Electronic Supplementary Material (ESI) for CrystEngComm.

Supramolecular organisation of sulphate salt hydrates exemplified with brucine sulphate

Doris E. Braun

*** Correspondence:** doris.braun@uibk.ac.at

Table of Contents

1. Long-time dehydration experiments of Brucine Sulphate

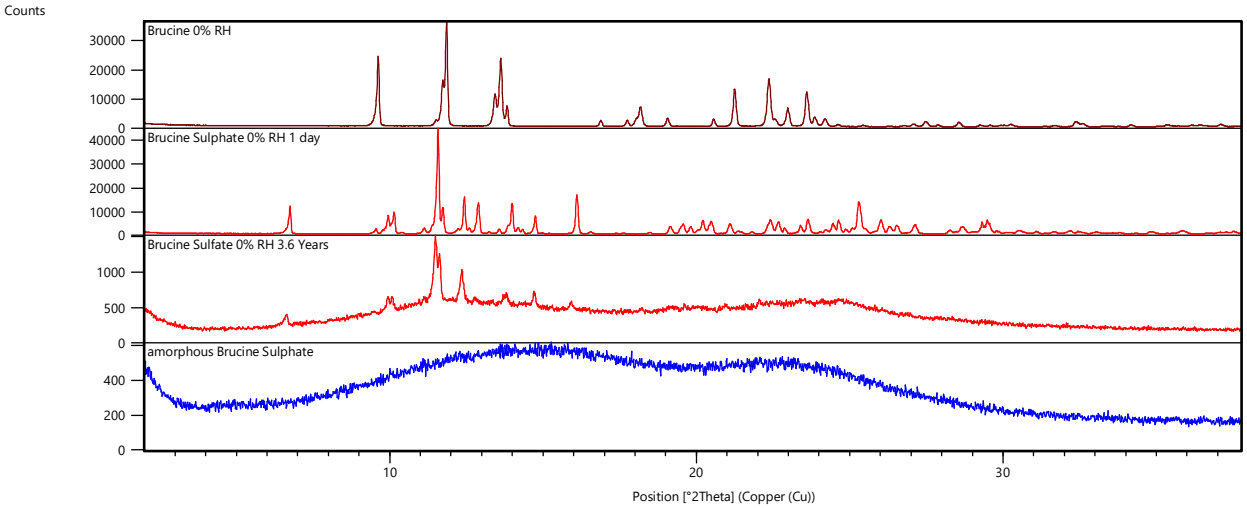

Figure S1. Comparison of Brucine and Brucine Sulphate samples. The first three samples were stored at approx. 0% RH. Amorphous Brucine Sulphate was stored at ambient conditions.

2. Crystal Explorer Calculations – HyA

Table S1. Overview of pairwise interaction energies[a] of Brucine Sulphate **HyA** water molecules (Fig. 8b of the manuscript).

