Supplementary Materials

Synthesis and characterization of crystalline structures

based on phenylboronate ligands bound to alkaline earth cations

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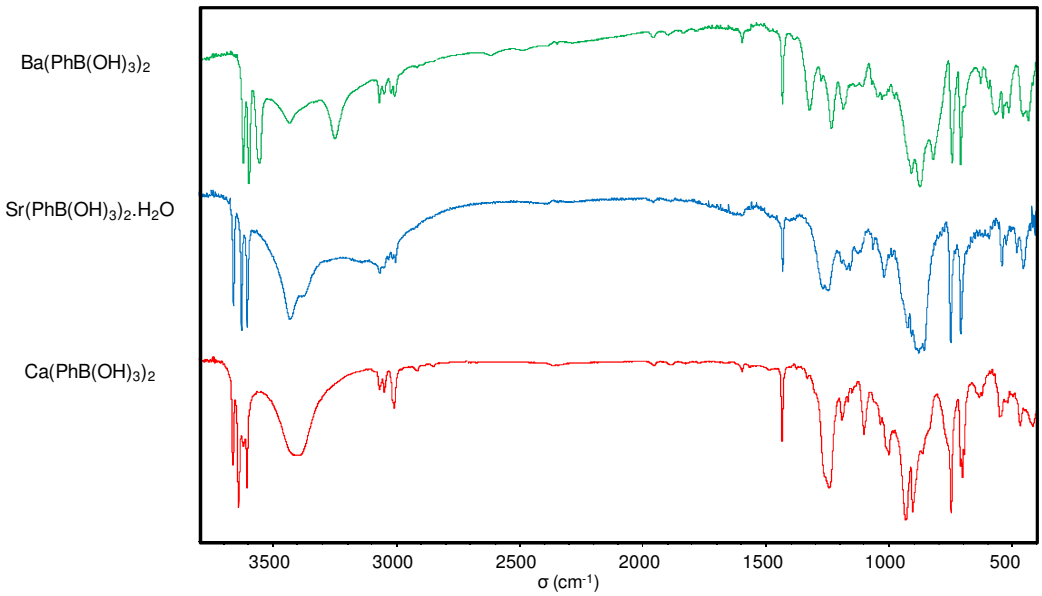
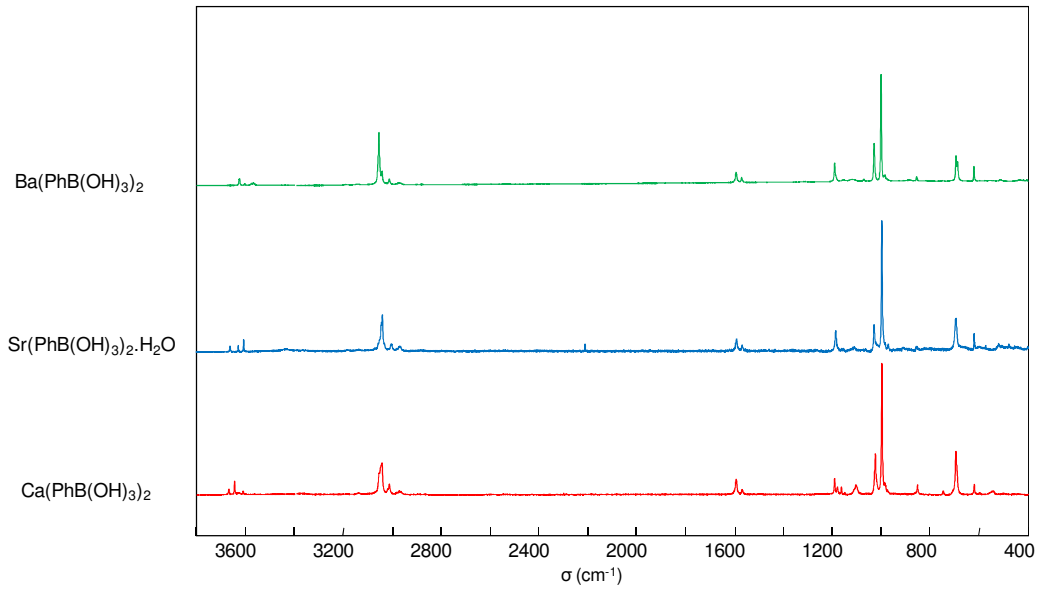
Supplementary Materials: Figures

Figure S1. IR and Raman[1] spectra of $Ca(PhB(OH)_3)_2$, $Sr(PhB(OH)_3)_2.H_2O$ and $Ba(PhB(OH)_3)_2$.

