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Multiarylpolycarboxylate-Mediated Hybrid Cobalt Phosphate Frameworks with Supramolecular Zeolitic Topology and Unusual I^2O^2 Connectivity

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Supporting Information

ABSTRACT: Two novel organic−inorganic hybrid frameworks containing multiarylpolycarboxylate linkers and cobalt phosphate layers, $[H_2DABCO]\cdot[Co(HPO_4)(bpdc)]$ (**1**) and $[H_2DABCO]_3\cdot[Co_{10}(npa)_3(PO_4)_6Cl_2]$ (**2**), where bpdc = 4,4′-biphenyldicarboxylate, npa = 2,6-naphthalenedicarboxylate, and DABCO = 1,4-diazabicyclo[2.2.2]octane, have been solvothermally synthesized. Compound **1** features a 3D zeolite-like supramolecular network with ABW topology, and compound **2** is a 3D framework structure with unusual I^2O^2 connectivity.

In recent years, the synthesis of crystalline open frameworks has received increasing research interest because of their potential applications in gas storage, magnetism, and catalysis.[1] Inorganic frameworks (IFs), including zeolites and transition-metal phosphates, and metal−organic frameworks (MOFs) are the two most important kinds of porous materials, both of which have been widely investigated.[2] However, hybrid framework materials based on the combination of robust inorganic structures in IFs and versatile organic ligands in MOFs have been relatively less studied.[3] This family of combined hybrid frameworks can represent enhanced porosity, physical stability, and chemical flexibility. To date, all of the reported IF−MOF hybrid materials belong to organometallophosphates (OMPOs), and most of them are functionalized by oxalate and polyamine ligands.[4] Arylcarboxylate linkers that are extensively used in the area of MOFs have found very rare application in the construction of OMPOs. Wang reported the only three arylcarboxylate-functionalizing OMPOs that comprise benzene-1,4-dicarboxylate or benzene-1,2,4,5-tetracarboxylate.[5] All of these examples are constructed from zinc cationic nodes. Extension of OMPOs to other transition metals and multiarylcarboxylate ligands still needs to be developed.

Classified by Cheetham and co-workers, the dimensionality of organic−inorganic hybrid frameworks can be represented with the notation I^nO^m ($n, m = 0, 1, 2, 3$), where I and O (I = inorganic and O = organic) refer to the dimensionalities of M−X−M (X = O, N, Cl, and S) and M−L−M (L = organic ligands) connectivity, respectively.[6] The whole dimensionality of most hybrid frameworks is between 0 and 3 ($m + n \leq 3$). To the best of our knowledge, only a few hybrid compounds have superimposed dimensionality over 3 ($m + n > 3$).[7]

We are interested in cobalt-based OMPOs because of their import applications in the areas of catalytic and redox chemistry.[8] We have previously demonstrated that organic amine can be applied as templates for the construction of chiral cobalt phosphite.[9] In this work, we report two organic−inorganic hybrid frameworks, $[H_2DABCO]\cdot[Co(HPO_4)(bpdc)]$ (**1**) and $[H_2DABCO]_3\cdot[Co_{10}(npa)_3(PO_4)_6Cl_2]$ (**2**), where bpdc = 4,4′-biphenyldicarboxylate, npa = 2,6-naphthalenedicarboxylate, and DABCO = 1,4-diazabicyclo[2.2.2]octane, both of which contain 2D cobalt phosphate layers. Compound **1** features a 3D zeolite-like supramolecular network with ABW topology, while compound **2** is a 3D hybrid framework structure with unusual I^2O^2 connectivity. They are the first examples of cobalt-based OMPOs mediated by arylcarboxylate linkers. Moreover, in these two compounds, multiarylcarboxylate ligands are successfully used for the construction of OMPOs for the first time.

Crystals of compound **1** were prepared by the solvothermal reaction of $CoCl_2\cdot 6H_2O$, DABCO, H_3PO_4, and H_2bpdc in *N*,*N*-dimethylformamide (DMF).[10a] Single-crystal X-ray diffraction reveals that compound **1** crystallizes in space group $P2_1/c$.[11a] The asymmetric unit of **1** contains one Co^{II} atom, one HPO_4^{2-} unit, one bpdc, and one protonated DABCO. Each Co center is coordinated by four O atoms, of which three are from the HPO_4^{2-} unit and one is from the carboxylate group, giving rise to a distorted tetrahedral coordination geometry. The average Co−O bond length is 1.949 Å, and the O−Co−O angles are in the range of 101.18(16)−117.12(18)° (Table S1 in the Supporting Information, SI). Each tetrahedral HPO_4^{2-} unit contains one terminal OH group and connects three Co centers, with the separated Co···Co distances being 4.506(11), 5.578(3), and 6.132(12) Å, respectively. Only one carboxylate group of the bpdc ligand is connected to one Co center, and the other remains uncoordinated.

