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Acentric and Centric Interpenetrations of an Anionic Framework Mediated by Cation Sizes: The Alkali-Metal Tin(II) Benzenedicarboxylates $A_2Sn_2(bdc)_3(H_2O)_x$ (A = Li, Na, K, Rb, Cs)

Xiqu Wang, Lumei Liu, Tatyana Makarenko, and Allan J. Jacobson*

Department of Chemistry, University of Houston, Houston, Texas 77204-5003

ABSTRACT: A series of alkali-metal tin benzenedicarboxylates $A_2Sn_2(bdc)_3(H_2O)_x$, A = Li, Na, K, Rb, Cs, in single crystal forms have been synthesized by using a hydrothermal technique. The compounds all have cubic crystal structures based on a very open anionic $[Sn_2(bdc)_3]^{2-}$ framework which is 8-fold interpenetrated noncentrosymmetrically (space group $I23$) in $Li_2Sn_2(bdc)_3(H_2O)_2$, **1**, $K_2Sn_2(bdc)_3$, **3**, $Rb_2Sn_2(bdc)_3$, **4**, and $Cs_2Sn_2(bdc)_3$, **5**, but centrosymmetrically (space group $Pn\overline{3}$) in $Na_2Sn_2(bdc)_3(H_2O)$, **2**. The ion size and coordination requirements of the alkali ions play an important role in the interpenetration of the anionic framework and the symmetry of the structures.

Introduction

The rapid development in inorganic−organic hybrid compounds has led to the discovery of many structurally unusual and technologically useful materials.[1−7] Design of such hybrid crystal structures can take advantage of both the specific physical properties of inorganic structural units and the huge variety of suitable organic linkers. A particularly well studied organic linker is the dianion of 1,4-benzenedicarboxylic acid (bdc). Compounds with various structures ranging from one-dimensional chains to highly porous frameworks have been synthesized by using this ligand to connect together metal oxide clusters or extended building units.[8−11] Sometimes, to facilitate the formation of structures with low dimensionality or with large voids the bdc linker may be partially replaced by terminating ligands such as 2,2-bipyridine or water molecules.[12] A similar terminating role may also be played by electron lone pairs of metal cations such as Sn^{2+} which tend to have an asymmetric "one-sided" coordination environment.[13−15] Very few structures of divalent tin benzenedicarboxylates are known despite the fact that some organotin polycarboxylates have found wide applications in biology and catalysis.[16−18] We have synthesized a series of alkali-metal tin benzenedicarboxylates $A_2Sn_2(bdc)_3(H_2O)_x$, A = Li, Na, K, Rb, Cs, in single crystal forms by using a hydrothermal technique. The crystal structures of the compounds are all based on a very open anionic $[Sn_2(bdc)_3]^{2-}$ framework which is 8-fold interpenetrated noncentrosymmetrically in $Li_2Sn_2(bdc)_3(H_2O)_2$, **1**, $K_2Sn_2(bdc)_3$, **3**, $Rb_2Sn_2(bdc)_3$, **4** and $Cs_2Sn_2(bdc)_3$, **5**, but centrosymmetrically in $Na_2Sn_2(bdc)_3(H_2O)$, **2**.

Experimental Section

Synthesis. In a typical synthesis of compound **1**, $SnSO_4$, $LiOH \cdot H_2O$, 1,4-benzenedicarboxylic acid, and H_2O were mixed in mole ratios of 1:2:1.5:55. The mixture was sealed in a Teflon-lined Parr autoclave (23 mL inner volume) in air and heated at 200 °C for 6 days. Colorless polyhedral crystals of **1** were recovered by vacuum filtering and washing with water. Compounds **2−5** were similarly synthesized by replacing the lithium hydroxide with the other alkali

*Corresponding author. Tel: 713-742-2785. Fax 713-742-2785. E-mail: ajjacob@uh.edu.

metal hydroxides. We were able to obtain single phase products for **1** and **2** with high yields (ca. 70% based on Sn). Compounds **3−5** were obtained as major phases together with minor-phase impurities. Synthesis conditions that minimized the impurities ($<20\%$) were developed using tetramethylamonium hydroxide to adjust the initial pH to a narrow range of 5−6, and using a reaction temperature of 170 °C. Efforts to eliminate completely the impurities by varying the reagent ratios and reaction temperatures have not yet been successful. Since the crystals have typical shapes (Figure 1), they could easily be separated from the impurities for characterization.