Water	N[b]	A[c]	B[c]	Distance (Å)	E_E / kJ mol^{-1}	E_P / kJ mol^{-1}	E_D / kJ mol^{-1}	E_R / kJ mol^{-1}	E_{tot} / kJ mol^{-1}
W1	2	W1	Brucine	7.20	–18.9	–5.2	–6.3	10.4	–22.9
	2	W1	W3	2.85	–23.4	–6.2	–3.2	28.6	–14.4
	2	W1	Brucine	9.19	–1.6	–0.8	–2.2	1.0	–3.6
	2	W1	W2	4.31	–1.9	–0.3	–0.6	0.1	–2.7
	2	W1	Brucine	6.23	12.4	–1.7	–2.4	0.3	10.0
W2	1/1	W2	Sulphate	3.73/3.70	–84.5/–106.5	–42.5/–57.2	–5.2/–5.1	21.0/49.2	–111.4/–128.9
	2	W2	W3	2.78	–40.9	–8.6	–3.2	43.9	–25.3
	2	W2	W4	2.72	–35.3	–9.6	–4.3	55.6	–13.8
	2	W2	Brucine	8.59	–5.1	–1.4	–2.6	1.5	–7.6
	2	W2	Brucine	6.6	0.7	–4.9	-6.2	5.4	–4.9
	2	W2	Brucine	9.89	–3.8	–0.3	–0.6	0.0	–4.8
	2	W2	W1	4.31	–1.9	–0.3	–0.6	0.1	–2.7
	2	W2	Brucine	5.24	7.1	–5.2	–9.2	7.2	0.2
	2	W2	W2B	4.61	5.2	–0.4	–0.7	0.1	4.7
W3	1/1	W3	Sulphate	4.13/4.15	–47.2/–60.0	–32/–39.2	–3.4/–3.0	10.8/31.6	–69.8/–75.6
	2	W3	Brucine	6.54	–20.9	–6.7	–8.4	11.3	–27.4
	2	W3	W2	2.78	–40.9	–8.6	–3.2	43.9	–25.3
	2	W3	W1	2.85	–23.4	–6.2	–3.2	28.6	–14.4
	2	W3	Brucine	9.65	–5.9	–0.8	–1.5	0.8	–7.7
	2	W3	Brucine	6.60	0.2	–1.1	–1.9	0.2	–2.2
	2	W3	W4	4.77	2.8	–0.1	–0.3	0.0	2.7
	2	W3	Brucine	8.27	9.7	–1.3	–2.9	0.9	7.3
	2	W3	Brucine	6.09	12.5	–3.9	–8.3	8.2	8.2
W4	1/1	W4	Sulphate	3.83/3.78	–65.3/–73.6	–35.9/46.7	–4.6/–4.6	21.2/33.5	–86.4/–95.7
	2	W4	Brucine	5.77	–37.3	–6.4	–8.2	37	–28.5
	2	W4	Brucine	8.02	–12.2	–1.3	–1.6	0.4	–15.0
	2	W4	W2	2.72	–35.3	–9.6	–4.3	55.6	–13.8
	2	W4	Brucine	8.30	–3.5	–1.7	–1.2	0.1	–6.1
	2	W4	Brucine	4.71	1.6	–2.9	–7.6	3.2	–5.1
	2	W4	W3	4.77	2.8	–0.1	–0.3	0.0	2.7
	2	W4	Brucine	6.02	11.8	–2.8	–4.3	0.8	7.1

[a]Electrostatic (E_E), polarisation (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]Interactions present either once (1) or twice (2). [c]Molecules involved. [d]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

Table S2. Pairwise intermolecular interaction energies[a] of Brucine Sulphate **Hy A** ($P2_1$ setting).