As shown in Figure 1a, the tetrahedral HPO_4^{2-} units alternately link the tetrahedral Co centers into an inorganic $\{Co(HPO_4)\}_n$ layer, of which the bpdc ligands are extended on both sides. These layers are connected to each other by N−H···O hydrogen-bonding interactions between HPO_4^{2-} units and carboxylates and the protonated DABCO guests, further giving rise to a 3D supramolecular framework (Figure S3 in the SI). Also, the distances between the N and O atoms range from 2.62 to 3.18 Å (Table S1 in the SI). It is interesting that this

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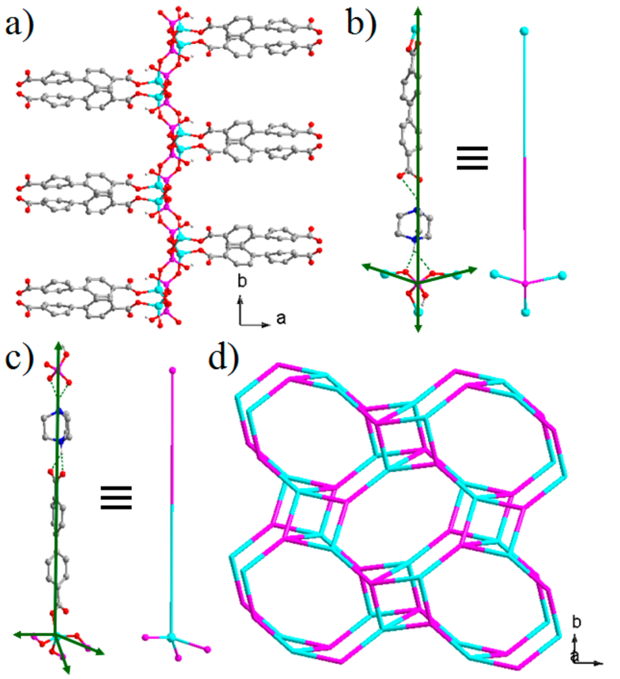

Figure 1. Structural representations of compound **1**: (a) inorganic $\{Co(HPO_4)\}_n$ layer with bpdc ligands on both sides; (b) reduction of the tetrahedral HPO_4^{3-} unit as a 4-connected node; (c) reduction of the tetrahedral $\{CoO_4\}$ unit as a 4-connected node; (d) ABW net of **1**.

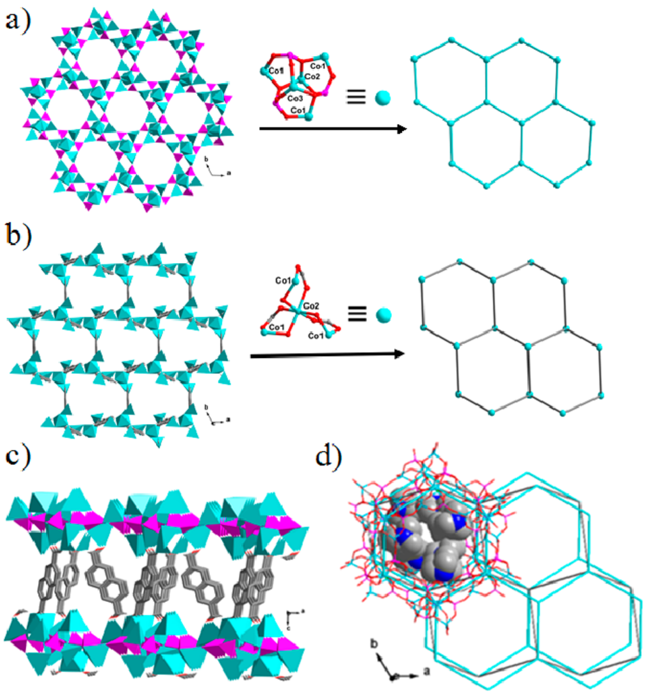

Figure 2. Structural features of compound **2**: (a) metal phosphate layer formed by interconnecting $\{Co_5\}$ clusters; (b) metal−organic layer formed by linking $\{Co_4\}$ clusters through npa ligands; (c) 3D framework of **2**; (d) 6-connected acs net of **2**, highlighting the protonated DABCO templates in the six-ring 1D channels.

supramolecular framework can be topologically represented as a 4-connected, zeolite-like ABW network (Figure 1d) by reducing each tetrahedral HPO_4^{2-} and $\{CoO_4\}$ unit as a 4-connected node (Figure 1b,c). The Schläfli symbol of this ABW net is $(4^2.6^3.8)$.

