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Alkaline earth metal–organic frameworks supported by ditopic carboxylates

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Hydrothermal reactions of alkaline earth metal nitrates with two ditopic carboxylic acids, *trans*-1,4-cyclohexanedicarboxylic acid (H₂CDC) and 1,4-phenylenedipropionic acid (H₂PDP), generate two 3-D metal–organic frameworks (MOFs) with empirical formulas [Ca(CDC)(H₂O)₂]·H₂O (**1**) and [Sr(PDP)(H₂O)] (**2**), respectively. Compound **1** consists of Ca–COO–H₂O chains cross-linked through the –C₆H₁₀– spacers of the CDC anions, showing slightly open 1-D channels along the crystallographic *c* axis that accommodate the guest water molecules. Compound **2** exhibits a MOF consisting of wavy 2-D Sr–COO–H₂O nets linked by –CH₂CH₂C₆H₄CH₂CH₂– tethers, and the condensed structure appears to arise from conformational flexibility of the ligand spacer.

Keywords: Calcium complexes; Strontium complexes; Coordination polymers; Metal–organic frameworks

1. Introduction

Metal–organic frameworks (MOFs) have attracted intense interest owing to novel and diverse supramolecular architectures, as well as potential applications as porous materials for gas storage and separation as well as size- and shape-selective catalysis [1–9]. Although the majority of MOFs involve d-block and lanthanide metal ions as nodes to bind organic linkers, there have appeared in the literature an increasing number of MOFs centered on main group metal ions, and examples for Li(I), M(II) (M = Mg, Ca, Sr, Ba), and Al(III) can be found [10–17]. Not only does the use of main group metal ions lead to distinct MOF structures, the incorporation of such lightweight metals as Li(I) and Ca(II) in place of heavier d-block and lanthanide metals also reduces the densities of the resulting MOFs, thereby increasing gas adsorption capacity per unit mass. Reported alkaline earth MOFs are generally supported by rigid aromatic ring ligands, such as 2,6-benzenedicarboxylate and 2,6-naphthalenedicarboxylate.

We have utilized less rigid multicarboxylate ligands to construct MOFs centered on d-block and lanthanide metal ions, which include saturated ring carboxylates

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(e.g. 1,3,5-cyclohexanetricarboxylate) and kinked flexible carboxylates (e.g. 1,4-phenylene-diacetate) [18–21]. We have more recently extended this investigation into the s-block, noticing that there has been no prior report of exploring such ligands in supporting s-MOFs. In this work, we employ two such ligands in hydrothermal reactions with alkaline earth metal nitrates, which generate two 3-D MOFs with empirical formulas $[\text{Ca}(\text{CDC})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Sr}(\text{PDP})(\text{H}_2\text{O})]$ (**2**), where CDC = *trans*-1,4-cyclohexanedicarboxylate and PDP = 1,4-phenylenedipropionate.

2. Experimental

2.1. Materials and methods

Reagent-grade *trans*-1,4-cyclohexanedicarboxylic acid (H_2CDC), 1,4-phenylenedipropionic acid (H_2PDP), triethylamine (TEA), and calcium and strontium nitrates were purchased from commercial suppliers and used without purification. Infrared spectra (IR) were recorded on a Thermo–Nicolet Avatar 360 FTIR spectrometer from neat solids placed on the diamond window of a horizontal attenuated total reflectance accessory. Thermogravimetric (TG) analyzes were performed under a flow of N_2 gas at a scan rate of $5^\circ\text{C}/\text{min}$ using a TGA-Q50 system.

2.2. Syntheses of $[\text{Ca}(\text{CDC})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Sr}(\text{PDP})(\text{H}_2\text{O})]$ (**2**)

Identical procedures were employed to prepare the two compounds; the procedure for **1** is described here in detail. To a Teflon-lined Parr bomb containing 5 mL of deionized water was added $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ (0.106 g, 0.45 mmol), H_2CDC (0.052 g, 0.25 mmol), and TEA (167 μL , 1.2 mmol). The bomb was sealed, heated at 160°C for 3 days, and then allowed to cool to room temperature. Colorless crystals were isolated by decanting the supernatant, washed thoroughly with deionized water, and air-dried to give 0.031 g of product (47%). Main IR absorption bands (cm^{-1}): 3506 (br), 3416 (br), 2929 (w), 1534 (s), 1444 (s), 1423 (s), 1366 (m), 1330 (m), 1285 (s), 1215 (m), 1050 (w), 975 (w), 935 (m), 890 (w), 860 (w), 800 (m), 785 (m), 690 (s).