Characterization. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). Energy dispersive X-ray (EDX) analyses were carried out using a JEOL JSM 6400 scanning electron microscope with a Link Analytical EXL spectrometer. The IR spectra were measured on a Galaxy Series FTIR 5000 spectrometer with pressed KBr pellets. Thermogravimetric analysis (TGA) measurements were carried out using a TA Instruments Hi-Res 2950 system in dry air or in nitrogen flow, employing a heating rate of 3 °C min^{-1}. Single-crystal X-ray structure analyses were performed on a Siemens SMART platform diffractometer outfitted with an Apex II area detector and monochromatized Mo K_α radiation. The structures were solved by direct methods and refined using *SHELXTL*.[19] Crystal data for the compounds **1−5** are summarized in Table 1.

Results and Discussion

Characterization. The presence of tin and the corresponding alkali metals in the compounds were qualitatively confirmed by EDX analysis on single crystals. Chemical analyses were performed for compounds **1−5**. The results are shown in Table 2. For compound **1** which occurs in the form of clean crystals the results are in very good agreement with the formula derived from crystal structure refinements and TGA results. For compounds **3**, **4**, and **5**, the C, H, Sn results are satisfactory, but the alkali metal contents are systematically low. Compound **2** is the least satisfactory with low values for both Sn and Na. Subsequent studies have shown that the low alkali metal contents are due to the sensitivity of the compounds to water. Hydrolysis leads to decomposition at the crystal surfaces and reduction of the alkali metal content. This was confirmed by the observation that crystals of **3** converted to $Sn_3(OH)_2(bdc)_2$ after immersion in water at room temperature for several days.

The infrared spectra of **1**−**5** all show strong bands characteristic of bidentate O−C−O of the bdc anion at approximately 1580 cm^{-1} and 1350 cm^{-1} (Figure 2). The differences between the two bands in each phase are between those typical for bidentate and unidentate coordinated carboxylate anions,[20] consistent with the one short and one long Sn−O bond of the chelating bdc observed in the crystal structures. The spectra of **1** and **2** show characteristic bands for the water molecules at approximately 3600 cm^{-1} and 1690 cm^{-1}. Similar bands were also observed for the samples of **3**, **4**, and **5** which are either due to partial substitution of
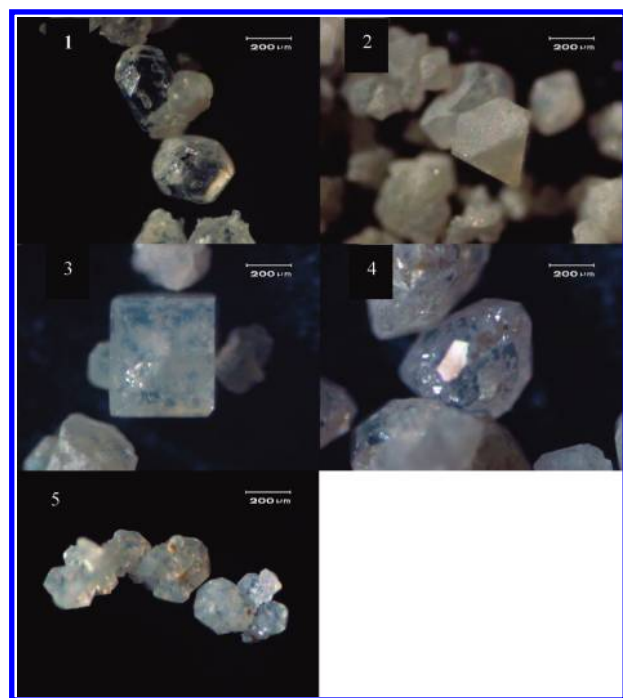
H_3O^+ for A^+ or to the presence of surface water. The thermogravimetric analysis data for **3** and **4** suggest the presence of a small amount of lattice water (< 0.4 H_2O per formula unit) that is lost at ~215 °C, but this could not be confirmed by structure refinements.

The thermogravimetric analysis (TGA) data in air indicate that compound **1** decomposes in one step between ca. 215−325 °C to form Li_2CO_3 + $2SnO_2$ (51.94% obs, 51.86% calcd). TGA data in air for $Na_2Sn_2(bdc)_3(H_2O)$, **2**, show a weight loss of 1.94% between 200 and 250 °C corresponding to a loss of 0.85 H_2O per formula unit. The anhydrous compound then decomposes between 420 and 500 °C to form a residue of Na_2CO_3 + $2SnO_2$ (50.06% obs, 51.50% calcd). Similarly, $K_2Sn_2(bdc)_3$, **3**, $Rb_2Sn_2(bdc)_3$, **4**, and $Cs_2Sn_2(bdc)_3$, **5**, decompose in air between 400 and 500 °C,

