$Cd[B_2(SO_4)_4]$ & $H_2[B_2(SO_4)_4]$ – A phyllosilicate analogue borosulfate and its homeotypic heteropolyacid

Matthias Hämmer[a], Leonard C. Pasqualini[b], Sean S. Sebastian[c], Hubert Huppertz[b], Henning A. Höppe[a]*, and Jörn Bruns[c*]

[a] Dr. Matthias Hämmer, and Prof. Dr. Henning A. Höppe,
Institut für Physik
Universität Augsburg
Universitätsstraße 1, 86159 Augsburg, Germany.
E-mail: henning@ak-hoeppe.de

[b] Leonard C. Pasqualini, M.Sc., and Univ.-Prof. Dr. Hubert Huppertz
Institute of General, Inorganic and Theoretical Chemistry
University of Innsbruck
Innrain 80-82, 6020 Innsbruck, Austria
E-mail: Hubert.Huppertz@uibk.ac.at

[c] Sean S. Sebastian, M.Sc., and Dr. Jörn Bruns*
Institute of Inorganic Chemistry
University of Cologne
Greinstrasse 6, 50939 Cologne, Germany
E-mail: j.bruns@uni-koeln.de

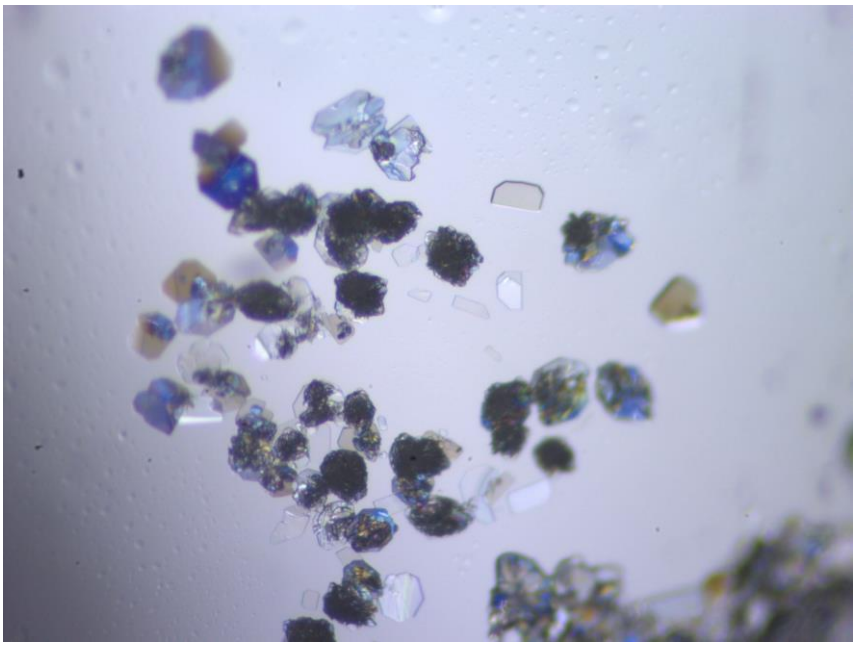

Figure S1. Single crystals of $H_2[B_2(SO_4)_2]$ under a polarization microscope.