Inter-action	N[a]	A	B	Distance (Å)	E_E (kJ mol^{-1})	E_P (kJ mol^{-1})	E_D (kJ mol^{-1})	E_R (kJ mol^{-1})	E_{tot}[b] (kJ mol^{-1})
1	2	Brucine	Sulphate	6.51	–708.8	–223.3	–18.6	73.9	–885.1
2	2	Brucine	Sulphate	6.52	–676.4	–197.4	–18	41.7	–851.1
3	2	Brucine	Sulphate	6.88	–466.4	–154.1	–11.9	25.2	–602
4	2	Brucine	Sulphate	6.92	–447	–129.8	–11.3	7.7	–573.8
5	2	Water	Sulphate	3.7	–106.5	–57.2	–5.1	49.2	–128.9
6	2	Water	Sulphate	3.73	–84.5	–42.5	–5.2	21	–112.4
7	2	Water	Sulphate	3.78	–73.6	–46.7	–4.6	33.5	–95.7
8	2	Water	Sulphate	3.83	–65.3	–35.9	–4.6	21.2	–86.4
9	2	Water	Sulphate	4.15	–60	–39.2	–3	31.6	–75.6
10	2	Water	Sulphate	4.13	–47.2	–32	–3.4	10.8	–69.8
11	4	Water	Brucine	5.77	–37.3	–6.4	–8.2	37	–28.5
12	4	Water	Brucine	6.54	–20.9	–6.7	–8.4	11.3	–27.4
13	4	Water	Water	2.78	–40.9	–8.6	–3.2	43.9	–25.3
14	4	Brucine	Water	7.2	–18.9	–5.2	–6.3	10.4	–22.9
15	4	Brucine	Water	8.02	–12.2	–1.3	–1.6	0.4	–15
16	4	Water	Water	2.85	–23.4	–6.2	–3.2	28.6	–14.4
17	4	Water	Water	2.72	–35.3	–9.6	–4.3	55.6	–13.8
18	4	Brucine	Water	9.65	–5.9	–0.8	–1.5	0.8	–7.7
19	4	Brucine	Water	8.59	–5.1	–1.4	–2.6	1.5	–7.6
20	4	Brucine	Water	8.3	–3.5	–1.7	–1.2	0.1	–6.1
21	4	Brucine	Water	4.71	1.6	–2.9	–7.6	3.2	–5.1
22	4	Brucine	Water	6.6	0.6	–4.9	–6.2	5.4	–4.9
23	4	Brucine	Water	9.89	–3.8	–0.3	–0.6	0	–4.8
24	4	Brucine	Water	9.19	–1.6	–0.8	–2.2	1	–3.6
25	4	Water	Water	4.31	–1.9	–0.3	–0.6	0.1	–2.7
26	4	Brucine	Water	6.6	0.2	–1.1	–1.9	0.2	–2.2
27	4	Brucine	Water	5.24	7.1	–5.2	–9.2	7.2	0.2
28	4	Water	Water	4.77	2.8	–0.1	–0.3	0	2.7
29	2	Water	Water	4.61	5.2	–0.4	–0.7	0.1	4.7
30	4	Brucine	Water	6.02	11.8	–2.8	–4.3	0.8	7.1
31	4	Brucine	Water	8.27	9.7	–1.3	–2.9	0.9	7.3
32	4	Brucine	Water	6.09	12.5	–3.9	–8.3	8.2	8.2
33	4	Brucine	Water	6.23	12.5	–1.7	–2.4	0.3	10
34	2	Brucine	Brucine	6.36	88.3	–19.5	–96	71.3	39.4
35	2	Brucine	Brucine	7.43	86.9	–22.5	–77.8	57.4	42.9
36	2	Brucine	Brucine	7.43	87.3	–22.5	–77.8	57.5	43.4
38	2	Brucine	Brucine	13.74	79.5	–2.1	–1.7	0	81.1
39	2	Brucine	Brucine	12.18	117.5	–7.2	–14.1	11.7	113.8
40	2	Brucine	Brucine	12.18	117.5	–7.2	–14.1	11.7	113.9
41	2	Brucine	Brucine	9.37	150.1	–13.4	–9.6	1.5	141.4
42	2	Brucine	Brucine	9.37	150.3	–13.4	–9.6	1.5	141.5
43	2	Brucine	Brucine	9.37	158.6	–16.5	–9.2	0.9	148
44	2	Brucine	Brucine	9.37	158.7	–16.5	–9.2	0.9	148.2

[a](2) – interaction present twice, (4) – interaction present four times. [b]Electrostatic (E_E), polarisation (E_P), dispersion (E_D) and exchange-repulsion energy (E_R) contributions. [b]$E_{tot} = k_E E_E + k_P E_P + k_D E_D + k_R E_R$, with k being scale factors.

