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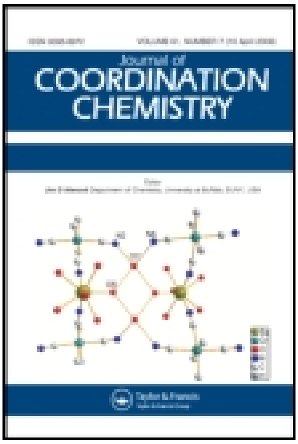

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Synthesis and characterization of calcium(II) coordination polymers based on phenylacetic acid§

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The syntheses, crystal structures, and thermal properties of the coordination polymers $[Ca(H_2O)_2(L_1)_2]\cdot H_2O$ (**1**) ($L_1 =$ 4-methoxyphenylacetate) and $[Ca(H_2O)_2(L_2)_2]\cdot 2H_2O$ (**2**) ($L_2 =$ 2-chlorophenylacetate) are described. **1** and **2** can be dehydrated to the anhydrous $[Ca(L_1)_2]$ (**1a**) or $[Ca(L_2)_2]$ (**2a**), respectively. Compounds **1** and **2** crystallize in the non-centrosymmetric monoclinic space group $P2_1$ and the structures consist of a central Ca(II), two terminal waters, and two crystallographically unique L_1 (or L_2) anions, one of which functions as a chelating bidentate ligand. The second independent L_1 (or L_2) is tetradentate, coordinated in a μ_3-bridging mode leading to the formation of a 1-D coordination polymer. In the infinite chain extending along the *b*-axis, each Ca(II) is eight-coordinate and bonded to two terminal waters and six oxygens from four different L_1 or L_2 ligands.

Keywords: Coordination polymer; Calcium; 4-Methoxyphenylacetate; 2-Chlorophenylacetate

1. Introduction

Coordination polymers (CPs), also known as metal organic frameworks (MOFs), have attracted attention because of their topology and applications in catalysis, adsorption (gas storage), separation, and luminescence [1–3]. Compared to the extensive chemistry of CPs based on transition metals, the coordination chemistry of group 1 and 2 metals with organic linkers is less explored. The reluctance in using alkaline earth cations as building blocks for open framework materials can be attributed to their unpredictable coordination numbers and geometries, as no ligand field stabilization governs their bonding. Although closed shell s-block metal cations lack useful properties like magnetism or variable oxidation states, alkali and alkaline-earth metals are preferred to transition or lanthanide metal ions because many of the s-block cations have the advantage of being non-toxic, cheap, and soluble in aqueous media. The growing interest in coordination chemistry of s-block elements can be evidenced by several

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§Dedicated to Prof. Dr M. S. Wadia on the occasion of his 74th Birthday.

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recent reports [4–16]. In a recent manuscript, Fromm [17] reviewed the different ligand and polymer types of s-block compounds.

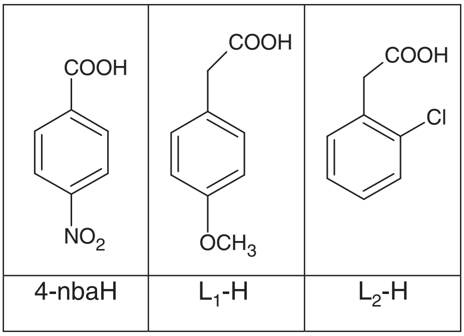
Depending on electronic and steric requirements of the central metal, flexibility, binding modes, and hydrogen-bonding characteristics of the organic ligand, CPs of differing dimensionalities can be constructed. For oxophilic s-block metals, carboxylic acids are useful linkers as the metals can be linked into an extended chain with bridging of the carboxylate. In view of their known affinity for oxygen donors, especially water, s-block metal carboxylates are normally synthesized in aqueous medium by reactions between alkaline earth metal sources and aromatic carboxylic acids under ambient conditions [18–36]. Many groups employ hydrothermal reactions of metal sources with carboxylic acids for compound synthesis [4–13].

As part of our longstanding research interest in the chemistry of alkaline earth carboxylates [32] we have investigated the reactions of alkaline earth metal carbonates with 4-nitrobenzoic acid (4-nbaH) [33–35], 2-nitrobenzoic acid (2-nbaH) [15, 16], and 2-carbamoyl-4-nitrobenzoic acid [36, 37] in aqueous media and have prepared several 1-D CPs [13–16, 34–36]. In this study, we have investigated the reactions of $CaCO_3$ with 4-methoxyphenylacetic acid (L_1-H) and 2-chlorophenylacetic acid (L_2-H) (scheme 1) and have synthesized two new non-centrosymmetric Ca(II) CPs. The carboxylic acid functionality in phenylacetic acid is more flexible than nitrobenzoic acids where the −COOH group is linked to a rigid six-membered ring.