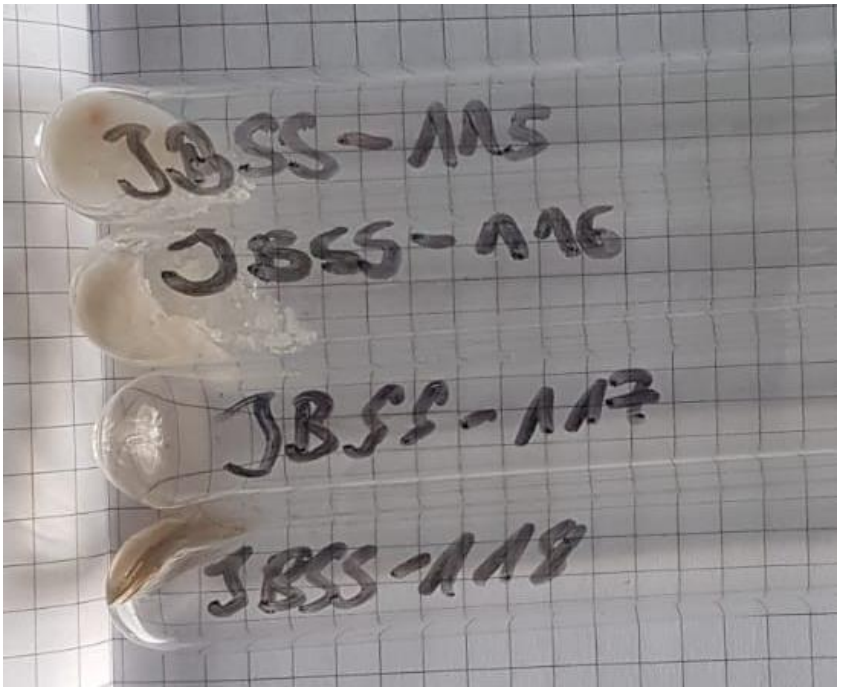

Figure S2. Top two ampoules: Single crystals and bulk material of $H_2[B_2(SO_4)_2]$ (starting materials: 200 mg B_2O_3 and 0.4 mL SO_3); Bottom two ampoules: Liquid product of an identical reaction as performed for the first two ampoules, however with exactly 0.1 mL less SO_3 (starting materials: 200 mg B_2O_3 and 0.3 mL SO_3).

Figure S3. Destroyed polyacetate foil after 10 minutes contact of crystals of $H_2[B_2(SO_4)_2]$ for PXRD.

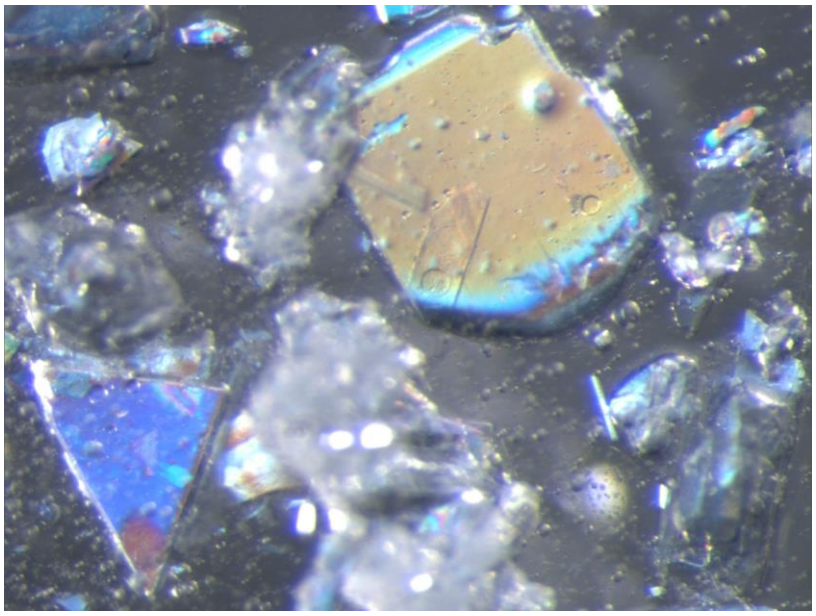

Figure S4. Single crystals of $Cd[B_2(SO_4)_2]$ under a polarization microscope.