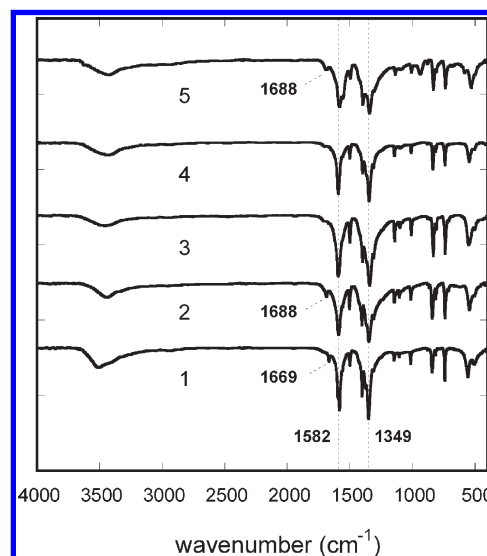**Figure 1.** Optical micrographs of the crystals of compounds **1**−**5**.

Figure 2. Infrared spectra for compounds **1**−**5**.

Table 1. Crystal Data and Structure Refinement Details for Compounds 1−5^a

compound	1	2	3	4	5
formula	$C_{24}H_{16}Li_2O_{14}Sn_2$	$C_{24}H_{14}Na_2O_{13}Sn_2$	$C_{24}H_{12}K_2O_{12}Sn_2$	$C_{24}H_{12}Rb_2O_{12}Sn_2$	$C_{24}H_{12}Cs_2O_{12}Sn_2$
F.W.	779.63	793.71	807.92	900.66	995.54
temperature/K	293(2)	293(2)	293(2)	293(2)	293(2)
space group	$I23$	$Pn\overline{3}$	$I23$	$I23$	$I23$
a/Å	13.7784(2)	13.903(1)	13.956(2)	13.9985(3)	14.0924(3)
V/Å^3	2615.75(7)	2687.5(4)	2718.1(7)	2743.1(1)	2798.7(1)
Z	4	4	4	4	4
D_{calc}/g(cm)$^{-3}$	1.980	1.962	1.974	2.181	2.363
μ/mm^{-1}	1.983	1.959	2.206	5.409	4.410
refln. collected/unique	8306/1116	4454/1099	4842/1117	4688/1137	8956/1208
R_{int}	0.0459	0.0297	0.0613	0.0256	0.0271
data/parameters	1116/71	1099/67	1117/62	1137/62	1208/117
goodness-of-fit	1.093	1.060	1.039	1.028	1.051
R_1/wR_2 ($I > 2\sigma(I)$)	0.0145/0.0386	0.0275/0.0607	0.0381/0.0637	0.0211/0.0469	0.0218/0.0481
R_1/wR_2 (all data)	0.0146/0.0387	0.0425/0.0662	0.0569/0.0670	0.0250/0.0478	0.0252/0.0491
absol. struct. parameter	−0.02(3)		−0.08(5)	−0.01(1)	0.46(7)^b

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma(wF_o^2)^2]^{1/2}$. ^{b} Racemic twin.

