zn(H_2O)(ur)(oFBPDC)]$ (2). The single crystals of 2 suitable for X-ray diffraction analysis were found in the reaction mixture containing $Zn(OH)_2$ prepared from $Zn(NO_3)_2 \cdot 6H_2O$ (0.010g, 0.034 mmol), $H_2oFBPDC$ (0.013 g, 0.032 mmol), urotropine (0.0047 g, 0.034 mmol) and 1.5 mL of EtOH after its ultrasonication, prolonged dwelling (*ca.* 3 months) at room temperature and further heating up to 60 °C for 1 day. Structure and the chemical formula of 2 were determined by single-crystal X-ray diffraction.

Synthesis of $[Zn(CH_3OH)_2(CH_3OCH_2CH_2OH)(oFBPDC)]$ (3). The mixture of $Zn(OH)_2$ prepared from $Zn(NO_3)_2 \cdot 6H_2O$ (0.010g, 0.034 mmol), H₂oFBPDC (0.013 g, 0.032 mmol) was dissolved in the mixture of CH₃OH and 2-methoxyethanol (v:v = 1:1, 3 mL in total), placed in a 4.5 mL screw cap vial and thoroughly sonicated. Then the vial was heated in the oven at 40 °C for 72 h to obtain a crystalline precipitate. Structure and the chemical formula of **3** were determined by single-crystal X-ray diffraction.

Synthesis of $[Zn_2(CH_3CN)_2(oFBPDC)_2]\cdot 2C_6H_6 \cdot 2CH_3CN$ (4). $Zn(NO_3)_2 \cdot 6H_2O$ (0.200 g, 0.66 mmol), H₂oFBPDC (0.250 g, 0.64 mmol) were dissolved in the mixture containing 8.0 mL of CH₃CN and 4.0 mL C₆H₆. The solution was placed in a 20 mL screw cap vial and heated at 80 °C for 48 h. The solid obtained was filtered off, washed with CH₃CN and dried in air. Yield 0.090 g (25%). Upon the isolation of 4 from the mother liquor it loses guest molecules, and the final composition is $[Zn_2(CH_3CN)_2(oFBPDC)_2]$ ·0.3C₆H₆·1.6CH₃CN. Found, %: C 40.55, H 1.09, N 4.60, F 27.96; calculated for C₃₇H_{12.6}F₁₆N_{3.6}O₈Zn₂, %: C 41.52, H 1.19, N 4,71, F 28.40. FT-IR, v/cm⁻¹: 3511 (w), 3420 (w), 3358 (w), 3282 (w), 2361 (w), 2322 (w), 2295 (w), 2258 (w), 1694 (s), 1656 (s), 1616 (s), 1591 (s), 1470 (s), 1403 (s), 1251 (w), 1133 (w), 1000 (s), 978 (s), 816 (s), 768 (s), 718 (s), 690 (w), 678 (w), 655 (w), 597 (w), 517 (w), 479 (w), 440 (w).

Synthesis of $[Zn_2(H_2O)_2(oFBPDC)_2]\cdot 4(CH_3)_2CO$ (5). The mixture of $Zn(OH)_2$ prepared from $Zn(NO_3)_2 \cdot 6H_2O$ (0.010g, 0.034 mmol), $H_2oFBPDC$ (0.013 g, 0.032 mmol), 3.0 mL of acetone and 25 µL (1.4 mmol) of distilled water was placed in a 4.5 mL screw cap vial without ultrasonication. When the vial was heated in the oven at 40 °C for 10 days, colourless block crystals were obtained. The crystals were filtered off, washed with acetone and dried in air. Yield 0.0075 g (45%). Upon the isolation of **5** from the mother liquor it

loses guest molecules of acetone and the final composition is $[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 1.3(CH_3)_2CO$. Found, %: C 37.56, H 1.18, F 29.70; calculated for $C_{31.9}H_{11.8}F_{16}O_{11.3}Zn_2$, %: C 37.91, H 1.18, F 30.08. FT-IR, v/cm⁻¹: 3576 (s, br), 1617 (s), 1560 (w), 1469 (s), 1452 (s), 1370 (s), 1264 (w), 1006 (s), 977 (s), 3371 (w), 98170 (w), 774 (s), 722 (s), 697 (w), 406 (w).