3. Moisture-dependent PXRD measurements

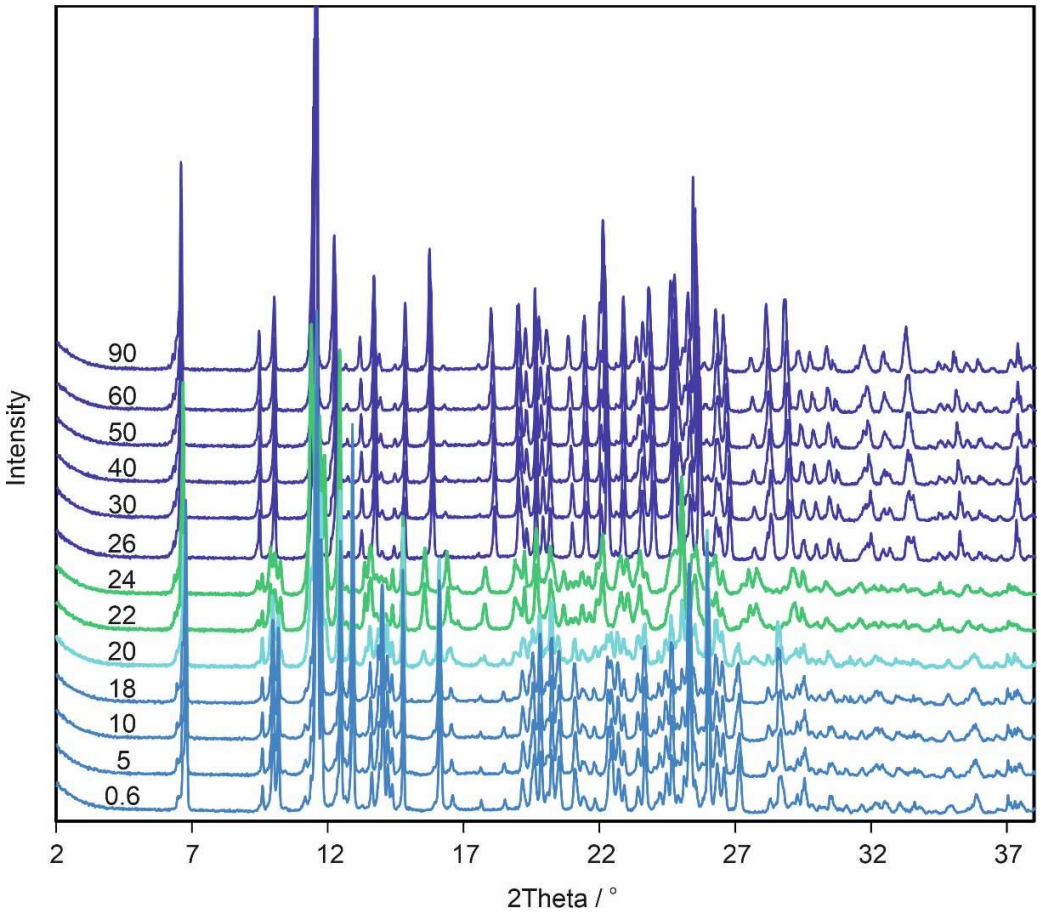

Figure S2. Moisture-dependent PXRD measurements of **BS** hydrates, indicating three different hydrates. The numbers given correspond to the relative humidity in % at which the PXRD pattern was recorded.