Table 2. Chemical Analysis Data for 1−5

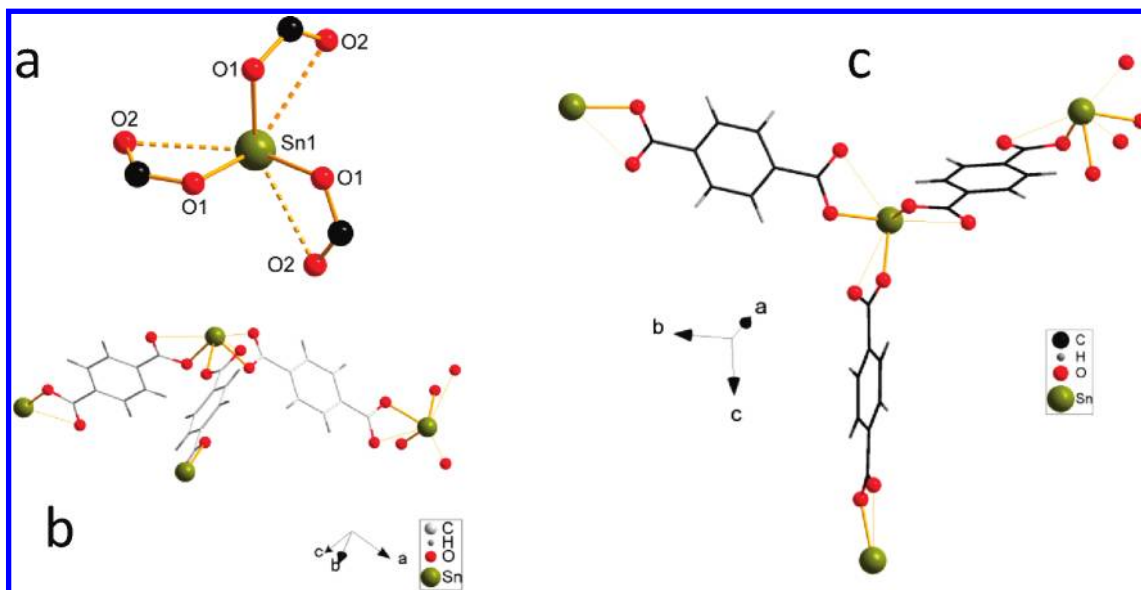|	C		H		M = Li, Na, K, Rb, Cs		Sn	
	obs %	calc %	obs %	calc %	obs %	calc %	obs %	calc %
$Li_2Sn_2(bdc)_3(H_2O)_2$, **1**	36.98	36.94	2.05	2.05	1.67	1.78	29.6	30.45
$Na_2Sn_2(bdc)_3(H_2O)$, **2**	34.48	36.28	1.73	1.76	5.09	5.79	26.4	29.91
$K_2Sn_2(bdc)_3$, **3**	34.58	35.65	1.46	1.48	8.06	9.68	29.40	29.39
$Rb_2Sn_2(bdc)_3$, **4**	31.78	32.0	1.48	1.33	18.0	19.0	27.4	26.4
$Cs_2Sn_2(bdc)_3$, **5**	28.72	28.9	1.26	1.21	24.05	26.7	24.7	23.9

Figure 3. The $Sn(bdc)_{3/2}$ expanded trigonal pyramid. Thick and thin brown lines represent the short and long Sn−O bonds, respectively.

Table 3. Selected Bond Distances and Angles for $A_2Sn_2bdc_3$ Compounds

compound	cation	d(Sn-O) Å	d(Sn-O) Å	∠O−Sn−O °	∠Sn−Sn−Sn °
1	Li	2.179(1)	2.859(1)	82.06(5)	103.611(1)
2	Na	2.215(2)	2.754(3)	76.947(7)	104.796(2)
3	K	2.177(3)	2.845(5)	80.46(10)	105.363(5)
4	Rb	2.196(2)	2.809(3)	80.54(7)	105.296(2)
5	Cs[a]	2.12(2)	2.85(2)	78.1(9)	105.470(3)
		2.32(2)	2.70(1)	84.0(8)	

[a] Distances for two disordered bdc anions, averages 2.22 Å, 2.78 Å.

to form residues of $A_2CO_3 + 2SnO_2$ (56.78% obs, 54.41% calcd for **3**, 59.10% obs, 57.16% calcd for **4**; 63.22% obs, 61.58% calcd for **5**). Further weight loss corresponding to carbonate decomposition is observed to occur at higher temperatures for A = Cs (610 °C) and Rb (740 °C).

Crystal Structures. The Anionic Framework. The structures of the compounds **1**−**5** are all based on a chiral anionic $[Sn_2(bdc)_3]^{2-}$ framework in which the single symmetry-nonequivalent Sn atom is linked by three chelating bdc ligands to three neighboring Sn atoms (see Figure 3). The tin atom is located on a 3-fold rotation axis. The chelating bdc ligands are asymmetrically coordinated to the tin atom with one short and one long Sn−O bond giving the 3 + 3 coordination that is typical for Sn^{2+} ions (Figure 3a). The three short Sn−O bonds ranging from 2.19 to 2.22 Å form a trigonal pyramid that is complemented by three long Sn−O bonds in the range 2.75−2.86 Å in each of the five structures (see Table 3).

Bond angles between the short Sn−O bonds are in the range of 76.9−82.5°. Even with the long Sn−O bonds included, the Sn atoms still have a one-sided coordination (Figure 3b) because of the repulsion between the bonding electron pairs and the lone electron pair of Sn^{2+}. Each benzenedicarboxylate anion is coordinated to two tin cations (Figure 3c).