2. Experimental

2.1. *Materials and methods*

All chemicals used in this study were reagent grade and used as received. The starting materials and reaction products are air stable and hence were prepared under normal laboratory conditions. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000 to 400 cm^{-1}. Diffuse-reflectance spectra were recorded on a Shimadzu UV-2450 double beam spectrophotometer using $BaSO_4$ as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk function ($a/S = (1 - R)^2/2R$, where a is the absorption coefficient, R the reflectance, and S the scattering coefficient).



Scheme 1. Nomenclature of ligands relevant to this study.

TG-DTA studies were performed in flowing air in Al_2O_3 crucibles on a STA-409PC simultaneous thermal analyzer from Netzsch. A heating rate of $10\,K\,min^{-1}$ was employed for all measurements. Isothermal weight loss studies were performed in an electric furnace. BET surface area of freshly prepared anhydrous compounds **1a** and **1b** was measured using micromeritics surface area and porosimetry analyzer (Tristar 3000, Norcross, GA) and N_2 gas as adsorbate. X-ray powder patterns were recorded on a Rigaku Miniflex II powder diffractometer using Cu-Kα radiation with a Ni-filter.

2.2. *Preparation of* $[Ca(H_2O)_2(L_1)_2]\cdot H_2O$ (**1**) *and* $[Ca(H_2O)_2(L_2)_2]\cdot 2H_2O$ (**2**)

To a slurry of $CaCO_3$ (0.500 g, 5 mmol) in water (50 mL) was added L_1-H (1.66 g, 10 mmol) and the reaction mixture was heated on a water bath. The insoluble $CaCO_3$ slowly dissolved accompanied by brisk effervescence. Heating was stopped when effervescence ceased resulting in the formation of an almost clear solution. The hot reaction mixture was filtered and left undisturbed for 6–7 days to obtain colorless crystalline needles of **1** in 84% yield; these were filtered, washed with water followed by ether, and dried in air. Use of L_2-H (1.7 g, 10 mmol) in the above reaction instead of L_1-H resulted in the formation of **2** in 70% yield.

Anal. Calcd for $CaC_{18}H_{24}O_9$ (424.46) **1** (%): Ca, 9.44; C, 50.93; H, 5.70; CaO, 13.19. Found (%): Ca, 9.4; C, 50.92; H, 5.79; CaO, 13.28. IR data: 3610 ν(–OH), 3427, 3001, 2961, 2928, 2838, 2050, 1612, 1567 ν_{as}(–COO), 1546, 1512, 1444, 1416, 1401 ν_s(–COO), 1287, 1250 ν_{as}(–COC–), 1201, 1177, 1153, 1105, 1036, 950, 926, 824, 790, 736, 696, 627, 600, 543 cm^{-1}. DTA (in °C): 116 (endo), 375 (exo), 492 (exo).

Anal. Calcd for $CaC_{16}H_{20}Cl_2O_8$ (451.31) **2** (%): Ca, 8.88; C, 42.58; H, 4.47; CaO, 12.42. Found (%): Ca, 8.5; C, 42.5; H, 4.40; CaO, 12.3. IR data: 3636 ν(–OH), 3326, 3062, 1618, 1556 ν_{as}(–COO), 1500, 1452, 1431, 1402 ν_s(–COO), 1292, 1146, 1076, 1031, 939, 842, 733, 706, 695, 659 cm^{-1}. DTA (in °C): 121 (endo), 318 (exo), 588 (exo).

2.3. *Dehydration and rehydration studies*

A powdered sample (0.500 g) of **1** or **2** was heated at 130°C for 15 min. The observed mass losses of 12.65% (for **1**) and 15.57% (for **2**) are in good agreement with the expected values for the formation of the anhydrous compounds $[Ca(L_1)_2]$ **1a** or $[Ca(L_2)_2]$ **2a**.

Anal. Calcd for $CaC_{18}H_{18}O_6$ (370.41) **1a** (%): CaO, 15.14. Found (%): CaO, 15.02. IR data: 3000, 2953, 2934, 2910, 2833, 1551 ν_{as}(–COO), 1512, 1429, 1406 ν_s(–COO), 1300, 1279, 1248, 1177, 1105, 1036, 947, 818, 799, 729, 696 cm^{-1}.

Anal. Calcd for $CaC_{16}H_{12}Cl_2O_4$ (379.25) **2a** (%): CaO, 14.79. Found (%): CaO, 14.63%. IR data: 3066, 1566, 1556 ν_{as}(–COO), 1474, 1425, 1396 ν_s(–COO), 1302, 1269, 1177, 1122, 1053, 1040, 934, 843, 743, 687, 619, 577 cm^{-1}.

2.4. *X-ray crystal structure determination*

Intensity data for **1** and **2** were collected on a Bruker Smart Apex charged coupled device (CCD) diffractometer using graphite-monochromated Mo-Kα radiation.

Table 1. Selected refinement data for $[Ca(H_2O)_2(L_1)_2] \cdot H_2O$ (**1**) and $[Ca(H_2O)_2(L_2)_2] \cdot 2H_2O$ (**2**).