Synthesis of

[{ $Zn_4(\mu_3-OCH_3)_4$ }(CH₃OH)₄(oFBPDC)₂]·[{ $Zn_4(\mu_3-OCH_3)_4$ }(H₂O)(CH₃OH)₃(oFBPDC)₂]·13CH₃OH (6). The mixture of Zn(OH)₂ prepared from Zn(NO₃)₂·6H₂O (0.010g, 0.034 mmol), H₂oFBPDC (0.010 g, 0.026 mmol), 2.9 mL of CH₃OH and 100 µL (1.80 mmol) of ethylene glycol was placed in a 4.5 mL screw cap vial and thoroughly sonicated. Then the vial was heated in the oven at 60 °C for 3 weeks. After that, the reaction mixture represents an amorphous solid and a few single crystals suitable for X-ray diffraction analysis. Structure and the chemical formula of **6** were determined by single-crystal X-ray diffraction. FT-IR, v/cm⁻¹: 3400 (s, br), 2953 (w), 2837 (w), 2384 (w), 1620 (s), 1468 (s), 1389 (s), 1252 (w), 1132 (w), 1002 (s), 978 (s), 843 (w), 816 (w), 772 (s), 719 (s), 513 (w).

Results and discussion

The majority of already described $Zn(II)^{17}$ and $Cu(II)^{15}$ complexes with oFBPDC^{2–} dianion were synthesized in methanol or its mixtures with DMF where methanol is the major component of the mixture. We tried other alcohols, polyols, and their derivatives, mixtures with methanol as well as CH₃CN and acetone and check whether these solvents are favourable for the formation of Zn complexes.

Synthesis and crystal structure of complex 1

Vicinal diols, *e.g.* ethylene glycol (eg), can act not only as a viscous polar solvent but also as a chelating ligand producing 1D and 2D coordination polymers with non-fluorinated^{23–25} and perfluorinated carboxylates²⁶. Nevertheless, the mixture of $Zn(OH)_2$ and $H_2oFBPDC$ completely dissolves in eg, and the heating of this solution at 40 °C leads to the formation of the non-polymeric complex [$Zn(eg)_3$](oFBPDC) (1). Each Zn(II) cation is in a distorted octahedral coordination environment consisting of six O atoms of three eg molecules, which produce [$Zn(eg)_3$]²⁺ cation. Zn–O distances are in the range 2.061(4)–2.124(4) Å. The oFBPDC²⁻ anion is not bounded to Zn and act as a counter-ion in this salt. The carboxylic group of oFBPDC²⁻ takes part in multiple hydrogen bonding interactions with H atoms of coordinated eg to form a supramolecular chain running along [–103] direction. O…O distances are 2.564–2.679 Å. The chains are stacked along *c* axis to form the hydrogen-bonded layer parallel to the *ac* plane (Fig. 1). The layers are stacked in ABAB fashion along the *b* axis.



Fig. 1. Fragment of hydrogen-bonded layer in the structure **1**. Hydrogen bonds are shown with dashed lines. Hydrogen atoms are omitted for clarity.

Syntheses and crystal structures of complexes 2-3

The mixture of $Zn(OH)_2$, $H_2oFBPDC$ and ur in 1:1:1 molar ratio reacts in methanol and gave the complex $[Zn(CH_3OH)_3(ur)(oFBPDC)]$ of the chain-like polymeric structure.¹⁷ In this complex, each Zn(II) cation is in a distorted octahedral coordination environment, consisting of two O atoms of carboxylate, one N atom of terminal ur and three O atoms of CH₃OH molecules. Meanwhile, the same mixture of $H_2oFBPDC$, ur, and the metal source in ethanol leads to the zigzag chain-like polymer. According to the X-ray crystallography, it has the chemical formula $[Zn(H_2O)(ur)(oFBPDC)]$ (2). In the compound 2, each Zn(II) cation is in a distorted tetrahedral coordination environment, which is presented by one N atom of terminal ur, two O atoms of dicarboxylate and one O atom of a water molecule (Fig. 2a). Zn–O distances are 1.950(4)–1.979(4) Å, Zn–N distance is 2.037(7) Å. The zigzag chains stack along *b* axis to form layers parallel to *bc* plane. Then the layers are stacked along the *a* axis to form double-layer crystal packing (Fig. S4). Careful inspection of interatomic distances revealed the absence of any hydrogen bonding interaction in the crystal structure of **2**.