Compound **2** was prepared analogously using a mixture of $\text{Sr}(\text{NO}_3)_2$ (0.095 g, 0.45 mmol), H_2PDP (0.056 g, 0.25 mmol), and TEA (167 μL , 1.2 mmol). Colorless crystals were isolated (0.045 g, 55%). Main IR absorption bands (cm^{-1}): 3500 (br), 3050 (br), 2945 (w), 2917 (w), 1543(s), 1441 (s), 1421 (s), 1338 (m), 1240 (m), 1028 (w), 940 (w), 860 (m), 826 (s), 679 (s).

2.3. Thermal analyzes

A TG analysis performed on a sample of **1** showed continuous weight decrease (20.51%) between 50 and 210°C , which corresponded to loss of three water molecules per formula unit (Calcd 20.45%). There was no further weight loss up to 455°C , at which point the sample began to decompose with a large weight loss (38.06%) recorded at 535°C . Further decomposition began at 574°C with a significant weight loss (16.82%) recorded at 680°C . A TG analysis performed on a sample of **2** showed a continuous weight decrease (5.61%)

Table 1. Crystal data and structure refinement.

Empirical formula	C ₈ H ₁₆ O ₇ Ca (1)	C ₁₂ H ₁₄ O ₅ Sr (2)
Formula weight	264.29	325.85
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P2(1)/c</i>	<i>Pca2₁</i>
<i>a</i> (Å)	7.8623(16)	11.770(2)
<i>b</i> (Å)	18.323(4)	14.540(3)
<i>c</i> (Å)	7.7159(15)	7.1924(14)
β (°)	95.70(3)	90
<i>V</i> (Å ³)	1106.1(4)	1230.9(4)
<i>Z</i>	4	4
<i>T</i> (K)	293(2)	293(2)
Wavelength (Å)	0.710747	0.710747
<i>d</i> _{calcd} (g/cm ³)	1.587	1.758
μ (mm ⁻¹)	0.586	4.390
Independent reflections	2430 [<i>R</i> _{int} = 0.0294]	2238 [<i>R</i> _{int} = 0.0698]
Data/restraints/parameters	2430/0/170	2238/4/172
Final <i>R</i> indices ^a [<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> ₁	0.0333	0.0363
<i>wR</i> ₂	0.0822	0.0963
<i>R</i> indices (all data)		
<i>R</i> ₁	0.0349	0.0371
<i>wR</i> ₂	0.0845	0.0970
Largest peak and hole (e Å ⁻³)	0.362 and -0.255	0.581 and -0.981

$$^a R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}; wR_2 = \frac{[\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}}{}$$

between 148 and 200 °C, which corresponded to loss of one water per formula unit (Calcd 5.53%). There was no further weight loss up to 446 °C, at which point the sample began to decompose continuously, with a large weight loss (29.62%) recorded at 556 °C.

2.4. X-ray crystallography

Intensity data for **1** and **2** were collected at 293 K on a Rigaku Saturn724 diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the ω -scan technique. The structures were solved by direct methods and subsequent difference Fourier syntheses and were refined using the SHELXTL software package [22,23]. All non-hydrogen atoms were refined anisotropically. Hydrogens of water were located from the Fourier maps, and all other hydrogens were added in calculated positions. The crystallographic data for the two compounds are summarized in table 1.

3. Results and discussion

3.1. Syntheses

Compounds **1** and **2** have been synthesized from hydrothermal reactions of Ca (NO₃)₂/H₂CDC/TEA and Sr(NO₃)₂/H₂PDP/TEA mixtures, respectively. The soluble base TEA promotes deprotonation of the carboxylic acids, affording the strongly ligating carboxylates. These crystalline solids, as expected of MOFs, do not dissolve in water or common organic solvents such as acetone and ethanol. The IR spectra of the two compounds indicate formation of MOFs, with two strong absorption bands around 1540

and 1420 cm^{-1} that are diagnostic of the asymmetrical and symmetrical stretches of coordinated carboxylates [24]. The disappearance of the strong carboxyl absorption bands at 1684 cm^{-1} for H_2CDC and at 1702 cm^{-1} for H_2PDP shows complete deprotonation of the acids.