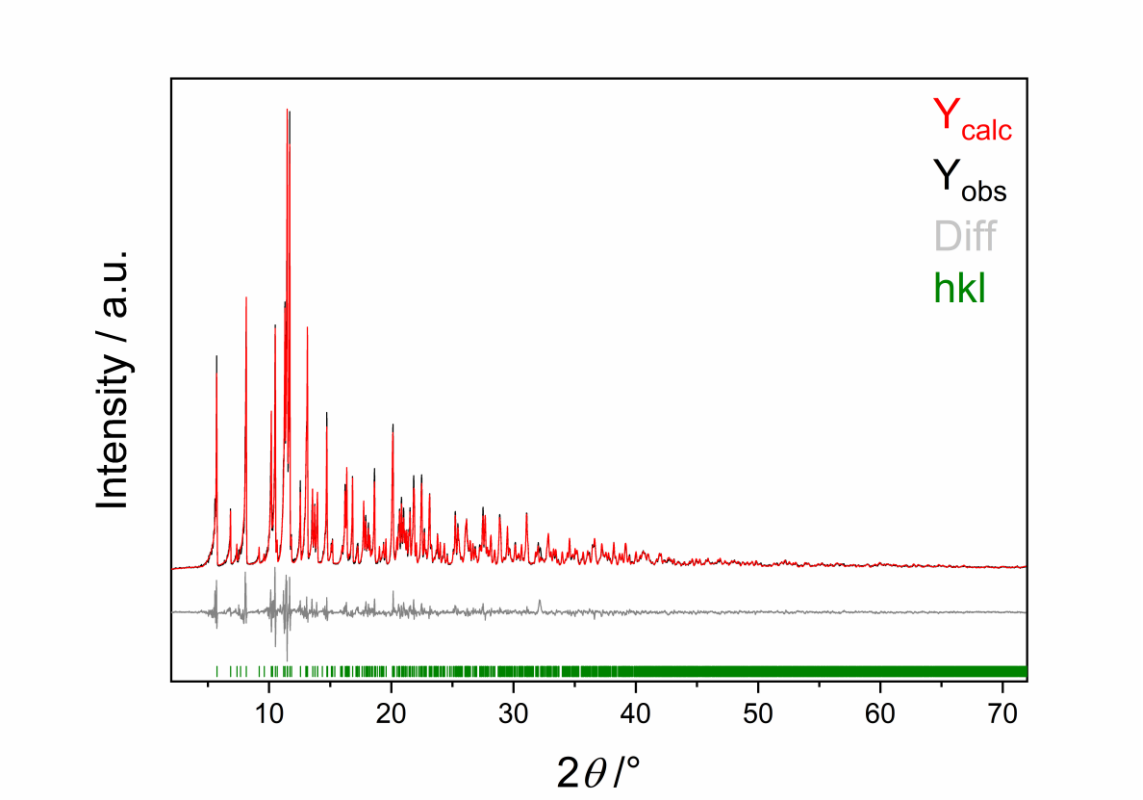

Figure S5. Rietveld refinement of the powder X-ray diffraction pattern of $Cd[B_2(SO_4)_2]$ prepared by synthesis method **I**.