The very open chiral framework is built by interconnecting the $Sn(bdc)_{3/2}$ units as shown in Figure 3c. The angles between three connected Sn atoms all fall in the narrow range 103.6−105.5°. A wide channel system outlined by helical walls run along the [111], [$\bar{1}$11], [1$\bar{1}$1], and [11$\bar{1}$] directions of the framework (Figures 4 and 5). In **5** the bdc
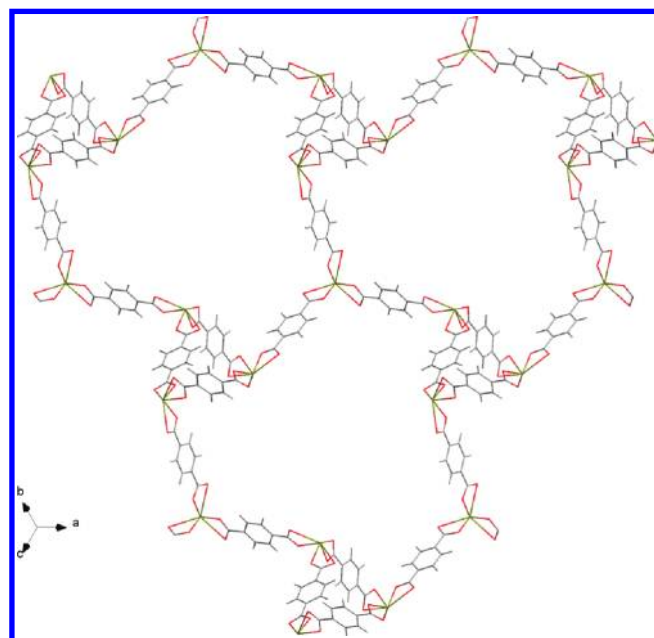

Figure 4. A view along [111] of one of the eight $[Sn_2(bdc)_3]^{2-}$ frameworks.

ligand is disordered over two roughly parallel orientations separated by less than 1 Å from each other (Figure 6). The frameworks in **1**−**4** are ordered.

Interpenetrations of the Anionic Framework. The $[Sn_2(bdc)_3]^{2-}$ frameworks are 8-fold interpenetrated in all the structures (Figure 7). In **1**, **3**, **4**, **5** the interpenetrations are the same and the individual frameworks are related by the 2-fold and 3-fold rotation axes and the body-centering translation symmetry, space group *I*23, while in **2** the eight interpenetrating frameworks are related by *n*-glide planes, 3-fold rotation axes and inversion symmetry centers, space group $Pn\bar{3}$. Therefore, only the structure of **2** is centrosymmetric. The interpenetration leads to a tetrahedral arrangement of Sn_4 atoms with Sn···Sn edge lengths in the range of 3.9−4.5 Å. Four separate frameworks come together to form a tetrahedron as shown in Figure 7a looking along the 100 direction and in Figure 7b along 111.

The lone electron pairs of the Sn atoms, assumed to lie on the opposite side of the three short Sn−O bonds, point to the centers of the Sn_4 tetrahedra. In **2**, the neighboring Sn_4 tetrahedra are related by a inversion symmetry center while in **1**, **3**, **4**, **5** they are related by a translation of a half diagonal of the cubic unit cell.
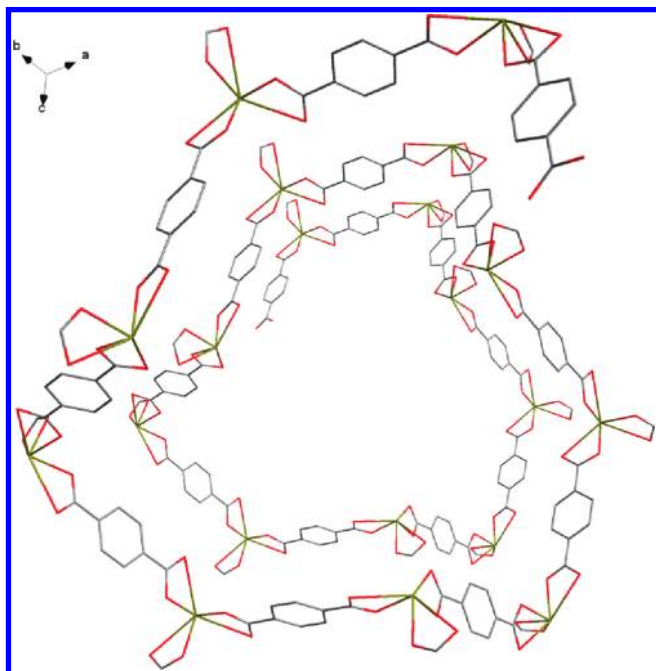

Figure 5. The helical wall of the [111] channels of an individual $[Sn_2(bdc)_3]^{2-}$ framework.

