

## Two-dimensional Cobalt-Carboxylate Framework with Hourglass Trinuclear $\text{Co}_3(\text{COO})_6(\text{DMA})_3$ Secondary Building Unit

Anna Goldman,<sup>[a]</sup> Katharina Nardin,<sup>[a]</sup> Simon-Patrick Höfert,<sup>[a]</sup> Simon Millan,<sup>[a]</sup> and Christoph Janiak\*<sup>[a]</sup>

*Dedicated to Professor Bernt Krebs on the Occasion of his 80th Birthday*

**Abstract.** The two-dimensional (2D) cobalt-carboxylate framework of the **hxl** type with the formula  $[\text{Co}_3(\text{bc}(\text{d}))_3(\text{DMA})_3]\cdot\text{DMA}$  was synthesized in a mixture of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate  $[\text{BMIm}][\text{BF}_4]$ ,  $\text{HBF}_4$  and *N,N*-dimethylacetamide (DMA) via solvothermal reaction. The structure of  $[\text{Co}_3(\text{bc}(\text{d}))_3(\text{DMA})_3]\cdot\text{DMA}$  ( $\text{bc}(\text{d})^{2-}$  = benzene-1,4-dicarboxylate) con-

sists of an hourglass trinuclear secondary building unit (SBU) with the first octahedral (oct)-octahedral and square-pyramidal (sq-pyr) coordinated cobalt atoms in the sequence  $\text{Co}_{\text{oct}}-\text{Co}_{\text{oct}}-\text{Co}_{\text{sq-pyr}}$  with terminally coordinated DMA molecules. These SBUs are bridged by six  $\text{bc}(\text{d})^{2-}$  ligands into a two-dimensional layered structure.

### Introduction

Metal-organic frameworks (MOFs) are typically composed of multinuclear secondary building units (SBUs) as metal containing nodes and bridging organic linkers.<sup>[1,2]</sup> The design of the SBUs is influenced by the coordination arrangement of the metal sources and the orientation of the bridging donor atoms in organic linkers. Depending on the synthetic conditions, SBUs with a different arrangement and connectivity may be formed for a given metal.<sup>[3]</sup> Terephthalate (benzene-1,4-dicarboxylate,  $\text{bc}(\text{d})^{2-}$ ) is a common ligand used in prototypical MOFs such as MOF-5, MIL-53, and MIL-101.<sup>[4–8]</sup> The construction of MOFs composed of cobalt carboxylate SBUs is difficult to predict as the coordination number and arrangement of cobalt(II) can range from four (tetrahedral) to six (octahedral). For example, cobalt exhibits tetrahedral coordination in the Co-MOF-5-analog, square-pyramidal coordination in paddle-wheel based MOFs, chains of corner-sharing  $\text{CoO}_6$  octahedra in Co-MOF-71 and clusters of higher nuclearity.<sup>[9–14]</sup>

To the best of our knowledge ten crystallographically different hourglass-like  $\text{Co}_3(\text{COO})_6$ -SBUs with the  $\text{bc}(\text{d})^{2-}$  ligand are known until now, including  $[\text{Co}_3(\text{bc}(\text{d}))_3(\text{DMA})_3]\cdot\text{DMA}$  reported in this work, highlighting the complexity of the cobalt coordination chemistry (Figure 1).<sup>[15–23]</sup> The main difference lies in the local coordination environment of the cobalt atoms. In general the central cobalt atom of the trinuclear  $\text{Co}_3(\text{COO})_6$  cluster is coordinated to six oxygen atoms from different carboxylate ligands. Depending on the synthetic conditions the terminal cobalt atoms can be coordinated to solvent molecules

like dimethylformamide (DMF), neutral N-donor ligands (e.g. pyridine), or they are fully ligated by the terephthalate linkers, to form different coordination environments. If the terminal cobalt atoms are coordinated by bridging ligands, then the SBUs assemble into a three-dimensional (3D) framework.