3.2. X-ray crystal structures

As revealed by single-crystal X-ray diffraction, **1** crystallizes in the monoclinic $P2_1/n$ space group and the asymmetric unit contains one Ca(II), two half-CDC anions, two coordinated waters, and one guest water. Ca(II) is coordinated by eight oxygens, six from four carboxylates of different CDC units, and two from waters (O5 and O6) (figure 1). Two of the carboxylate groups ligate bidentate and the other two in a bis-monodentate form. The Ca(II) coordination geometry in **1** is that of a distorted dodecahedron, a common structure

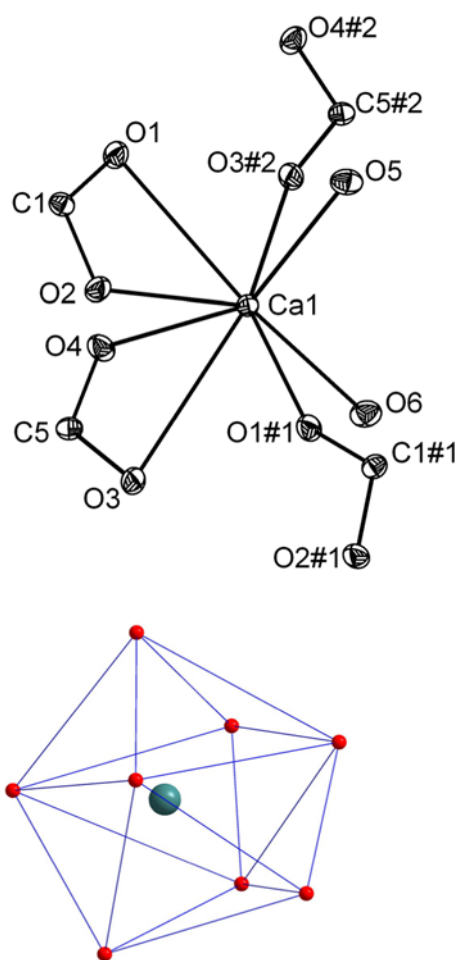


Figure 1. An ORTEP diagram with thermal ellipsoids at 50% probability showing the Ca(II) coordination environment in **1** (top) and a representation for the dodecahedral coordination geometry of Ca(II) (bottom). Symmetry transformations used to generate equivalent atoms: #1, $x, -y+1/2, z-1/2$; #2, $x, -y+1/2, z+1/2$.

for eight-coordinate metal ions. Ca–O bond distances range from 2.3254(13) to 2.6315(13) Å, comparable with those reported for Ca–O (carboxylate) and Ca–O (aqua) bonds in other eight-coordinate calcium coordination polymers [14,25,26]. Selected bond distances are presented in table 2.

The network structure of **1** can be viewed as follows. Ca(H₂O)₂ moieties are interconnected through two bridging COO ligands, forming an infinite Ca(H₂O)₂–(OOC)₂ chain that extends along the crystallographic *a*-axis (figure 2(a)). Within the chain, each Ca(II) acts as a node joining four COO groups and each COO ligand bridges two adjacent Ca(II) ions in tridentate coordination. There are two classes of intra-chain hydrogen bonds between coordinated water and COO oxygens, as indicated, respectively, by blue and black dashed lines in figure 2a, and the donor (aqua O)···acceptor (carboxylate O) distances are 2.8181 Å for O5···O2 (blue) and 2.7440 Å for O6···O4 (black). A representation of the 1-D chain highlighting the Ca(II) coordination polyhedra is also shown (figure 2b).

These infinite 1-D chains constitute supramolecular secondary building units (SBUs), which are cross-linked via –C₆H₁₀– tethers of the CDC anions, affording a 3-D MOF (figure 3). Note that we and others have previously put forth the concept of supramolecular infinite SBUs [20,27]. As shown in figure 3, the MOF of **1** contains lozenge-shaped channels running along the *c* axis, where the guest water molecules reside. Furthermore, the guest water is engaged in a total of four hydrogen-bonding interactions with the host network: two of them with coordinated water and another two with carboxylate oxygens (O2 and O4). A space-filling model analysis of **1** shows the 3-D MOF with slightly open channels, and a PLATON calculation reveals that the void space accessible by guest water accounts for 3.8% of the crystal volume [28].