IR spectra

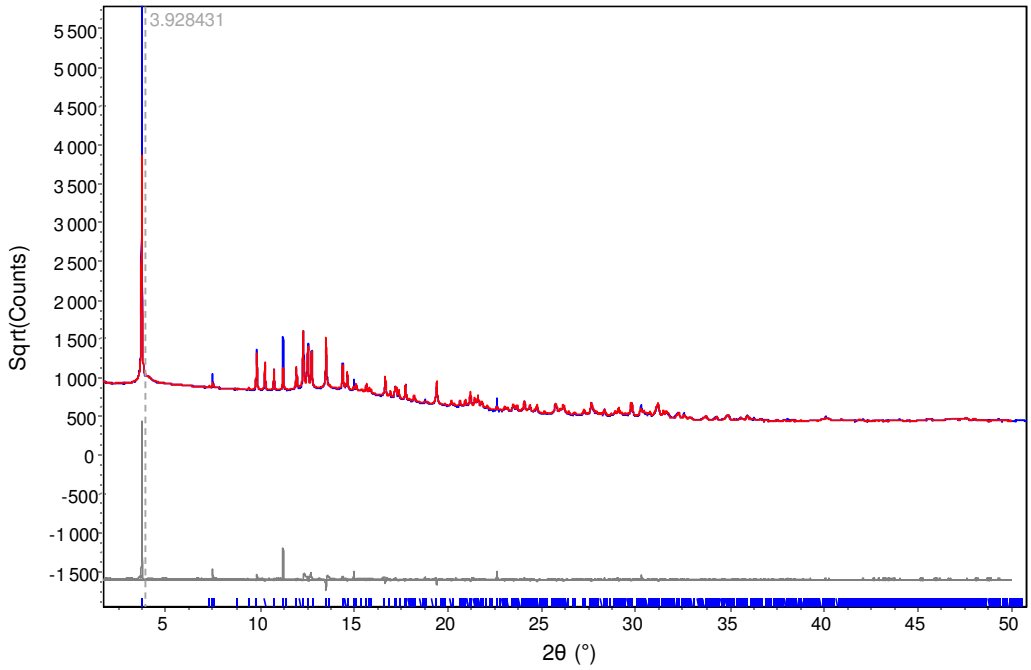


Raman spectra



[1] Raman spectroscopy measurements were performed on a LabRAM Aramis IR[2] spectrometer from Horiba Jobin Yvon using a red HeNe laser beam (λ = 633 nm). Spectra were recorded between 50 and 4000 cm^{-1} wavenumbers by accumulating 1 to 5 scans during 1 to 60 s per scan depending on the eventual fluorescence of the sample.

Figure S2. Rietveld plot for the refinement of the structure of $Ca(PhB(OH)_3)_2$.



In blue the observed diffractogram, in red the calculated diffractogram and in grey the difference plot. The peak at 2θ = 3.928° is due to the kapton foil in the beampipe.

Attempts to refine the XRD powder pattern without taking into account the most intense peak at small angles did not lead to better results. Different preferential orientation models were also tested.

Below, a zoom of the higher 2θ region of the diffractograms and difference plot above is given.

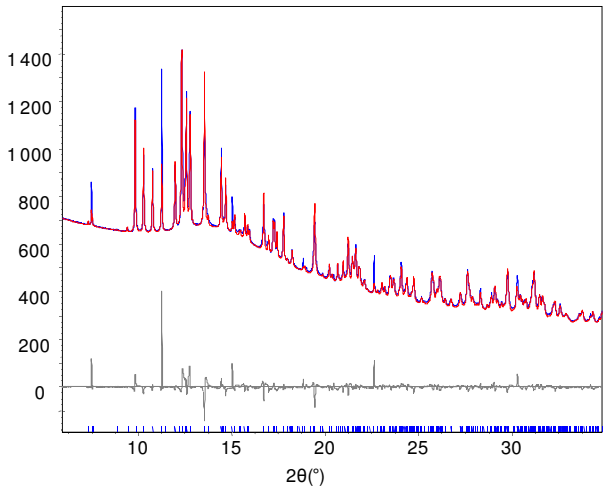
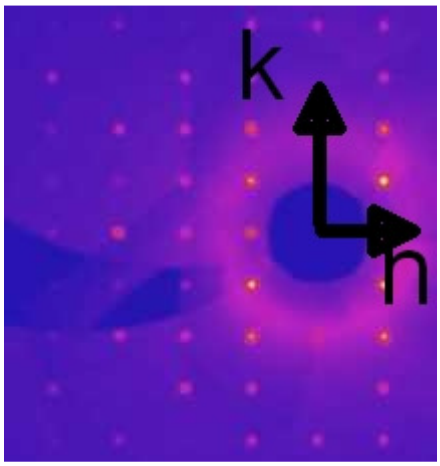
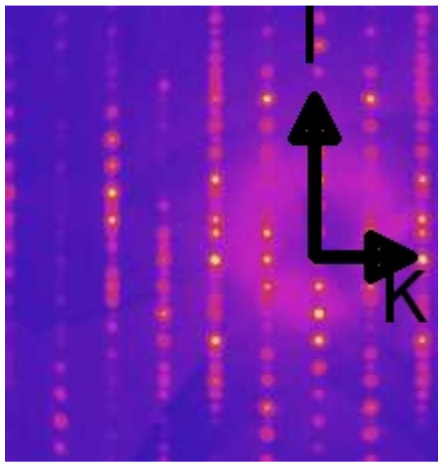


Figure S3. Selection of reconstructed diffraction images for $Sr(PhB(OH)_3)_2.H_2O$.