Empirical formula	$[Ca(H_2O)_2(L_1)_2] \cdot H_2O$	$[Ca(H_2O)_2(L_2)_2] \cdot 2H_2O$
Formula weight ($g\,mol^{-1}$)	424.45	451.30
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
Unit cell dimensions (Å, °)		
a	9.568(2)	11.669(3)
b	6.6381(16)	6.6737(18)
c	16.165(4)	13.508(4)
β	99.196(4)	105.295(5)
Volume (Å^3), Z	1013.5(4), 2	1014.7(5), 2
Calculated density ($Mg\,m^{-3}$)	1.391	1.477
Absorption coefficient (mm^{-1})	0.356	0.612
$F(000)$	448	468
θ range for data collection (°)	2.16–28.33	2.69–28.49
Limiting indices	$-8 \le h \le 12$; $-8 \le k \le 8$; $-21 \le l \le 21$	$-15 \le h \le 13$; $-8 \le k \le 8$; $-17 \le l \le 15$
Reflections collected	6663	6740
Independent reflections	4544 [R(int) = 0.0447]	4597 [R(int) = 0.0312]
Completeness to θ (%)	98.3	97.4
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4544/1/248	4597/1/244
Goodness-of-fit on F^2	1.103	1.117
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0711$, $wR_2 = 0.1840$	$R_1 = 0.0501$, $wR_2 = 0.1140$
R indices (all data)	$R_1 = 0.0989$, $wR_2 = 0.2385$	$R_1 = 0.0763$, $wR_2 = 0.1516$
Flack X parameter	0.00(14)	−0.03(6)
Largest difference peak and hole (e Å^{-3})	0.799 and −0.647	0.389 and −0.490

Data integration and reduction were processed with SAINT software [38]. An empirical absorption correction was applied to the collected reflections with the Siemens Area Detector Absorption (SADABS) [38]. Structures were solved with direct methods using SHELXS-97 [39] and refinement was done against F^2 using SHELXL-97 [39]. All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens were introduced in calculated positions and included in the refinement riding on their respective parent atoms. Hydrogen attached to O21 in **1** and an H-atom attached to O22 in **2** could not be located. All other hydrogens of the coordinated and lattice waters were located in the difference Fourier map but were positioned with idealized geometry and refined using a riding model. Selected crystal refinement results for **1** and **2** are summarized in table 1.

3. Results and discussion

3.1. *Synthesis, spectra, and thermal investigations*

In earlier work we demonstrated that crystalline hydrates of metal carboxylates can be prepared in good yields under ambient conditions, by an aqueous reaction of alkaline earth metal carbonate with aromatic carboxylic acids. The generality of this reaction for the preparation of hydrated alkaline earth metal carboxylates can be evidenced by the synthesis of several such compounds [15, 16, 32–37]. In the present work, the same methodology has been employed for the synthesis of **1** and **2**. Thus the aqueous reaction of $CaCO_3$ with the substituted phenylacetic acid L_1-H (or L_2-H) resulted in the formation of **1** (or **2**) in good yield. Compounds **1** and **2** were also prepared in a two-step reaction. In the first step the sodium salt of L_1-**H** or L_2-**H** was generated *in situ* by the reaction of the acids with $NaHCO_3$. In the second step the aqueous solution of the Na-salt was reacted with $CaCl_2$ and the title compounds were then crystallized from the reaction mixture. Both **1** and **2** can be dehydrated to the corresponding anhydrous compounds **1a** or **2a** by heating at 130°C. On reaction with dilute HCl, **1**, **1a**, **2**, and **2a** decompose resulting in the separation of the insoluble L_1-**H** or L_2-**H**. Analytical and thermal data show that **1** and **2** which are differently hydrated contain Ca : carboxylate in a 1 : 2 mole ratio. The X-ray powder diffractograms (figure S1) reveal the crystalline nature of **1** and **2**, and the anhydrous compounds **1a** and **2a**. A comparison of the powder pattern of **1** and **1a** or **2** and **2a** clearly indicates that dehydration of **1** or **2** leads to changes in structure as evidenced by the appearance of new peaks in the diffractogram of the anhydrous compound. On pyrolysis at 800°C, **1** and **2** are converted into calcium oxide as shown by X-ray powder pattern (figure S1). Compound **1** (or **2**) was characterized as a 1-D CP based on single crystal X-ray work. It has been reported [6–10] that use of di or tricarboxylic acids and/or hydrothermal reactions result in the formation of CPs of higher dimensionality, unlike the 1-D polymers obtained in the present work.

