Coordination Polymers Based on Alkylboronate Ligands: Synthesis, Characterization, and Computational Modelling


Keywords: Boronates / Coordination polymers / Density functional calculations / Solid-state NMR spectroscopy / Alkaline earth metals / IR spectroscopy

Boronic acids \([\text{R–B(OH)}_2]^-\) are a family of molecules with a very broad variety of applications, ranging from organic synthesis to materials chemistry.[1] In particular, they can serve as building blocks for the elaboration of porous molecular materials such as covalent organic frameworks (COFs),[2] which are promising compounds for gas storage applications or for the development of photoconductive materials. More recently, we demonstrated that boronate anions \([\text{R–B(OH)}_3^-]\) can also be used for the preparation of coordination polymers by reacting boronate ligands with alkaline earth metal cations.[3,4] These preliminary studies suggested that boronate anions are promising candidates for the elaboration of new coordination networks [including metal–organic frameworks (MOFs)], because their coordination modes with respect to cations such as \(\text{Ca}^{2+}\) are complementary to those of other anionic ligands such as phosphonates \([\text{R–PO}_2(OH)–]\) and \(\text{R–PO}_3^{2–}\).[5]

Our initial studies on metal boronates led to the isolation of four different crystalline phases: \(\text{Ca[Ph–B(OH)}_3^2\text{]·H}_2\text{O}}\), \(\text{Sr[Ph–B(OH)}_3^2\text{]·H}_2\text{O}}\), \(\text{Ba[Ph–B(OH)}_3^2\text{]·H}_2\text{O}}\), and \(\text{Ca[Bu–B(OH)}_3^2\text{]·H}_2\text{O}}\), all of which presented a lamellar structure.[3,4]

The mode of binding of the boronate anion to alkaline earth metals was found to depend on the nature of the organic chain attached to the boron atom (phenyl or butyl) and the metal ion involved. Moreover, hydrogen bonding was found to play an important role in the formation of these phases, and the exact nature of the H-bond network within these materials could be obtained by combining IR and \(^1\text{H}\) solid-state NMR characterization with DFT-based calculations. This allowed relationships to be established between the IR O–H stretching frequencies or the \(^1\text{H}\) chemical shift of the boronate and the O–H···O bond length within the structures.[4]

Despite these first studies on metal boronates, there is a real dearth in the number of structures reported to date, as only four crystalline phases involving metal–boronate coordination bonds have been described. This is far below what has been done so far for other anionic ligands such as carboxylates, sulfonates and phosphonates, and much work is still required to fully understand how to make the best use of boronate ligands for the elaboration of coordination polymers.
of boronate ligands for materials applications. Thus, the purpose of this manuscript is to go one step further in the investigation of metal boronate crystal structures through the study of three new phases: Sr[Bu–B(OH)₃]₂ and M[Oct–B(OH)₃]₂ (M = Ca, Sr; Oct = C₈H₁₇). The longer octyl chains were chosen to evaluate the propensity of alkylboronate anions to assemble into dense and ordered hydrophobic layers. First, we will detail the synthesis of the materials and describe the corresponding crystal structures. Then, their spectroscopic characteristics will be provided with particular emphasis on IR and multinuclear solid-state NMR (¹¹B, ¹³C, ⁴³Ca and ⁸⁷Sr) spectroscopy characterizations. Finally, the ¹H solid-state NMR and IR spectroscopic signatures of the OH groups in Sr[Bu–B(OH)₃]₂ will be discussed on the basis of computational modelling and compared to those obtained for Sr[Ph–B(OH)₃]₂·H₂O and Ca[Bu–B(OH)₃]₂.

Results and Discussion

Synthesis and Crystal Structures

The Sr[Bu–B(OH)₃]₂ (SrBBu), Ca[Oct–B(OH)₃]₂ (CaBOct) and Sr[Oct–B(OH)₃]₂ (SrBOct) phases were synthesized by precipitation (Scheme 1) by applying similar reaction conditions as those for the synthesis of Ca[Bu–B(OH)₃]₂ (CaBBu).¹⁹ Temperatures above 25 °C needed to be avoided to ensure that pure phases were obtained. All of the compounds were isolated as microcrystalline powders. Scanning electron microscopy (SEM) analyses revealed that they are composed of platelets of uneven shape, with dimensions generally ranging from ca. 3 to 20 μm and a thickness of several hundreds of nm (see Figure S1, Supporting Information).