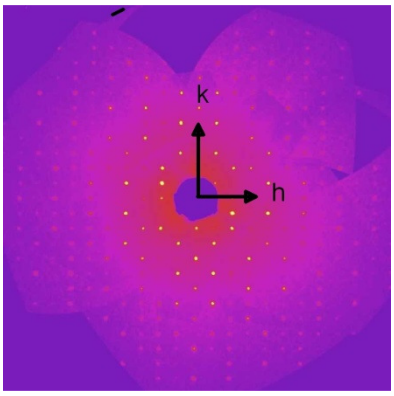


hk0

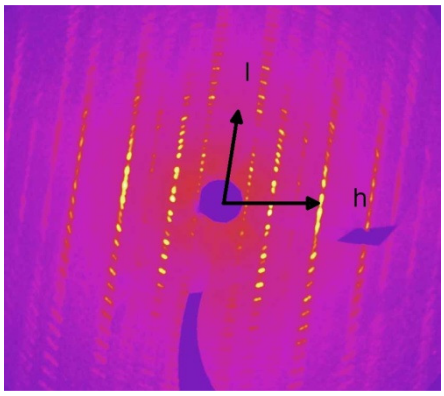


1kl

Figure S4. Selection of reconstructed diffraction images for $Ba(PhB(OH)_3)_2$.

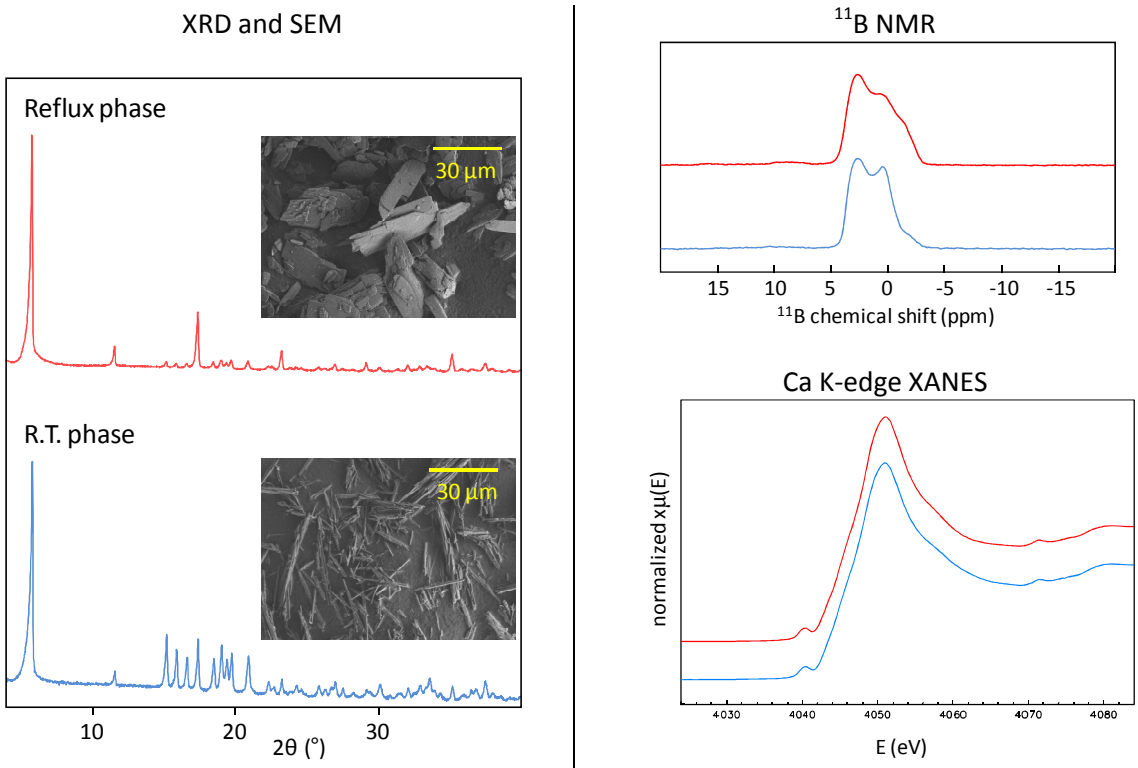


hk0



h1l

Figure S5. Comparison of the SEM, XRD, ^{11}B NMR and Ca K-edge XANES data of $Ca(PhB(OH)_3)_2$ phases prepared at room temperature (R. T.) (in blue) or under reflux (in red).



The SEM, XRD and ^{11}B solid state NMR analyses presented here were carried out in the same conditions as in the experimental section in the main text.