Diffuse reflectance spectra of the title compounds are nearly identical to that of the corresponding free acid and the signals at 265 nm can be assigned to intraligand charge transfer of the organic acid. IR spectra of **1** or **2** (figure S2) exhibit several signals in the mid-IR region, indicating the presence of the organic moiety. The intense band at 3610 (in **1**) and 3636 cm^{-1} (in **2**) can be assigned as O–H stretch of water; this signal is not observed in anhydrous **1a** or **2a**. Characteristic signals due to the symmetric and asymmetric stretching of the carboxylate are observed at 1567 and 1401 cm^{-1} (in **1**) and 1556 and 1402 cm^{-1} (in **2**). The N_2 adsorption–desorption isotherms of the anhydrous compounds **1a** or **2a** show very little uptake of N_2, suggesting non-porous nature of **1** and **2**. On heating to 800°C, **1** or **2** can be decomposed to the binary oxide as evidenced by weight loss and the featureless IR spectra of the residues. The thermal profiles of **1** and **2** which exhibit an initial endothermic event at 116 and 121°C, respectively, assignable for the loss of coordinated and lattice water followed by exothermic events at higher temperatures (figure S3) due to the decomposition of the organic linker are in accord with the isothermal weight loss studies.

3.2. *Crystal structure description of* $[Ca(H_2O)_2(L_1)_2]\cdot H_2O$ *(1) and* $[Ca(H_2O)_2(L_2)_2]\cdot 2H_2O$ *(2)*

The polymeric compounds **1** and **2** crystallize in the chiral non-centrosymmetric monoclinic space group $P2_1$ with all atoms situated in general positions. The structures of **1** and **2** consist of a central Ca(II), two terminal waters, and two crystallographically unique (L_1) or (L_2) ligands (figure 1), one of which functions as a chelating bidentate ligand. The second independent L_1 (or L_2) is a tetradentate μ_3-bridging ligand. The geometric parameters of the organic ligands are in the normal range. Compounds **1** and

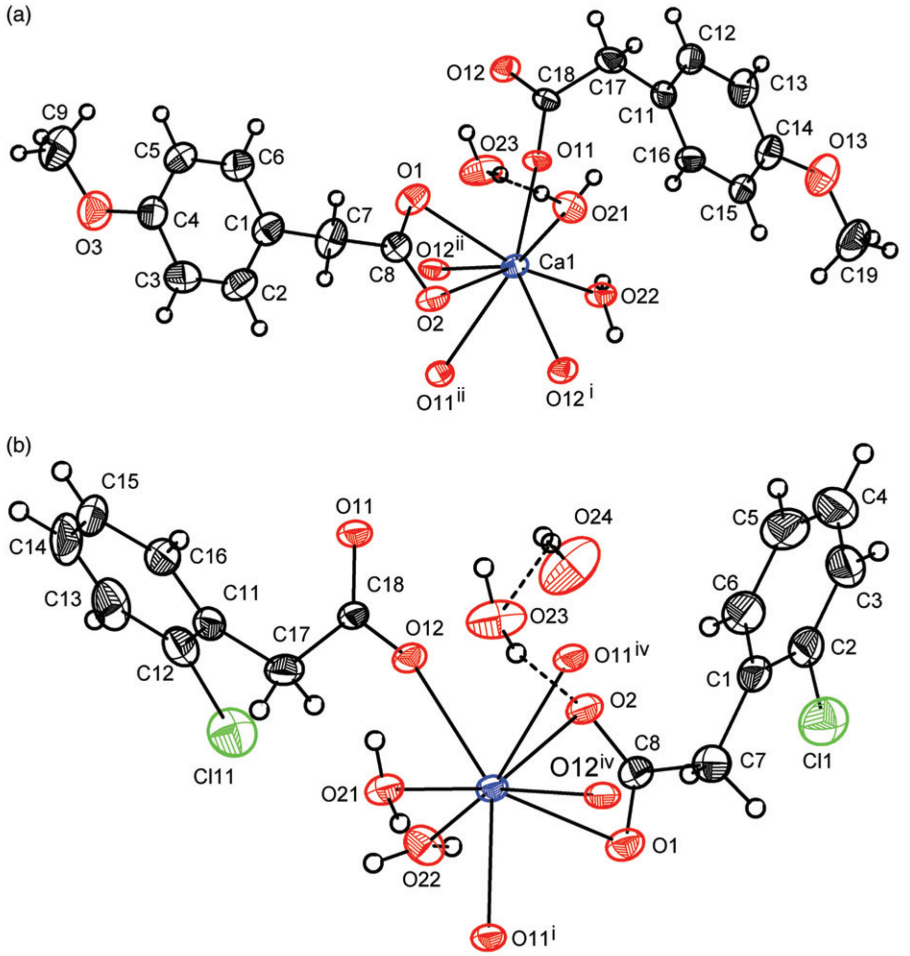
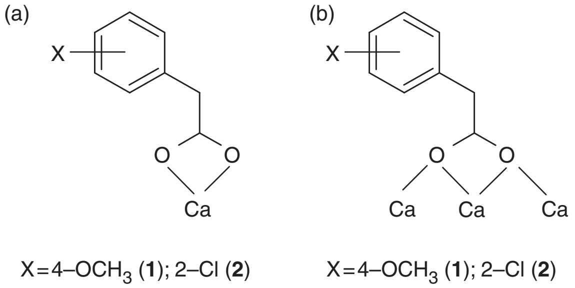


Figure 1. The coordination sphere of Ca(II) in $[Ca(H_2O)_2(L_1)_2]\cdot H_2O$, **1** (a) and $[Ca(H_2O)_2(L_2)_2]\cdot 2H_2O$, **2** (b) showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level except for hydrogens, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown as broken lines. Symmetry codes: (i) x, $y-1$, z; (ii) $-x+1$, $y-1/2$, $-z+1$; (iv) $-x+2$, $y-1/2$, $-z+1$.