All of the samples were characterized by synchrotron powder X-ray diffraction analyses. Rietveld refinements were performed on the diffractograms, as illustrated in Figure 1 for CaBOct. The three phases present a layered structure, similar to the one previously reported for CaBBu: they are composed of planes of Ca²⁺ or Sr²⁺ cations interconnected by boronate ligands with the alkyl chains facing each other in the interlayer space. Both octylboronate phases are isostructural, and the SrBBu phase is isostructural to CaBBu. In each structure, there are two independent ligands in the unit cell, and the modes of coordination of the butyl- and octylboronate anions towards the Ca²⁺ and Sr²⁺ ions are all identical; the metal ions are linked to eight different oxygen atoms belonging to six different boronate ligands. In contrast, for phenylboronate ligands, different binding modes had been observed when switching from calcium to strontium. It should be noted that owing to the identical binding modes observed for both alkylboronate anions, solid solutions involving mixtures of butyl- and octylboronate ligands were also prepared (data not shown); these solid solutions could be interesting for the intercalation of hydrophobic molecules in the interlayer space.

Spectroscopic Characterization

In line with our previous studies on metal boronate phases, we characterized each sample by IR, Raman and multinuclear solid-state NMR spectroscopy, as these techniques are useful for identifying the H-bonding networks in the materials and proposing the positions of the hydroxy H atoms, which could not be located from the powder X-ray diffraction data.

The IR spectra are shown in Figure 2, and the corresponding Raman spectra are shown in Figure S2 (Supporting Information). In the O–H stretching vibration region of the spectra between σ = 3100 and 3700 cm⁻¹, similarities can be found between the different phases, and, in all cases, one strong vibration at σ ≈ 3340 cm⁻¹ corresponds to an OH group involved in a fairly strong H bond. The profiles of the spectra in this region are analogous for all compounds, and the similarities are the strongest between CaBOct and CaBBu, and between SrBOct and SrBBu. Thus, these spectra provide complementary information to XRD characterization: not only are the binding modes of the octyl- and butylboronate ligands towards Ca²⁺ and Sr²⁺ ions identical but the H-bond networks are also similar in the resulting coordination polymers.

The ¹¹B and ¹³C magic-angle spinning (MAS) solid-state NMR spectra of the SrBBu and SrBOct samples are shown in Figure 3, and those of the CaBOct phase are shown in Figure S3 (Supporting Information). These ¹¹B NMR spectra are consistent with the presence of two independent boronate anions in the materials, as illustrated in Figure S4 for SrBBu. In the ¹³C NMR spectra, the signals from the organic chains are nicely resolved, as was previously observed for CaBBu. The assignment of the ¹³C NMR resonances was made by using ¹³C{¹¹B} rotational echo double resonance (REDOR) NMR experiments for SrBBu and quantum chemical calculations for SrBOct (Figures S5 and S6).

The characterizations of the local environments of the calcium and strontium ions were also performed for SrBBu and CaBOct by natural-abundance ⁴³Ca and ⁸⁷Sr NMR experiments. For SrBBu, the ⁸⁷Sr NMR spectrum is consis-
Figure 1. (A) Rietveld plots of Ca\textsubscript{Oct–B(OH)\textsubscript{3}}\textsubscript{2} under two different measurement conditions (see Experimental Section). (a) Observed (red dots) and calculated (solid lines) synchrotron (λ = 0.697751 Å) powder diffraction patterns, (b) difference curves and (c) Bragg peak positions. (B) Representations of the crystal structure of Ca\textsubscript{Oct–B(OH)\textsubscript{3}}\textsubscript{2} along different projections; H atoms are not shown in this representation.

Figure 2. IR spectra of the Ca and Sr butyl- and octylboronate phases.

Figure 3. (A) \textsuperscript{11}B, (B) \textsuperscript{87}Sr and (C) \textsuperscript{13}C solid-state NMR spectra of the Sr butyl- and octylboronate phases (SrBBu and SrBOct). The deconvolution of the \textsuperscript{11}B MAS spectrum of SrBBu can be found in Figure S4. For the \textsuperscript{87}Sr NMR spectroscopic data, the dashed blue line represents the simulation of the line shape. Assignments for the \textsuperscript{13}C NMR resonances are proposed, as detailed in the main text.