Ca K-edge XANES (X-ray Absorption Near Edge Structure) measurements were performed on the LUCIA beamline[2] at the Soleil Synchrotron (Saint-Aubin, France). The Soleil ring energy was 2.75 GeV and the current was 400 mA. XANES analyses were performed on $Ca(PhB(OH)_3)_2$ samples synthesized at room temperature and under reflux. Both samples were ground to a fine powder, diluted in polyvinyl pyrrolidone (average molecular weight 40,000, Sigma-Aldrich, "PVP40"), pressed into pellets, and run at room temperature in transmission mode. Spectra were collected at the Ca K-edge at 4038 eV. The X-ray incident energy on the sample was defined using a double-crystal Si(111) monochromator. The instrument was evacuated to ~1 Pa. An energy resolution of ~0.5 eV at the Ca K-edge was achieved and the energy was calibrated with a Ti foil (by setting the maximum of the 1st derivative at 4966 eV). The pre-edge (3950–4017 eV), edge (4017.2–4080 eV) and post-edge (4081–4200 eV) regions were scanned in 5.0, 0.2 and 1.0 eV steps respectively, with dwell times per point of 2.0 s. Data reduction was performed using the Athena software package.[3] Typically, three XANES data sets were collected for each sample, which were averaged and normalised with Athena.

[2] Flank, A. M. ; Cauchon, G. ; Lagarde, P. ; Bac, S. ; Janousch, M. ; Wetter, R. ; Dubuisson, J. M. ; Idir, M. ; Langlois, F. ; Moreno, T. ; Vantelon. D. *Nucl Instr and Meth in Phys Rev B* **2006**, *246*, 269.
[3] Ravel, B.; Newville, M. *J Synchrotron Radiat* **2005**; *12*: 537.

Figure S6. Structural representation of $Ba(PhB(OH)_3)_2$, resulting from preliminary refinement tests.

Ba, B, C, H, and O atoms are represented in green, brown, grey, white and red, respectively. The H atoms of the phenyls were positioned geometrically, whereas those of the OH groups were not positioned.

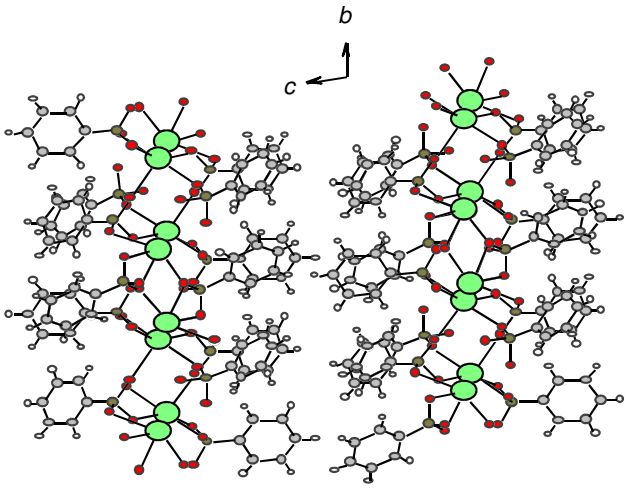
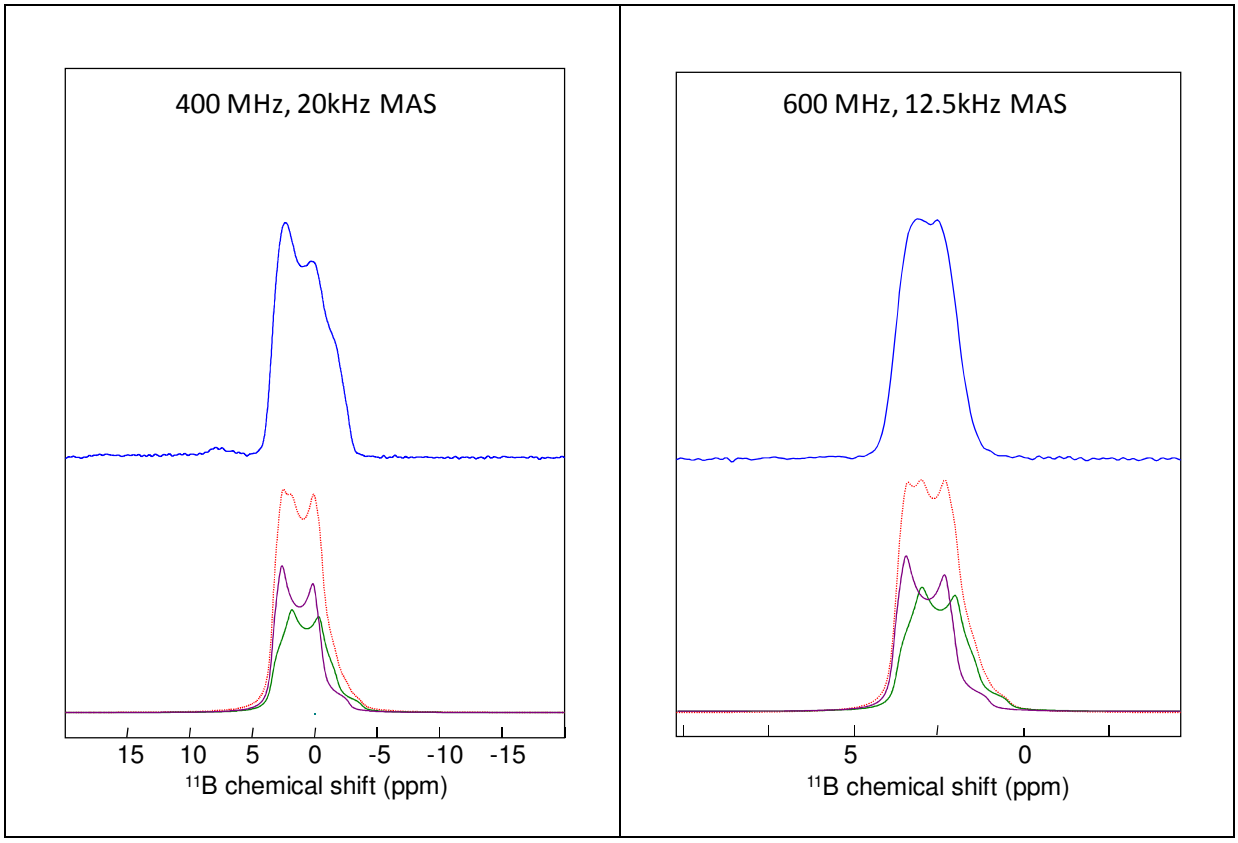