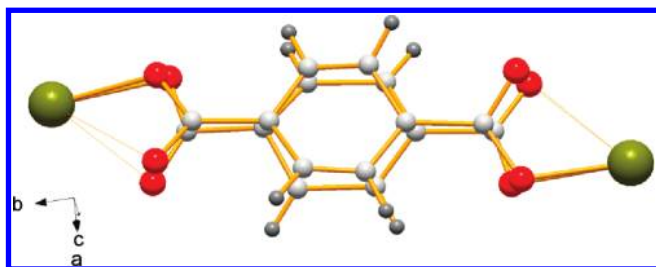**Figure 6.** Two disordered positions of the bdc ligand in compound **5**.

The arrangement of the frameworks leads to another part of the structure that lies between the Sn tetrahedra. This open part of the framework is lined with the oxygen atoms from the bdc ligands and provides the coordination environment for the cations. The arrangement for the potassium ion is shown in Figure 8a along 100 and in Figure 8b perpendicular to 111, as a representative example. The details of the K^+ coordination are discussed below.

Coordination of the Alkali Metal Ions. In the anhydrous structures of compounds **3**, **4**, **5**, the larger alkali ions all have a distorted octahedral coordination by oxygen ions with bond lengths K−O [2.695(3) Å × 3, 3.093(3) Å × 3], Rb−O [2.789(3) Å × 3, 3.095(2) Å × 3], and Cs−O [2.827(14) Å × 3, 3.093(26) Å × 3, 3.024(12) Å × 3, 3.211(28) Å × 3], respectively. The geometry of the coordination site is shown in Figure 8 and in a simplified view in Figure 9c for K^+ ions. The extra distances and the greater errors for the Cs compound arise from the disorder of the bdc anion described above. The Li ion in **1** has a tetrahedral coordination from three carboxylate oxygen atoms with a Li−O bond length of 1.916(3) Å × 3 and one water oxygen atom with the bond length 1.842(3) Å. The water molecule is randomly disordered over three orientations related by a 3-fold rotation axis (see Figure 9a).

The arrangement of the Na^+ cations is more complex than found for the other alkali metal cations. There are two symmetry-independent Na sites in **2**. The Na1 atom has a site symmetry $\bar{3}$, and has a distorted octahedral coordination with six Na−O bond lengths of 2.467(2) Å. The NaO_6 octahedron is very elongated with O−Na−O bond angles of 67.9° rather than 90°. The Na2 atom is tetrahedrally coordinated by oxygen ions in a similar way to the Li ions in **1**. The Na−O distances to the framework oxygen atoms are 2.270(3) Å × 3 and to the oxygen atom of the water molecule 2.263(5) Å. The Na2 atom and the water oxygen atom bonded to it are randomly disordered leading to two disordered positions of the Na_2O_4 tetrahedra related by an inversion symmetry center. This is shown in Figure 9b where the two disordered sodium ion positions are shown in green and light green. The symmetry differences between the structure of **2** of the others is apparent in Figure 9. In Figure 9b the Sn tetrahedra are related by an inversion center, whereas in Figure 9a,c they are related by a translation.