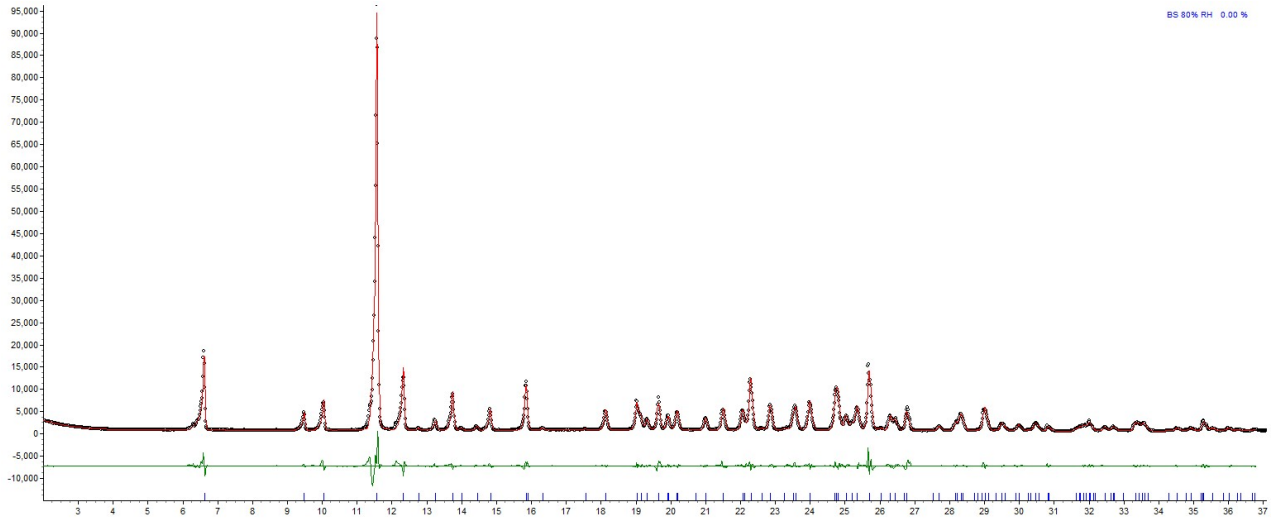

Figure S3. Observed (black points), calculated (red line) and difference (green line) profiles for the Pawley fit of **HyA** (measured at 26% RH). Blue tick marks denote the peak positions.

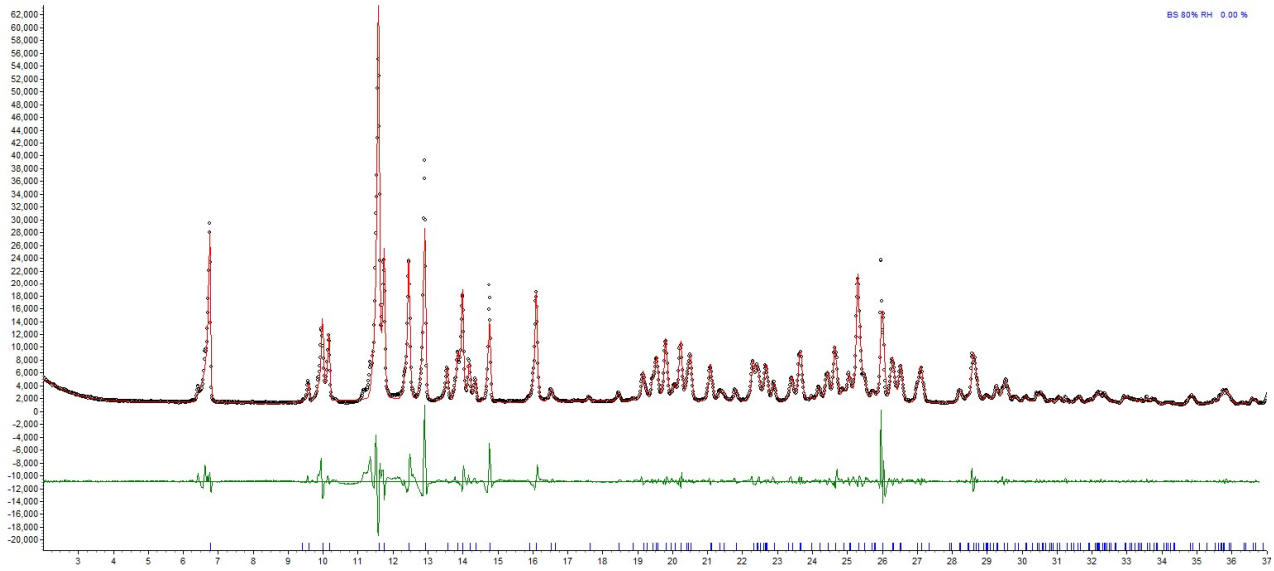

Figure S4. Observed (black points), calculated (red line) and difference (green line) profiles for the Pawley fit of **HyC** (measured at 18% RH). Blue tick marks denote the peak positions.

Table S3. Refined unit-cell parameters of **Brucine Sulphate** hydrates.

