



## Solvothermal synthesis and characterization of new calcium carboxylates based on cluster- and rod-like building blocks



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### ABSTRACT

Four new calcium carboxylate frameworks, namely  $\text{Ca}_2(1,3\text{-bdc})_2(\text{nmp}) \cdot 0.5\text{H}_2\text{O}$  (**1**),  $\text{Ca}(1,3\text{-bdc})(\text{pyr})$  (**2**),  $\text{Ca}_3(1,4\text{-bdc})_3(\text{nmp})_2$  (**3**), and  $\text{Ca}_3(1,4\text{-bdc})_3(\text{dmi})_4$  (**4**), have been prepared under solvothermal conditions. Compounds **1–3** have 3D framework structures based on rod-like building blocks, while compound **4** has a layered structure constructed from  $\text{Ca}_3(\text{CO}_2)_6$  clusters. Topological analyses reveal that compounds **2–4** have lvt-b, pcu, and sql topologies, respectively.

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Functional coordination polymers have drawn enormous scientific attentions due to their potential applications in many areas, such as gas storage, separation, catalysis and sensing [1–3]. The structures of these crystalline materials consist of metal ions or metal clusters as nodes, and organic ligands as linkers. Most of the research works so far have focused on transition metal ions [4–6]. In comparison, the synthesis of open-framework structures based on s-block metals has been much less explored [7–10]. As an environmentally abundant element, calcium is of current interest in the synthesis of new open-framework coordination polymers for its high gas adsorption enthalpies and its important role in many biological and biochemical processes [11–13]. Different from transition metals that can form regular secondary building units (SBUs), such as  $\text{M}_2(\text{CO}_2)_4$  paddlewheel and  $\text{M}_4\text{O}(\text{CO}_2)_6$  octahedron, calcium(II) coordination polymers often contain rod-like SBUs [14–17]. An illustrative example is porous CYCU-1 constructed from inorganic chains of  $\text{CaO}_7$  polyhedra, which exhibits high thermal stability up to 450 °C [18].

A common way to tune the framework structures of coordination polymers is the use of different organic ligands as the bridging linkers between metal centers. The variation of the synthetic parameters, such as temperature, time, and solvent, can also affect the structures of resulting products. For example, the synthesis of magnesium naphthalene-1,4-dicarboxylates in different organic solvents has resulted in the formation of several different networks with sql, pts, lvt-b, ABW, and ACO topologies [19,20]. In these solvothermal reactions,

organic solvents can imprint their structural information to the frameworks of coordination polymer by serving as terminal ligands, bridging ligands, charge-balancing agents, and structure-directing agents.

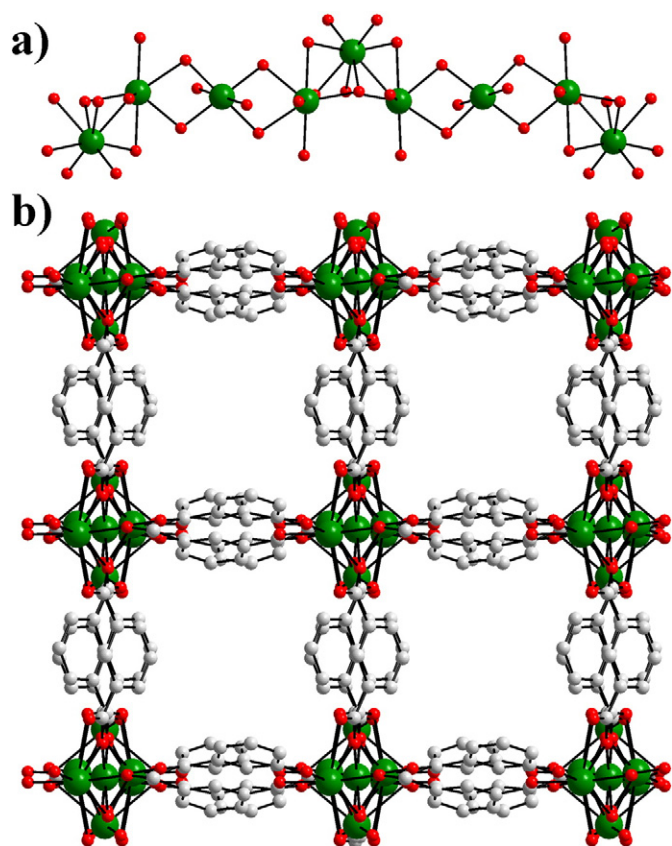
In this work, we report the solvothermal synthesis and characterization of four new calcium carboxylate frameworks, formulated as  $\text{Ca}_2(1,3\text{-bdc})_2(\text{nmp}) \cdot 0.5\text{H}_2\text{O}$  (**1**),  $\text{Ca}(1,3\text{-bdc})(\text{pyr})$  (**2**),  $\text{Ca}_3(1,4\text{-bdc})_3(\text{nmp})_2$  (**3**), and  $\text{Ca}_3(1,4\text{-bdc})_3(\text{dmi})_4$  (**4**), where bdc = benzenedicarboxylate, nmp = 1-methyl-2-pyrrolidinone, pyr = 2-pyrrolidinone, and dmi = 1,3-dimethyl-2-imidazolidinone. Structural analyses reveal that compounds **1–3** have 3D framework structures based on rod-like building blocks, while compound **4** has a layered structure constructed from cluster-like building blocks [21].