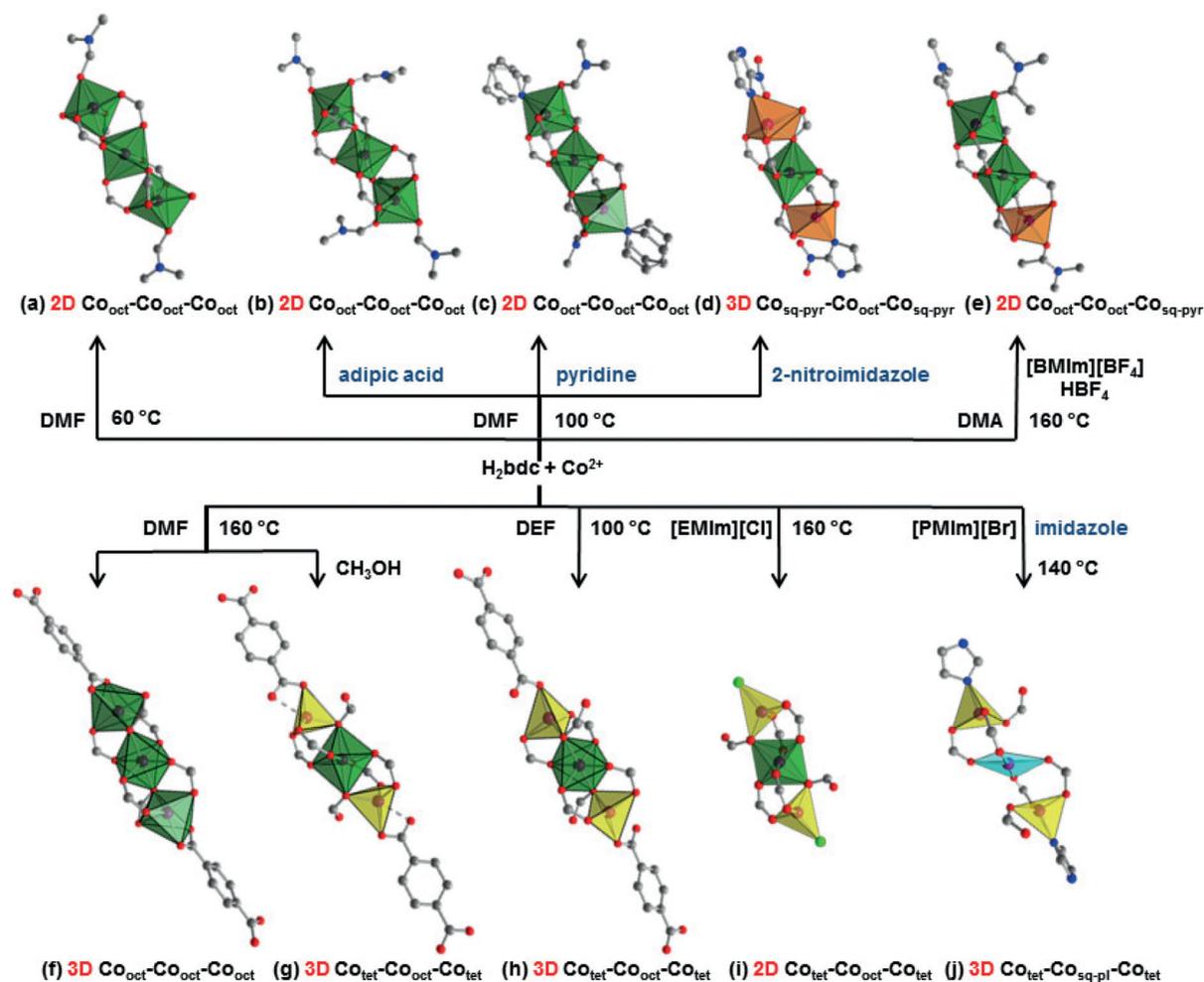
For example, the coordination environment in the SBU of  $3\text{D}-[\text{Co}_7(\text{bc}(\text{d}))_6(\text{nIm})_2(\text{H}_2\text{O})_6]\cdot 3\text{H}_2\text{O}\cdot 3\text{DMF}$  ( $\text{nIm}$  = 2-nitroimidazole) is  $\text{Co}_{\text{sq-pyr}}-\text{Co}_{\text{oct}}-\text{Co}_{\text{sq-pyr}}$  (sq-pyr = square-pyramidal, oct = octahedral) (Figure 1d).<sup>[16]</sup> Here one site of the terminal cobalt atoms is occupied with one N-donor atom from a bridging 2-nitroimidazole, which pillars the otherwise 2D-Co-bcd network to a 3D framework. The coordination of solvent molecules like DMF leads to the construction of 2D structures. The SBU of the  $2\text{D}-[\text{Co}_3(\text{bc}(\text{d}))_3(\text{DMF})_2(\text{H}_2\text{O})_2]$  structure is built from trinuclear  $\text{Co}_3(\text{COO})_6$  clusters, where the terminal cobalt sites are occupied by one DMF oxygen atom and one water molecule to complete the vertices of an octahedron (Figure 1a).<sup>[15]</sup>

Various strategies have been used in the literature to synthesize MOFs (solvothermal, mechanochemical, sonochemical, dry-gel conversion).<sup>[24–26]</sup> One promising procedure is the use of ionic liquids (ILs) as solvents or additives to synthesize MOFs.<sup>[27–35]</sup> When they are incorporated into the framework, they often induce anionic networks.<sup>[36,37]</sup> On the other hand, they can exert a structure-directing effect (e.g. templating) on the crystallization process of MOFs.<sup>[38–41]</sup> The ionothermal synthesis of  $2\text{D}-[\text{RMIm}]_2[\text{M}_3(\text{bc}(\text{d}))_3\text{X}_2]$  networks ( $[\text{RMIm}]\text{X}$  ( $R$  = ethyl, propyl, butyl, amyl;  $\text{MIm}$  = methylimidazolium;  $M$  = Zn, Co, Mn;  $X$  =  $\text{Cl}^-$ ,  $\text{I}^-$ ), was previously investigated for the influence of the  $\text{RIm}^+$  cation, which acts as a template and the halide anion with the function as a monodentate terminal ligand determining the 2D structural fashion of the network.<sup>[22,42–44]</sup> Herein, we report the synthesis and crystal structure of a 2D cobalt network with the formula  $[\text{Co}_3(\text{bc}(\text{d}))_3(\text{DMA})_3]\cdot\text{DMA}$  via an ionic liquid (IL)-assisted solvothermal reaction.