Methyl cellosolve (2-methoxyethanol), the methylated derivative of ethylene glycol, is often used as a solvent for the synthesis of organic and coordination compounds. Heating of $Zn(OH)_2$ and $H_2oFBPDC$ in the mixture of CH₃OH and 2-methoxyethanol (v:v = 1:1) at 40 °C gives also a chain-like coordination polymer [$Zn(CH_3OH)_2(CH_3OCH_2CH_2OH)(oFBPDC)$] (3). Zn(II) cations are in a distorted octahedral environment consisting of two O atoms of oFBPDC^{2–}, two O atoms of CH₃OH molecules and two O atoms of 2-

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methoxyethanol. Zn–O distances are 2.0375(13)-2.288(2) Å. In this case, 2-methoxyethanol acts as a chelating ligand. Coordinated CH₃OH and 2-methoxyethanol molecules are disordered over two orientations (Fig. S5). Each carboxylic group is coordinated in a monodentate fashion, oFBPDC^{2–} dianion acts as a bridging digand connecting the adjacent Zn(II) cations to form almost linear chains (Fig. 2b). These chains form a supramolecular layer in *bc* plane due to hydrogen bonding interactions between non-coordinated O atom of carboxylic group of one chain and H atom of coordinated methanol molecule of the adjacent chain. O...O distances are 2.612–2.684 Å. The supramolecular layers stack along *c* axis producing double-layer crystal packing.



Fig. 2. Fragments of the polymeric chains **a**) in the structure **2**; **b**) in the structure **3** (major orientation of coordinated methanol and 2-methoxyethanol is shown). Hydrogen atoms are omitted for clarity. Hydrogen **bonds** are/shownowith dashed lines.

Syntheses and crystal structures of complexes 4-5

A dinuclear $[M_2(CO_2)_2L_2]$ paddle wheel building unit appeared to be a typical motif in Zn coordination with oFBPDC²⁻ dianion. The paddle polymers wheel unit is found in complexes [Zn₂(CH₃CONH₂)₂(oFBPDC)₂]·3CH₃CN and [Zn₂(dabco)(oFBPDC)₂]·4.5CH₃OH ¹⁷ as well as in complexes $[Zn_2(CH_3CN)_2(oFBPDC)_2] \cdot 2C_6H_6 \cdot 2CH_3CN$ (4) and $[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 4(CH_3)_2CO$ (5). All of them have layers formed by Zn paddle wheel units and oFBPDC²⁻ dianions (Fig. 3). The differences between the layered structures 4 and 5 are in the nature of apical ligands L and the deviation from the ideal square grid network (Fig. 3). Zn–O distances are 2.0286(12)–2.0468(12) Å, Zn–N distance in 4 is 2.0185(15) Å, Zn–OH₂ distance in 5 is 1.952(4) Å. The compound 4 was obtained by a reaction between $Zn(NO_3)_2 \cdot 6H_2O$ and H₂oFBPDC in the mixture of solvents CH₃CN/C₆H₆ (v:v = 2:1) at 80 °C. Interestingly, 4 formed as large single crystals of a few millimeters in size (Fig. S6). It was expected that benzene could take part in π - π interactions with fluorine-substituted phenyl rings^{27,28} of oFBPDC linkers, playing the role of the template and leading to a coordination polymer with the different crystal structure under the same synthetic conditions. Indeed, owing to rapid crystallization of 4 there was no acid-catalyzed hydrolysis, and CH₃CN is coordinated to Zn(II) cations in contrast to CH₃CONH₂ in the synthesis of [Zn₂(CH₃CONH₂)₂(oFBPDC)₂]·3CH₃CN. Guest molecules of benzene take part in π - π interactions with fluorine substituted phenyl rings. The shortest C...C distances are 3.618 Å and 3.679 Å (Fig. 3a). The layered coordination polymer 4 can be a perfect starting material for the synthesis of porous coordination polymers of the 3D structure via heterogeneous pillar insertion strategy²⁹ since Zn(II) cations are coordinated by weakly bounded and easily displaced CH₃CN molecules.