Figure S7. Experimental ^{11}B MAS NMR spectra of $Ca(PhB(OH)_3)_2$ recorded at 9.4 T and 14.1 T, and their simulation.

Experimental ^{11}B MAS NMR spectra of $Ca(PhB(OH)_3)_2$, recorded on 400 and 600 MHz NMR spectrometers (in blue), together with their simulation at both magnetic fields considering the presence of 2 boron sites, and using the "best" set of NMR parameters.[4]



Simulations performed using the following ^{11}B NMR parameters

Site 1: δ_{iso} = 3.8 ± 0.3 ppm, C_Q = 1.4 ± 0.2 MHz, η = 0.4 ± 0.2

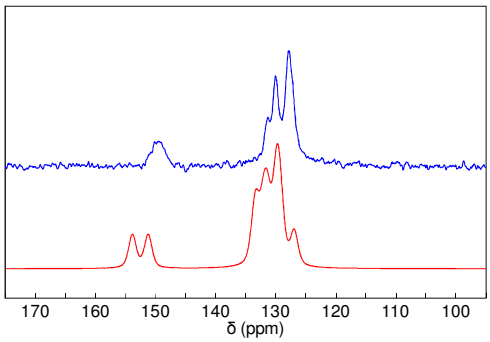
Site 2: δ_{iso} = 4.0 ± 0.2 ppm, C_Q = 1.3 ± 0.1 MHz, η = 0.2 ± 0.1

[4] The DMFit software was used for the NMR simulations (Massiot, D. et al. *Magn. Reson. Chem.* **2002** *40*,70).

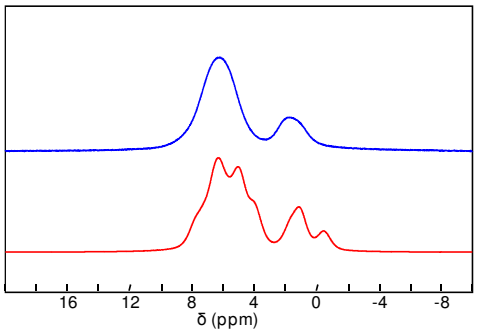
Figure S8. Experimental (blue) and calculated (red) ^{1}H, ^{11}B and ^{13}C NMR spectra of $Sr(PhB(OH)_3)_2.H_2O$ and Ba $(PhB(OH)_3)_2$.

$Sr(PhB(OH)_3)_2.H_2O$[5]