\* Prof. Dr. C. Janiak  
E-Mail: janiak@uni-duesseldorf.de

[a] Institut für Anorganische Chemie und Strukturchemie  
Heinrich-Heine Universität Düsseldorf  
40204 Düsseldorf, Germany

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**Figure 1.** Polyhedral presentations and reaction conditions for the formation of ten types of SBUs built-up from trinuclear  $\text{Co}_3(\text{COO})_6$  clusters, with the Co coordination environment indicated as oct = octahedral, sq-pyr = square-pyramidal, sq-pl = square-planar, and tet = tetrahedral. (a) In  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMF})_2(\text{H}_2\text{O})_2]$  (DMF = dimethylformamide) (CSD-Refcode DUCQUP);<sup>[15]</sup> (b) in  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMF})_4]_n$  (CSD-Refcode LOMQIP);<sup>[21]</sup> (c) in  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMF})_2(\text{py})_2]$  (py = pyridine) (CSD-Refcode NAJDUA);<sup>[17]</sup> (d) in  $3\text{D}-[\text{Co}_7(\text{bdc})_6(\text{nIm})_2(\text{H}_2\text{O})_6]\cdot 3\text{H}_2\text{O}\cdot 3\text{DMF}$  (nIm = 2-nitroimidazole) (CSD-Refcode LACBID);<sup>[16]</sup> (e) in  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot \text{DMA}$  this work; (f) in  $3\text{D}-[\text{Me}_2\text{NH}_2]_2[\text{Co}_3(\text{bdc})_4]\cdot 4\text{DMF}$  (CSD-Refcode VAKREG);<sup>[18]</sup> (g) in  $3\text{D}-[\text{Me}_2\text{NH}_2]_2[\text{Co}_3(\text{bdc})_4]\cdot 2\text{DMF}$  (CSD-Refcode MOXDIN);<sup>[20]</sup> (h) in  $3\text{D}-[\text{C}_4\text{H}_{12}\text{N}_2][\text{Co}_3(\text{bdc})_4]_2\cdot 3\text{C}_5\text{H}_{11}\text{NO}$  (CSD-Refcode VEGMIE);<sup>[19]</sup> (i) in  $2\text{D}-[\text{EMIm}]_2[\text{Co}_3(\text{bdc})_3\text{Cl}_2]$  (CSD-Refcode TACHUD);<sup>[22]</sup> (j) in  $3\text{D}-[\text{Co}_3(\text{bdc})_3(\text{Im})_2]_n$  (Im = imidazole) (CSD-Refcode XAPSOY).<sup>[23]</sup>

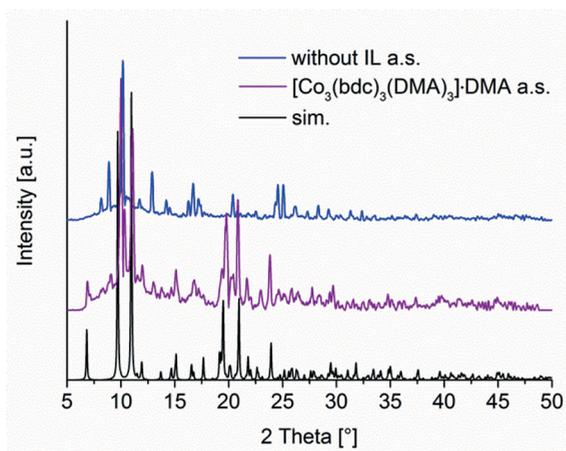
## Results and Discussion

Single crystals of  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot \text{DMA}$  could be obtained by the reaction of  $\text{Co}(\text{BF}_4)_2\cdot 6\text{H}_2\text{O}$  and  $\text{H}_2\text{bdc}$  in a mixture of the ionic liquid [BMIm][BF<sub>4</sub>] with DMA as the solvent at 160 °C (see Experimental Section for details). Additionally, tetrafluoroboric acid, HBF<sub>4</sub>, as a modulator was added to insure a slow crystallization due to the protonation of the  $\text{bdc}^{2-}$  ligand.<sup>[45,46]</sup> As only the proton through its pH adjustment was intended as modulator, we chose HBF<sub>4</sub>, which has the same weakly-coordinating anion as the IL in order to perturb the system as little as possible. Therefore, no other modulator such as often-used acetic acid was tested.

The representative nature of the single crystal for the bulk as-synthesized sample was verified by comparison of the experimental with the simulated powder X-ray diffractogram (PXRD) from the single crystal structure data (Figure 2).

The comparison between the experimental diffraction pattern of these phase with the simulated PXRD of  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot \text{DMA}$  confirmed the identity of the major crystalline part of the sample. However, it is also evident that a minor contribution of another still undefined crystalline phase was obtained (Figure 2). Without the addition of the IL under otherwise same reaction conditions, this yet undefined phase is formed in very small and unidentifiable crystals, which did not have sufficient quality for single crystal data analysis (Figure S2, Supporting Information). At the same time, this reaction shows the influence of the IL on the product formation. The IL is important for the controlled crystallization growth and functions as a structure-directing agent.