The compound $[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 4(CH_3)_2CO$ (5) has a very similar layered structure (Fig. 3b). For the first time, the single crystals of 5 were found in the mixture of freshly prepared $Zn(OH)_2$ and $H_2oFBPDC$ in acetone after ultrasonication and *ca*. 1 month of dwelling at room temperature. Afterwards, the procedure was optimized in order to get an only crystalline precipitate. The optimized procedure implies the addition of a small amount of water and heating up to 40 °C. In this complex, apical ligand is water disordered over two orientation (Fig. S9). According to X-ray crystallography data, there are four guest molecules of acetone per Zn_2 unit, which are linked to coordinated water molecules via hydrogen bonding (Fig 5a, S9). O...O distances are 2.646 and 2.723 Å. The metal-organic polymeric layers in both 4 and 5 are packed in a double-layer fashion with the apical ligands pointing in the square openings of the adjacent layer (Fig. S7, S10, S11).



a)

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Fig. 3. The structure of the metal-organic polymeric layer a) in complex 4, b) in complex 5. Hydrogen atoms in structure 5 are omitted for clarity. The shortest C...C distances between guest molecules of benzene and oFBPDC linker in structure 4 and hydrogen bonds between coordinated water molecules and acetone guest molecules in structure 5 are shown with dashed lines.

Synthesis and crystal structure of complex 6

As it was shown above, the solvent often plays the crucial role in the formation for Zn(II) perfluorinated carboxylates. Using significant amounts of chelating solvents like ethylene glycol and 2-methoxyethanol leads to 0D and 1D structures **1** and **2**, respectively. On the other hand, synthesis in pure methanol results in the formation of previously described $[Zn(CH_3OH)_3(oFBPDC)]^{17}$ of the layered polymeric structure. Interestingly, prolonged heating (*ca*. 1 month) at 60 °C of Zn(OH)₂, H₂oFBPDC in CH₃OH with a small additive of eg gives an unidentified amorphous precipitate together with crystals of unusual complex [$\{Zn_4(\mu_3-OCH_3)_4\}(CH_3OH)_4(oFBPDC)_2$]·[$\{Zn_4(\mu_3-OCH_3)_4\}(H_2O)(CH_3OH)_3(oFBPDC)_2$]·13CH₃OH (**6**). Compound **6**

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has a layered polymeric structure with a very unusual $\{Zn_4(\mu_3-OCH_3)_4\}$ cuboidal building unit. Zn(II) and O

atoms are located in the vertices of a slightly distorted cube, each CH₃O⁻-group acts as a µ₃-lidand. The unit is typical for organometallic compounds, obtained by the controlled oxidation of zinc alkers, 30-632/but for Zn coordination polymers. To the best of our knowledge, compound 6 is the first example of Zn coordination polymer based on $\{Zn_4(\mu_3-OCH_3)_4\}$ units. In the structure 6, there are two distinct cuboidal units, which are different in the ligands completing the coordination environment of Zn(II). The unit of the first type comprises $[Zn_4(\mu_3-OCH_3)_4(CH_3OH)_4(RCO_2)_4]$ block, in which all four Zn(II) cations are coordinated by four CH₃OH (Fig. 4a). In the unit of the second type, one of the terminal methanol molecules is substituted by aqua-ligand: [Zn₄(µ₃-OCH₃)₄(H₂O)(CH₃OH)₃(RCO₂)₄] (Fig. 4b). Each carboxylic group links two adjacent Zn(II) cations in one cuboidal unit. Zn-OCH₃ distances are 2.028(10)-2.139(10) Å, Zn-OCO distances range from 2.066(7) Å to 2.168(7) Å. Perfluorinated biphenyl moiety of oFBPDC²⁻ linker connects cuboidal building units in two perpendicular directions producing a square grid layer (Fig. 5). Each layer contains the cuboidal units of only one type. There is a system of hydrogen bonding interactions between O atoms of oFBPDC²⁻. coordinated methanol, and water molecules. O...O distances are 2.676-2.836 Å. These interactions make adjacent Zn₄(OCH₃)₄ units to be situated close to each other (Fig. 6, S13). The spatial arrangement of the layers is described as a four-layer packing (Fig. 6). The crystal structure has the system of isolated helical channels, which are presumably filled by highly disordered solvent guest molecules (Fig. S14). According to the PLATON/SQUEEZE estimation, there are 13 methanol guest molecules by formula unit of the compound 6.