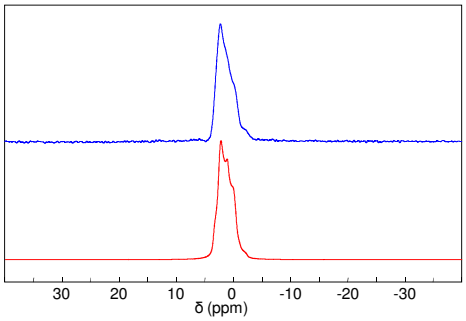
a/ ^{13}C NMR



b/ ^{1}H NMR

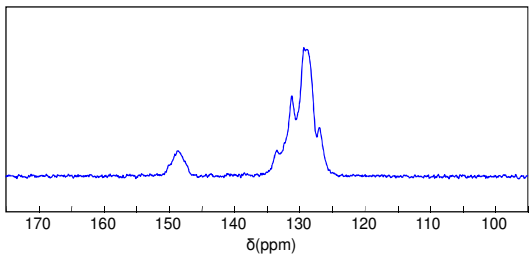


c/ ^{11}B NMR

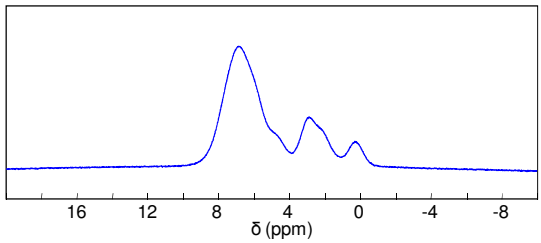


$Ba(PhB(OH)_3)_2$

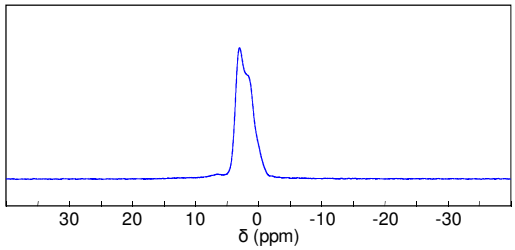
a/ ^{13}C NMR



b/ ^{1}H NMR



c/ ^{11}B NMR



[5] It is noteworthy that for the strontium structure, the discrepancy between experimental and calculated data is stronger than for the calcium one (Figure 5 in main text). This could be due to the higher difficulty in positioning H atoms in the Sr structure and/or to some mobility of the OH groups within this sample (as this can affect the overall aspect of solid state NMR spectra).

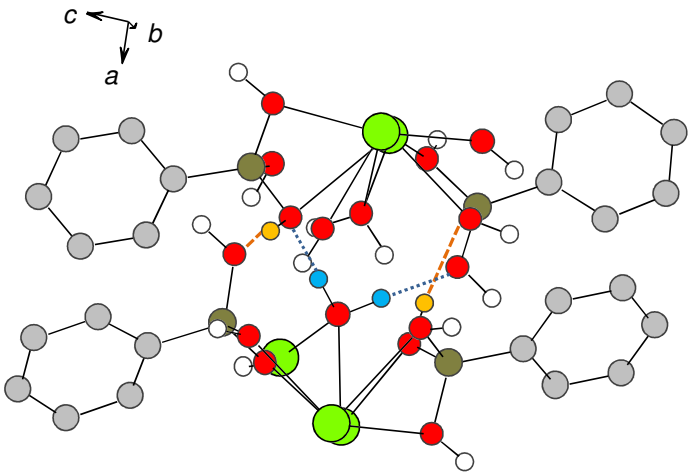
Figure S9. Representation of the inter-chain H bonds in the best DFT model of $Sr(PhB(OH)_3)_2.H_2O$.

The strongest H-bonds involve the water ligand. They are represented in dotted blue lines (with the water protons in blue).[6]

The other moderate H bonds mentioned in the main text involve the boronate hydroxyls. They are shown in dashed orange lines (with the corresponding hydroxyl protons in orange).[7]

The aromatic protons have been removed for clarity.

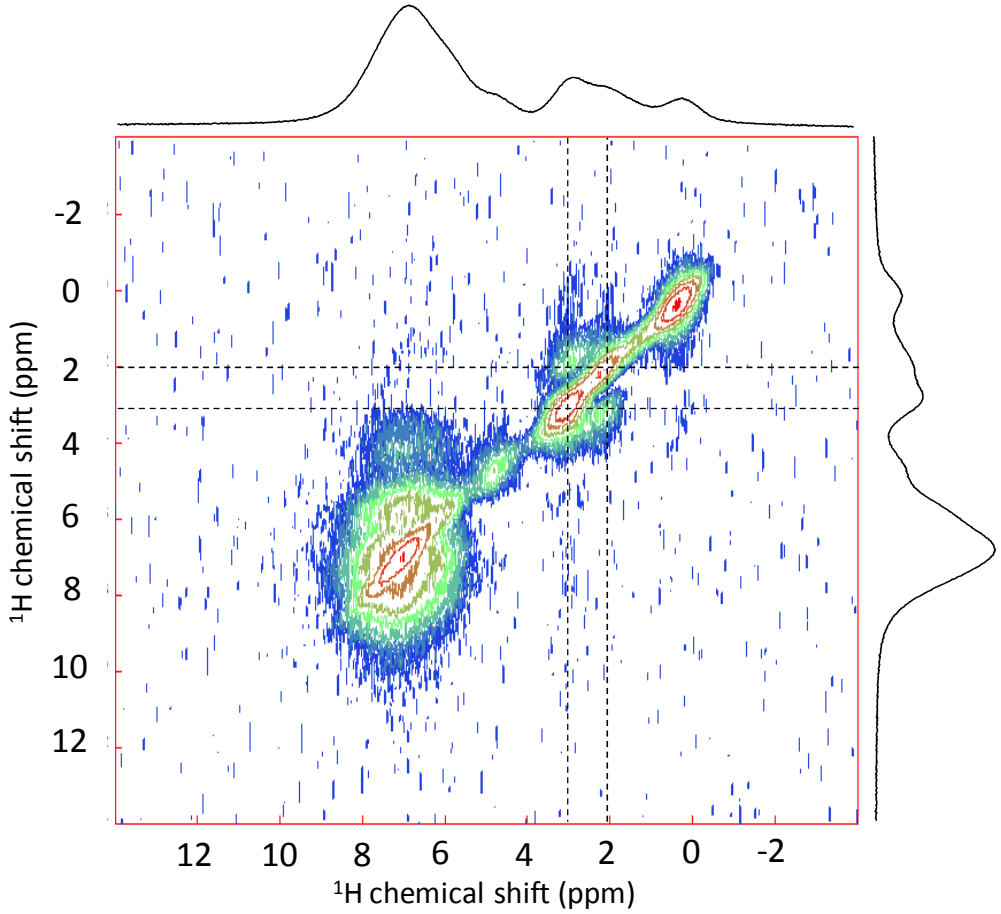
The B, C, Sr, O, and remaining H atoms are in brown, grey, green, red and white, respectively.