$[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot \text{DMA}$  crystallizes in the monoclinic crystal system with the space group  $Pn$ . The asymmetric unit consists of three  $\text{Co}^{\text{II}}$  ions, three  $\text{bdc}^{2-}$  ligands, three coordi-

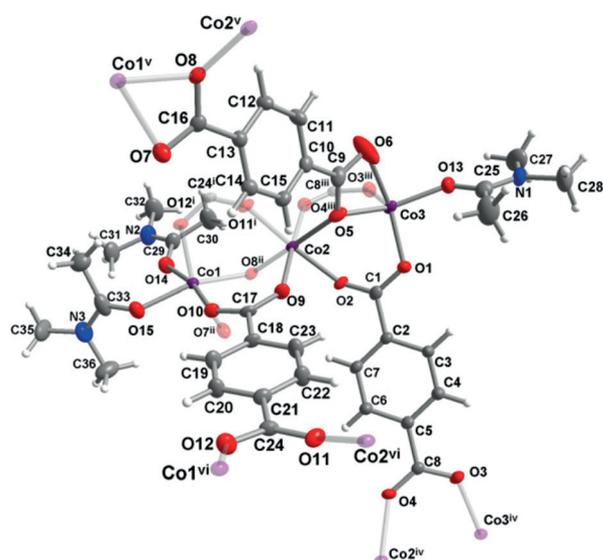


**Figure 2.** PXRD pattern of  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot\text{DMA}$  [simulated (black) and as-synthesized (purple)] and the PXRD pattern of the undefined phase obtained without the addition of the ionic liquid (blue).

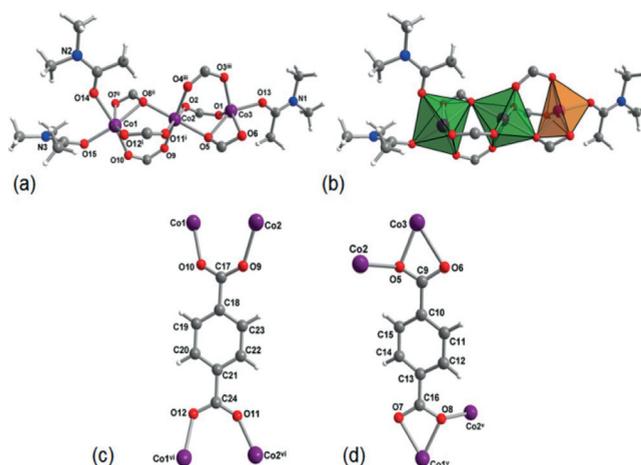
nated DMA molecules, and one non-coordinated DMA molecule (Figure 3). The three Co atoms form an hourglass-like trinuclear SBU, where the terminal cobalt atoms have an octahedral and square-pyramidal coordination environment  $\text{Co}_{\text{oct}}\text{--Co}_{\text{oct}}\text{--Co}_{\text{sq-pyr}}$ , respectively (Figure 4a, b). The SBU  $\{\text{Co}_3(\text{COO})_6(\text{DMA})_3\}$  possesses three crystallographic different  $\text{Co}^{\text{II}}$  ions, six carboxylate groups from six bridging  $\text{bdc}^{2-}$  ligands, and three terminal coordinated DMA molecules (Figure 4a). As shown in Figure 4 the bridging carboxylate ligands show different coordination modes. Two of the three crystallographically different ligands are bridging bidentate via a  $\mu_4\text{--}(\kappa^1\kappa^1\kappa^1\kappa^1)$  mode (Figure 4c) and the third linker is chelating/bridging bidentate in a  $\mu_4\text{--}(\kappa^1\kappa^2\kappa^1\kappa^2)$  mode (Figure 4d).

$\text{Co1}$  adopts an octahedral arrangement, surrounded by two oxygen atoms from two  $\text{bdc}^{2-}$  bidentate bridging ligands, two oxygen atoms from one chelating bridging carboxylate group, and two oxygen atoms from two coordinated DMA molecules. The lengths of the  $\text{Co1}_{\text{oct}}\text{--O}$  bonds are in the range of 2.02(4)–2.27(4) Å. The central  $\text{Co2}$  atom is surrounded by four oxygen atoms from different  $\text{bdc}^{2-}$  bridging ligands in the equatorial position and two oxygen atoms from two other  $\text{bdc}^{2-}$  ligands in the axial plane completing the octahedral coordination environment. The lengths of the  $\text{Co2}_{\text{oct}}\text{--O}$  bonds are in the range of 2.02(4)–2.17(5) Å. The coordination sphere on  $\text{Co3}$  consists of two oxygen atoms of a bidentate bridging and two oxygen atoms from one chelating bridging carboxylate group. The fivefold coordination of  $\text{Co3}$  is completed by a coordinated oxygen atom from a DMA molecule to a square-pyramidal coordination. The tau parameter ( $\tau$ ) defined by Addison et al. of  $\tau = 0.3$  indicates a closer to square-pyramidal (ideally  $\tau = 0$ ) coordination environment of  $\text{Co3}$ .<sup>[47]</sup> The lengths of the  $\text{Co3}_{\text{sq-pyr}}\text{--O}$  bonds are in the range of 1.97(4)–2.33(6) Å.