2 are structurally similar in terms of the coordination environment of calcium and the binding modes of the crystallographically unique carboxylates but differ in disposition of the methoxy or chloro substituents with respect to the carboxylate in the aromatic ring (scheme 2) and the number of lattice waters. In **1**, which contains a single lattice water, the $-OCH_3$ group is *trans* to the carboxylate, while in **2**, which has two lattice waters, the –Cl group is *ortho* to the $-COO$ functionality.

In view of similar structures, identical labels namely O1, O2 for the bidentate ligand, O11, O12 for the bridging ligand, and O21, O22 for coordinated waters are used for the oxygens in **1** and **2**. In the crystal structure, each Ca(II) in **1** or **2** is eight coordinate, bonded to two oxygens (O21 and O22) from water and six oxygens from four different L_1 or L_2 ligands resulting in a distorted triangular dodecahedron $\{CaO_8\}$ around Ca (figure 2). Compounds **1** and **2** exhibit a very long Ca–O distance of 2.753(4) and



Scheme 2. Bidentate (a) and μ_3-bridging (b) binding modes of L$_1$ and L$_2$ in **1** and **2**.

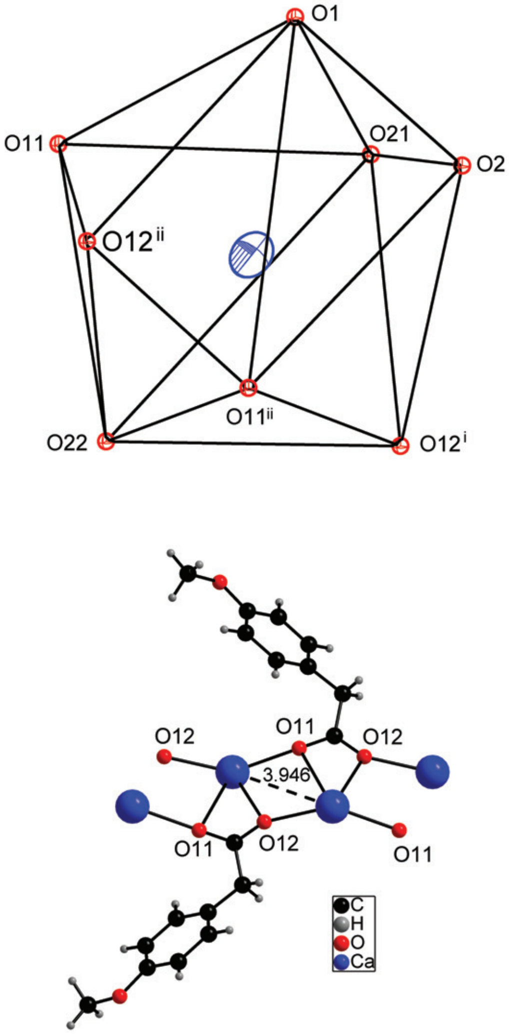


Figure 2. (a) The distorted triangular dodecahedral coordination around Ca(II) in **1**. (b) A pair of μ_3–$\eta^2:\eta^2$ ligands form a tricyclic dicalcium–dicarboxylate unit. Symmetry codes: (i) x, $y-1$, z; (ii) $-x+1$, $y-1/2$, $-z+1$. (For the basic building block of **2** see figure S4.)

Table 2. Selected bond distances (Å) and angles (°) for **1** and **2**.