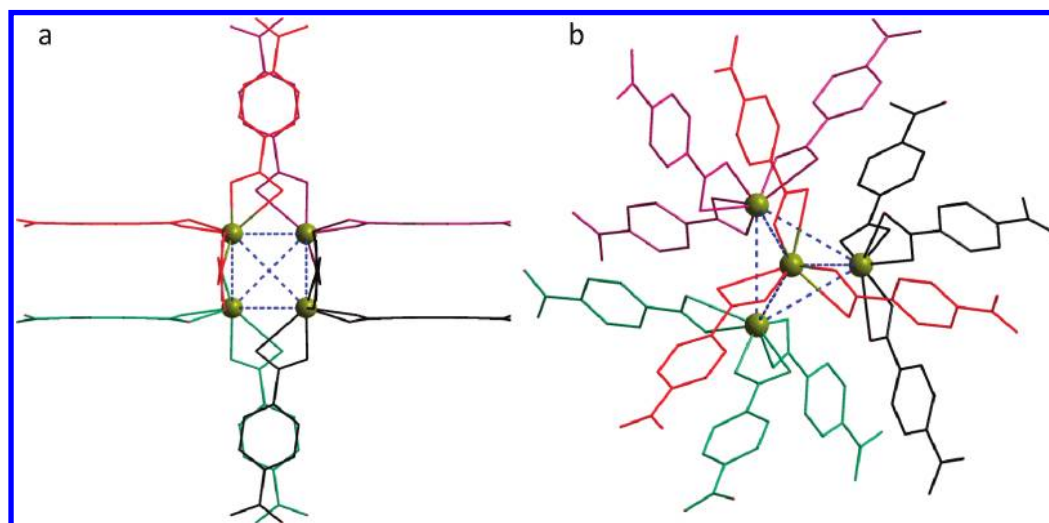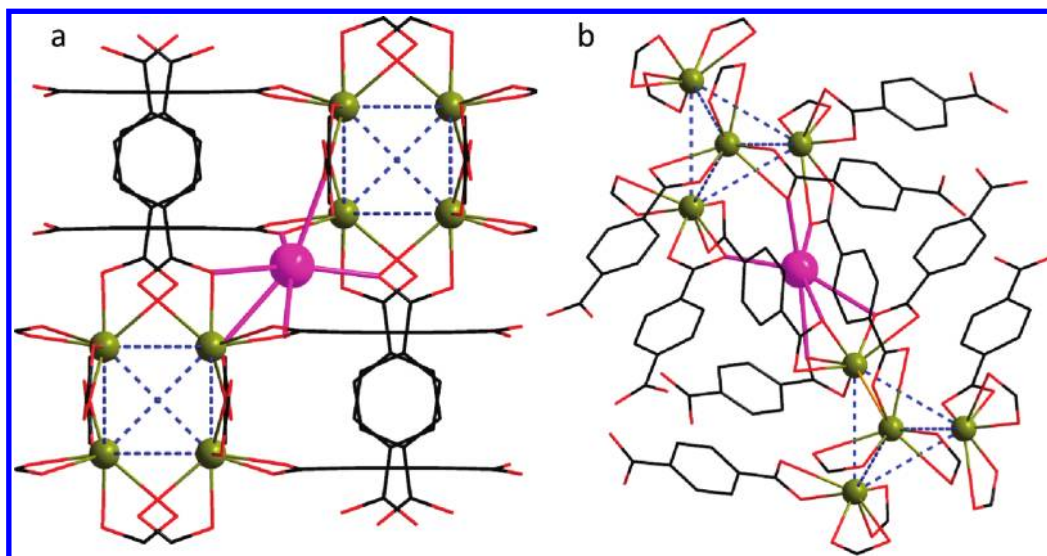**Figure 7.** Four independent $Sn(bdc)_{3/2}$ frameworks come together to give a tetrahedral arrangement of Sn atoms viewed in (a) along 100 and in (b) along 111. The four different frameworks are colored black, red, purple, and green.

Figure 8. Views of the potassium ion coordination by bdc oxygen atoms lying between the Sn tetrahedra, (a) along 100 and (b) perpendicular to 111. Sn tetrahedra have been outlined in dotted blue lines.
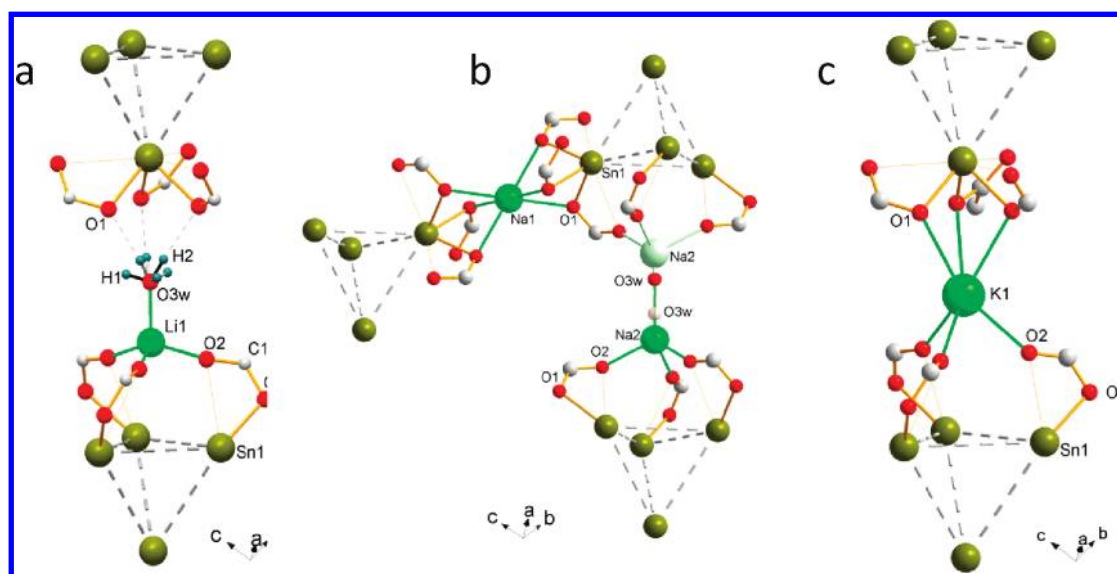