tent with the presence of one Sr site and could be simulated with the following NMR parameters: δ\textsubscript{iso} = 40 ± 100 ppm, C\textsubscript{Q} = 20.5 ± 0.8 MHz and η\textsubscript{Q} = 0.55 ± 0.10 (Figure 3B). It is worth noting that the quadrupolar coupling constant is consistent with that previously observed for Sr[Ph–B(OH)\textsubscript{3}]\textsubscript{2}·H\textsubscript{2}O (SrBPh).\textsuperscript{6} For CaBOct, natural-abundance \textsuperscript{43}Ca NMR experiments were performed at three different magnetic fields (Figure 4) to ensure that accurate NMR pa-
were found to be nearly identical above 3100 cm⁻¹ but calculations on the CaBBu and Ca[Ph–B(OH)₃]₂ (CaBPh) combined experimental and computational approach involving OH groups could provide details of the OH···O bond in both phases.

The calculated ¹H NMR chemical shifts of the hydroxy groups were also tested, but they all led to structures of higher energy after geometry optimization. For SrBPh, although we had proposed previously a model for OH orientations,[3] we were not fully satisfied with the B–O–H angles around one of the boron atoms. Thus, several other starting configurations were tested for the OH groups. Of all the models for which a reasonable geometry was found, the one of lowest energy was considered. It should be noted that the OH orientation in this model differs from what we had previously proposed.[3]

Details on the local geometry around the “H-bonded” OH groups within the “best” structural models of SrBBu and SrBPh are provided in Figure 5. For SrBBu, there are two fairly strong H bonds, one per butylboronate anion. The final orientation of the OH groups after geometry optimization differs somewhat from those observed for the CaBBu phase (see Figure S7). For SrBPh, several H bonds are present in the final structure, and the strongest are those involving the water ligand.

DFT calculations of the NMR parameters were performed on the selected models of SrBBu and SrBPh by using the gauge including projector augmented wave (GIPAW) method (Table S1).[10] The agreement between the calculated and experimental ¹³C, ¹¹B and ⁸⁷Sr NMR parameters was reasonable, as shown in Figures S8 and S9. The calculated ⁸⁷Sr NMR coupling constants for both phases were overestimated by ca. 5 MHz, but such discrepancies remain in the range of those of previously reported ⁸⁷Sr NMR studies.[6,11] Systematic shifts in the ¹³C NMR resonances were also observed for the SrBBu model, but the relative order of the calculated shifts of the ¹³C NMR resonances agrees with that determined experimentally by the ¹³C(¹¹B) REDOR experiments. It should be noted that variable-temperature experiments were performed to see if the discrepancy between the experimental and calculated ¹³C NMR chemical shifts could be reduced, but the changes were minimal (Figure S5B).

The calculated ¹H NMR chemical shifts of the hydroxy groups and the anharmonic O–H stretching frequencies for SrBBu and SrBPh are reported in Figure 5 and Table S2, and comparisons with the experimental spectra are shown in Figures 6 and 7. The previously reported results on CaBBu and CaBPh have also been included in these figures. Although discrepancies appear between the calculated and experimental values (as previously observed for the Ca systems),[4] several trends are well reproduced when the IR data of SrBBu and CaBBu are compared (Figures 6 and S10):

(1) The calculated O–H stretching frequency of the strongest H bond is at a higher wavenumber for the strontium phase, in agreement with the experimental data, and, along the same lines, the highest ¹H NMR chemical shift is calculated for the Ca phase.

(2) The highest calculated O–H stretching frequency is found for the SrBBu phase, in agreement with experimental observations.

(3) One intermediate O–H frequency is calculated for the SrBBu phase, which is consistent with the presence of two
Figure 5. Geometries of the strongest H bonds in the SrBBu and SrBPh models after geometry optimization. For SrBPh, H bonds involving the water ligand are shown at the bottom right. O, B, H, Sr and C atoms are in blue, brown, white, red and grey, respectively.

Figure 6. Comparison of experimental IR and $^1$H solid-state NMR spectra of Ca and Sr butylboronate phases. The calculated O–H stretching modes and $^1$H NMR chemical shifts of the hydroxy groups (only) are shown as vertical bars below the experimental data. A zoom on the low-intensity $^1$H NMR signals of the hydroxy groups is provided in Figure S10.

Calculations of IR wavenumbers and $^1$H NMR chemical shifts can clearly account for some similarities and discrepancies between the experimental spectra:

1. In the $^1$H NMR spectra for both phases, several calculated $^1$H NMR chemical shifts are grouped between $\delta = 0$ and 4 ppm and correspond to the O–H groups not involved in H bonds; this explains the similarity of both spectra in this region of the spectrum.