Fig. 4. Zn_4O_4 cuboidal units in the crystal structure of 6: a) [$\{Zn_4(\mu_3-OCH_3)_4\}(CH_3OH)_4(RCO_2)_4$], b) [$\{Zn_4(\mu_3-OCH_3)_4\}(H_2O)(CH_3OH)_3(RCO_2)_4$].



Fig. 5. The structure of the metal-organic polymeric layer in complex 6. Hydrogen atoms are omitted for clarity.

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Fig. 6. Packing of the layers in 6. View along the *a* axis. Hydrogen atoms are omitted for clarity.

Guest removal and thermal stability of 4 and 5

Complexes 4–5 contain a lot of solvent guest molecules and have similar layered crystal structures. The of CHNF well with formulas results elemental analysis match chemical $[Zn_2(CH_3CN)_2(oFBPDC)_2]$ · 0.3C₆H₆ · 1.6CH₃CN for 4 and $[Zn_2(H_2O)_2(oFBPDC)_2]$ · 1.3(CH₃)₂CO for 5. These formulas are in a good agreement with the composition revealed by single crystal X-ray diffraction and a partial loss of guest molecules while the isolation of these solids from the mother liquor. The amounts of guest molecules are also confirmed by thermal analysis data (Fig. S17). TG curve of 4 shows the loss of C_6H_6 and CH₃CN guest molecules (ca. 8%) and one of the coordinated CH₃CN ligand (ca. 4%) in the temperature region 90-150 °C. The second stage up to 215 °C corresponding to the loss of the second coordinated CH₃CN ligand results in the formation of $[Zn_2(oFBPDC)_2]$. The following step in the temperature range 240–400 °C is attributed to the coordination polymer degradation with the formation of zinc- and amorphous carboncontaining products. The mass loss of compound 5 is ca. 8.5% up to 160 °C which corresponds to the release of 1.4 molecules of acetone. Compound 5 does not undergo further mass loss up to 280 °C, followed by the coordination polymer degradation with the formation of amorphous products.

For further gas adsorption measurements we carried out the activation of synthesized frameworks in high vacuum at 150 °C as the optimal temperature to remove all guest molecules as well as weakly coordinated CH₃CN ligands in polymer **4**. The FT-IR spectra (Fig. S18) confirm the successful guest removal. In FT-IR spectra of activated **4** the peaks of CN valence vibrations in 2500–2300 cm⁻¹ range completely disappear confirming removal of both guest and coordinated CH₃CN molecules. A broad peak in the region of 3600–

 3100 cm^{-1} confirms the presence of coordinated water molecules in the activated compound **5**, while slight changes of v(CO) line profiles is attributed to the removal of acetone guest molecules.

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Adsorption properties of coordination polymers 4 and 5

The analysis of crystal packing of coordination polymers 4 and 5 allows us to suggest that they should demonstrate permanent porosity after complete removal of guest molecules. Indeed, the accessible void volumes could be estimated by Mercury software routine as 30.5% and 35.5% for 4 and 5, respectively. Nevertheless, activated 5 does not adsorb N2 in a measurable amount, and we have failed to measure this isotherm, while N₂ uptake of 4 is only *ca*. 16 cm³/g (Fig. 7). It should be the consequence of narrow pore necks which do not allow N2 molecules to penetrate into pores and channels. Unlike N2, CO2 has a smaller kinetic diameter and a quadrupole moment. Therefore, CO₂ adsorption at 195 K is often used to determine the textural properties of such solids instead of N2 adsorption. According to the official IUPAC classification, the isotherms of CO₂ adsorption for both 4 and 5 belong to I type. CO₂ uptake of 4 (89 cm³/g) is slightly less than the estimated volume (110 cm³/g), while complex 5 demonstrates lower CO₂ uptake, though the estimated accessible void volume is larger than for 4. Such discrepancy for 5 can be explained by significant changes in the packing of the polymeric layers upon the removal of all acetone guest molecules, which could involve hydrogen bonding interaction between coordinated water molecules of adjacent layers of the same type (Fig. S11). The BET surface areas calculated on the basis of the isotherms of CO₂ adsorption are 334.8 m^2/g and 150.6 m²/g, pore volumes are 0.187 cm³/g and 0.094 cm³/g for 4 and 5, respectively. Pore size distribution Ac curves were calculated using DFT approach (Fig. S19). Pore diameters obtained are in agreement with the estimation made on the basis of the single crystal data.