Compound **2** crystallizes in the orthorhombic space group *Pca*2₁ and the asymmetric unit contains one Sr(II), one PDP anion, and one coordinated water. The Sr(II) is eight-coordinate to six carboxylate oxygens and two waters with a distorted dodecahedron geometry (figure 4). The Sr–O bond distances range from 2.491(3) to 2.721(3) Å, slightly longer than the Ca–O bond distances in **1**, consistent with Sr being located below Ca in group 2A. In addition, the Sr–O coordination bonds are comparable in length with those reported for other eight-coordinate strontium frameworks [14,29]. Selected bond distances are presented in table 2.

It should be noted that PDP, as indicated by OOC(9)C(8)H₂C(7)H₂C₆H₄C(10)H₂C(11)H₂C(12)OO, adopts a non-centrosymmetric conformation with a C(8)–C(7)···C(10)–C(11) torsion angle of –97.19°. This factor, along with the local Sr(II) coordination environment and the extended framework structure, accounts for the non-centrosymmetric space group for **2**. Specifically, the interconnection of the distorted SrO₈ dodecahedra about a 2₁ screw

Table 2. Selected bond lengths [Å].

<i>Compound 1</i>			
Ca1–O1	2.5219(13)	Ca1–O2	2.5301(13)
Ca1–O3	2.6315(13)	Ca1–O4	2.4802(13)
Ca1–O5(aqua)	2.4265(14)	Ca1–O6(aqua)	2.4280(14)
Ca1–O1#1	2.3254(13)	Ca1–O3#2	2.3298(13)
<i>Compound 2</i>			
Sr1–O1	2.497(3)	Sr1–O2#2	2.576(3)
Sr1–O2#3	2.578(3)	Sr1–O3#1	2.491(3)
Sr1–O3#4	2.721(3)	Sr1–O4#4	2.602(3)
Sr1–O5	2.639(3)	Sr1–O5#5	2.674(3)

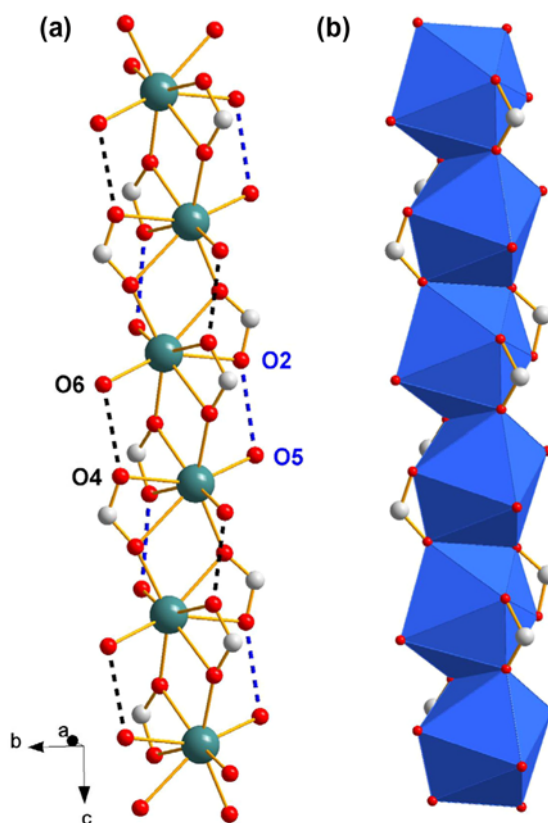


Figure 2. (a) A ball-and-stick representation of the 1-D $\text{Ca}(\text{H}_2\text{O})_2-(\text{OOC})_2$ chain showing interconnections between calcium ions, as well as intra-chain hydrogen bonds (dashed lines). (b) A representation highlighting calcium coordination polyhedra. Hydrogens are omitted for clarity. Color scheme (here and hereafter): Ca, teal; O, red; C, gray.