Each  $\{\text{Co}_3(\text{COO})_6(\text{DMA})_3\}$  SBU acts as a 6-c-node and is linked by six bridging  $\text{bdc}^{2-}$  ligands (Figure 5a). The overall structure is a 2D-network of **hxl** topology with the short Schläfli symbol  $3^6\cdot 4^6\cdot 5^3$  comprising triangular channels. The **hxl** sheets stack in an AB fashion (Figure 5b and c).<sup>[48,49]</sup> A 6-connected **hxl** topology is also known in the 2D manganese



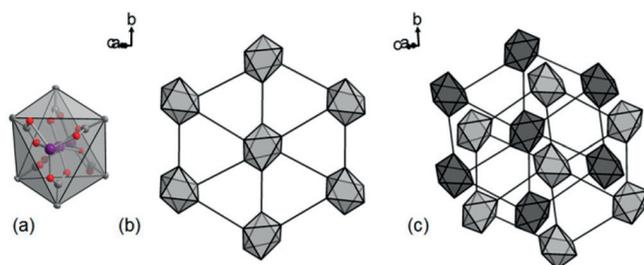
**Figure 3.** Thermal ellipsoid plot (50%) of the extended asymmetric unit in  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot\text{DMA}$  to show the complete coordination sphere for each Co atom and the bridging action of each ligand. Symmetry transformations: (i)  $\frac{1}{2} + x, 2 - y, \frac{1}{2} + z$ ; (ii)  $-\frac{1}{2} + x, -y, -\frac{1}{2} + z$ ; (iii)  $x, -\frac{1}{2} + x, 1 - y, -\frac{1}{2} + z$ ; (iv)  $x, -1 + y, z$ ; (v)  $\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$ ; (vi)  $\frac{1}{2} + x, 1 - y, \frac{1}{2} + z$ ; (vii)  $x, 1 + y, z$ ; (viii)  $\frac{1}{2} + x, -y, \frac{1}{2} + z$ ; (ix)  $-\frac{1}{2} + x, 2 - y, -\frac{1}{2} + z$ . The non-coordinated DMA solvent molecule of crystallization is omitted for clarity.



**Figure 4.** (a) Ball and stick presentation and (b) polyhedral view of the trinuclear hourglass-like SBU with  $\text{Co}_{\text{oct}}\text{--Co}_{\text{oct}}\text{--Co}_{\text{sq-pyr}}$  cobalt coordination environments. The two different coordination modes of the  $\text{bdc}^{2-}$  ligand (c) bridging bidentate ( $\mu_4 = \kappa^1\kappa^1\kappa^1\kappa^1$ ) and (d) chelating/bridging bidentate ( $\mu_4 = \kappa^1\kappa^2\kappa^1\kappa^2$ ).

network  $[\text{Mn}_{1.5}(\text{bdc})_{1.5}(\text{DMA})_2]$ , which is built from trinuclear  $\{\text{Mn}_3(\text{COO})_6\}$  SBUs.<sup>[50]</sup>

Further,  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3]\cdot\text{DMA}$  was characterized by IR spectroscopy (Figure S4, Supporting Information). The characteristic absorption bands for the coordinated ligands at  $1585\text{ cm}^{-1}$  correspond to the asymmetric stretching vibration ( $\nu_{\text{as}}$ ) and the band at  $1385\text{ cm}^{-1}$  to the symmetric stretching vibration ( $\nu_{\text{s}}$ ) of the carboxylate group. The frequency gap ( $\Delta\nu$ ) between these bands  $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$  of  $200\text{ cm}^{-1}$  reveals that the carboxylate ligation is in the biden-



**Figure 5.** (a) Trinuclear hourglass-like SBU as 6-c-node by considering the carboxylate-carbon atoms as the point-of-extension and Co2 as central point. (b) 2D **hxl** topology with the short Schläfli symbol  $3^6.4^6.5^3$  including triangular channels. (c) AB-stacking of two adjacent 2D nets. Non-coordinated DMA is omitted for clarity in all images.

tate bridging mode ( $\mu_{1,3^-}$  or  $\eta^1:\eta^1:\mu_2^-$ ).<sup>[51,52]</sup> The band at  $1169\text{ cm}^{-1}$  can be assigned to the C–N stretching vibration and the band at  $1019\text{ cm}^{-1}$  is compatible to the C–CH<sub>3</sub> rocking vibration from DMA.

Previously, the ionothermal synthesis of Co-bdc structures based on similar trinuclear  $\{\text{Co}_3(\text{COO})_6\text{X}_2\}$  SBUs ( $X = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) in the IL  $[\text{RMIm}][\text{X}]$  ( $R = \text{ethyl}$ ,  $n\text{-propyl}$ ,  $n\text{-butyl}$ , and  $\text{amyl}$ ;  $X = \text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) as solvent was investigated for the effect of the  $[\text{RMIm}]^+$  cation by varying the length of the  $N$ -alkyl chain and/or by changing the halide anion  $X$ .

Although in the compound presented in this work neither the IL cation nor the anion is incorporated into the network structure, the  $[\text{BMIm}]^+$  cation could favor the formation of the 2D network. Otherwise the use of an IL with a larger  $N$ -alkyl chain could potentially lead to an expansion of the structure in the third direction. Such an influence of  $[\text{RMIm}]^+$  cation size on the final structures was shown in the ionothermal reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{H}_2\text{bdc}$  in a series of ILs, such as  $[\text{EMIm}][\text{Br}]$  ( $E = \text{ethyl}$ ),  $[\text{PMIm}][\text{Br}]$  ( $P = \text{propyl}$ ),  $[\text{BMIm}][\text{Br}]$  ( $B = \text{butyl}$ ) and  $[\text{AMIm}][\text{Br}]$  ( $A = \text{amyl}$ ). It was observed that the synthesis in ILs with smaller cations led to similar  $2\text{D}-[\text{RMIm}]_2[\text{Co}_3(\text{bdc})_3\text{Br}_2]$  structures, where the IL cation and  $\text{Br}^-$  anion are incorporated in the structure.<sup>[44]</sup> These compounds are built from similar trinuclear  $\{\text{Co}_3(\text{COO})_6\text{Br}_2\}$  SBUs, where the terminal cobalt atoms have a distorted tetrahedral coordination sphere surrounded by three oxygen atoms from  $\text{bdc}^{2-}$  ligands and one monodentate  $\text{Br}^-$  ligand (akin to Figure 1i). Whereas with the larger  $N$ -alkyl chain in the  $[\text{AMIm}]^+$  cation under otherwise same reaction conditions a  $3\text{D}-[\text{AMIm}]_2[\text{Co}_3(\text{bdc})_4]$  framework was obtained. It consists of similar trinuclear  $\{\text{Co}_3(\text{COO})_8\}$  building units except in the place of the terminal  $\text{Br}^-$  ligand, two carboxylate groups from one  $\text{bdc}^{2-}$  ligand pillar the 2D layers into a 3D framework (akin to Figure 1g and h). In this case the  $[\text{RMIm}]^+$  cation acts as template and through its size has a structure directing effect.