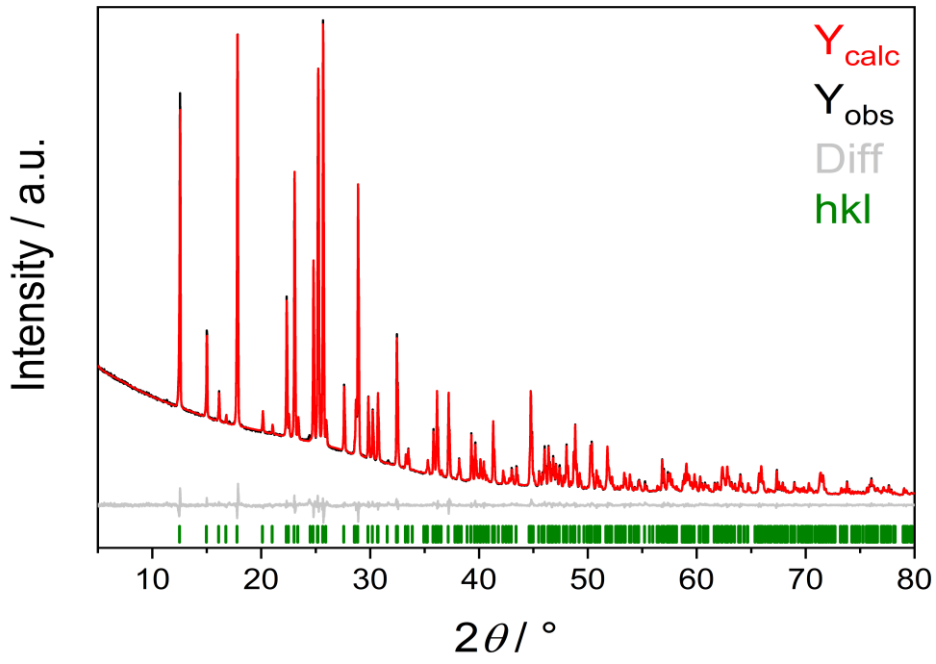

Figure S6. Rietveld refinement of the powder X-ray diffraction pattern of $Cd[B_2(SO_4)_2]$ prepared by synthesis method **II**; details are found in table S1.

Table S1. Crystal data and structure refinements of $Cd[B_2(SO_4)_4]$ determined from powder XRD data via Rietveld refinement

M / g mol^{-1}	518.26
Temperature / K	298(2)
Space group	$P2_1/n$ (no. 14)
a / pm	809.25(1)
b / pm	797.00(1)
c / pm	938.48(2)
β / °	109.857(1)
Volume / 10^6 pm^3	569.31(1)
Z	2
ρ_{calcd} / g cm^{-3}	3.02
Radiation; wavelength λ / Å	CuK_α; 1.54184
Diffractometer	Bruker D8 Advance
θ range / deg	2.5–40
Observed reflections	350
Refined parameters	67
R_{Bragg}	0.010
R_p	0.014
R_{wp}	0.021
GooF	2.35

Table S2. Crystal data and structure refinement for $H_2[B_2(SO_4)_4]$.

Formula weight	203.94
Temperature/K	173(2)
Crystal system	triclinic
Space group	$P\bar{1}$ (no. 2)
a/ Å	7.7014(7)
b/ Å	8.5004(8)
c/ Å	8.7264(8)
α/ °	92.41(1)
β/ °	97.85(1)
γ/ °	90.31(1)
Volume/ Å^3	565.39(9)
Z	2
ρ_{calc}/ g cm^{-3}	2.396
Absorption coefficient/ mm^{-1}	0.942
F(000)	408
Crystal size/ mm^3	0.1 × 0.095 × 0.09
2*θ* range for data collection	4.7 to 75.8°
Index ranges	$-13 \le h \le 13$; $-14 \le k \le 14$; $-15 \le l \le 15$
Reflections collected	46145
Independent reflections	6113 [R_{int} = 0.0366]
Completeness to *θ*	100%
Absorption correction	multi-scan
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6113 / 0 / 208
Goodness-of-fit on F^2	1.039
Final *R* indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0252; wR_2 = 0.0683
Final *R* indexes [all data]	R_1 = 0.0302; wR_2 = 0.0707
Largest diff. peak/hole/ e$^-$/Å^{-3}	1.03 / -0.62
CSD number	2207483