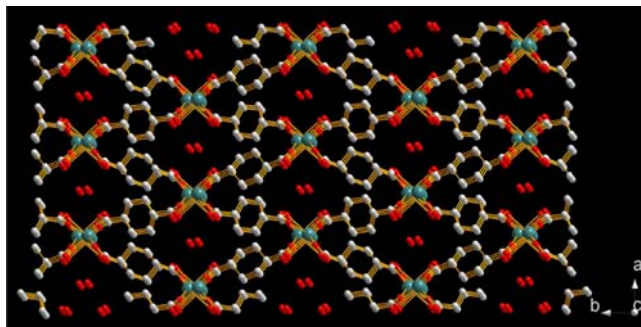


Figure 3. A ball-and-stick representation of the 3-D MOF structure of 1. Hydrogens are omitted for clarity.

axis forms a helix along the c direction that also contains the C(12)OO carbon, and adjacent helices are interconnected through the C(9)OO carbon along the a -axis, forming a layer that expands approximately in the crystallographic ac plane (figure 5). These 2-D

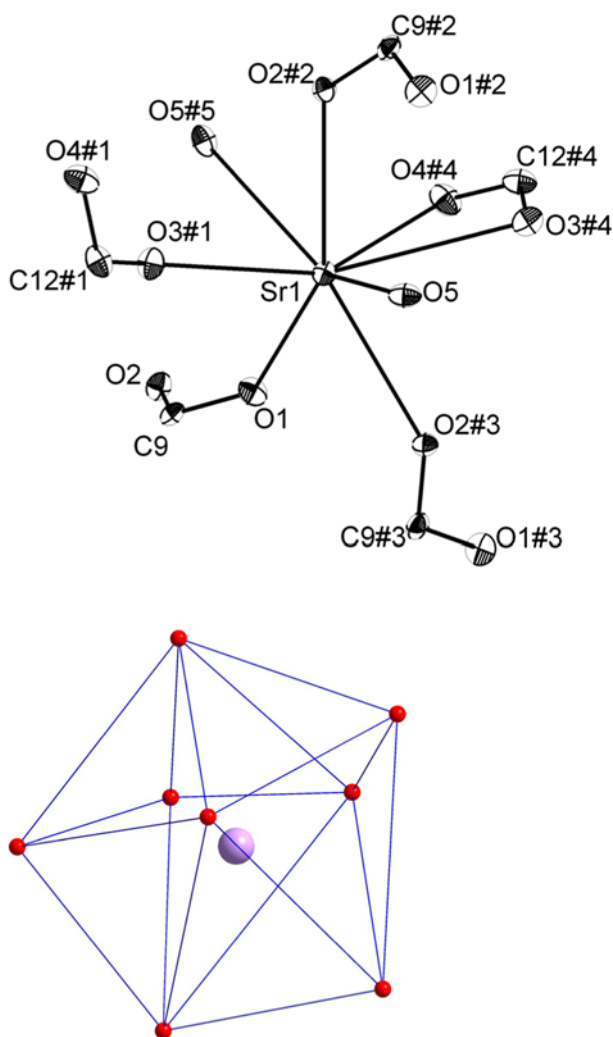


Figure 4. An ORTEP diagram with thermal ellipsoids at 50% probability showing the Sr(II) coordination environment in **2** (top), and a representation for the dodecahedral coordination geometry of Sr(II) (bottom). Symmetry transformations used to generate equivalent atoms: #1, $x-1/2, -y+1, z$; #2, $x-1/2, -y, z$; #3, $-x+1/2, y, z-1/2$; #4, $-x+1/2, y-1, z-1/2$; #5, $-x, -y, z+1/2$.

layers, which spread out undulatingly as viewed along the crystallographic b -axis, are further cross-linked by non-centrosymmetric $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2-$ tethers in an AA sequence, affording a 3-D network solid of non-centrosymmetry (figure 6).

A space-filling model analysis of the 3-D MOF of **2** shows no sufficiently large void to include guest species, which explains why **2** contains only coordinated water and no guest water, and this is corroborated by a PLATON calculation indicating that **2** has no solvent-accessible void space. Compared with **1**, **2** has a more condensed structure, which we attribute to the more flexible $-\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2-$ tether that holds atoms closer to one another, leaving little empty space in the channels.