$[Ca(H_2O)_2(L_1)_2]\cdot H_2O$ (**1**)		$[Ca(H_2O)_2(L_2)_2]\cdot 2H_2O$ (**2**)	
Ca(1)–O(12)^{i}	2.346(4)	Ca(1)–O(12)	2.361(3)
Ca(1)–O(11)	2.358(4)	Ca(1)–O(11)^{i}	2.368(3)
Ca(1)–O(22)	2.410(2)	Ca(1)–O(22)	2.387(3)
Ca(1)–O(21)	2.417(2)	Ca(1)–O(21)	2.415(3)
Ca(1)–O(12)^{ii}	2.454(4)	Ca(1)–O(12)^{iv}	2.460(3)
Ca(1)–O(2)	2.501(5)	Ca(1)–O(2)	2.495(4)
Ca(1)–O(1)	2.512(5)	Ca(1)–O(1)	2.529(4)
Ca(1)–O(11)^{ii}	2.753(4)	Ca(1)–O(11)^{iv}	2.704(3)
Ca(1)–Ca(1)^{iii}	3.9461(11)	Ca(1)–Ca(1)^{iv}	3.9533(11)
O(12)^{i}–Ca(1)–O(11)	145.32(13)	O(12)–Ca(1)–O(11)^{i}	145.61(10)
O(12)^{i}–Ca(1)–O(22)	75.55(14)	O(12)–Ca(1)–O(22)	88.38(14)
O(11)–Ca(1)–O(22)	75.54(13)	O(11)^{i}–Ca(1)–O(22)	83.62(13)
O(12)^{i}–Ca(1)–O(21)	89.11(13)	O(12)–Ca(1)–O(21)	74.80(13)
O(11)–Ca(1)–O(21)	82.77(13)	O(11)^{i}–Ca(1)–O(21)	76.13(13)
O(22)–Ca(1)–O(21)	109.34(9)	O(22)–Ca(1)–O(21)	108.27(10)
O(12)^{i}–Ca(1)–O(12)^{ii}	118.51(11)	O(12)–Ca(1)–O(12)^{iv}	119.22(9)
O(11)–Ca(1)–O(12)^{ii}	77.04(13)	O(11)^{i}–Ca(1)–O(12)^{iv}	76.05(10)
O(22)–Ca(1)–O(12)^{ii}	84.45(12)	O(22)–Ca(1)–O(12)^{iv}	151.94(13)
O(21)–Ca(1)–O(12)^{ii}	151.88(12)	O(21)–Ca(1)–O(12)^{iv}	85.60(11)
O(12)^{i}–Ca(1)–O(2)	78.29(16)	O(12)–Ca(1)–O(2)	79.13(12)
O(11)–Ca(1)–O(2)	132.73(15)	O(11)^{i}–Ca(1)–O(2)	132.23(12)
O(22)–Ca(1)–O(2)	151.65(13)	O(22)–Ca(1)–O(2)	82.20(11)
O(21)–Ca(1)–O(2)	80.80(11)	O(21)–Ca(1)–O(2)	151.43(13)
O(12)^{ii}–Ca(1)–O(2)	98.73(14)	O(12)^{iv}–Ca(1)–O(2)	97.24(12)
O(12)^{i}–Ca(1)–O(1)	129.60(16)	O(12)–Ca(1)–O(1)	130.21(12)
O(11)–Ca(1)–O(1)	82.33(15)	O(11)^{i}–Ca(1)–O(1)	80.94(12)
O(22)–Ca(1)–O(1)	154.04(13)	O(22)–Ca(1)–O(1)	79.10(12)
O(21)–Ca(1)–O(1)	80.67(12)	O(21)–Ca(1)–O(1)	154.79(13)
O(12)^{ii}–Ca(1)–O(1)	77.43(15)	O(12)^{iv}–Ca(1)–O(1)	78.76(12)
O(2)–Ca(1)–O(1)	51.42(11)	O(2)–Ca(1)–O(1)	51.64(8)
O(12)^{i}–Ca(1)–O(11)^{ii}	71.51(13)	O(12)–Ca(1)–O(11)^{iv}	71.58(10)
O(11)–Ca(1)–O(11)^{ii}	124.49(11)	O(11)^{i}–Ca(1)–O(11)^{iv}	123.83(9)
O(22)–Ca(1)–O(11)^{ii}	85.60(11)	O(22)–Ca(1)–O(11)^{iv}	152.08(13)
O(21)–Ca(1)–O(11)^{ii}	152.12(11)	O(21)–Ca(1)–O(11)^{iv}	85.54(11)
O(12)^{ii}–Ca(1)–O(11)^{ii}	49.13(10)	O(12)^{iv}–Ca(1)–O(11)^{iv}	49.62(8)
O(2)–Ca(1)–O(11)^{ii}	75.85(13)	O(2)–Ca(1)–O(11)^{iv}	75.22(11)
O(1)–Ca(1)–O(11)^{ii}	96.13(14)	O(1)–Ca(1)–O(11)^{iv}	98.84(12)

Symmetry transformations used to generate equivalent atoms: $^{(i)}$ $x, y-1, z$; $^{(ii)}$ $-x+1, y-1/2, -z+1$; $^{(iii)}$ $-x+1, y+1/2, -z+1$; $^{(iv)}$ $-x+2, y-1/2, -z+1$.

2.704(3) Å, respectively. The other seven Ca–O bond distances in **1** vary in a small range between 2.346(4) and 2.512(5) Å, while in **2** these Ca–O bond lengths range from 2.361(3) to 2.529(4) Å (table 2). Recently Dietzel *et al.* [8] reported a long Ca–O distance of 2.8384(16) Å in $[Ca(H_2dhtp)(H_2O)_2]$ (H_4dhtp = 2,5-dihydroxyterephthalic acid). The O–Ca–O angles (49.13(10)°–154.04(13)° in **1**; 49.62(8)°–154.79(13)° in **2**) scatter in a very wide range.