2. In the IR spectra, the vibration bands at $\sigma \approx 3400$ cm$^{-1}$, which correspond to the H bonds around the phenylboronate ligands, are shifted towards slightly higher wavenumbers for the SrBPh phase, in line with DFT calculations.

3. In the IR spectrum of SrBPh, the broad band between $\sigma = 3000$ and 3200 cm$^{-1}$ (which overlaps with the C–H stretching frequencies) can be unambiguously ascribed to the O–H stretching frequencies of the H$_2$O molecule (blue arrow in Figure 7) on the basis of the DFT-calculated frequencies.

Overall, this comparison of the experimental and calculated IR frequencies and $^1$H NMR chemical shifts shows how DFT calculations can be useful in the interpretation of the spectra of alkaline earth metal boronates. More generally, through this study of four different Sr and Ca boronate phases, it can be seen more clearly how different regions of these spectra are informative about the different types of O–H groups within such materials and how this can be used in future investigations of boronate phases of unknown structure.
Figure 7. Comparison of experimental IR and $^1$H solid-state NMR spectra of Ca and Sr phenylboronate phases. The calculated O–H stretching modes and $^1$H chemical shifts of the hydroxy groups (only) are shown as vertical bars below the experimental data. The blue arrow indicates the region of the O–H stretching vibrations of the H$_2$O ligand in SrBPh.

Conclusions

Three new metal boronate structures involving butyl- and octylboronate ligands have been synthesized and characterized by a wide variety of spectroscopic techniques. A combined experimental–computational approach was used to position the protons and help interpret the spectroscopic data of the Sr butylboronate phases. It was confirmed that such calculations can provide clues about the nature of some O–H vibration bands and, thus, about the differences in H-bonding networks between different boronate phases.

In the butyl- and octylboronate phases described to date, the alkyl chains are closely packed to each other, and such a configuration recalls what one may expect for a self-assembled monolayer (SAM) of boronates at the surface of an inorganic material. Thus, as a follow-up to this work, one may try to look into grafting boronate SAMs at the surface of materials with exposed Ca$^{2+}$ cations such as hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$] or calcite (CaCO$_3$). We have started to pursue studies along this line, and this should open the way to a much broader variety of boronate-based materials.

Experimental Section

Chemicals and Materials: Butylyboronic acid [C$_4$H$_9$–B(OH)$_2$, Alfa Aesar, >98%], octylboronic acid [C$_8$H$_{17}$–B(OH)$_2$, Alfa Aesar, >97%],[12] calcium chloride dihydrate (CaCl$_2$·2H$_2$O, Acros Organics, >99% purity), strontium chloride hexahydrate (SrCl$_2$·6H$_2$O, Acros Organics, >99% purity) and sodium hydroxide (NaOH, Acros Organics) were used as received, and reactions were performed with ultrapure water and absolute ethanol. The syntheses and characterization of Ca[Ph–B(OH)$_3$]$_2$, Ca[But–B(OH)$_3$]$_2$ and Sr[Ph–B(OH)$_3$]$_2$·H$_2$O can be found in previous publications.[1,4]

General Materials Characterization: Elemental analyses were performed by the Service Central d’Analyse of the CNRS (Vernaison, France). IR spectra were recorded in transmission mode by using an Avatar 320 FTIR spectrometer with samples as KBr pellets. SEM measurements were conducted with a Hitachi S$^4$800 instrument under an excitation voltage of 2–8 kV depending on the surface charging of the powder. Powdered samples were deposited on double-face tape and then Pt-metallized by sputtering under vacuum.

Sr[But–B(OH)$_3$]$_2$ (Sr Butylboronate, SrBBu): Microbeads of NaOH (194 mg, 4.85 mmol) were dissolved in an H$_2$O/EtOH (1:1) mixture (14 mL). Butylboronic acid (490 mg, 4.81 mmol) was then added to the solution under magnetic stirring. After dissolution of the boronic acid, an aqueous solution of SrCl$_2$·6H$_2$O at (214.09 g L$^{-1}$, 2.41 mmol, 3 mL) was added dropwise; this led to the immediate formation of a white precipitate. The suspension was stirred at room temperature for ca. 30 min. The suspension was then filtered through a sintered glass frit under vacuum, and the vacuum was maintained for 15 min. The precipitate was washed twice with an H$_2$O/EtOH (1:1) mixture (10 mL; the vacuum was maintained after each wash for 5 min). The white powder was then dried in a furnace at 40 °C for ca. 3 d. Yield: 690 mg (87%). C$_{36}$H$_{48}$B$_2$O$_6$Sr (325.214): calc. C 29.5, H 7.4, B 6.6, Sr 26.9; found C 28.6, H 7.0, B 6.1, Sr 27.0.