Fig. 7. Isotherms of adsorption on 4 and 5.

Despite moderate surface areas and pore volumes both compounds 4 and 5 demonstrate high selectivity of adsorption of CO₂ over N₂. It should be noted that the similar behaviour was observed earlier for compound $[Zn_2(CH_3CONH_2)_2(oFBPDC)_2]$ with almost the same layered structure.¹⁷

Conclusions

Perfluorination of an organic carboxylate ligand results in its distinctive electronic and acidic properties and the coordination ability. The synthesis of perfluorinated coordination polymers occurs at moderate temperature in comparison with many other MOFs based on non-fluorinated aromatic carboxylates. The literature data together with our present experiments have shown that the oFBPDC^{2–} metal complexes do form in a weakly coordinating solvent (CH₃CN, acetone, alcohols, THF) or its mixtures with a small additive of coordinating solvent (DMF, water, eg) or extra N-donor ligand (ur, dabco, bpy).

Different coordination numbers of Zn(II) cation and ability to form secondary building units of diverse structure allow us to get six new metal complexes containing oFBPDC^{2–}. Thus, ethylene glycol appeared to be a strongly coordinating solvent, and the heating of the reaction mixture results in complex [Zn(eg)₃](oFBPDC) of non-polymeric structure, while the reaction in the mixture of CH₃OH and 2-methoxyethanol produces chain-like polymer [Zn(CH₃OH)₂(CH₃OCH₂CH₂OH)(oFBPDC)]. In contrast to the reaction of Zn(OH)₂, H₂oFBPDC and ur in methanol giving [Zn(CH₃OH)₃(ur)(oFBPDC)] with octahedral

coordination of Zn(II) cations, the same reaction in ethanol gives $[Zn(H_2O)(ur)(oFBPDC)]$ with CN=4. Dinuclear $[Zn_2(CO_2)_2L_2]$ paddle wheel unit is found in the layered coordination polymers $[Zn_2(CH_3CN)_2(oFBPDC)_2] \cdot 2C_6H_6 \cdot 2CH_3CN$ and $[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 4(CH_3)_2CO$ with CH3CN and H2O as apical ligands, respectively. Finally, prolonged heating of the mixture of $Zn(OH)_2$, $H_2oFBPDC$ and ethylene glycol in methanol gives the polymer of layered structure based on unique for coordination polymers $Zn_4(OCH_3)_4$ cuboidal units. Heating of the layered $[Zn_2(CH_3CN)_2(oFBPDC)_2] \cdot 2C_6H_6 \cdot 2CH_3CN$ and $[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 4(CH_3)_2CO$ in vacuum results in the removal of volatile guest molecules and lead to permanently porous solids. The BET surface areas calculated on the basis of isotherms of CO_2 adsorption at 195 K are 334.8 and 150.6 m²/g, respectively.

Conflicts of interest

There are no conflicts to declare.