The first independent L_1 (or L_2) is coordinated to calcium through O1 and O2 with Ca–O distances of 2.501(5) and 2.512(5) Å in **1** (2.495(5) and 2.529(4) Å in **2**), indicating the symmetrical bidentate behavior of this ligand. The second L_1 (or L_2) which binds through O11 and O12 is tetradentate in a μ_3–$\eta^2:\eta^2$ binding mode, resulting in a 1-D CP. Both O11 and O12 are bonded to two Ca(II)s, of which one Ca(II) is common to both. The polymeric structure of **1** and **2** is based on a dimer and can be visualized as follows. A pair of μ_3-bridging L_1 (or L_2) ligands link a pair of $\{Ca(H_2O)_2(L_1)\}$ (or $\{Ca(H_2O)_2(L_2)\}$)

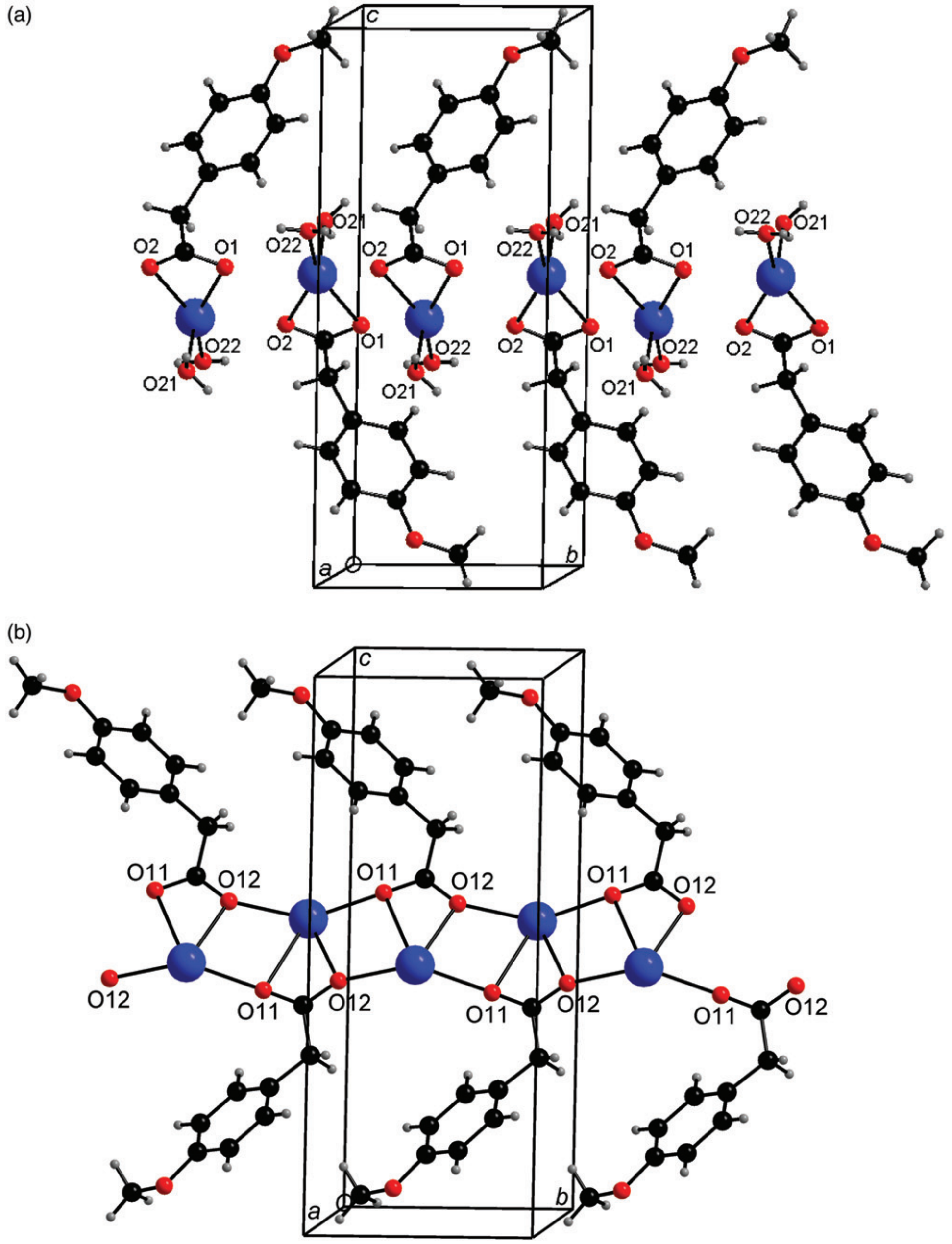


Figure 3. (a) The crystal structure of **1** along the *a*-axis showing only the bidentate L_1 ligand (O1, O2) and the coordinated waters (O21, O22) around Ca(II). (b) A portion of the polymeric chain in **1** extending along the *b*-axis only due to the μ_3–$\eta^2:\eta^2$ bridging binding mode of the L_1 (O11, O12) ligand, showing the linking of each Ca(II) to three different bridging ligands. (c) The crystallographic packing of **1** showing the eight-coordinate Ca(II) due to terminal aqua ligands and the chelating and bridging L_1. The $\{CaO_8\}$ units are represented as polyhedra. (For the crystallographic packing of **2** see figure S5.)

