

Diverse Structures and Dimensionalities in Hybrid Frameworks of Strontium and Lanthanum with Isomeric Dihydroxybenzoates

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Investigations of Sr and La derivatives of 2,3-, 2,4-, 3,5-, and 2,6-dihydroxybenzoic acids have revealed that it is possible to obtain chain and layered structures of these materials. $[\text{Sr}_2(2,3\text{-DHB})_4(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$, **I**, and $[\text{Sr}(2,4\text{-DHB})_2(\text{H}_2\text{O})_4]\cdot \text{H}_2\text{O}$, **II**, are both one-dimensional coordination polymers based on dimers; both the carboxylate and phenolic oxygens bond to the metal in **I** and only the carboxylate oxygens bond to the metal in **II**. $[\text{Sr}(3,5\text{-DHB})_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$, **III**, has a one-dimensional chain structure with large channels and involves extended Sr–O–Sr connectivity. $[\text{Sr}(\text{CH}_3\text{CO}_2)(2,4\text{-DHB})(\text{H}_2\text{O})_3]\cdot \text{H}_2\text{O}$, **IV**, also has a chain structure with extended Sr–O–Sr connectivity, but the chain structure is formed by bridging acetate units, unlike in **III** where the Dihydroxybenzoate (DHB) is the bridging unit. $[\text{Sr}(2,6\text{-DHB})_2(\text{H}_2\text{O})_2]\cdot 0.5\text{H}_2\text{O}$, **V**, is a two-dimensional coordination polymer where both carboxylate and phenolic oxygens coordinate to the metal. A lanthanum compound with the composition $[\text{La}(\text{CH}_3\text{CO}_2)_2(2,4\text{-DHB})(\text{H}_2\text{O})]\cdot 0.18\text{H}_2\text{O}$, **VI**, with a one-dimensional chain structure with extended La–O–La connectivity, has been prepared. Besides these chain and layered structures, zero-dimensional dimers of rare-earth DHBs with the general formula $[\text{La}(\text{CH}_3\text{CO}_2)_2(\text{DHB})(\text{H}_2\text{O})_2]$, with 3,5- (**VII**), 2,6- (**VIII**), and 2,3-dihydroxybenzoic acids (**IX**) have been synthesized. The diverse structures of the strontium and lanthanum DHBs are described. The study demonstrates that it is possible to obtain interesting structures of metal DHBs with different dimensionalities. The structures appear to be controlled largely by geometrical rather than electronic factors.

1. Introduction

Organically templated open-framework metal silicates and phosphates have been reported widely in the literature.^{1,2} In the early 1990s, Robson and Hoskins³ used organic linkers for the first time, to construct open-framework materials. Since then, there have been many reports in the literature on the synthesis and characterization of open-framework metal carboxylates of varying dimensionalities.⁴ Design and synthesis of hybrid materials employing carboxylate linkers

constitute an important endeavor in view of potential applications of these materials in sorption, gas storage, and luminescence.^{5–7} Research on hybrid materials has been generally centered on the assembly of organic linkers with d-block metal ions, with predictable coordination geometries.^{8–10} The

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Table 1. Crystal Data and Structure Refinement Parameters for Compounds I–V

parameter	I	II	III	IV	V
empirical formula	Sr ₂ C ₂₈ H ₃₁ O ₂₃	SrC ₁₄ H ₂₀ O ₁₃	SrC ₁₄ H ₁₈ O ₁₄	SrC ₉ H ₁₅ O ₁₀	SrC ₁₄ H ₁₄ O _{10.5}
crystal system	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>C2/c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
crystal size (mm)	0.28 × 0.26 × 0.25	0.21 × 0.25 × 0.27	0.2 × 0.25 × 0.4	0.22 × 0.20 × 0.22	0.24 × 0.15 × 0.2
<i>a</i> (Å)	10.240(2)	6.796(2)	11.703(4)	7.047(2)	7.5989(4)
<i>b</i> (Å)	10.502(2)	10.461(2)	21.409(6)	7.719(2)	9.3805(5)
<i>c</i> (Å)	16.441(4)	13.095(3)	7.841(2)	13.786(3)	11.3938(6)
α (deg)	98.156(4)	101.380(3)	90.0	99.96(2)	91.871(1)
β (deg)	96.206(4)	91.542(4)	90.131(5)	100.05(1)	95.303(2)
γ (deg)	96.373(4)	97.946(4)	90.0	105.38(3)	90.687(2)
volume (Å ³)	1725.5(7)	902.5(3)	1964.6(10)	692.7(3)	808.17(7)
<i>Z</i>	2	2	4	2	2
formula mass	910.77	483.92	497.90	370.83	437.87
ρ_{calcd} (g cm ⁻³)	1.753	1.781	1.683	1.778	1.799
λ (Mo K α ; Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	3.186	3.057	2.815	3.937	3.393
Θ range (deg)	1.98–26.37	2.01–28.04	1.90–28.38	1.54–23.27	1.80–23.37
total data collected	18642	7921	7869	2850	3387
limiting indices	$-12 \leq h \leq 12,$ $-13 \leq k \leq 13,$ $-20 \leq l \leq 20$	$-8 \leq h \leq 8,$ $-13 \leq k \leq 13,$ $-17 \leq l \leq 17$	$-14 \leq h \leq 15,$ $-28 \leq k \leq 28,$ $-10 \leq l \leq 10$	$-6 \leq h \leq 7,$ $-8 \leq k \leq 8,$ $-15 \leq l \leq 12$	$-6 \leq h \leq 8,$ $-9 \leq k \leq 10,$ $-12 \leq l \leq 12$
unique data	7016	4102	2276	1948	2318
refinement method	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $
R_{int}	0.0423	0.0183	0.0427	0.0479	0.0267
R indexes [$I > 2\sigma(I)$]	$R_1 = 0.0399,$ $wR_2 = 0.0777$	$R_1 = 0.0310,$ $wR_2 = 0.0720$	$R_1 = 0.0530,$ $wR_2 = 0.1202$	$R_1 = 0.0394,$ $wR_2 = 0.0950$	$R_1 = 0.0283,$ $wR_2 = 0.0673$
R (all data)	$R_1 = 0.0684,$ $wR_2 = 0.0886$	$R_1 = 0.0387,$ $wR_2 = 0.0751$	$R_1 = 0.0629,$ $wR_2 = 0.1238$	$R_1 = 0.0444,$ $wR_2 = 0.0972$	$R_1 = 0.0359,$ $wR_2 = 0.0692$
goodness of fit	1.009	1.049	1.194	0.974	0.983
no. of variables	554	291	152	221	259
largest difference map peak and hole e Å ⁻³	0.497 and -0.354	0.637 and -0.458	0.773 and -1.480	0.541 and -0.836	0.433 and -0.503

f-block and main group elements are also gaining attention, the former because they afford materials with high coordination numbers and variable geometry as well as properties arising from the f–f electronic transitions. A careful choice of the organic ligands coupled with the lanthanide ions can thus lead to new and interesting luminescent materials.^{7,11} Of the many carboxylic acids employed in recent years for building hybrid networks, special mention must be made of the isomeric dicarboxylic acids of benzene, cyclohexane, and cyclohexene.^{6,9,10}

Dihydroxybenzoic acids are attractive candidates for forming hybrid frameworks because they can, in principle, bind to the metal ions by making use of the carboxylate and hydroxyl oxygens. There are not many reports of metal dihydroxybenzoates (DHBs) whose structures have been determined, and most of them are monomeric or one-dimensional polymeric metal complexes.^{12–14} No chain with continuous M–O–M connectivity or layered structures have been reported hitherto. In the present study, we have investigated the compounds formed by different isomeric dihydroxybenzoic acids with a rare earth ion (La³⁺) and an equally large alkaline earth metal ion (Sr²⁺). We have thus been able to synthesize and characterize several lanthanum

and strontium DHBs possessing zero-, one-, and two-dimensional structures.