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Metal	Chemical formula	Starting materials	Synthetic conditions	Dimensi onality	Ref
Cu	[Cu ₂ (CH ₃ OH) ₂ (oFBPDC) ₂]·0.5CH ₃ OH (MOFF-1)	Cu(NO ₃) ₂ ·2.5H ₂ O, H ₂ oFBPDC, 1:1	CH ₃ OH/DMF/H ₂ O (v:v:v =18:1:1), 40 °C, 4 days	2D	15
	[Cu ₂ (dabco)(oFBPDC) ₂] (MOFF-2)	Cu(NO ₃) ₂ ·2.5H ₂ O, H ₂ oFBPDC, dabco 2:2:1	CH ₃ OH/DMF/H ₂ O (v:v:v =20:3.33:1), 60 °C, 2 days	3D	15
Zn	[Zn(eg) ₃](oFBPDC)	Zn(OH) ₂ , H ₂ oFBPDC, 1:1	eg, 40 °C, 48 h	0D	This work
	[Zn(H ₂ O)(ur)(oFBPDC)]	Zn(OH) ₂ , H ₂ oFBPDC, ur, 1:1:1	C ₂ H ₅ OH, 20–60 °C, 3 months	1D	This work
	[Zn(CH ₃ OH) ₂ (CH ₃ OCH ₂ CH ₂ OH)(oFBPDC)]	Zn(OH) ₂ , H ₂ oFBPDC, 1:1	CH ₃ OH/ 2-methoxyethanol (v:v = 1:1), 40 °C, 72 h	1D	This work
	[Zn(CH ₃ OH) ₃ (ur)(oFBPDC)]	Zn(OH) ₂ , H ₂ oFBPDC, ur, 1:1:1	CH ₃ OH, 40 °C, 24 h	1D	17
	[Zn ₂ (oFBPDC) ₂ (CH ₃ CONH ₂) ₂]·3CH ₃ CN	Zn(NO ₃) ₂ ·6H ₂ O, H ₂ oFBPDC, CH ₃ CONH ₂ 1:1:1	CH ₃ CN, 80 °C, 40 h	2D	17
	[Zn(CH ₃ OH) ₃ (oFBPDC)]	Zn(OH) ₂ , H ₂ oFBPDC, 1:1	CH ₃ OH, 60 °C, 24 h	2D	17
	$[Zn_2(CH_3CN)_2(oFBPDC)_2] \cdot 2C_6H_6 \cdot 2CH_3CN$	Zn(NO ₃) ₂ ·6H ₂ O, H ₂ oFBPDC, 1:1	CH_3CN/C_6H_6 (v:v = 2:1), 80 °C, 48 h	2D	This work
	$[Zn_2(H_2O)_2(oFBPDC)_2] \cdot 4(CH_3)_2CO$	Zn(OH) ₂ , H ₂ oFBPDC, 1:1	acetone, H_2O (v:v = 2:1), 40 °C, 10 days	2D	This work
	$\label{eq:charge} \fboxspace{-1.5mu} \begin{tabular}{lllllllllllllllllllllllllllllllllll$	Zn(OH) ₂ , H ₂ oFBPDC	CH ₃ OH/eg (v:v = 30:1), 60 °C, 3 weeks	2D	This work
	[Zn ₂ (H ₂ O) _{1.5} (thf) _{1.5} (oFBPDC) ₂]·3.5H ₂ O·2.5THF	Zn(OH) ₂ , H ₂ oFBPDC, 1:1	THF, 40 °C, 6 days	3D	17
	[Zn ₂ (oFBPDC) ₂ dabco]·4.5CH ₃ OH	Zn(OH) ₂ , H ₂ oFBPDC, dabco, 2:2:1	CH ₃ OH, 80 °C, 48 h	3D	17
	(H ₂ bipy)[Zn ₂ (bipy)(oFBPDC) ₃]	Zn(OH) ₂ , H ₂ oFBPDC, bpy, 2:3:2	H ₂ O, 70 °C, 72 h	3D	17
Ln =	$[Ln_2(H_2O)_4(oFBPDC)_3] \cdot 3H_2O$	Ln(OH) ₃ , H ₂ oFBPDC, 2:3	dissolution in water at room temperature with		16
Tb, Eu	[Ln ₂ (phen) ₂ (oFBPDC) ₃]·2H ₂ O	Ln(OH) ₃ , H ₂ oFBPDC, phen·H ₂ O, $2:3:2$	further precipitation by adding acetone/CH ₃ OH mixture ($v:v = 3:1$)		16
Zr	[Zr ₆ O ₄ (OH) ₄ (oFBPDC) _{4.27} ((OH)(OH ₂)) _{3.46}]	ZrOCl ₂ ·8H ₂ O, H ₂ oFBPDC, 1:1	THF/HCl _{conc.} (v:v = 96:1), 80 °C, 24 h	3D	18