Table S3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $H_2[B_2(SO_4)_4]$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	U_{eq}
S1	8091.1(3)	11403.3(2)	1847.5(2)	8.49(4)
S2	3384.1(3)	9208.8(3)	3498.1(2)	8.67(4)
S3	8153.1(3)	6405.3(2)	3943.5(2)	7.52(4)
S4	3277.6(3)	4503.0(2)	1140.9(2)	8.50(4)
B1	6876(1)	9374(1)	3787(1)	8.5(1)
B2	6799(1)	4314(1)	1656(1)	8.8(1)
O1	7099(1)	10394(1)	569.9(9)	20.3(2)
O2	9741(1)	11942(1)	1569(1)	18.1(1)
O3	8202.6(9)	10418.6(8)	3241.4(8)	10.6(1)
O4	7204.9(9)	9429.5(8)	5469.5(8)	10.9(1)
O5	7154.5(9)	7757.4(8)	3195.9(8)	10.7(1)
O6	5140.2(9)	9852.8(8)	3096.2(8)	10.3(1)
O7	2176(1)	9192.1(1)	2092.8(8)	16.0(1)
O8	3635(1)	7808.3(8)	4320.6(9)	13.4(1)
O9	9845.6(9)	6802.4(9)	4689.8(9)	14.5(1)
O10	6952(1)	5694.2(9)	4942.8(9)	14.4(1)
O11	8222.6(9)	5273.7(8)	2584.5(8)	10.0(1)
O12	7147(1)	4219.1(8)	52.8(8)	11.3(1)
O13	6862.1(9)	2702.4(8)	2223.4(8)	11.9(1)
O14	2129(0)	4832.4(1)	2279.4(8)	14.8(1)
O15	3280(1)	2986.0(8)	402.5(9)	15.9(1)
O16	5130.5(9)	4996.2(8)	1914.7(8)	10.7(1)
H1	7380(30)	10550(30)	-280(30)	53(7)
H2	7340(30)	5560(30)	5850(30)	58(8)

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $H_2[B_2(SO_4)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	11.17(8)	5.45(8)	9.52(8)	1.22(6)	3.52(6)	0.16(6)
S2	9.99(8)	9.20(8)	6.75(8)	-0.58(6)	1.21(6)	0.61(6)
S3	8.78(8)	6.05(8)	7.48(8)	0.20(6)	0.26(6)	0.46(6)
S4	9.45(8)	8.54(8)	7.72(8)	0.87(6)	1.77(6)	-1.10(6)
B1	10.7(3)	6.8(3)	8.1(3)	0.9(3)	1.9(3)	1.4(3)
B2	10.6(3)	7.2(3)	8.6(3)	0.9(3)	1.3(3)	1.3(3)
O1	33.9(4)	17.0(3)	10.1(3)	-4.4(2)	5.2(3)	-10.2(3)
O2	12.8(3)	17.0(3)	26.7(4)	8.5(3)	8.5(3)	0.6(2)
O3	11.8(3)	9.0(2)	11.2(3)	4.3(2)	1.4(2)	-0.1(2)
O4	15.2(3)	10.1(3)	7.4(2)	0.2(2)	2.1(2)	4.2(2)
O5	16.6(3)	5.6(2)	9.4(2)	0.8(2)	0.2(2)	2.9(2)
O6	10.0(2)	10.9(3)	10.5(2)	3.7(2)	2.2(2)	1.2(2)
O7	13.9(3)	25.0(4)	8.2(3)	-2.1(2)	-1.4(2)	0.2(3)
O8	17.3(3)	8.2(3)	15.4(3)	1.9(2)	4.1(2)	-0.4(2)
O9	11.2(3)	15.1(3)	15.6(3)	-2.2(2)	-3.0(2)	-1.5(2)
O10	15.0(3)	18.2(3)	10.6(3)	5.8(2)	2.7(2)	-1.8(2)
O11	9.6(2)	9.0(2)	10.8(2)	-3.3(2)	0.85(19)	1.4(2)
O12	16.2(3)	10.4(3)	7.6(2)	2.0(2)	2.3(2)	4.0(2)
O13	14.9(3)	7.0(2)	15.0(3)	3.4(2)	5.6(2)	3.0(2)
O14	12.4(3)	23.2(3)	9.9(3)	2.7(2)	4.6(2)	-0.3(2)
O15	20.8(3)	8.1(3)	18.0(3)	-1.6(2)	0.4(3)	-2.3(2)
O16	8.6(2)	10.7(3)	12.0(3)	-1.9(2)	0.0(2)	1.5(2)