2. Experimental Section

Synthesis. Strontium DHBs, I–V. Compounds I–V were prepared under mild conditions. For the synthesis of I–III and V, 0.5 mmol of the dihydroxybenzoic acid was dissolved in 5 mL of deionized water, and 0.5 mmol of strontium carbonate was added slowly to the solution under constant stirring. The reaction mixture was heated to 50 °C and stirred for 30 min. Compounds I–III and V could also be prepared by adding 0.5 mmol of strontium acetate to a solution of 0.5 mmol of the dihydroxybenzoic acid in 5 mL of deionized water. For the synthesis of IV, 0.5 mmol of strontium carbonate was dispersed in 5 mL of deionized water, to which 1.5 mmol of acetic acid was added dropwise, and the mixture was stirred for 10 min until it formed a clear solution. To this solution,

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Table 2. Crystal Data and Structure Refinement Parameters for Compound VI–IX

parameter	VI	VII ^a	VIII	IX
empirical formula	LaC ₁₁ H ₁₃ O _{9.18}	LaC ₁₁ H ₁₅ O ₁₀	LaC ₁₁ H ₁₅ O ₁₀	LaC ₁₁ H ₁₄ O ₁₀
crystal system	orthorhombic	triclinic	monoclinic	monoclinic
space group	<i>Pbcn</i>	<i>P</i> $\bar{1}$	<i>P2(1)/n</i>	<i>P2(1)/n</i>
crystal size (mm)	0.22 × 0.20 × 0.18	0.28 × 0.25 × 0.20	0.3 × 0.27 × 0.3	0.25 × 0.27 × 0.22
<i>a</i> (Å)	15.226(4)	8.5452(18)	11.1858(3)	11.5638(2)
<i>b</i> (Å)	8.322(2)	9.1824(19)	8.3939(1)	8.2409(2)
<i>c</i> (Å)	23.698(5)	10.910(2)	16.5029(3)	16.6299(2)
α (deg)	90.0	103.651(3)	90.0	90.0
β (deg)	90.0	101.304(3)	104.069(1)	105.601(1)
γ (deg)	90.0	110.923(3)	90.0	90.0
volume (Å ³)	3002.7(12)	739.0(3)	1503.02(5)	1526.38(5)
<i>Z</i>	8	2	4	4
formula mass	430.92	446.14	446.14	446.13
ρ_{calcd} (g cm ⁻³)	1.906	2.005	1.972	1.937
λ (Mo K α ; Å)	0.71073	0.71073	0.71073	0.71073
μ (mm ⁻¹)	2.886	2.939	2.890	2.846
Θ range (deg)	2.18–25.40	2.02–28.37	2.00–23.26	1.93–23.28
total data collected	20487	6160	5842	5982
limiting indices	–18 ≤ <i>h</i> ≤ 18, –9 ≤ <i>k</i> ≤ 10, –25 ≤ <i>l</i> ≤ 28	–11 ≤ <i>h</i> ≤ 11, –11 ≤ <i>k</i> ≤ 11, –14 ≤ <i>l</i> ≤ 14	–7 ≤ <i>h</i> ≤ 12, –8 ≤ <i>k</i> ≤ 9, –18 ≤ <i>l</i> ≤ 18	–12 ≤ <i>h</i> ≤ 12, –9 ≤ <i>k</i> ≤ 8, –18 ≤ <i>l</i> ≤ 13
unique data	2722	3262	2158	2196
refinement method	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $	full-matrix least squares on $ F^2 $
R_{int}	0.0290	0.0190	0.0344	0.0570
R indexes [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0246$, $wR_2 = 0.0481$	$R_1 = 0.0224$, $wR_2 = 0.0532$	$R_1 = 0.0240$, $wR_2 = 0.0587$	$R_1 = 0.0296$, $wR_2 = 0.0610$
R (all data)	$R_1 = 0.0366$, $wR_2 = 0.0513$	$R_1 = 0.0249$, $wR_2 = 0.0544$	$R_1 = 0.0275$, $wR_2 = 0.0597$	$R_1 = 0.0366$, $wR_2 = 0.0627$
goodness of fit	1.047	1.038	1.034	0.925
no. of variables	207	221	215	211
largest difference map peak and hole e Å ⁻³	0.962 and –0.343	0.761 and –0.924	0.618 and –0.936	0.551 and –1.014

^a The unit cell dimensions of the isostructural Y and Gd compound are, for Y, *a* = 8.415(6), *b* = 8.966(6), *c* = 10.713(8) Å, and vol = 697.1(8) Å³ and, for Gd, *a* = 8.464(2), *b* = 9.006(3), *c* = 10.778(3) Å, and vol = 707.4(3) Å³.

0.5 mmol of 2,4-DHB was added slowly, and the mixture stirred for 30 min. The solutions were filtered and kept undisturbed at 50 °C for 24 h, from which the strontium DHBs, I–V, crystallized out.

Lanthanum DHBs, VI–IX. Compounds VI–IX were prepared under mild conditions starting with 0.5 mmol of the dihydroxybenzoic acid dissolved in 5 mL of deionized water. To this solution, 0.5 mmol of lanthanum acetate was added slowly under constant stirring. The clear solutions were kept undisturbed at 50 °C for 24 h, from which the lanthanum DHBs crystallized out. In the case of VI and IX good quality crystals suitable for single crystal structure solution could be obtained only by layer diffusion, wherein a solution of 0.5 mmol of the corresponding dihydroxybenzoic acid in 2 mL of *n*-butanol was layered on top of a solution of the 0.5 mmol of the lanthanum acetate in 2 mL of deionized water.

The products, I–IX, were vacuum filtered and washed with water. The yields generally exceeded 80%. The compounds were characterized by powder X-ray diffraction (XRD), which indicated the products to be new materials and monophasic, the patterns being consistent with those generated from single-crystal X-ray diffraction. The simulated and experimental powder XRD patterns for the compounds are provided in the Supporting Information. The products form over a wide pH range (4–8) of the starting reaction mixture and over a range of temperatures varying from room temperature to 100 °C for both the La and the Sr compounds. Elemental analyses of I–IX were satisfactory. For I, calcd for Sr₂C₂₈O₂₃H₃₄: C, 36.8%; H, 3.79%. Found: C, 36.87%; H, 3.71%. For II, calcd for SrC₁₄O₁₃H₂₀: C, 34.74%; H, 4.14%. Found: C, 34.85%; H, 3.97%. For III, calcd for SrC₁₄O₁₄H₂₂: C, 33.5%; H, 4.4%. Found: C, 33.75%; H, 4.55%. For IV, calcd for

SrC₉O₁₀H₁₆: C, 29.06%; H, 4.3%. Found: C, 29.47%; H, 4.41%. For V, calcd for SrC₁₄O_{10.5}H₁₅: C, 38.3%; H, 3.42%. Found: C, 38.25%; H, 3.81%; %. For VI, calcd for LaC₁₁O_{9.18}H_{13.36}: C, 30.2%; H, 3.2%. Found: C, 30.43%; H, 3.15%. For VII, VIII, IX, calcd for LaC₁₁O₁₀H₁₅: C, 29.6%; H, 3.36%. Found for VII, C, 29.4%; H, 3.48%. Found for VIII, C, 29.33%; H, 3.40%. Found for IX, C, 29.8%; H, 3.33.

Single-Crystal Structure Determination. A suitable single crystal of each of the compounds I–IX was carefully selected under a polarizing microscope and glued at the tip of a thin glass fiber with cyano-acrylate (superglue) adhesive. Single-crystal structure determination by XRD was performed on a Siemens Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo K α radiation, $\lambda = 0.71073$ Å) operating at 40 kV and 40 mA. A hemisphere of intensity data was collected at room temperature with ω space scans (width of 0.30° and exposure time of 10 s per frame). Pertinent experimental details of the structure determination for compounds I–V and VI–IX are presented in Tables 1 and 2, respectively.

The structures were solved by direct methods using SHELXS-86,¹⁵ which readily established the heavy atom position (La and Sr) and facilitated the identification of the light atoms (O, C, H) from difference Fourier maps. An empirical absorption correction based on symmetry equivalent reflections was applied using the SADABS program.¹⁶ All the hydrogen positions were initially