Figure 9. (a) The coordination of the Li ion and the Sn_4 tetrahedra in **1**; the water molecule is disordered over three positions marked by light, middle, and dark gray bonds; the O3w—H···O1 hydrogen bonds are represented by thin fragmented lines, (b) the coordination of the Na ions and the Sn_4 tetrahedra in **2**; the two disordered $Na2O_4$ tetrahedra are marked by green and pale green bonds, respectively, (c) the coordination of the K ion in **3**.

Change of Interpenetration with Alkali Ions. The alkali ions are localized inside the voids between the interpenetrated anionic frameworks and bind the frameworks together through the A—O bonds. The bonding and size requirement of different alkali ions affects the interpenetration. The void between the two neighboring Sn_4 tetrahedra in **1** is too large for a Li^+ ion. Therefore, a water molecule accompanies the Li ion to fill the void and forms a corner of the LiO_4 tetrahedron. The Li—O bonds in a LiO_4 tetrahedron each require an ideal bond valence of 0.25 v.u. that can be provided by the O2 atom of the bdc ligand because the O2—Sn bond is weak. The O1 atom that is strongly bonded to the Sn atom cannot participate in forming a LiO_4 tetrahedron; it is connected, however, to the LiO_4 tetrahedron through a hydrogen bond to the water oxygen atom (O1···O3w: 2.870 Å) (Figure 9a).

The same void found in **1** would be also too large for a Na^+ ion, but would be too small for a similar NaO_3O_w tetrahedron.

To accommodate the Na^+ ions the interpenetration of the anionic framework in **2** changes by flipping half of the Sn_4 tetrahedra so that neighboring Sn_4 tetrahedra are related by an inversion symmetry center (see Figure 9b). This change leads to two different cation sites. The site between the parallel bases of two neighboring Sn_4 tetrahedra is large enough to be filled by a Na^+ ion and a water molecule to form a NaO_3O_w tetrahedron. Because of the inversion symmetry of the void the NaO_3O_w tetrahedron is randomly disordered over two positions. The other void between the apical corners of two neighboring Sn_4 tetrahedra is smaller and is occupied by a Na^+ ion alone with a distorted octahedral coordination (Figure 9b). Since the Na—O bonds in a NaO_6 octahedron require an ideal bond valence of only 1/6 v.u., the Na1 atom is able to bond to the O1 atoms in spite of the short Sn—O1 bond. The Sn—O1 bond in **2** is considerably weakened (2.215(2) Å) compared to in **1** (2.177(3) Å) (see Table 3).

For the larger alkali ions in **3**, **4**, **5**, the void similar to that present in **1** can be filled solely by an A^+ cation with a distorted octahedral coordination (Figure 9c). Therefore, the interpenetration of the anionic frameworks in **1**, **3**, **4**, and **5** is identical. The relatively smaller K^+ ion in **3** is shifted from the center of the void forming three short $K-O2$ bonds (2.692 Å) and three long $K-O1$ bonds (3.091 Å). As the size of the A ions increases they tend to be closer to the center of the voids, with slight strengthening of the $A-O1$ bonds. The strengthening of $A-O1$ bonds requires corresponding weakening of the $Sn-O1$ bonds. In **5**, such cooperative bond strength changes probably reach a limit so that the coordinating bdc ligands around the Sn atoms are disordered.

Conclusions

A complete series of alkali-metal tin(II) benzenedicarboxylates has been synthesized. The crystal structures of the five new compounds are all based on a novel chiral anionic framework. The ion size and coordination requirements of the alkali metal ions play an important role in the interpenetration of the framework and the symmetry of the structures. All of the alkali-metal compounds $A_2Sn_2bdc_3$ have chiral space group symmetry $I23$ except for Na that crystallizes in the centrosymmetric space group $Pn\overline{3}$. The small size of the Li ion is compensated by bonding to additional water molecules, which leads to the same chiral structure as the compounds with alkali cations larger than Na. These observations should be helpful to materials design since noncentrosymmetry is a prerequisite for many interesting physical properties such as ferroelectricity and second harmonic generation.

Supporting Information Available: Powder X-ray diffraction data for compounds **2** and **3** and an additional figure are available together with X-ray crystallographic information files (CIF) for compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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