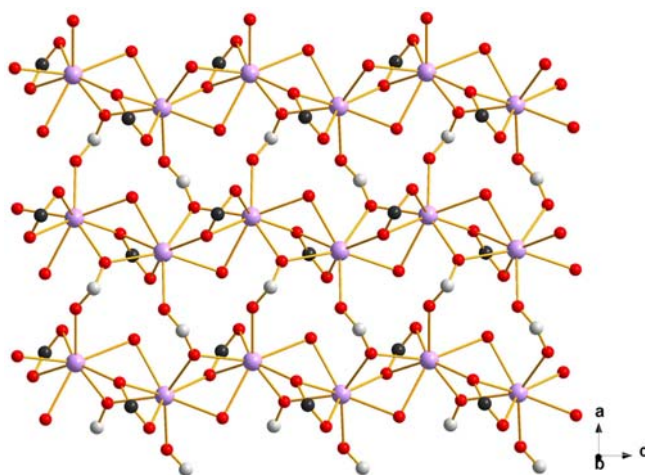


Figure 5. A ball-and-stick representation of the 2-D layer in **2** viewed along the crystallographic *b* axis. Hydrogens are omitted for clarity. Color scheme (here and hereafter): Sr, lavender; O, red; C9, gray-25%; C12, gray-80%.

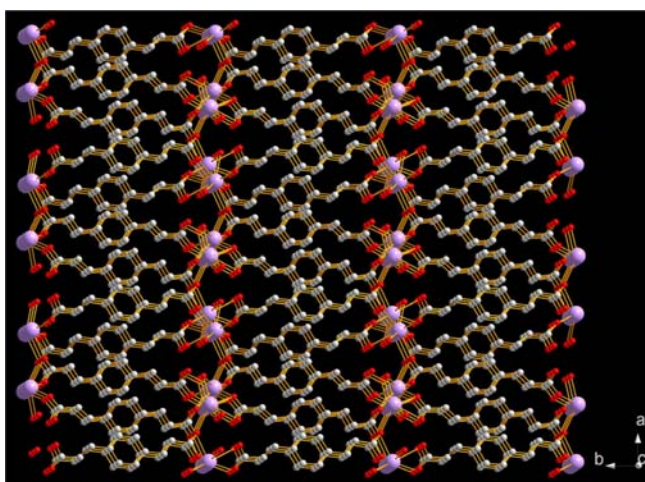


Figure 6. A ball-and-stick representation of the 3-D MOF structure of **2**. Hydrogens are omitted for clarity.

4. Conclusions

We have synthesized via hydrothermolysis $[\text{Ca}(\text{CDC})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Sr}(\text{PDP})(\text{H}_2\text{O})]$ (**2**), two new alkaline earth metal–organic coordination polymers. The MOFs of both compounds contain supramolecular SBUs that are interconnected through organic spacers to form infinite 3-D networks. Compound **1** has a slightly open framework and represents an example of a 3-D calcium–organic framework. Compound **2** is a condensed 3-D MOF, apparently due to the more flexible organic ligand. This work adds to the growing number of main group MOFs in general and calcium and strontium coordination polymers in particular, and it is useful to make some comparisons of the structural features of **1** and **2**

with those of the previously reported calcium- and strontium-organic frameworks [14,25,26,29,30–33]. In all of these structures, the Ca(II) and Sr(II) ions exhibit high coordination numbers (seven or larger), binding to hard donors like oxygen and forming infinite chains of calcium and strontium polyhedra. In addition, these MOFs generally show condensed or only slightly open frameworks without much void space accessible by solvent and other guest molecules. Prior to this work, the known calcium and strontium coordination polymers are generally linked by structurally rigid organic ligands, whereas **1** and **2** are supported by more flexible carboxylates. While the rigid ligands have led to 1-D, 2-D, and 3-D calcium and strontium coordination frameworks, the kinked flexible linkers in **1** and **2** favor high framework dimensionality, as seen in the 3-D networks of both compounds. The ligand structures also result in lozenge-shaped channels in **1** and undulating layers in **2**.

There remains the objective to create significantly porous calcium and strontium coordination polymers, which could be accomplished by the judicious choice of organic linkers and ancillary ligands. Currently, we are working toward this goal by investigating other ditopic carboxylates in MOF-generating reactions with calcium and strontium salts.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 822883 (**1**) and 822884 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223336033; Email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/data_request/cif).

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