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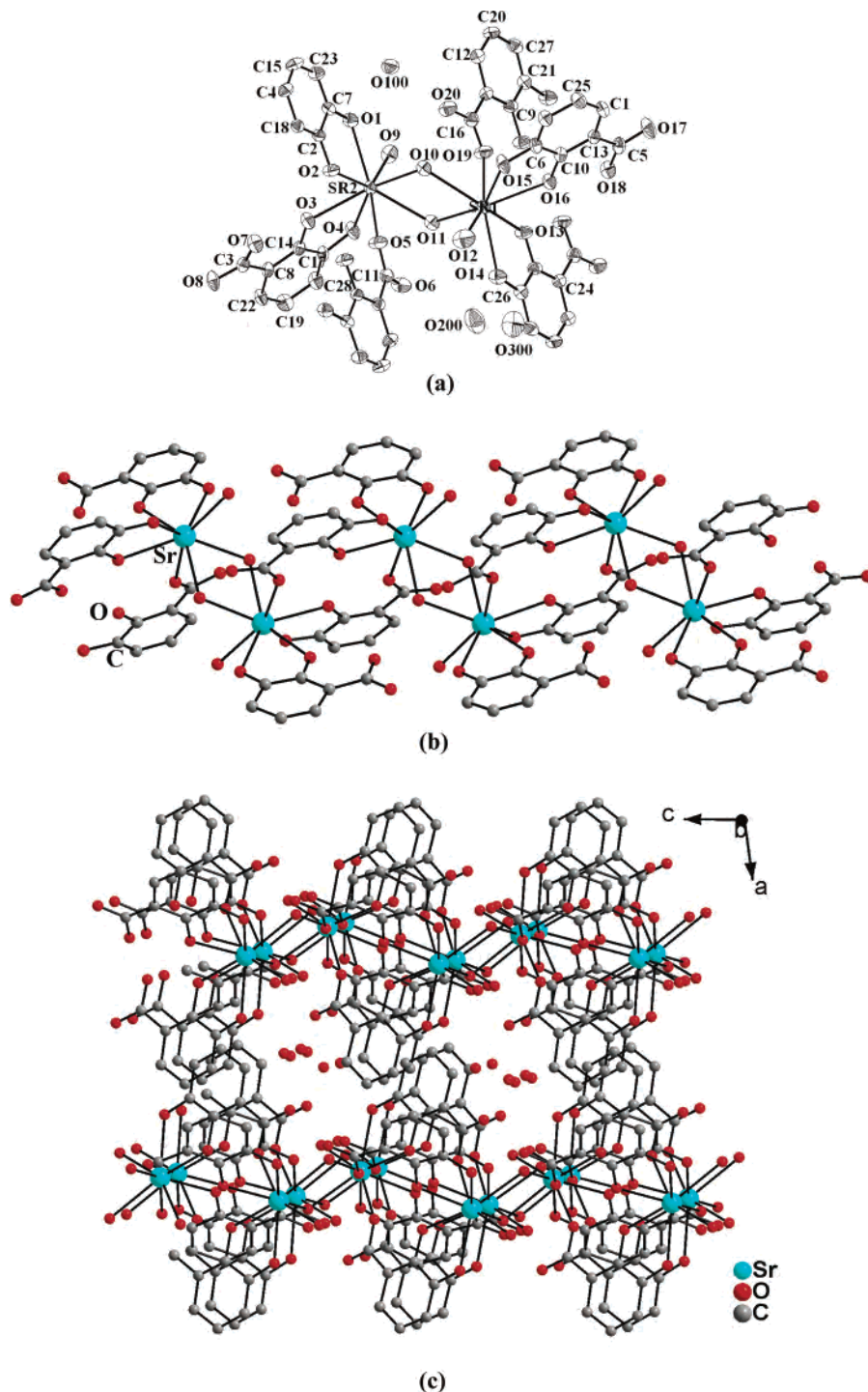


Figure 1. (a) ORTEP plot of $[\text{Sr}_2(2,3\text{-DHB})_4(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$, **I**. Thermal ellipsoids are shown at 50% probability. Only the asymmetric part is labeled. Hydrogen atoms are not shown for clarity. (b) One-dimensional chain structure formed in **I**. Note one of the 2,3-DHB molecules uses its hydroxyl groups to bond to the Sr atoms with the carboxylate end remaining free. (c) The three-dimensional packing diagram of **I**, with the interstitial molecules residing in the channels.

located in the difference Fourier maps, and the hydrogen atoms were placed geometrically and held in the riding mode for the final refinement. With the single-crystal X-ray data collected at room temperature, few of the hydrogen atoms of the water molecules could not be located from difference Fourier maps. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against $|F^2|$ was carried out using the SHELXTL-PLUS package of programs.¹⁷

Thermogravimetric analysis was carried out with a heating rate of $2\text{ }^\circ\text{C min}^{-1}$ in an oxygen atmosphere using a Mettler 851eTG/sDTA coupled to a Blazers ThermoStar 300 AMU mass spectrometer. X-ray thermodiffractionometry (Cu $K\alpha$ radiation, $\lambda = 1.5418\text{ \AA}$) was performed under static air in a Bruker D8 Advance diffractometer outfitted with a M. Braun Position Sensitive Detector and an Anton Paar HTK 16 high-temperature stage.

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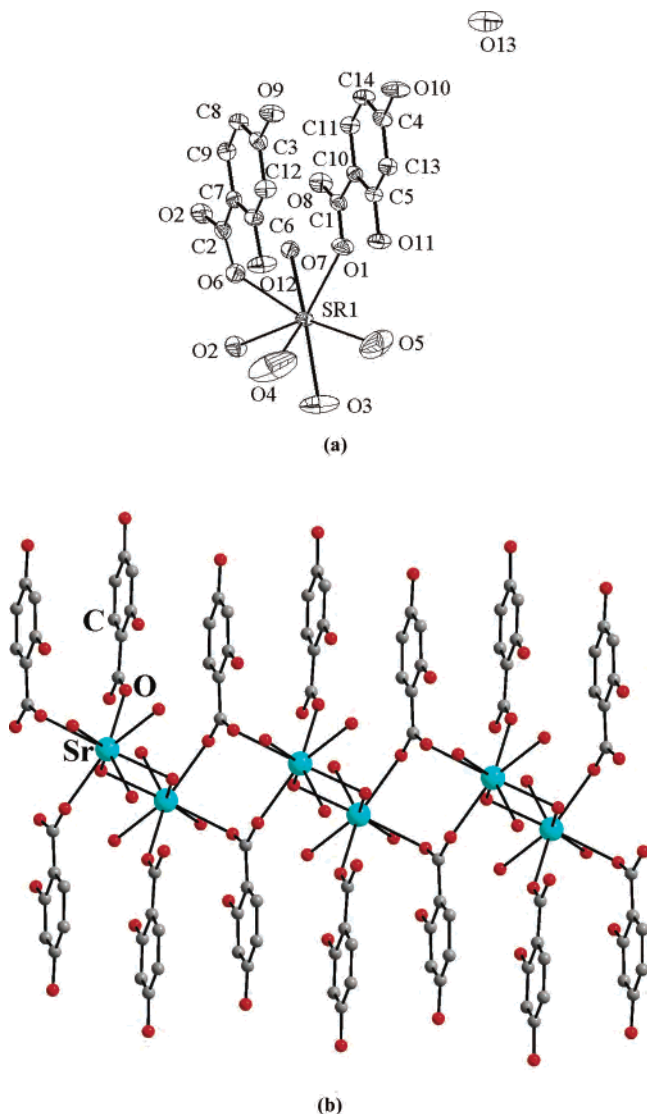


Figure 2. (a) ORTEP plot of $[\text{Sr}(2,4\text{-DHB})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$, **II**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are not shown for clarity. (b) The one-dimensional chain structure formed in **II** by the bridging of the dimers by the carboxylate end of the DHB molecule, resulting in the formation of four-membered rings in the chain.

3. Results and Discussion

3.1. Strontium DHBs, I–V. With the various DHBs strontium forms one-dimensional coordination polymers and chain structures as well as two-dimensional networks. Thus, with 2,3-DHB, Sr forms a one-dimensional coordination polymer with the formula $[\text{Sr}_2(2,3\text{-DHB})_4(\text{H}_2\text{O})_4]\cdot 3\text{H}_2\text{O}$, **I**. The asymmetric unit of **I** contains two Sr atoms, 20 oxygen atoms belonging to the four DHB molecules and four coordinated water molecules, 28 carbon atoms, and 3 interstitial water molecules (Figure 1a). The Sr atoms are eight-coordinated and are bridged by coordinating water molecules to form dimers with Sr–O–Sr connectivity (Figure 1b). The bridging units were not hydroxo groups because we could not locate the hydrogens of the bridging water in **I** and also the subsequent structures described in the article. Furthermore, hydroxo groups would not compensate the charge correctly. Attempts to locate or fix the hydrogens at the carboxylate end of the DHB groups were also unsuccessful.