Ca[Oct–B(OH)$_3$]$_2$ (Ca Octylboronate, CaBOct): Microbeads of NaOH (192 mg, 4.80 mmol) were dissolved in an H$_2$O/EtOH (1:1) mixture (14 mL). Octylboronic acid (758 mg, 4.80 mmol) was then added to the solution under magnetic stirring. After dissolution of the boronic acid, an aqueous solution of CaCl$_2$·2H$_2$O (118.09 g L$^{-1}$, 2.41 mmol, 3 mL) was added dropwise; this led to the immediate formation of a white precipitate. The suspension was stirred at room temperature for ca. 30 min. The suspension was then filtered through a sintered glass frit under vacuum, and the vacuum was maintained for 15 min. The white precipitate was washed and dried as described previously for SrBBu. The white powder was then dried in a furnace at 80 °C for ca. 2 d. Yield: 711 mg (76%). Amorphous calcium borate impurities were found in this sample.[12] and this led to discrepancies between the experimental and expected elemental analyses. The quantification of this impurity by $^{11}$B solid-state NMR is proposed in Figure S3.

Sr[Oct–B(OH)$_3$]$_2$ (Sr Octylboronate, SrBOct): Microbeads of NaOH (96 mg, 2.41 mmol) were dissolved in an H$_2$O/EtOH (1:1) mixture (7 mL). Octylboronic acid (380 mg, 2.40 mmol) was then added to the solution under magnetic stirring. After dissolution of the boronic acid, an aqueous solution of SrCl$_2$·6H$_2$O (214.09 g L$^{-1}$,
1.20 mmol, 1.5 mL) was added dropwise; this led to the immediate formation of a white precipitate. The suspension was stirred at room temperature for ca. 30 min. The suspension was then filtered through a sintered glass frit under vacuum, and the vacuum was maintained for 15 min. The white precipitate was then dried in a furnace at 80 °C for ca. 2 d. Yield: 406 mg (78%). Amorphous strontium borate impurities were found in this sample[12] (this led to discrepancies between the experimental and expected elemental analyses.

Synchrotron Powder X-ray Diffraction Measurements, Indexation and Structure Analysis

Lattices and Space Groups: As no crystals suitable for single-crystal X-ray diffraction were obtained, high-resolution X-ray diffraction powder patterns were recorded. The synchrotron powder diffraction data were obtained at the Swiss–Norwegian Beam Line at ESRF (Grenoble, France). The samples were introduced into 0.5 mm diameter glass capillaries. Data collections were performed at 295 K with a MAR345 Image Plate detector by using a monochromatic wavelength of $\lambda = 0.697751$ Å. Two sample-to-detector distances were used (150 and 400 mm) to combine the advantages of high structural and angular resolutions. Owing to the very high relative intensity of the first diffraction ring, two exposure times were used for each sample-to-detector distance: one measurement with an unsaturated first ring (to have the exact relative intensities for all the diffraction peaks) and one measurement with a saturated first ring to increase the counting statistics for the low-relative-intensity diffraction peaks. The detector parameters and the wavelength were calibrated with NIST LaB$_6$. The highest resolution of the MAR345 detector was used with 3450 × 3450 pixels with a pixel size of 100 μm. During the exposure time, the capillaries were rotated by 60°. The 2D data were integrated with the Fit2D program.[13] Highly accurate integrated intensities were obtained thanks to a good powder average achieved by projecting the whole scattering information on the 2D detector. The uncertainties of the integrated intensities were calculated at each 2θ point by applying Poisson statistics to the intensity data and considering the geometry of the detector.[14] The first 20 observed reflections from the unsaturated data with the large sample-to-detector distance (high angular resolution) were used to index the unknown patterns. The DICVOL04 indexing program[15] was successfully used to reveal a monoclinic lattice for the three samples, and systematic extinctions also indicated space group $P2_1/c$ for the three samples. A Le Bail fitting was performed by using the FullProf.2k program.[16] The peak shape was described with a Thomson–Cox–Hasting function. The profile matching refinements for the unsaturated measurements recorded with a sample-to-detector distance of 400 mm agree with the monoclinic $P2_1/c$ space group; the lattice parameters are indicated in Table 1.