An example, where the IL is not incorporated into the framework was presented in the synthesis of a neutral framework with the chemical formula  $3\text{D}-[\text{Co}_3(\text{bdc})_3(\text{Im})_2]_n$  from the reaction of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with  $\text{H}_2\text{bdc}$  in  $[\text{EMIm}][\text{Br}]$  with the addition of imidazole (Figure 1j).<sup>[23]</sup> This compound possesses  $\{\text{Co}_3(\text{COO})_6\text{Im}_2\}$  SBUs, where the central cobalt atom adopts a square-planar coordination environment sur-

rounded by four oxygen atoms from four different  $\text{bdc}^{2-}$  ligands and the terminal cobalt atoms adopt a tetrahedral coordination sphere by the coordination to three oxygen atoms from three  $\text{bdc}^{2-}$  and one nitrogen atom from the terminal imidazole ligand.

In contrast to the syntheses described above, where only the IL was used as solvent, in this work the formation of  $[\text{Co}_3(\text{bdc})_3(\text{DMA})_3] \cdot \text{DMA}$  was achieved in a mixture of  $[\text{BMIm}][\text{BF}_4]$  with DMA. The addition of DMA has a pivotal role in the construction of the 2D structure confirmed through the coordination by the DMA oxygen atom on terminal cobalt atoms of the trinuclear SBU. The structural environments of the  $\text{Co}_3$  hourglass compounds shown in Figure 1 are determined by the synthesis temperature, the solvent or the addition of (terminating) co-ligands. Solvothermal reactions of  $\text{Co}^{2+}$  salts with  $\text{H}_2\text{bdc}$  in  $N,N$ -dimethylformamide (DMF) show a temperature dependent transition from 2D- to 3D-Co-bdc-networks. At lower temperatures (60–100 °C) DMF solvent molecules potentially coordinate as mono-dentate terminal ligands on the peripheral sites of the  $\text{Co}_3$ -SBU, whereas at higher temperatures about 160 °C the carboxylate group of the  $\text{bdc}^{2-}$  ligand has a stronger ability to coordinate on these terminal sites.

The reaction of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  with  $\text{H}_2\text{bdc}$  in DMF at 60 °C leads to the formation of  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMF})_2(\text{H}_2\text{O})_2]$  built-up from trinuclear  $\text{Co}_3(\text{COO})_6$  clusters with the Co sequence  $\text{Co}_{\text{oct}}-\text{Co}_{\text{oct}}-\text{Co}_{\text{oct}}$  (Figure 1a).<sup>[15]</sup> A similar  $\text{Co}_{\text{oct}}-\text{Co}_{\text{oct}}-\text{Co}_{\text{oct}}$  environment was achieved for  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMF})_4]$  in the reaction with  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  instead of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and with the addition of adipic acid at 100 °C (Figure 1b).<sup>[21]</sup> Without the addition of adipic acid but at an elevated temperature of 160 °C  $3\text{D}-[\text{Me}_2\text{NH}_2]_2[\text{Co}_3(\text{bdc})_4] \cdot 4\text{DMF}$  was formed (Figure 1f).<sup>[18]</sup> The octahedral environment of the terminal cobalt atoms in  $3\text{D}-[\text{Me}_2\text{NH}_2]_2[\text{Co}_3(\text{bdc})_4] \cdot 4\text{DMF}$  is completed by the coordination from two oxygen atoms from two bridging carboxylate groups and two oxygen atoms from one chelate carboxylate group. One  $\text{bdc}^{2-}$  ligand acts as a pillar to form a 3D coordination framework. The formation of  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMA})_3] \cdot \text{DMA}$  presented in this work at also 160 °C could be due the modulator effect of  $\text{HBF}_4$ , which slows and modulates the deprotonation of  $\text{H}_2\text{bdc}$ . In similar reactions,  $N$ -donor additives like pyridine, nitroimidazole or imidazole coordinate preferably on the terminal cobalt sites of the  $\text{Co}_3$ -SBU (Figure 1c, d, and j). 2D networks are formed with the addition of mono-dentate  $N$ -donor co-ligands such as pyridine in  $[\text{Co}_3(\text{bdc})_3(\text{DMF})_2(\text{py})_2]$ , where each terminal  $\text{Co}^{2+}$  atom is saturated by one O-donor atom from DMF and one N-donor atom from pyridine to an octahedral coordination environment (Figure 1c).<sup>[17]</sup> 3D networks can be achieved with the use of bidentate co-ligands like imidazole or 2-nitroimidazole, which pillar the adjacent layers in the third direction. (Figure 1 d and j).<sup>[16,23]</sup>