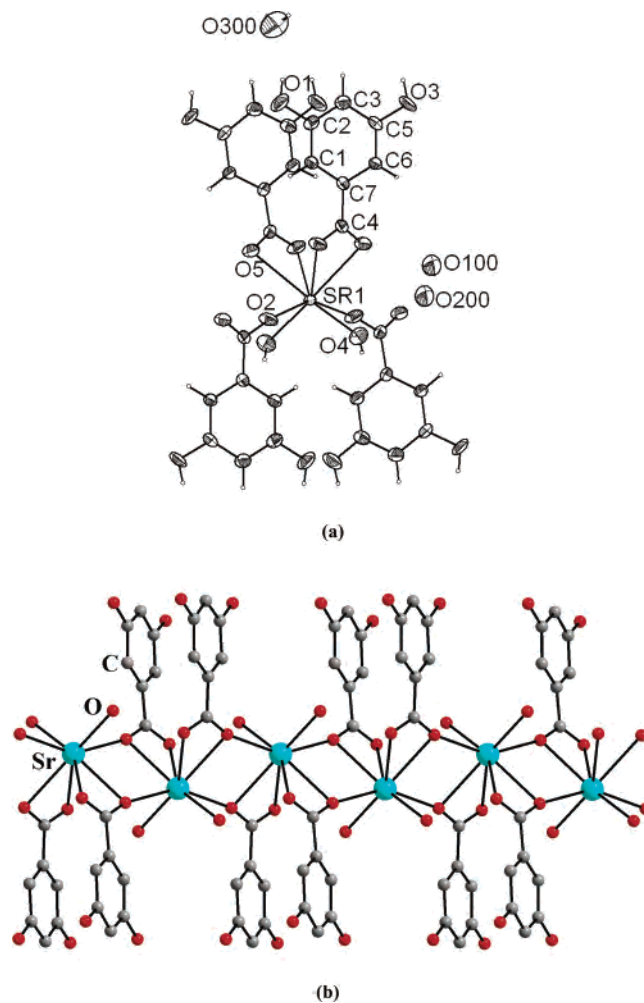


Figure 3. (a) ORTEP plot of $[\text{Sr}(3,5\text{-DHB})_2(\text{H}_2\text{O})_2]\cdot 4\text{H}_2\text{O}$, **III**. Thermal ellipsoids are shown at 50% probability. Only the asymmetric part is labeled. (b) The chain structure of **III** with one-dimensional Sr–O–Sr connectivity.

The DHB units exhibit two different types of coordination modes that are quite different from those formed in the DHBs to be discussed later. Both types of DHB unit bind to the Sr atom in a chelating fashion through the adjacent hydroxyl groups in the benzene ring with an O–Sr–O bite angle of 60° . Such a coordination mode of the 2,3-dihydroxybenzoic acid has been observed earlier too.^{12d,e} The carboxylate end of one type of DHB unit remains free, whereas the other type binds to the Sr atom of the adjacent dimer in a monodentate fashion through its carboxylate end. This leads to the formation of 4-rings (defined by two DHB units and two Sr atoms) which connect the dimers to form chains parallel to the *c* axis of the unit cell (Figure 1b). The Sr–O–Sr connectivity does not run across the entire length of the chain but is limited to the dimers. The chains are arranged parallel to the *bc* plane of the unit cell. Such a stacking results in the formation of channels along the *c* axis of the unit cell, where the interstitial water molecules reside and form hydrogen bonds with the framework oxygen atoms (Figure 1c).

Sr with 2,4-DHB forms a dimer-based one-dimensional coordination polymer with the formula $[\text{Sr}(2,4\text{-DHB})_2(\text{H}_2\text{O})_4]\cdot\text{H}_2\text{O}$, **II**. The asymmetric unit of **II** contains one Sr

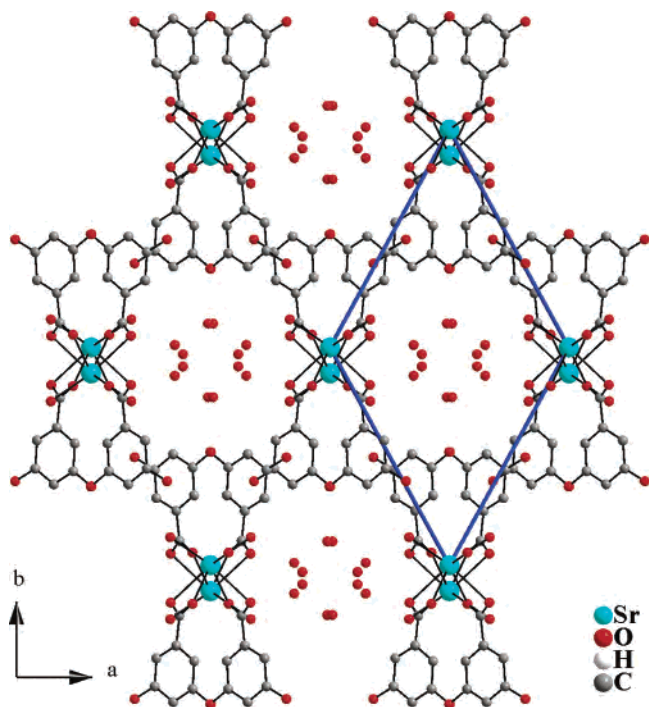


Figure 4. Three-dimensional packing diagram of **III**. Note the presence of the rhombohedral channel (marked by the blue line) down the c axis of the unit cell.

atom, 12 oxygen atoms belonging to two DHB molecules and the four coordinated water molecules, 14 carbon atoms, and one interstitial water molecule (Figure 2a). There are two types of DHB units in the structure, one binding to a Sr atom in a monodentate fashion through its carboxylate and the other binding to two Sr atoms in a monodentate fashion through the carboxylate (Figure 2b). As in **I**, the Sr atoms are eight-coordinated and are bridged by coordinating water molecules to form dimers with Sr–O–Sr connectivity. The dimers are joined by carboxylate bridges to form chains parallel to the a axis of the unit cell and also forming 4-rings in the chain, as in structure **I**. Similar to **I**, the Sr–O–Sr connection in **II** is limited to the dimers and does not run across the entire length of the chain (Figure 2b). There is extensive hydrogen bonding between the chains and the interstitial water molecules.

With 3,5-DHB, Sr forms a chain structure of the composition, $[\text{Sr}(3,5\text{-DHB})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, **III**. The asymmetric unit of **III** contains one Sr atom in a special position, seven oxygen atoms of which three belong to the interstitial water molecules, and seven carbon atoms (Figure 3a). Two of the interstitial water molecules are disordered with 50% occupancy in each site. The Sr atom is eight-coordinated. The DHB binds only through carboxylate, and it coordinates to one Sr atom in a chelating fashion and further bridges two Sr atoms through a three-coordinating oxygen, thus forming a one-dimensional chain with Sr–O–Sr connectivity parallel to the c axis of the unit cell (Figure 3b). The chains are separated by a unit-cell length along the a axis and are stacked parallel to each other along the ac plane of the unit cell. Such layers, in turn, are separated by half a unit-cell length along the b axis and are shifted by half a unit-cell length along the a axis, to form large rhombohedral

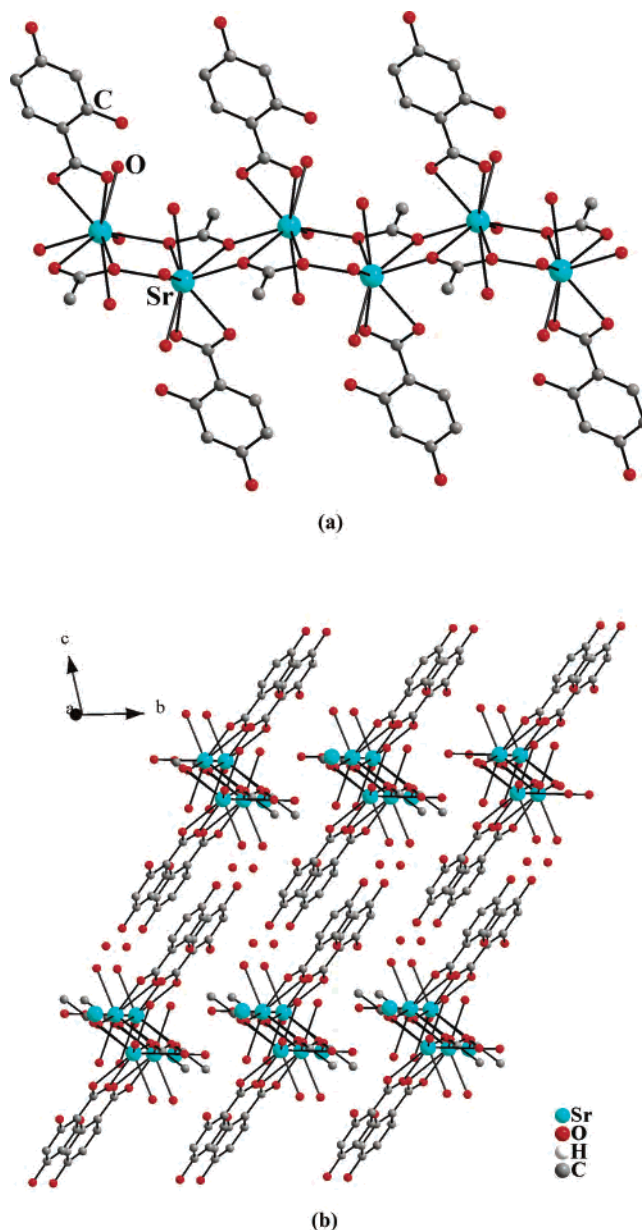


Figure 5. (a) One-dimensional chain structure formed in $[\text{Sr}(\text{CH}_3\text{CO}_2)(2,4\text{-DHB})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, **IV**. Note the presence of the acetate molecules in the structure. (b) Three-dimensional packing diagram of **IV**.

hydrogen-bonded channels with an aperture of 12.19×12.19 Å, measured from Sr to Sr, running down the c axis of the unit cell (Figure 4). The presence of the channel results in the large unit cell volume of **III**, the volume per Sr atom being the highest of all the Sr DHBs investigated by us. Interstitial water molecules residing in the interchain region form multipoint hydrogen bonds with the oxygen atoms of the chain to stabilize the structure.