Colorless block crystals of compound **1** were obtained by heating a mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 1,3- $\text{H}_2\text{bdc}$ , and nmp at 150 °C for 5 days (62% yield based on calcium). The compound crystallizes in the monoclinic space group  $P2_1/n$  (no. 13). The asymmetric unit contains three crystallographically independent calcium atoms, which are six-, seven-, and eight-coordinated by oxygen atoms, respectively. The Ca–O bond lengths range from 2.244(4) to 2.703(4) Å. The Ca-centered polyhedra share their edges or faces to form chain-like building blocks, as shown in Fig. 1a. These inorganic chains are further bridged by 1,3-bdc ligands to form a three-dimensional framework with rectangle-shaped channels of  $7.2 \times 7.6 \text{ \AA}^2$ , as shown in Fig. 1b. The nmp molecules attach to the walls of calcium carboxylate framework, which occupy 37.3% of the unit cell volume.

Colorless block crystals of compound **2** were obtained by heating a mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 1,3- $\text{H}_2\text{bdc}$ , and pyr at 190 °C for 6 days (57% yield based on calcium). The compound crystallizes in the

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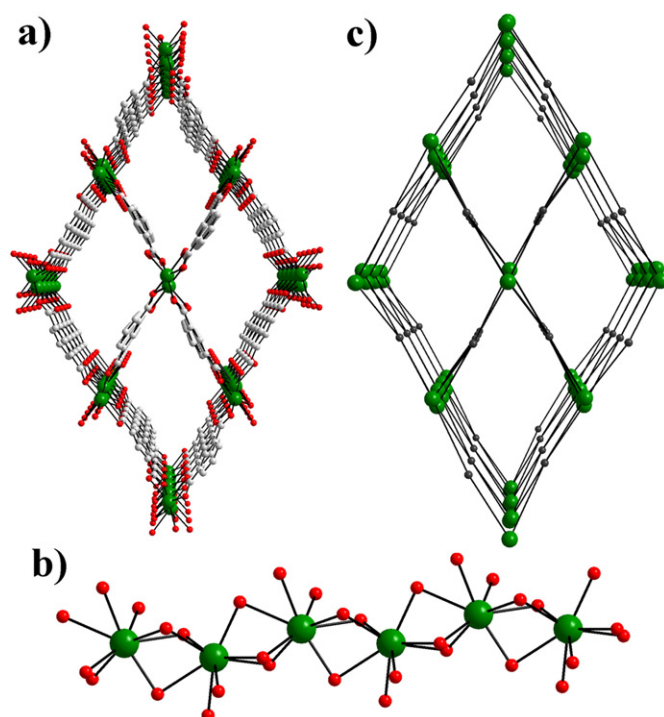
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**Fig. 1.** (a) A view of the inorganic chain constructed from  $\text{CaO}_6$ ,  $\text{CaO}_7$ , and  $\text{CaO}_8$  polyhedra. (b) A view of the framework structure of **1** with rectangle-shaped channels. Solvent molecules are omitted for clarity.