When using npa ligands instead of bpdc ligands, a new 3D framework structure **2** with unusual I^2O^2 connectivity was obtained.[10b] X-ray crystallography reveals that compound **2** crystallizes in trigonal space group $P\bar{3}c_1$.[11b] The asymmetric unit of compound **2** contains three crystallographically independent Co^{II} cations (Co1, Co2, and Co3). Although the Co1 and Co3 atoms have similar tetrahedral coordination environments, Co1 is coordinated by four O atoms, with three of them belonging to PO_4^{3-} units and the remaining one coming from carboxylate, while the Co3 atom is coordinated by three O atoms from PO_4^{3-} units and one terminal Cl^-. Moreover, Co2 is six-coordinated by three O atoms from three carboxylate groups of different npa ligands and three O atoms from PO_4^{3-} units. The average Co−O distance is 2.016 Å, and the Co−Cl distance is 2.301 Å. The O−Co−O angles are in the range between 86.28(13)° and 174.92(12)° (Table S3 in the SI). In compound **2**, each carboxylate group of the npa ligand bridges two Co centers (Co1 and Co2) in a bidentate coordination mode (Figure S4 in the SI).

The outstanding structural feature of **2** is the simultaneous presence of honeycomb $\{Co_5(PO_4)_3Cl\}_n$ metal phosphate layers and $\{Co(npa)\}_n$ metal−organic layers that are crosswise-linked to form a 3D hybrid framework. In the $\{Co_5(PO_4)_3Cl\}_n$ layer, $\{Co_5\}$ clusters (3Co1, Co2, and Co3) are connected to each other through the O atoms of the PO_4^{3-} units (Figure 2a), corresponding to the inorganic connectivity of I^2. In the $\{Co(npa)\}_n$ layer, npa ligands are linked together by $\{Co_4\}$ clusters (3Co1 and Co2), giving rise to the organic connectivity of O^2. Thus, the whole dimensionality of framework **2** can be classified as I^2O^2. For comparison, the whole dimensionality of framework **1** can be classified as traditional I^2O^0. As shown in Figure 2d, the protonated DABCO resides in the free voids of the six-ring 1D channels along the *c* axis as template molecules. From the viewpoint of topology, the whole framework can be represented as a 6-connected acs network by reducing each $\{Co_5(PO_4)_3Cl\}$ cluster as a 6-connected node (Figure 2d). Also, the Schläfli symbol of this acs net is $(4^9.6^6)$.

Magnetic susceptibility studies of these two compounds were carried out on powdered microcrystalline samples at 1 kOe in the temperature range 2−300 K (Figures 3 and 4). The room temperature $\chi_m T$ values are 2.51 and 4.48 $cm^3\ mol^{-1}$ K for **1** and **2**, respectively. When the temperature is lowered to 100 K, the $\chi_m T$ values decrease smoothly to 1.97 $cm^3\ mol^{-1}$ K for **1** and 4.03 $cm^3\ mol^{-1}$ K for **2**. Below 100 K, the $\chi_m T$ values of **1** and **2** begin to decrease more steeply, reaching the lowest values of 0.14 and 0.86 $cm^3\ mol^{-1}$ K at 2 K. The magnitudes of the magnetic interactions in **1** and **2** can be quantified by Weiss constants

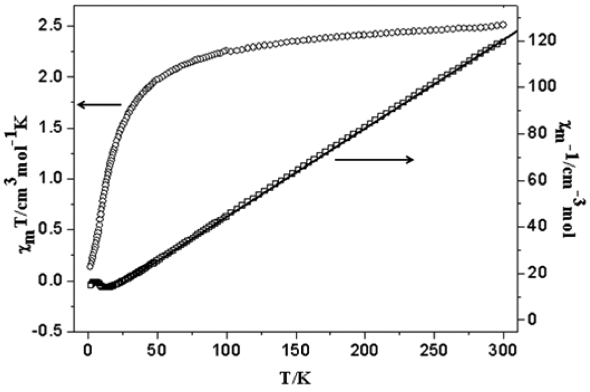

Figure 3. Temperature dependence of $\chi_m T$ and $1/\chi_m$ for compound **1**.