Strontium forms a chain structure with 2,4-DHB as well, the formula being $[\text{Sr}(\text{CH}_3\text{CO}_2)(2,4\text{-DHB})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$, **IV**. Here, the Sr atom is nine-coordinated and binds to one DHB unit, one acetate, and three water molecules. The asymmetric unit of **IV** contains one Sr atom, nine oxygen atoms, nine carbon atoms, and one interstitial water molecule. Both the DHB and acetate units bind to the Sr atom through the carboxylate oxygens. The acetate unit bridges the Sr atoms

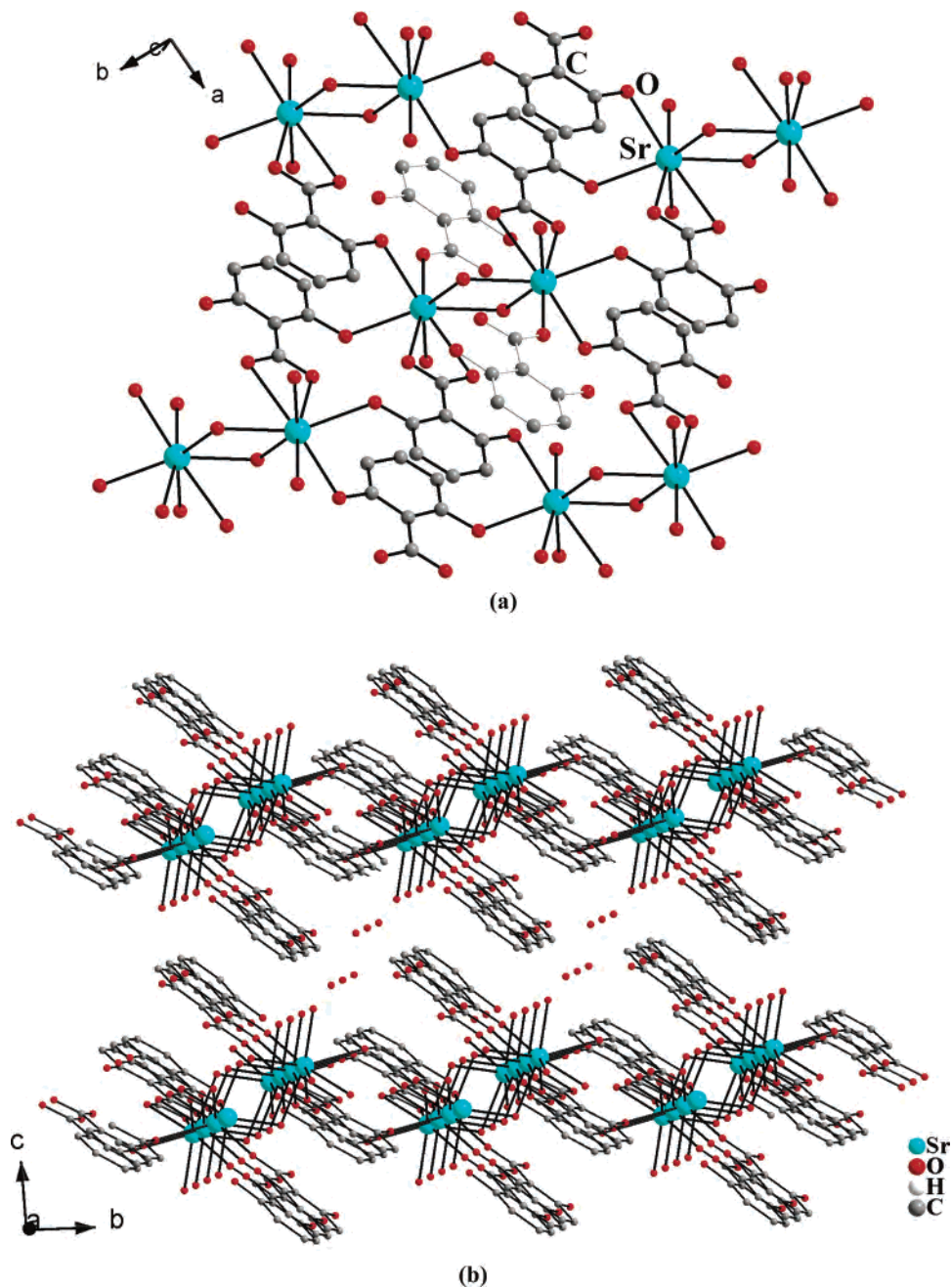


Figure 6. (a) Top view of the layer formed in $[\text{Sr}(\text{2,6-DHB})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$, **V**, by the joining of the dimers; the monodentate DHB molecules of the dimers are shown in a lighter shade. Note the two different coordination modes of the 2,6-DHB molecule present in the structure. (b) Three-dimensional packing diagram of the layers; note the presence of 4-ring channels running across the layer.

through the three-coordinating carboxylate oxygens, forming chains parallel to the *a* axis of the unit cell, with pendant DHB groups (Figure 5a). The chains, which have extended Sr–O–Sr connectivity, are separated by a unit cell length along the *b* axis and are arranged in layers within the *ab* plane of the unit cell. The layers are separated by a unit cell length along the *c* axis with the DHB units protruding from the layers in an interdigitated manner (Figure 5b). The interstitial water molecules reside in the interlamellar region. Hydrogen bonding between the chains and with the interstitial water molecules renders additional stability to the structure.

With 2,6-DHB, strontium forms a layer structure, $[\text{Sr}(\text{2,6-DHB})_2(\text{H}_2\text{O})_2] \cdot 0.5\text{H}_2\text{O}$, **V**. The asymmetric unit of **V** con-

tains one Sr atom, 10 oxygen atoms belonging to two DHB units and two coordinated water molecules, 14 carbon atoms, and one interstitial water molecule with 50% occupancy. The Sr atoms are bridged by coordinating water molecules to form dimers having Sr–O–Sr connectivity. The DHB unit exhibits two different coordination modes in this structure. One 2,6-DHB unit binds to a Sr atom in a monodentate fashion through the carboxylate end, and the other 2,6-DHB unit binds to a Sr atom in a chelating fashion through the carboxylate end and further connects the dimers by bonding to the Sr atoms of the neighboring dimers through the hydroxyl groups, thus forming layers parallel to the *ab* plane of the unit cell (Figure 6a). Such connectivity results in the

Table 3. Selected Bond Distances in I–V^a

	moiety	distance (Å)	moiety	distance (Å)
I	Sr(1)–O(19)	2.524(2)	Sr(2)–O(5)	2.507(2)
	Sr(1)–O(12)	2.550(4)	Sr(2)–O(9)	2.565(3)
	Sr(1)–O(16)	2.570(3)	Sr(2)–O(3)	2.572(3)
	Sr(1)–O(13)	2.589(3)	Sr(2)–O(1)	2.602(3)
	Sr(1)–O(14)	2.603(3)	Sr(2)–O(10)	2.631(3)
	Sr(1)–O(11)	2.616(3)	Sr(2)–O(2)	2.633(3)
	Sr(1)–O(15)	2.652(3)	Sr(2)–O(4)	2.652(3)
	Sr(1)–O(10)	2.671(3)	Sr(2)–O(11)	2.677(3)
II	Sr(1)–O(1)	2.523(2)	Sr(1)–O(5)	2.617(3)
	Sr(1)–O(2)	2.542(2)	Sr(1)–O(6)	2.665(2)
	Sr(1)–O(4)	2.613(4)	Sr(1)–O(7) ¹	2.666(2)
	Sr(1)–O(3)	2.590(2)	Sr(1)–O(7)	2.681(2)
III	Sr(1)–O(2)	2.492(3)	Sr(1)–O(2) ²	2.683(3)
	Sr(1)–O(2) ¹	2.492(3)	Sr(1)–O(2) ³	2.683(3)
	Sr(1)–O(4) ¹	2.603(4)	Sr(1)–O(5)	2.698(3)
	Sr(1)–O(4)	2.603(4)	Sr(1)–O(5) ¹	2.698(3)
IV	Sr(1)–O(1)	2.515(4)	Sr(1)–O(6)	2.670(5)
	Sr(1)–O(2) ¹	2.532(4)	Sr(1)–O(2)	2.719(3)
	Sr(1)–O(4)	2.656(5)	Sr(1)–O(1) ²	2.755(4)
	Sr(1)–O(3)	2.660(4)	Sr(1)–O(7)	2.778(4)
	Sr(1)–O(5)	2.661(5)		
V	Sr(1)–O(1)	2.544(3)	Sr(1)–O(4)	2.616(2)
	Sr(1)–O(2)	2.565(2)	Sr(1)–O(5)	2.625(2)
	Sr(1)–O(4) ¹	2.569(2)	Sr(1)–O(6) ²	2.657(2)
	Sr(1)–O(3)	2.573(2)	Sr(1)–O(7)	2.921(2)