Table 2. Crystal data and structure refinement for 1	-6
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Table 2. Crystal data and structure refinement for 1–6.								
Identification code	1	2	3	4	5	6		
Empirical formula	$C_{20}H_{18}F_8O_{10}Zn$	$C_{20}H_{14}F_8N_4O_5Zn$	$C_{19}H_{16}F_8O_8Zn$	$C_{24}H_{12}F_8N_2O_4Zn$	$C_{40}H_{28}F_{16}O_{14}Zn_2$	$C_{84}H_{106}F_{32}O_{45}Zr$		
<i>M</i> , g/mol	635.71	607.72	589.69	609.73	1167.36	2966.64		
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic		
Space group	<i>I</i> 2	$P2_{1}/c$	$P2_{1}/c$	C2/c	<i>I</i> 222	$P2_1$		
<i>a</i> , Å	12.6244(3)	14.9250(12)	13.3346(4)	19.7538(4)	10.2288(5)	17.6709(4)		
b, Å	15.2868(4)	5.4485(4)	15.4645(4)	10.5400(2)	15.2173(7)	18.1755(7)		
<i>c</i> , Å	38.1764(8)	27.4123(15)	10.9486(3)	23.0099(5)	15.2087(6)	17.7050(4)		
α, deg.								
β, deg.	97.201(2)	101.413(6)	94.460(3)	90.091(2)		91.349(2)		
γ, deg.								
<i>V</i> , Å ³	7309.4(3)	2185.1(3)	2250.91(11)	4790.79(18)	2367.31(18)	5684.9(3		
Ζ	12	4	4	8	2	2		
$D(\text{calc.}), \text{g/cm}^3$	1.733	1.847	1.740	1.691	1.638	1.733		
μ , mm ⁻¹	1.123	1.236	1.201	1.123	1.139	1.795		
<i>F</i> (000)	3840	1216	1184	2432	1168	2996		
Crystal size, mm	$0.31 \times 0.14 \times 0.13$	$0.66 \times 0.14 \times 0.02$	$0.23 \times 0.16 \times 0.11$	$0.34 \times 0.18 \times 0.12$	$0.25 \times 0.13 \times 0.05$	$0.27 \times 0.22 \times 0.$		
θ range for data collection, deg.	3.30-28.45	3.42-25.35	3.34–29.06	3.44-28.88	3.60-25.68	3.22-25.68		
Index ranges	$-16 \le h \le 13,$ $-19 \le k \le 15,$ $-47 \le l \le 50$	$-17 \le h \le 15,$ $-6 \le k \le 5,$ $-33 \le l \le 27$	$-17 \le h \le 16,$ $-20 \le k \le 20,$ $-14 \le l \le 14$	$-26 \le h \le 26,$ $-12 \le k \le 14,$ $-29 \le l \le 29$	$-9 \le h \le 12,$ -17 $\le k \le 18,$ -17 $\le l \le 18$	$-21 \le h \le 21,$ $-22 \le k \le 22,$ $-21 \le l \le 21$		
Reflections collected / independent	20127 / 12281	8828 / 3969	35566 / 5531	12581 / 5279	3739 / 2123	33516 / 19128		
$R_{\rm int}$	0.0136	0.0307	0.0258	0.0180	0.0199	0.0245		
Reflections with $I > 2\sigma(I)$	10116	3168	4678	4696	2083	17906		
Goodness-of-fit on F^2	1.044	1.050	1.044	1.047	1.034	1.032		
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0284;$ $wR_2 = 0.0709$	$R_1 = 0.0730;$ $wR_2 = 0.2119$	$R_1 = 0.0307;$ $wR_2 = 0.0684$	$R_1 = 0.0264;$ $wR_2 = 0.0628$	$R_1 = 0.0314;$ $wR_2 = 0.0770$	$R_1 = 0.0670;$ $wR_2 = 0.1851$		
R indices (all data)	$R_1 = 0.0393;$ $wR_2 = 0.0771$	$R_1 = 0.0886;$ $wR_2 = 0.2278$	$R_1 = 0.0416;$ $wR_2 = 0.0732$	$R_1 = 0.0320;$ $wR_2 = 0.0652$	$R_1 = 0.0326;$ $wR_2 = 0.0782$	$R_1 = 0.0702;$ $wR_2 = 0.1882$		

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Largest diff. peak / hole, e/A	Å ³ 0.360 / -0.216	2.204 / -0.929	0.642 / -0.459	0.379 / -0.345	0.473 / -0.595	1.449 / -1.069		
CCDC no.	1879950	1879951	1879952	1879953	1879954	1879955		

Certain modifications of the synthetic conditions lead to six novel Zn(II) complexes with octafluorobiphenyl-4,4'-dicarboxylate, thus enriching the knowledge on the coordination chemistry of perfluorinated ligands.