T /°C	RH /%	Space group	*a* /Å	*b* /Å	*c* /Å	*β* /°	Vol /Å^3	R_{wp}	R_{exp}	R_p	Solid Form
25	90	$C222_1$	12.239(<1)	14.486(<1)	26.866(1)	90	4763.20(34)	8.51	2.18	5.97	HyA
25	80	$C222_1$	12.240(<1)	14.472(<1)	26.848(1)	90	4755.23(22)	8.44	2.19	5.98	HyA
25	70	$C222_1$	12.239(<1)	14.456(<1)	26.820(1)	90	4745.00(33)	8.50	2.18	6.00	HyA
25	60	$C222_1$	12.240(1)	14.439(<1)	26.797(1)	90	4735.81(35)	9.00	2.19	6.32	HyA
25	50	$C222_1$	12.242(<1)	14.422(<1)	26.775(1)	90	4727.36(33)	8.53	2.18	5.98	HyA
25	40	$C222_1$	12.245(<1)	14.399(<1)	26.750(1)	90	4716.47(34)	8.94	2.18	6.18	HyA
25	30	$C222_1$	12.250(1)	14.366(<1)	26.715(2)	90	4701.45(37)	9.41	2.18	6.49	HyA
25	26	$C222_1$	12.251(1)	14.357(<1)	26.707(2)	90	4697.53(38)	9.51	2.18	6.53	HyA
25	18	$P2_1$	9.494(1)	26.088(3)	9.298(1)	98.111(3)	2279.94(32)	11.75	1.67	7.80	HyC
25	10	$P2_1$	9.487(1)	26.060(2)	9.297(1)	98.074(3)	2275.62(29)	11.33	2.17	7.62	HyC
25	5	$P2_1$	9.484(1)	26.041(2)	9.295(1)	98.063(3)	2272.83(29)	11.27	2.16	7.62	HyC
25	0.6	$P2_1$	9.490(1)	25.970(3)	9.292(1)	98.086(3)	2267.14(30)	11.32	2.16	7.61	HyC

4. Computational dehydration modelling

Table S4. Total CASTEP energies, lattice energy differences (same hydrate stoichiometry) and energy required to remove water molecules (averaged per water).

Structure	PBE-TS / kJ mol^{-1}	ΔE_{latt} / kJ mol^{-1}	Energy required to remove 1 water molecule / kJ mol^{-1}	PBE-D2 / kJ mol^{-1}	ΔE_{latt} / kJ mol^{-1}	Energy required to remove 1 water molecule / kJ mol^{-1}
Hept_A	–1725936.47	0.73		–1726016.84	1.67	
Hept_B	–1725937.19	0.00		–1726018.51	0.00	
Hex_B1	–1680618.97	14.39	–83.59	–1680702.16	12.23	–82.36
Hex_B2	–1680602.76	30.60	–99.80	–1680685.89	28.50	–98.63
Hex_B3	–1680600.84	32.52	–101.72	–1680689.99	24.41	–94.53
Hex_B4	–1680633.36	0.00	–69.20	–1680714.39	0.00	–70.13
Hex_B5	–1680624.79	8.56	–77.76	–1680710.73	3.66	–73.79
Hex_B6	–1680596.77	36.59	–105.79	–1680683.77	30.62	–100.75
Hex_B7	–1680605.74	27.61	–96.81	–1680688.35	26.05	–96.17
Penta_B1	–1635309.281	0.00	–80.05	–1635394.05	0.00	–74.12
Penta_B2	–1635298.064	11.22	–85.65	–1635379.76	14.29	–88.41
Penta_B3	–1635306.372	2.91	–81.50	–1635388.74	5.32	–79.43
Penta_B4	–1635307.534	1.75	–80.92	–1635392.88	1.17	–75.29
Penta_B5	–1635292.092	17.19	–88.64	–1635376.82	17.24	–91.36
Penta_B6	–1635294.046	15.24	–87.66	–1635379.03	15.03	–89.15
Isomorphic dehydrate	–1408693.74		–86.58	–1408794.15		–83.78