^a Symmetry transformations used to generate equivalent atoms: (1) $-x + 1, -y + 1, -z + 1$ and (2) $-x + 1, -y + 1, -z$ in **I**; (1) $-x + 1, -y + 1, -z + 1$ and (2) $-x, -y + 1, -z$ in **II**; (1) $-x + 2, -y, -z + 0.5$; (2) $-x + 2, -y + 2, -z$; (3) $x, -y + 2, z + 0.5$; and (4) $-x + 2, -y + 2, -z + 1$ in **III**; (1) $-x - 1, -y, -z$ and (2) $-x - 2, -y, -z$ in **IV**; and (1) $-x + 2, -y + 1, -z + 2$; (2) $x + 1, y, z$; (3) $x - 1, y, z$; and (4) $-x + 2, -y, -z + 2$ in **V**.

formation of 4-ring channels running across the layer along the *a* axis, and the pendant DHB molecules protrude out from the layer (Figure 6b). Because the Sr–O–Sr connectivity is confined to the dimers, the structure can be regarded as two-dimensional coordination polymer. The interstitial water molecules reside in the interlamellar region and form O–H···O type hydrogen bonds with the framework oxygen atoms.

π – π interactions with energies in the 3–10 kcal mol^{−1} range stabilize molecules in many crystals.¹⁸ Compounds **I**, **IV**, and **V** appear to have significant π – π interactions, with the minimum centroid-to-centroid distances between the participating aromatic rings being 3.485 Å and 3.539 Å (**I**) and 3.849 Å (**IV**) and 3.599 Å (**V**); the dihedral angles are 0.0° in **I**, **IV**, and **V**.

The average Sr–O bond distances in the Sr DHB frameworks are 2.597 (for Sr1) and 2.605 (for Sr2; **I**), 2.608 (**II**), 2.619 (**III**), 2.661 (**IV**), and 2.634 Å (**V**). The average carboxylate C–O bond distances of the DHB units in **I–V** are 1.263, 1.267, 1.260, 1.268, and 1.265 Å, respectively, consistent with the values observed in other metal DHBs.^{12–14} The carboxylate C–O bond distance of the acetate moiety in **IV** is 1.255 Å. Selected bond distances for compounds **I–V** are summarized in Table 3.

3.2. Lanthanum DHBs, VI–IX. With 2,4-DHB, lanthanum forms a one-dimensional chain structure of the formula [La(CH₃CO₂)₂(2,4-DHB)(H₂O)]·0.18H₂O, **VI**. The asymmetric

unit contains one La atom, 11 carbon atoms belonging to a DHB molecule and two acetates, nine O atoms coordinating to the La atom, of which two are from coordinating water molecules, and one interstitial water molecule with 36% occupancy (Figure 7a). The 2,4-DHB bridges the La centers through its carboxylate end, forming a one-dimensional chain structure parallel to the *b* axis of the unit cell. The La centers in the chain are further bridged by three-coordinating oxygen atoms of the chelating acetate molecules, thus giving rise to one-dimensional La–O–La connectivity along the chain (Figure 7b). Unlike the analogous Sr compound, **IV**, the chains in **VI** are formed by both the DHB and the acetate units. The chains are arranged parallel to each other in the *bc* plane. Two adjacent chains are separated by half a unit-cell length along the *c* axis. The layers are separated by half a unit-cell length along the *a* axis and are stacked over one another to complete the three-dimensional packing arrangement in the crystal structure (Figure 7c). The interstitial water molecules reside in the interlamellar region. The O–H···O type hydrogen bonds formed by the water molecules with the oxygen atoms of the chain stabilize the structure.

We have isolated and characterized three closely related lanthanum acetate DHBs **VII**, **VIII**, and **IX** of the general formula [La(CH₃CO₂)₂{CO₂C₆H₃(OH)₂}(H₂O)₂], with 3,5-DHB, 2,6-DHB, and 2,3-DHB, respectively. These compounds, which contain zero-dimensional (i.e., isolated) dimers, were obtained even when the reaction temperature was increased to 100 °C. [La(CH₃CO₂)₂(3,5-DHB)(H₂O)₂], **VII**, has an asymmetric unit containing 22 non-hydrogen atoms. There is one crystallographically independent La atom, 11 C atoms belonging to the two acetates and one DHB molecule, and 10 O atoms, of which two are from water molecules coordinating to the La center as shown in Figure 8a. The DHB molecule bridges the nine-coordinated La centers through the carboxylate end, forming the dimer. The La centers in the dimer are further bridged by the three coordinating oxygen atoms of the acetate ions, giving rise to La–O–La connectivity. The dimers are arranged linearly, parallel to the *a* axis of the unit cell, and the linear arrangements are parallel to the *ac* plane. The DHB rings in the different chains overlap with each other in an interdigitated fashion, indicating the presence of weak π – π interaction between the benzene rings of the adjacent chains (Figure 8b). The hydroxyl groups of the overlapping benzene rings are oriented in a staggered fashion, thereby minimizing the possible electrostatic repulsion between them. Such a stacking of the phenyl rings has been observed in a copper derivative of 3,5-DHB.¹³ The O–H···O type hydrogen bonds between the coordinated water molecules and the oxygen atoms of the carboxylate groups render additional stability to the structure.

In addition to the lanthanum compound, **VII**, isostructural yttrium and gadolinium compounds with the formulas [Y(CH₃CO₂)₂(3,5-DHB)(H₂O)₂] and [Gd(CH₃CO₂)₂(3,5-DHB)(H₂O)₂] were also synthesized, and the structures were solved by single-crystal XRD. The unit cell parameters of the compounds are listed in the footnote to Table 1. The

(18) Hunter, C. A. *Chem. Soc. Rev.* **1994**, *23*, 101.