[6] The two strongest H bonds involve the water ligand, as attested from the following geometrical parameters: (O)H…O distances ~1.75 Å, O(H)…O distances ~2.75 Å, and (OHO) angles ~174°; they can be considered as "moderate" to "strong" H bonds.

[7] The two more "moderate" H bonds have the following average geometrical characteristics: (O)H…O distances ~2.0 Å, O(H)…O distances ~2.98 Å, and (OHO) angles ~170°.

Figure S10. 2D ^{1}H-^{1}H NOESY NMR spectrum of Ba(PhB(OH)$_3$)$_2$.



The 2D ^{1}H-^{1}H NOESY spectrum of Ba(PhB(OH)$_3$)$_2$ was recorded on a Bruker Avance III 700 MHz (16.45 T) spectrometer at a frequency of 700.13 MHz, using a 1.3 mm Bruker HX MAS probe spinning at 65 kHz. A 90° pulse of 1.6 µs was used, and recycle delay of 24 s. The mixing time was of 5 ms. For each spectrum, 16 transients were acquired for each of the 200 t_1 increments. The total experimental time was 21 hours.

The 1D ^{1}H NMR projections shown on the figure above correspond to the ^{1}H MAS NMR spectrum of Ba(PhB(OH)$_3$)$_2$.

This experiment shows that the protons corresponding to ^{1}H NMR signals centered at 3.0 and 2.0 ppm are close to each other within the structure, whereas the others are more distant. Such information could be valuable in the future to propose good models for this structure (i.e. models in which the protons have been properly placed), provided that better X-ray diffraction data were available.

Supplementary materials : Tables

Table S1. Fractional coordinates of the atoms of $Ca(PhB(OH)_3)_2$ after relaxation of all atomic positions (model M1). The lattice parameters were not relaxed.

	x/a	y/b	z/c
B17	0.2836	0.5501	0.1153
B7	0.8676	0.0524	0.1465
C1	0.7642	0.0870	0.3104
C2	0.8031	0.1518	0.3997
C3	-0.0039	0.2580	0.4312
C4	0.1515	0.2977	0.3727
C5	0.1105	0.2316	0.2834
C6	0.9166	0.1251	0.2498
C11	0.5675	0.5545	0.2527
C12	0.6480	0.6109	0.3398
C13	0.5261	0.7295	0.3943
C14	0.3268	0.7905	0.3610
C15	0.2505	0.7343	0.2734
C16	0.3682	0.6139	0.2170
Ca1	0.9906	0.7530	0.0007
H11	0.6112	0.0046	0.2888
H21	0.6818	0.1184	0.4443
H31	0.0236	0.3101	0.5006
H41	0.3029	0.3809	0.3957
H51	0.2341	0.2667	0.2397
H111	0.6608	0.4574	0.2123
H121	0.8003	0.5576	0.3647
H131	0.5866	0.7730	0.4623
H141	0.2292	0.8830	0.4024
H151	0.09849	0.7900	0.2495
H81	0.7470	0.8289	0.1798
H101	0.6057	0.2114	0.1150
H191	0.4772	0.3820	0.03402
H201	0.5274	0.2396	0.9127
H181	0.0522	0.4628	0.8466
H91	0.7798	0.9696	0.8634
O8	0.7394	0.8789	0.1277
O9	0.0857	0.0281	0.0974
O10	0.7498	0.1662	0.0963
O18	0.0236	0.5346	0.0998
O19	0.3597	0.3771	0.0762
O20	0.3524	0.6744	0.0596