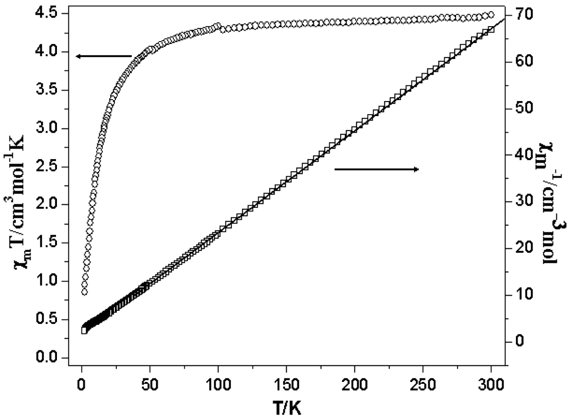

Figure 4. Temperature dependence of $\chi_m T$ and $1/\chi_m$ for compound **2**.

obtained from the fit of the magnetic susceptibility data to the Curie–Weiss law [$\chi_m = C/(T - \theta)$] above 10 K, leading to C = 2.70 cm^3 K mol^{-1} and $\theta = -23.22$ K for **1** and C = 4.58 cm^3 K mol^{-1} and $\theta = -8.22$ K for **2**. The effective magnetic moments of Co^{II} in these two systems are calculated to be 4.65 and 6.05 μ_B for **1** and **2**, respectively, both of which are higher than the spin-only magnetic moment 3.87 μ_B of the Co^{II} ion ($S = {}^3/_2$). This divergence might be due to the orbital moment contribution of Co^{II} in the oxygen tetrahedral environment.

In summary, two new organic–inorganic hybrid cobalt(II) phosphate frameworks have been prepared and structurally characterized. In compound **1**, the inorganic cobalt phosphate layers are assembled by hydrogen bonds between bridging ligands and templating cations to form a robust supramolecular 3D structure with zeolite-like ABW topology, while compound **2** is a crossed combination of cobalt phosphate and cobalt carboxylate layers, giving rise to a 3D hybrid framework, which shows unusual I^{2}O^2 dimensionality. Moreover, Co ions and multiarylcarboxylate ligands have been proven to be effective components for OMPOs, opening new ways for the development of these kinds of hybrid framework materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, additional figures and tables, TGA, powder X-ray diffraction patterns, IR spectra, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(10) (a) Synthesis of **1**: a mixture of H$_2$bpdc (0.061 g, 0.25 mmol), H$_3$PO$_4$ (0.049 g, 0.5 mmol), DABCO (0.08 g, 0.7 mmol), CoCl$_2$·6H$_2$O (0.119 g, 0.5 mmol), hydrogen peroxide (0.080 g), and DMF (4 mL) was added to a 20 mL vial and heated at 120 °C for 4 days. After washing with DMF, dark-blue crystals of **1** were obtained (yield: 70%). Elem anal. Calcd for C$_{20}$H$_{23}$O$_8$N$_2$PCo: C, 47.17; H, 4.55; N, 5.49. Found: C, 47.11; H, 4.63; N, 5.56. (b) Synthesis of **2**: **2** was obtained by the same solvothermal procedure as that for **1** only employing the H$_2$npa (0.054 g, 0.25 mmol) ligand instead of the H$_2$bpdc ligand. Dark-blue crystals of **2** were obtained in a yield of 65%. Elem anal. Calcd for C$_{54}$H$_{60}$O$_{36}$N$_6$P$_6$Cl$_2$Co$_{10}$: C, 29.27; H, 2.71; N, 3.79. Found: C, 29.12; H, 2.48; N, 3.71.

(11) (a) Crystal data for **1**: C$_{20}$H$_{23}$O$_8$N$_2$PCo, M = 509.3, monoclinic, space group $P2_1/c$, a = 20.1740(16) Å, b = 9.7329(7) Å, c = 10.7371(7) Å, V = 2102.5(3) Å^3, Z = 4, 7895 reflections measured, 3701 independent reflections (R_{int}= 0.0314). The final R1 value was 0.0759 [$I > 2\sigma(I)$]. The final wR2(F^2) value was 0.2572 [$I > 2\sigma(I)$]. The GOF on F^2 was 1.091. (b) Crystal data for **2**: C$_{54}$H$_{60}$O$_{36}$N$_6$P$_6$Cl$_2$Co$_{10}$, M = 2215.17, trigonal, space group $P\bar{3}c_1$, a = 13.809 Å, b = 13.809 Å, c = 30.004 Å, V = 4955.0 Å^3, Z = 4, 25517 reflections measured, 2914 independent reflections (R_{int} = 0.0539). The final R1 value was 0.0486 [$I > 2\sigma(I)$]. The final wR2(F^2) value was 0.1498 [$I > 2\sigma(I)$]. The GOF on F^2 was 1.132. The structures were solved by direct methods and refined on F^2 full-matrix least squares using the *SHELXTL-97* program package.