Table 1. Refined lattice parameters.

<table>
<thead>
<tr>
<th></th>
<th>CaBBu</th>
<th>CaBOct</th>
<th>SrBBu</th>
<th>SrBOct</th>
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<tr>
<td>$b$ [Å]</td>
<td>8.3969(4)</td>
<td>8.3415(7)</td>
<td>8.7353(10)</td>
<td>8.6858(19)</td>
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<td>$c$ [Å]</td>
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<td>9.9395(11)</td>
<td>9.9826(13)</td>
<td>9.9919(2)</td>
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<td>$\beta$ [°]</td>
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<td>97.298(11)</td>
<td>90.668(9)</td>
<td>103.251(14)</td>
</tr>
<tr>
<td>$V$ [Å$^3$]</td>
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<td>2169.3(4)</td>
<td>1426.13(13)</td>
<td>2245.71(10)</td>
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<td>2.27, 3.28</td>
<td>8.34, 6.94</td>
<td>6.52, 5.61</td>
</tr>
</tbody>
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Structure Solution for Ca Octylboronate: The structure of Ca octylboronate (CaBOct) was then solved in the centrosymmetrical group $P2_1/c$ by the global optimization of the structural model in direct space by using simulated annealing (in parallel mode) with the FOX program.[17] As a cost function, the integrated $wR$ factor of the unsaturated short sample-to-detector distance pattern[18] and an antibump function (based on the minimal lengths Ca–O 2.3, Ca–B 2.5, Ca–C 2.5 and Ca–Ca 3.5 Å) weighted at 0.60/0.40 were used. One independent Ca(B$_2$O$_3$)$_2$ object was considered (corresponding to four motifs per unit cell in agreement with the expected density of the compound). The introduced Ca(C$_8$BO$_3$)$_2$ object was described by 25 atoms (1 Ca, 2 B, 6 O and 16 C) with bond lengths Ca–O 2.40, B–O 1.50, B–C 1.60 and C–C 1.55 Å and angles O–B–O 109.5, O–B–C 109.5, O–C–C 115 and C–C–C 109°. The Ca–O and Ca–C angles were not restrained to solve the orientation of the organic chain around the alkaline earth cation. The H atoms were not considered here owing to their weak scattering contrast for X-rays. The position of the central Ca atom was allowed to vary, as were the two Ca–O–B angles, through the use of the Dynamical Occupancy Correction for the automatic identification of the special crystallographic positions. The solution with the $x$ coordinate of Ca close to 0 was slowly found with all atoms in the general 4e position. The crystal structure was refined by the joint Rietveld method by using the four synchrotron data sets and the FullProf.2k program.[16] No crystalline impurity was identified in the powdered sample. All site occupancies were fixed to unity, and restraints were applied. The refinement methodology used was the same as that in the previous study on CaBBu[19] with similar restrictive restraints for the alkyl boronate [interatomic distances set to B–O 1.51(1), B–C 1.62(1), C–C 1.54(1) Å, and angles set to O–B–O 105.5(1.0), O–B–C 113(1), C–C–C 114(1)°]. The corresponding Rietveld plots are shown in Figure 1 together with a general representation of the structure. The structure of Ca octylboronate is similar to that of the previously described Ca butylboronate.[20] The calcium local environment is essentially the same in both structures; the calcium atoms are eightfold coordinated with a square-based antiprism, the eight neighbours are hydroxy groups belonging to six organic molecules, and the average experimental interatomic Ca–OH distances are 2.50 Å for Ca butylboronate and 2.51 Å for Ca octylboronate. The only difference is due to the alkyl length (eight carbon atoms versus four), which leads to a longer $a$ axis and an increase of the $\beta$ angle.

Structure Solutions for Sr Compounds: The structures for both Sr butylboronate (SrBBu) and Sr octylboronate (SrBOct) have been solved by considering isostuctural descriptions to the Ca butylboronate and Ca octylboronate compounds, respectively (according to the similar lattice parameters and space group, see Table 1). Rietveld refinements of the Sr compounds with the initial atomic positions taken from the equivalent Ca compounds have confirmed the isostuctural features for M–butylboronate and for M–octylboronate (M = Ca and Sr). Similarly to the calcium cases, the eightfold coordination of the strontium atoms (from six organic molecules) and a layered structure with a slab along the (100) plane were observed. The Sr$^{2+}$ cations are also in square-based antiprisms polyhedra with average experimental Sr–OH distances of ca. 2.63 Å (in agreement with the larger cationic radius for Sr$^{2+}$ cation compared to Ca$^{2+}$ and with the slightly larger lattice parameters for Sr compounds).