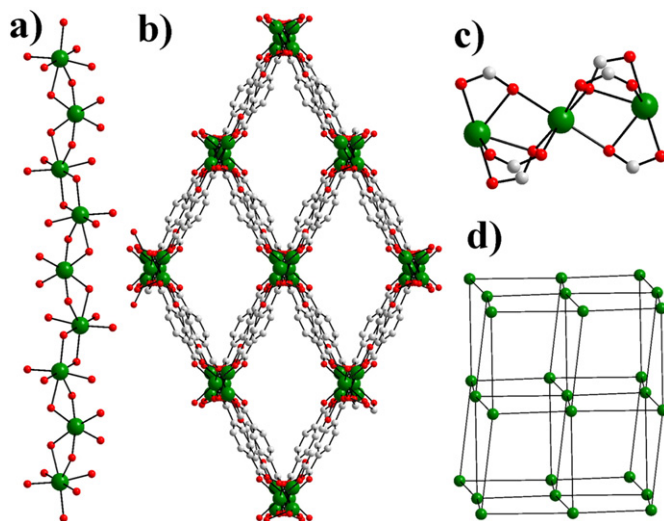
orthorhombic space group  $P2_12_12_1$  (no. 19). The asymmetric unit comprises one calcium atom, one bdc ligand, and one pyr molecule. The calcium atom is eight-coordinated by six carboxylate oxygen atoms and two oxygen atoms from pyr molecules. The Ca–O bond lengths are in the region 2.307(3)–2.609(4) Å. Each calcium atom connects four bdc ligands and vice versa. As a result, a three-dimensional framework with rhombus-like channels of  $8.8 \times 11.3 \text{ \AA}^2$  is created (Fig. 2a). The pyr molecules reside in the “free voids” and attach to the pore walls, which occupy 43.7% of the unit cell volume. The presence of inorganic chains of  $\text{CaO}_8$  polyhedra in the framework is noteworthy (Fig. 2b). By regarding calcium atom and bdc ligands as 4-connected nodes, the calcium carboxylate framework has a lvt-b topology, as shown in Fig. 2c.

Colorless bulk crystals of compound **3** were obtained by heating a mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 1,4- $\text{H}_2\text{bdc}$ , and nmp at  $150 \text{ }^\circ\text{C}$  for 5 days (83% yield based on calcium). The compound crystallizes in the monoclinic space group  $C2/c$  (no. 15). The asymmetric unit contains two crystallographically independent calcium atoms. The Ca(1) atom shows a distorted octahedral geometry coordinated by six carboxylate oxygen atoms. The Ca(2) atom is seven-coordinated by six carboxylate oxygen atoms and one oxygen atom from the coordinated nmp molecule. The Ca–O bond lengths range from 2.273(2) to 2.531(2) Å. The  $\text{CaO}_6$  octahedra and  $\text{CaO}_7$  pentagonal bipyramids share their edges to create rod-like building blocks, which are further connected by organic linkers to form a three-dimensional structure with rhombus-like channels (Fig. 3a, b). The pore size of the cross sections of the channels is about  $10.1 \text{ \AA} \times 18.1 \text{ \AA}$ . The nmp molecules attach to the pore walls, which occupy 40.4% of the unit cell volume. An alternative way to view the framework structure involves in cluster-like  $\text{Ca}_3(\text{CO}_2)_6$  building blocks (Fig. 3c). Each  $\text{Ca}_3(\text{CO}_2)_6$  cluster makes six connections to adjacent such building blocks, forming a pcu topology (Fig. 3d).



**Fig. 2.** (a) A view of the framework structure of **2** with rhombus-like channels. (b) A view of the inorganic chain constructed from  $\text{CaO}_8$  polyhedra. (c) Compound **2** has a 4-connected lvt-b topology. Solvent molecules are omitted for clarity.

Colorless bulk crystals of compound **4** were obtained by heating a mixture of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 1,4- $\text{H}_2\text{bdc}$ , and dmi at  $150 \text{ }^\circ\text{C}$  for 5 days (45% yield based on calcium). The compound crystallizes in the orthorhombic space group  $Pbcn$  (no. 60). Its layered structure is constructed from the cluster-like  $\text{Ca}_3(\text{CO}_2)_6$  SBUs, as shown in Fig. 4a. The Ca–O bond lengths range from 2.305(2) to 2.530(2) Å. Each  $\text{Ca}_3(\text{CO}_2)_6$  cluster connects four such SBUs through six bdc ligands, leading to the formation of a layered structure (Fig. 4b and c). The thickness of the layered structure is ca. 7.0 Å. One structural feature of the layered structure is the co-existence of single and double organic bridges between  $\text{Ca}_3(\text{CO}_2)_6$  clusters. By regarding  $\text{Ca}_3(\text{CO}_2)_6$  clusters as the nodes, the structure of **1** can be understood as a 4-connected framework with a



**Fig. 3.** (a) A view of the inorganic chain constructed from  $\text{CaO}_6$  and  $\text{CaO}_7$  polyhedra. (b) A view of the framework structure of **3** with rhombus-like channels. (c) The  $\text{Ca}_3(\text{CO}_2)_6$  cluster in the structure of **3**. (d) Compound **3** has a pcu topology by regarding  $\text{Ca}_3(\text{CO}_2)_6$  cluster as the building block. The solvent molecules are omitted for clarity.

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