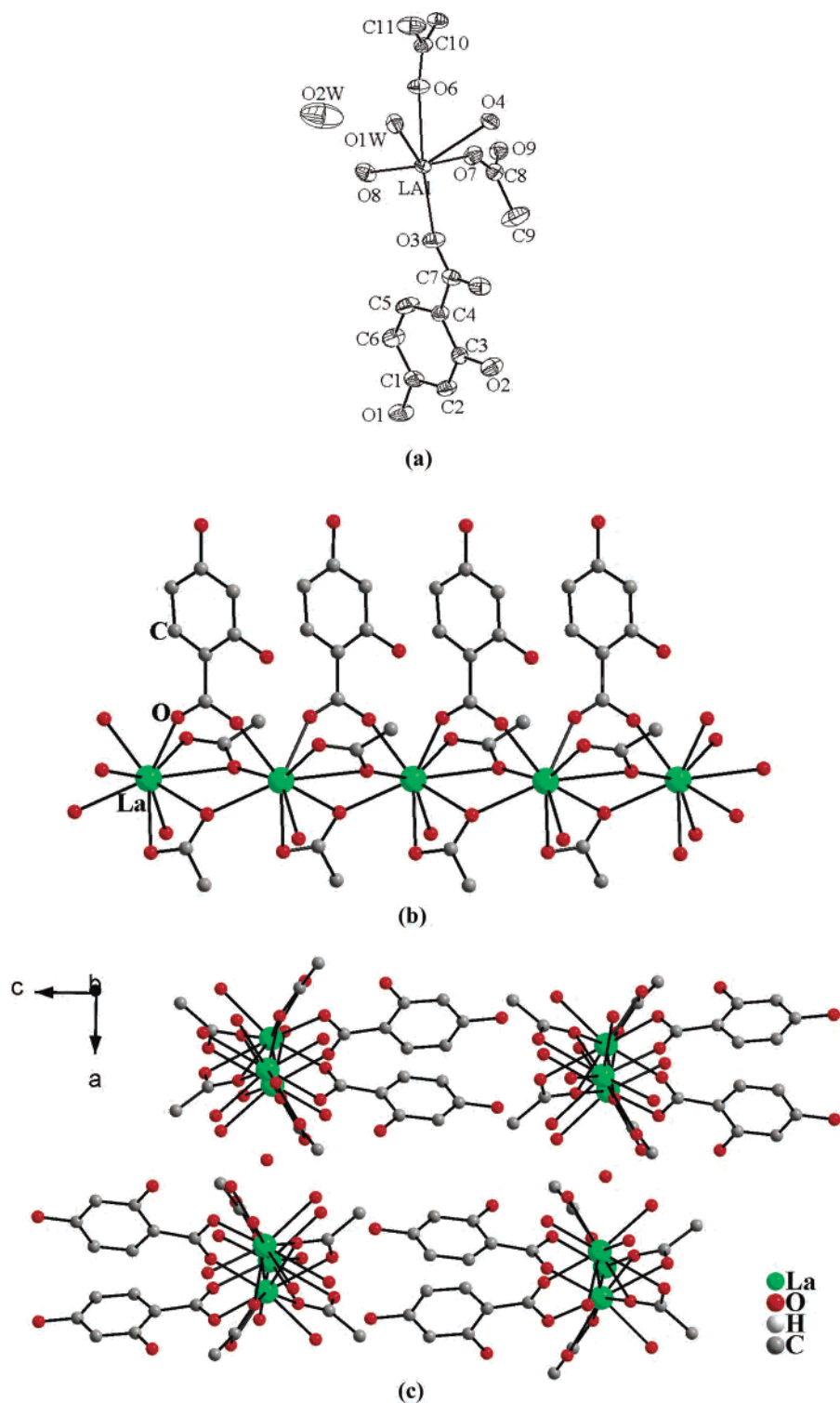


Figure 7. (a) ORTEP plot of $[\text{La}(\text{CH}_3\text{CO}_2)_2(2,4\text{-DHB})\text{H}_2\text{O}] \cdot 0.18\text{H}_2\text{O}$, **VI**. Thermal ellipsoids are shown at 50% probability. Hydrogen atoms are not shown for clarity. (b) The one-dimensional chain structure of **VI**, with one-dimensional La–O–La connectivity. (c) Three-dimensional packing diagram of **VI**.

cell dimensions and the volume are in the expected order $Y < Gd < La$.¹⁹

The zero-dimensional dimeric structures obtained with 2,6-DHB, $[\text{La}(\text{CH}_3\text{CO}_2)_2(2,6\text{-DHB})(\text{H}_2\text{O})_2]$, **VIII**, and 2,3-DHB, $[\text{La}(\text{CH}_3\text{CO}_2)_2(2,3\text{-DHB})(\text{H}_2\text{O})_2]$, **IX**, were similar to the structure of **VII** (Figure 8). The dimers, in **VIII** and **IX**, are arranged parallel to each other to form linear arrangements

parallel to the *b* axis of the unit cell. The hydroxyl groups of the overlapping benzene rings are oriented in a staggered fashion just as in **VII**.

The average La–O bond distances in **VI–IX** are 2.575, 2.560, 2.559, and 2.55 Å, respectively. The average car-

(19) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

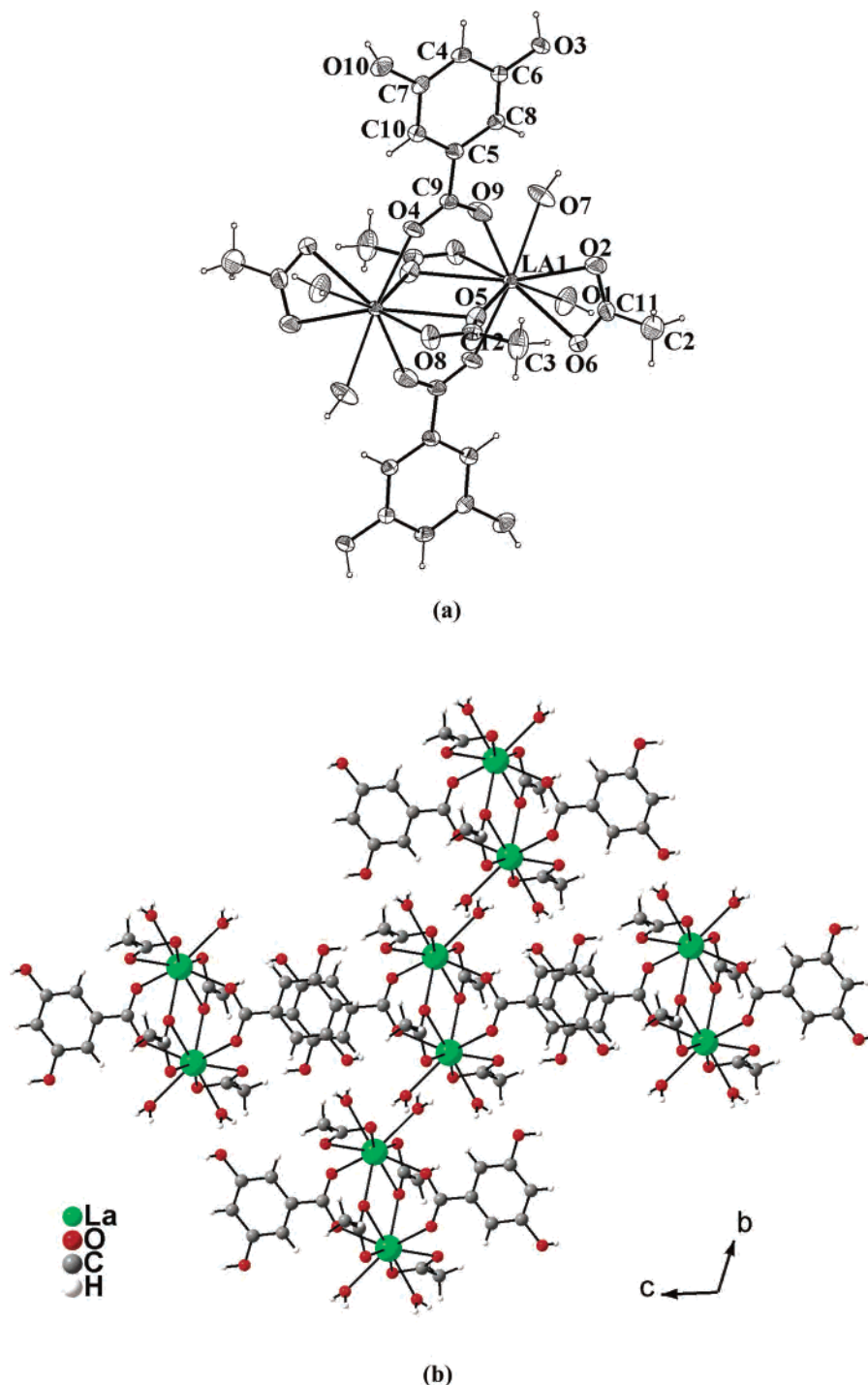


Figure 8. (a) ORTEP plot of $[\text{La}(\text{CH}_3\text{CO}_2)_2(3,5\text{-DHB})(\text{H}_2\text{O})_2]$, **VII**, with thermal ellipsoids shown at 50% probability. Only the asymmetric part is labeled. (b) Three-dimensional packing diagram of **VII**. Note the staggered alignment of the hydroxyl groups of the overlapping DHB rings.

boxylate C–O bond distances of the DHB group in **VI–IX** are 1.263, 1.257, 1.274, and 1.263 Å, respectively, and are consistent with the values observed in other metal DHBs.^{12–14} The average carboxylate C–O bond distances of the acetate group in **VI–IX** are 1.262, 1.261, 1.263, and 1.258 Å, respectively. In Table 4, we show the selected bond distances for compounds **VI–IX**.