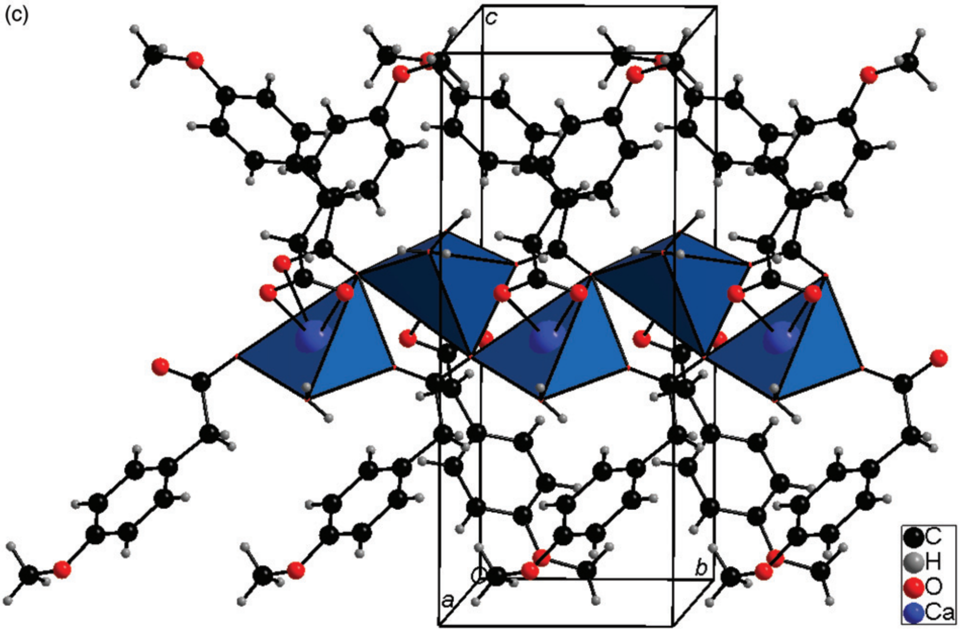


Figure 3. Continued.

units resulting in the formation of a tricyclic dicalcium–dicarboxylate block with a Ca · · · Ca separation of 3.9461(11) Å in **1** or 3.9533(11) Å in **2** (figure 2). This tricyclic unit can be considered as the basic building block of the 1-D polymer. A similar tricyclic unit has been reported recently in the 1-D polymers $[Ca(H_2O)_2(2\text{-nba})_2]_n$ (2-nba = 2-nitrobenzoate) [16] and $[Ca(H_2O)_2(2\text{-ca-4nba})_2]_n$ (2-ca-4nba = 2-carbamoyl-4-nitrobenzoate) [36]. In these compounds the organic linker coordinates in a μ_2–$\eta^2:\eta^1$ fashion leading to the formation of the tricyclic unit. The net result of the differing coordination modes of L_1 (or L_2) in **1** and **2** is the formation of a 1-D polymeric chain extending along the *b*-axis with two terminal waters (O21, O22), a chelating bidentate (O1, O2) L_1 (or L_2) accounting for four of the eight binding sites of each Ca(II) in the chain (figure 3). The remaining four oxygens for Ca(II) are provided by three symmetry-related μ_3-bridging L_1 (or L_2) ligands. Scrutiny of the structure reveals that hydrogens of the coordinated and lattice waters function as H-donors and are involved in several O–H · · · O interactions (table S1) and the oxygens of the chelating L_1 (or L_2) and the lattice waters function as H-donors.

4. Conclusions

Ca(II) CPs have been synthesized under hydrothermal conditions and structurally characterized in recent years [6–10]. Organic linkers containing two or more –COOH groups were used for the hydrothermal synthesis. In this work, we describe the synthesis under ambient conditions, structural characterization, and thermal properties of two new Ca(II) CPs, based on flexible monocarboxylic acid linkers. Based on an analysis of the structural features of several Ca-carboxylates, we had recently shown that when the number of coordinated waters in a Ca-carboxylate is 3 or less the carboxylate adopts a bridging binding mode [16]. In **1** and **2**, which contain two coordinated waters, the observation of bridging carboxylate for the flexible phenylacetate-based ligands L_1 (or L_2) in **1** (or **2**) is in accord with the earlier result. The title compounds constitute two new examples to the growing list of structurally characterized alkaline earth CPs.

Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 719744 (**1**) and 719743 (**2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-(0)1223-336033 or E-mail: deposit@ccdc.cam.ac.uk). Additional figures related to the crystal structure, IR spectra, thermograms, and table of H-bonding geometry of **1** and **2** are available as ''Supplementary data'' for this article and can be found in the online version.

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