## Conclusions

The  $2\text{D}-[\text{Co}_3(\text{bdc})_3(\text{DMA})_3] \cdot \text{DMA}$  framework with **hxl** topology was successfully synthesized via an IL-containing solvothermal reaction. The obtained structure consists of

{Co<sub>3</sub>(COO)<sub>6</sub>(DMA)<sub>3</sub>} secondary building units with an hourglass shape. In comparison to other previously reported Co-bdc hourglass SBUs a new coordination sequence of Co<sub>oct</sub>-Co<sub>oct</sub>-Co<sub>sq-pyr</sub> was achieved. Thereby, the presence of IL was important to obtain well-shaped and large enough crystals, whereas in the absence of IL under otherwise identical conditions only very small, unidentifiable crystals could be obtained. Further, the IL in the solvent mixture seemed to induce the noted SBU modification to known structure types and allowed to obtain a new Co<sub>3</sub> hourglass configuration. Also, DMA played a pivotal role in the construction of the 2D structure through the coordination to the terminal cobalt atoms of the trinuclear SBU.

## Experimental Section

The chemicals used were obtained from commercial sources. No further purification has been carried out. CHN analysis was performed with a Perkin-Elmer CHN 2400 (Perkin-Elmer, Waltham, MA, USA). IR spectra were recorded with a Bruker Tensor 37 IR spectrometer (Bruker Optics, Ettlingen, Germany) equipped with KBr unit. The intensity of adsorption is indicated as strong (s), medium (m), weak (w) and broad (br). The powder X-ray diffraction pattern (PXRD) was obtained with a Bruker D2 Phaser powder diffractometer with a flat silicon, low background sample holder, at 30 kV, 10 mA for Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

**Single Crystal X-ray Structure, Data Collection:** Under a polarizing microscope suitable crystals were carefully selected and placed in protective oil. A crystal of sufficient quality was measured with a Bruker Kappa APEX2 CCD diffractometer with microfocus tube using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). For data collection APEX2,<sup>[53]</sup> for cell refinement SAINT,<sup>[53]</sup> and for experimental absorption correction SADABS was used.<sup>[54]</sup> The structure was solved with SHELXT by intrinsic phasing and refined with SHELXL-2017 by full-matrix least-squares on  $F^2$ .<sup>[55,56]</sup> All hydrogen atoms were positioned geometrically (with C-H = 0.95  $\text{\AA}$  for aromatic CH and 0.98  $\text{\AA}$  for CH<sub>3</sub>) and refined using riding models (AFIX 43 and 137) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH})$  and 1.5  $U_{\text{eq}}(\text{CH}_3)$ . Crystallographic data and structure refinement results are summarized in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1857764 for [Co<sub>3</sub>(bdc)<sub>3</sub>(DMA)<sub>3</sub>] $\cdot$ DMA (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**[Co<sub>3</sub>(bdc)<sub>3</sub>(DMA)<sub>3</sub>] $\cdot$ DMA:** Co(BF<sub>4</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O (26 mg, 0.11 mmol) and H<sub>2</sub>bdc (22 mg, 0.12 mmol) were dissolved separately in a mixture of *N,N*-dimethylacetamide (4.5 mL) and [BMIm][BF<sub>4</sub>] (0.5 mL) with tetrafluoroboric acid HBF<sub>4</sub> (0.2 mL) as modulator. Both solutions were mixed, transferred in a Pyrex tube and heated to 160  $^{\circ}\text{C}$  for 40 h in a programmable oven and held at this temperature for 40 h, then cooled to room temperature over 30 h. Subsequently, single crystals of [Co<sub>3</sub>(bdc)<sub>3</sub>(DMA)<sub>3</sub>] $\cdot$ DMA were obtained. Yield: 16.8 mg (25%). C<sub>40</sub>H<sub>48</sub>Co<sub>3</sub>N<sub>4</sub>O<sub>16</sub>: calcd. C 47.21; H 4.75; N 5.51%; found: C 48.04; H 4.88; N 5.49%. IR (KBr):  $\tilde{\nu} = 3600$  (w), 3431 (br), 3147 (w), 3106 (w), 2961 (w), 2934 (w), 2871 (w), 1585 (m), 1504 (w), 1385 (s), 1169

**Table 1.** Crystallographic data for [Co<sub>3</sub>(bdc)<sub>3</sub>(DMA)<sub>3</sub>] $\cdot$ DMA.

[Co <sub>3</sub> (bdc) <sub>3</sub> (DMA) <sub>3</sub> ] $\cdot$ DMA	
Empirical formula	C <sub>36</sub> H <sub>39</sub> Co <sub>3</sub> N <sub>3</sub> O <sub>15</sub> ·C <sub>4</sub> H <sub>9</sub> NO
$M / \text{g}\cdot\text{mol}^{-1}$	1017.61
Crystal dimensions /mm	0.30 $\times$ 0.10 $\times$ 0.05
$T / \text{K}$	140
Crystal system	monoclinic
Space group	$Pn$ (no. 7)
$a / \text{\AA}$	15.716(2)
$b / \text{\AA}$	9.5722(13)
$c / \text{\AA}$	15.868(2)
$\beta / ^{\circ}$	109.658(6) <sup>o</sup>
$V / \text{\AA}^3$	2248.0(6)
$Z$	2
$D_{\text{calc}} / \text{g}\cdot\text{cm}^{-3}$	1.503
$\mu(\text{Mo-K}\alpha) / \text{mm}^{-1}$	1.17
$F(000)$	1050
$T_{\text{max}}, T_{\text{min}}$	1.000, 0.755
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} / \text{e}\ \text{\AA}^{-3}$	1.08, -0.63
$R_1, wR_2 [I > 2\sigma(I)]$	0.0395, 0.1018
$R_1, wR_2$ [all data]	0.0448, 0.1062
Goodness-of-fit on $F^2$	1.015