3.3. Thermal Properties. Thermogravimetric analysis of the strontium DHBs, **I–III** and **V**, in an oxygen atmosphere, showed two distinct mass losses. The Sr compounds lose

water molecules around 100 °C (percentage weight loss for **I**, calcd, 13.78%, found, 13.0%; for **II**, calcd, 18.61%, found, 18.11%; for **III**, calcd, 21.53%, found, 21.75%; for **V**, calcd, 10.26%, found, 10.50%). The second mass loss starts at 300 °C and is complete by 500 °C, corresponding to the pyrolysis of DHB, leaving SrO as the product, as verified by powder XRD (percentage weight loss for **I**, calcd, 63.51%, found, 63.80%; for **II**, calcd, 59.97%, found, 60.11%; for **III**, calcd, 57.81%, found, 57.55%; for **V**, calcd, 66.12%, found, 66.0%). In the case of **IV**, the mass losses occur in three

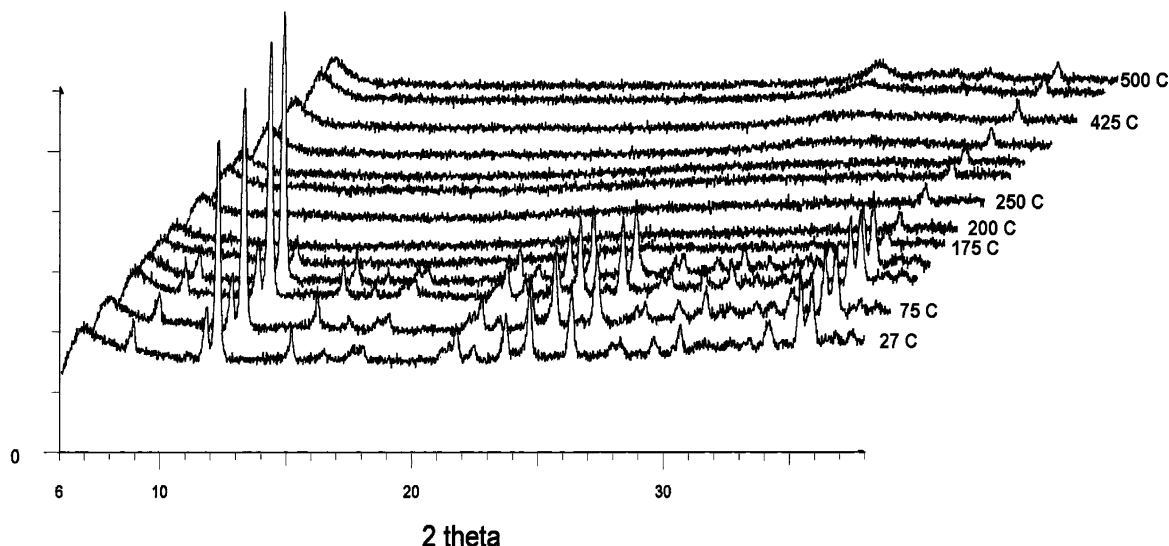


Figure 9. Thermodiffractograms of **VII** showing the loss of crystallinity above 200 °C.

Table 4. Selected Bond Distances in **VI–IX**^a

	moiety	distance (Å)	moiety	distance (Å)
VI	La(1)–O(3)	2.416(2)	La(1)–O(6)	2.588(2)
	La(1)–O(8)	2.494(2)	La(1)–O(4)	2.626(2)
	La(1)–O(1W)	2.510(2)	La(1)–O(6) ¹	2.673(2)
	La(1)–O(7)	2.515(2)	La(1)–O(7) ¹	2.770(2)
	La(1)–O(9) ¹	2.587(2)		
VII	La(1)–O(9)	2.464(2)	La(1)–O(8) ¹	2.564(2)
	La(1)–O(4) ¹	2.489(2)	La(1)–O(6)	2.577(2)
	La(1)–O(5)	2.510(2)	La(1)–O(2)	2.606(2)
	La(1)–O(1)	2.546(2)	La(1)–O(5) ¹	2.724(2)
	La(1)–O(7)	2.563(2)		
VIII	La(1)–O(1)	2.510(2)	La(1)–O(6)	2.550(3)
	La(1)–O(2) ¹	2.518(3)	La(1)–O(7)	2.564(3)
	La(1)–O(3)	2.530(3)	La(1)–O(8)	2.591(3)
	La(1)–O(4)	2.534(3)	La(1)–O(1) ¹	2.698(3)
	La(1)–O(5)	2.535(3)		
IX	La(1)–O(1)	2.484(3)	La(1)–O(9)	2.562(3)
	La(1)–O(2)	2.490(3)	La(1)–O(6)	2.562(3)
	La(1)–O(3)	2.500(3)	La(1)–O(7)	2.573(3)
	La(1)–O(4)	2.510(5)	La(1)–O(3) ¹	2.730(3)
	La(1)–O(5)	2.538(4)		

^a Symmetry transformations used to generate equivalent atoms: (1) $-x + 0.5, y - 0.5, z$ and (2) $-x + 0.5, y + 0.5, z$ in **VI**; (1) $-x + 1, -y + 1, -z + 1$ in **VII**; (1) $-x + 1, -y + 1, -z - 1$ in **VIII**; and (1) $-x + 1, -y, -z$ in **IX**.

steps. It loses the water molecules around 100 °C. The second mass loss occurs in the range 175–250 °C, corresponding to the loss of acetate molecules. The third mass loss corresponding to the loss of DHB starts at 325 °C, leaving behind SrO as the product (percentage weight loss for **IV**, calcd, 19.37%, found, 19.80% for water loss; calcd, 15.88%, found, 16.10% for the loss of acetate molecules; and calcd, 36.87%, found, 37.0% for DHB).

Thermogravimetric analysis of the lanthanum DHBs, **VI–IX**, in oxygen atmosphere, showed similar behavior, with mass losses occurring in three distinct stages. The first mass loss for **VI** occurs between 100 and 200 °C, corresponding to the loss of both interstitial and coordinated water molecules (percentage weight loss for **VI**, calcd, 4.92%, found, 4.80%), whereas for the three compounds, **VII–IX**, it occurs between 150 and 200 °C, corresponding to the loss

of coordinated water molecules (percentage weight loss for **VII**, **VIII**, and **IX**, calcd, 8.07%, found, 8.40% for **VII**, 8.00% for **VIII**, 8.23% for **IX**). Variable temperature XRD data show that sample **VII** loses its crystallinity at this stage. In Figure 9 we have given the thermodiffractogram data of compound **VII**. The second mass loss for compounds **VI–IX** occurs gradually in the 250–350 °C range, corresponding to the loss of acetates (percentage weight loss for **VI**, calcd, 27.40%, found, 27.22%; for **VII**, **VIII**, and **IX**, calcd, 26.46%, found, 27.00% for **VII**, 26.23% for **VIII**, 26.66% for **IX**). The loss of the DHB starts at 375 °C, most of it being lost at 400 °C (percentage weight loss for **VI**, calcd, 29.90%, found, 29.52%; for **VII**, **VIII** and **IX**, calcd, 28.93%, found, 28.10% for **VII**, 28.29% for **VIII**, 28.45% for **IX**). The final product was found to be La₂O₃, verified by powder XRD.

4. Concluding Remarks

We have demonstrated that dihydroxybenzoic acids form compounds with diverse structures and dimensionalities with both Sr and La. The chain and layered structures, which are reported here for the first time, are generally based on metal DHB dimers, sometimes in combination with acetate. It is noteworthy that some of the chains have metal–oxygen–metal connectivity and are therefore extended inorganic hybrid structures rather than coordination polymers. One of the strontium compounds with the chain structure, **III**, has large zeolite-like channels and is accordingly associated with the largest unit cell volume among the Sr DHBs reported here. By and large, the carboxylate unit is responsible for giving rise to the chain or layered structures, presumably because it is more acidic than the phenolic groups. We have examined the various structures in the light of the acid strengths of the different acids, which are approximately 2,6 > 2,4 > 2,3 > 3,5²⁰ but find no strong relation between the acidity and the mode of coordination to the metal. For example, the strongest and the second weakest acids, 2,6-DHB and 2,3-DHB, both exhibit coordination through carboxylate as well as phenolic groups. We, therefore, believe

that the bonding is largely dictated by geometrical factors. In view of this it is not surprising that we have not encountered three-dimensional structures. We would expect three-dimensional structures if we had another carboxylic group in the 4-position as suggested recently.⁹ In the case of the Sr 2,6-DHB structure, the Sr...Sr connectivity is achieved via the two phenolic groups, presumably on account of their convenient geometry. It is also interesting that we obtain only zero-dimensional dimeric lanthanum DHBs and that these do not transform to chains or layers at higher temperatures as found in many metal carboxylates.²¹ The present study suggests that it would be worthwhile to examine the structures of the DHBs formed by transition metals.

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Supporting Information Available: Simulated and experimental powder XRD patterns for compounds **I–IX**. Crystallographic information files (CIF) for the compounds **I–IX**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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