Table S2 : Fractional coordinates of the atoms of $Sr(PhB(OH)_3)_2.H_2O$ after relaxation of all atomic positions. The lattice parameters were not relaxed. [8]

	x/a	y/b	z/c
B3	0.2149	0.7122	0.1829
B14	0.2273	0.7220	0.3399
C10	0.1623	0.5841	0.0600
C11	0.2391	0.6036	0.1030
C17	0.3549	0.6916	0.3866
C18	0.5513	0.6038	0.3892
C19	0.6698	0.5781	0.4283
C20	0.5921	0.6421	0.4666
C21	0.3967	0.7280	0.4655
C22	0.2799	0.7528	0.4260
C6	0.1258	0.6992	0.1328
C7	0.9290	0.7686	0.1178
C8	0.8485	0.7512	0.5749
C9	0.9673	0.8428	0.5457
H101	0.2557	0.5101	0.0379
H111	0.3876	0.5388	0.1132
H121	0.1295	0.8233	0.4263
H121	0.1095	0.2457	0.2608
H122	0.1422	0.1899	0.2127
H131	0.2052	0.9778	0.3537
H151	0.6073	0.4642	0.6868
H161	0.9273	0.6686	0.3628
H181	0.6148	0.5515	0.3597
H191	0.8182	0.5053	0.4290
H201	0.6818	0.6206	0.4972
H21	0.9475	0.4347	0.3062
H211	0.3342	0.7742	0.4956
H41	0.0729	0.4863	0.1960
H51	0.4750	0.2432	0.3385
H71	0.8372	0.8444	0.1397
H81	0.6964	0.8078	0.0647
H91	0.9087	0.6433	0.0121
O2	0.0972	0.8341	0.2103
O4	0.2078	0.5447	0.2037
O5	0.4494	0.7661	0.1877
O12	0.2215	0.2009	0.2415
O13	0.2172	0.9074	0.3282
O15	0.3440	0.6459	0.3032
O16	0.0052	0.6505	0.3365
Sr1	0.4513	0.9269	0.2636

[8] It should be noted that in this model, some of the heavier atoms (including oxygen) have moved slightly compared to the experimental X-ray data, following the full-atomic position relaxation.

Table S3. ^{1}H, ^{11}B, ^{13}C and ^{43}Ca calculated NMR parameters for the various DFT models of $Ca(PhB(OH)_3)_2$.

	M1			M2			M3			M4		
	δ_{iso} (ppm)	C_Q (MHz)	η	δ_{iso} (ppm)	C_Q (MHz)	η	δ_{iso} (ppm)	C_Q (MHz)	η	δ_{iso} (ppm)	C_Q (MHz)	η
Ca1	26.1	-1.40	0.49	10.4	2.00	0.57	33.5	0.66	0.99	31.2	-1.34	0.69
B7	3.8	-1.39	0.36	3.2	-1.30	0.59	4.1	-1.60	0.15	4.0	-1.44	0.37
B17	4.0	-1.34	0.19	4.9	-1.37	0.30	4.6	-1.46	0.12	4.1	-1.35	0.20
C1	132.7			132.3			133.7			133.2		
C2	132.4			133.5			132.8			132.5		
C3	129.2			124.3			129.7			129.3		
C4	131.8			125.7			131.3			131.7		
C5	132.8			128.5			132.9			132.3		
C6	150.8			148.1			146.4			150.2		
C11	132.0			131.4			131.8			132.0		
C12	133.0			135.3			132.8			133.3		
C13	130.9			125.8			131.1			131.0		
C14	132.2			127.0			132.3			132.2		
C15	135.6			130.9			135.6			136.0		
C16	153.2			153.2			149.6			152.8		
H11	4.5			4.4			4.7			4.4		
H21	6.2			6.2			6.3			6.2		
H31	6.2			6.2			6.4			6.2		
H41	4.9			4.4			4.9			4.8		
H51	5.8			5.5			5.7			5.8		
H111	6.2			6.0			6.0			6.1		
H121	4.9			5.3			4.9			5.0		
H131	6.7			6.6			6.7			6.7		
H141	5.5			5.1			5.7			5.4		
H151	5.5			5.5			5.4			5.5		
H81	0.2			0.0			-0.4			0.2		
H101	3.1			3.1			4.7			3.0		
H191	5.6			6.1			4.2			5.1		
H201	5.8			6.7			5.1			6.1		
H181	1.4			2.0			2.0			1.3		
H91	1.4			1.6			1.8			1.5		

Table S4. ^{1}H, ^{11}B and ^{13}C calculated NMR parameters for the best DFT model of $Sr(PhB(OH)_3)_2.H_2O$.

	δ_{iso} (ppm)	C_Q (MHz)	η
B3	3.8	-1.12	0.43
B14	3.2	-1.21	0.15
C10	133.6		
C11	133.3		
C17	151.3		
C18	129.8		
C19	127.0		
C20	132.2		
C21	131.3		
C22	131.7		
C6	153.9		
C7	130.1		
C8	129.2		
C9	129.6		
H101	6.1		
H111	5.2		
H121	7.8		
H122	7.3		
H131	-0.5		
H151	1.7		
H161	1.1		
H181	6.4		
H191	4.1		
H201	5.7		
H21	5.0		
H211	6.5		
H221	5.0		
H41	3.9		
H51	1.1		
H71	6.2		
H81	4.8		
H91	6.7		

Table S5. Comparison of the calculated ^{43}Ca NMR parameters and the average Ca…O bond distance in the models of $Ca(PhB(OH)_3)_2$.

Model	Average d(Ca…O) (in Å)	Calculated δ_{iso} (in ppm)
M1	2.49	26.1
M2	2.55	10.4
M3	2.47	33.5
M4	2.48	31.2