CCDC-1008485 (for CaBOct), -1008486 (for SrBBu) and -1008487 (for SrBOct) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Solid-State NMR Characterizations: The $^{11}$B MAS NMR spectra of all samples were recorded with a Varian VNMRS 400 MHz
The 11B NMR chemical shifts were referenced externally. Experiments were performed with the pure samples (with no boronates). It is worth noting that all these 11B NMR dephasing time was applied by using rotor-synchronized experiments. For Sr[Oct–B(OH)3]2, the 13C{11B} REDOR NMR experiment was performed with a Bruker 4 mm triple resonance probe spinning at 12.5 kHz. For all experiments, a 2.5 μs 90°1H excitation pulse was used, followed by a ramped contact pulse of 2 ms. Spinal-64 1H decoupling (100 kHz RF) was applied during acquisition. The recycle delay was set to 2 s. Sixty-four transients were recorded. All 13C NMR chemical shifts were referenced externally to NaBH4 at δ = −42.05 ppm (used as a secondary reference).

For Sr[Oct–B(OH)3]2, 1H–13C cross-polarization MAS (CP-MAS) NMR spectra were recorded with a Varian VNMRS 600 MHz (14.1 T) spectrometer at a frequency of 150.83 MHz by using a 3.2 mm Varian T3 HX MAS probe spinning at 10 kHz. For Ca[Oct–B(OH)3]2 and Sr[Oct–B(OH)3]2, 1H–13C CP-MAS NMR spectra were recorded with a Bruker Avance II+ 600 MHz (14.1 T) NMR spectrometer at a frequency of 150.72 MHz by using a Bruker 4 mm triple resonance probe spinning at 14 kHz. For all experiments, a 2.5 μs 90° 1H excitation pulse was used, followed by a ramped contact pulse of 2 ms. Spinal-64 1H decoupling (100 kHz RF) was applied during acquisition. The recycle delay was set to 8 s, and the number of transients acquired were 100, 464 and 342 for Sr[Oct–B(OH)3]2, Ca[Oct–B(OH)3]2 and Sr[Oct–B(OH)3]2, respectively. All 13C NMR chemical shifts were referenced externally to adamantane as a secondary reference (high-frequency peak at δ = 38.5 ppm with respect to tetramethylsilane (TMS)).