a) Largest difference peak and hole. b)  $R_1 = [\sum(|F_o| - |F_c|) / \sum|F_o|]$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2]^{1/2}$ . c) Goodness-of-fit  $S = [\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$ .

**Table 2.** Selected bond length / $\text{\AA}$  and angles / $^{\circ}$  for [Co<sub>3</sub>(bdc)<sub>3</sub>(DMA)<sub>3</sub>] $\cdot$ DMA.

Bond lengths			
Co1-O15	2.017 (4)	Co2-O2	2.087 (4)
Co1-O12 <sup>i</sup>	2.033 (4)	Co2-O8 <sup>ii</sup>	2.110 (4)
Co1-O10	2.041 (4)	Co2-O5	2.171 (5)
Co1-O8 <sup>ii</sup>	2.116 (4)	Co3-O3 <sup>iii</sup>	1.969 (4)
Co1-O14	2.186 (4)	Co3-O1	1.970 (4)
Co1-O7 <sup>ii</sup>	2.271 (4)	Co3-O13	1.987 (5)
Co2-O9	2.022 (4)	Co3-O5	2.068 (4)
Co2-O11 <sup>i</sup>	2.041 (4)	Co3-O6	2.328 (6)
Co2-O4 <sup>iii</sup>	2.076 (4)		
Bond angles			
O15-Co1-O12 <sup>i</sup>	99.88 (18)	O4 <sup>iii</sup> -Co2-O2	92.59 (17)
O15-Co1-O10	85.70 (17)	O9-Co2-O8 <sup>ii</sup>	91.76 (17)
O12 <sup>i</sup> -Co1-O10	100.06 (18)	O11 <sup>i</sup> -Co2-O8 <sup>ii</sup>	89.46 (16)
O15-Co1-O8 <sup>ii</sup>	162.03 (18)	O4 <sup>iii</sup> -Co2-O8 <sup>ii</sup>	89.30 (16)
O12 <sup>i</sup> -Co1-O8 <sup>ii</sup>	97.72 (16)	O2-Co2-O8 <sup>ii</sup>	94.43 (15)
O10-Co1-O8 <sup>ii</sup>	94.84 (16)	O9-Co2-O5	88.67 (17)
O15-Co1-O14	85.12 (16)	O11 <sup>i</sup> -Co2-O5	89.90 (16)
O12 <sup>i</sup> -Co1-O14	85.29 (17)	O4 <sup>iii</sup> -Co2-O5	90.30 (17)
O10-Co1-O14	170.05 (17)	O2-Co2-O5	86.20 (16)
O8 <sup>ii</sup> -Co1-O14	92.72 (15)	O8 <sup>ii</sup> -Co2-O5	179.27 (18)
O15-Co1-O7 <sup>ii</sup>	102.08 (18)	O3 <sup>iii</sup> -Co3-O1	115.64 (19)
O12 <sup>i</sup> -Co1-O7 <sup>ii</sup>	155.41 (17)	O3 <sup>iii</sup> -Co3-O13	96.24 (19)
O10-Co1-O7 <sup>ii</sup>	92.52 (17)	O1-Co3-O13	97.79 (17)
O8 <sup>ii</sup> -Co1-O7 <sup>ii</sup>	59.94 (15)	O3 <sup>iii</sup> -Co3-O5	107.57 (18)
O14-Co1-O7 <sup>ii</sup>	85.67 (17)	O1-Co3-O5	91.83 (17)
O9-Co2-O11 <sup>i</sup>	96.21 (17)	O13-Co3-O5	147.3 (2)
O9-Co2-O4 <sup>iii</sup>	177.6 (2)	O3 <sup>iii</sup> -Co3-O6	99.5 (3)
O11 <sup>i</sup> -Co2-O4 <sup>iii</sup>	85.97 (18)	O1-Co3-O6	140.3 (2)
O9-Co2-O2	85.16 (17)	O13-Co3-O6	96.0 (2)
O11 <sup>i</sup> -Co2-O2	175.84 (19)	O5-Co3-O6	58.78 (19)
Symmetry codes: (i) $x + 1/2, -y + 1, z + 1/2$ ; (ii) $x, y + 1, z$ ; (iii) $x + 1/2, -y + 2, z + 1/2$ .			

(w), 1136 (w), 1019 (w), 1017 (w), 887 (w), 822 (w), 749 (w), 653 (w), 623 (w), 546 (w), 445 (w)  $\text{cm}^{-1}$ .

**Supporting Information** (see footnote on the first page of this article): Crystal images, IR spectrum, fractional atom coordinates, displacement and geometric parameters of X-ray structure.

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