For Sr[Bu–B(OH)3]2, the 13C(11B) REDOR NMR experiment was performed with a Varian VNMRS 600 MHz (14.1 T) spectrometer by using a 3.2 mm Varian T3 HXY MAS probe spinning at 20 kHz. The single-pulse experiments were performed with a ca. 45° solid pulse of 1.6 μs, a recycle delay of 6 s (full relaxation) and 100 kHz spin-64 1H decoupling during acquisition; 64 transients were recorded. The spectrum of Sr[Bu–B(OH)3]2 was also recorded at 14.1 T with a Varian VNMRS 600 MHz spectrometer by using a 3.2 mm Varian T3 HXY MAS probe spinning at 12.5 kHz. A single-pulse experiment was performed with a ca. 45° solid pulse of 1.6 μs, a recycle delay of 6 s (full relaxation) and 100 kHz spin-64 1H decoupling during acquisition; 64 transients were recorded. The spectrum of Sr[Oct–B(OH)3]2 was also recorded at 14.1 T but with an Avance II+ 600 MHz spectrometer by using a Bruker 4 mm triple resonance probe spinning at 12.5 kHz. In this case, a Hahn echo experiment was performed with an echo delay equal to one rotor period, a recycle delay of 8 s and 100 kHz spin-64 1H decoupling during acquisition; eight transients were recorded. The advantage of recording 11B MAS NMR spectra at different magnetic fields has already been demonstrated for other boronic acid derivatives including boronates. It is worth noting that all these 11B NMR experiments were performed with the pure samples (with no physical dilution of the powder), in contrast with our previous work on CaBBu.4 All 11B NMR chemical shifts were referenced externally to NaBH4 at δ = −42.05 ppm (used as a secondary reference).
were expanded on a plane-wave basis set with a kinetic energy cut-off of 1088 eV. The integration over the first Brillouin zone was performed by using a Monkhorst-Pack $2 \times 2 \times 2$ $k$-point grid. The isotropic chemical shift $\delta_{iso}$ is defined as $\delta_{iso} = [-\sigma - \sigma_{ad}]$; $\sigma$ is the isotropic shielding, and $\sigma_{ad}$ is the isotropic shielding of the same nucleus in a reference system as described previously.[13,33] For $^{1}H$, $^{13}C$ and $^{31}S$ NMR, $\sigma_{ad}$ was fixed so that the average sum of experimental and calculated shifts of a series of reference compounds coincided.[6,34] For $^{11}B$ NMR, the external referencing to crystalline phenylboronic acid (CCDC-654342) was chosen. The diagonalization of the symmetrical part of the calculated chemical shift tensor provides its principal components $\delta_{11}, \delta_{22}$ and $\delta_{33}$ from which the chemical shift components $\Delta \delta_{11}, \Delta \delta_{22}$ and $\Delta \delta_{33}$ can be calculated. $\sigma$, $\delta_{11}$, $\delta_{22}$ and $\delta_{33}$ are defined such that $\delta_{11} \geq \delta_{22} \geq \delta_{33}$ and $\delta_{iso} = 1/3(\delta_{11} + \delta_{22} + \delta_{33})$. The chemical shift anisotropy (CSA) parameters are defined by $\Omega = \delta_{22} - \delta_{11} = \delta_{33} - \delta_{11} = \delta_{33} - \delta_{22}$ and $\kappa = 3(\delta_{22} - \delta_{33})/\Omega$. The chemical shift anisotropy (CSA) parameters are obtained by diagonalization of the tensor. The quadrupolar interaction can then be characterized by the quadrupolar coupling constant $C_{Q}$ and the asymmetry parameter $\eta_{Q}$, which are defined as $C_{Q} = eQV_{zz}$ and $\eta_{Q} = (V_{yy} - V_{xx})/2V_{zz}$ ($e$ is the proton charge, $h$ is the Planck constant, and $Q$ is the quadrupole moment of the considered nucleus). The $Q$ values reported by Pykkö[35] were used in the calculations except for those for the $^{11}B$ calculations, because a systematic overestimation of $C_{Q}$ was observed in our $^{11}B$ NMR calculations and also in previous calculations on boronic acids and their cyclic derivatives.[19b,36] Charpentier et al. have proposed the application of a scaling factor to the $^{11}B$ quadrupolar parameters calculated by GIPAW to improve the agreement between experimental and calculated values.[37] Therefore, the $C_{Q}$ values for $^{11}B$ were calculated here with an “adjusted” $Q = 35$ mb instead of the value reported by Pykkö ($Q = 40.59$ mb). For the chemical shift calculations, the estimated errors in the calculated $\delta_{iso}$ values are 0.5 ppm for $^{1}H$, 1.0 ppm for $^{13}C$ and 1.0 ppm for $^{11}B$, as in previous studies on Ca boronates.[34]

**Supporting Information** (see footnote on the first page of this article): Additional SEM, Raman and solid-state NMR characterizations of SrBBr$_{6}$, SrBBr$_{8}$ and CaBBr$_{6}$; complementary information on the computational models (geometries, calculated IR and NMR parameters).

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8. As calcium-43 is a quadrupolar nucleus, the position and line shape of the $^{43}Ca$ NMR signal varies with the magnetic field $B_{0}$ (notably because the second-order quadrupolar broadening is inversely proportional to the magnetic field). In MAS, this lineshape mainly depends on three parameters: $\delta_{iso}, C_{Q}$ and $\eta_{Q}$. By recording the $^{43}Ca$ MAS NMR spectrum of a sample at different magnetic fields, it is possible to extract these NMR parameters with a higher accuracy, especially when there are several independent Ca sites in the structure.
12. In some of the commercial octylboronic acid precursors, $\text{B(OH)}_{3}$ impurities were detected by $^{11}B$ NMR spectroscopy. Attempts to purify these precursors by washing them with water or recrystallizing led, in all cases, to a very low yield of pure octylboronic acid. Thus, for some of the syntheses described, the experiments were performed with an impure octylboronic acid precursor to avoid yields that would be too low for characterization of the final material. A possible quantification of the amount of impurity in the final product is shown in Figure S3.


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