Table S5. Experimental bond lengths for $H_2[B_2(SO_4)_4]$.

atom	atom	bond length/ Å
S1	O1	1.4975(8)
S1	O2	1.4040(8)
S1	O3	1.4985(7)
S1	O13[1]	1.5128(7)
S2	O4[2]	1.5449(7)
S2	O6	1.5457(7)
S2	O7	1.4339(8)
S2	O8	1.4164(7)
S3	O5	1.5078(7)
S3	O9	1.4078(7)
S3	O10	1.4969(7)
S3	O11	1.5022(7)
S4	O12[3]	1.5420(7)
S4	O14	1.4381(7)
S4	O15	1.4172(8)
S4	O16	1.5410(7)
O3	B1	1.489(1)
04	B1	1.455(1)
O5	B1	1.474(1)
O6	B1	1.457(1)
O11	B2	1.488(1)
O12	B2	1.459(1)
O13	B2	1.475(1)
O16	B2	1.454(1)

[1]+*x*,1+*y*,+*z*; [2]1-*x*,2-*y*,1-*z*; [3]1-*x*,1-*y*,-*z*

Table S6. Experimental bond angles for $H_2[B_2(SO_4)_4]$.

atom	atom	atom	angle/°	atom	atom	atom	angle/°
O1	S1	O3	104.51(4)	O15	S4	O16	111.20(4)
O1	S1	O13[1]	106.30(5)	B1	O3	S1	130.74(6)
O2	S1	O1	115.48(5)	B1	O4	S2[2]	123.75(6)
O2	S1	O3	112.47(5)	B1	O5	S3	131.15(6)
O2	S1	O13[1]	114.05(5)	B1	O6	S2	125.44(6)
O3	S1	O13[1]	102.82(4)	B2	O11	S3	129.96(6)
O4[2]	S2	O6	101.95(4)	B2	O12	S4[3]	125.82(6)
O7	S2	O4[2]	105.57(4)	B2	O13	S1[4]	127.11(6)
O7	S2	O6	106.33(4)	B2	O16	S4	128.21(6)
O8	S2	O4[2]	111.23(4)	O4	B1	O3	107.22(7)
O8	S2	O6	111.18(4)	O4	B1	O5	109.21(7)
O8	S2	O7	119.06(5)	O4	B1	O6	116.30(7)
O9	S3	O5	114.60(4)	O5	B1	O3	107.82(7)
O9	S3	O10	115.43(5)	O6	B1	O3	108.41(7)
O9	S3	O11	111.38(4)	O6	B1	O5	107.59(7)
O10	S3	O5	105.37(4)	O12	B2	O11	108.14(7)
O10	S3	O11	107.01(4)	O12	B2	O13	107.70(7)
O11	S3	O5	101.88(4)	O13	B2	O11	108.74(7)
O14	S4	O12[3]	104.38(4)	O006	B2	O11	108.04(7)
O14	S4	O16	106.03(4)	O006	B2	O12	115.89(7)
O15	S4	O12[3]	111.13(4)	O006	B2	O13	108.16(7)
O15	S4	O14	120.23(5)				

[1]+*x*,1+*y*,+*z*; [2]1-*x*,2-*y*,1-*z*; [3]1-*x*,1-*y*,-*z*; [4]+*x*,-1+*y*,+*z*

Table S7. Hydrogen bonds in $H_2[B_2(SO_4)_4]$.

D	H	A	*d*(D-H)/ Å	*d*(H-A)/ Å	*d*(D-A) / Å	D-H-A/ °
O1[1]	H1	O7[2]	0.82	1.69	2.501(1)	175.9
O10	H2	O14[3]	0.82	1.68	2.491(1)	172.2

[1]1-x,2-y,1-z; [2]x,y,1+z; [3]1-x,1-y,1-z

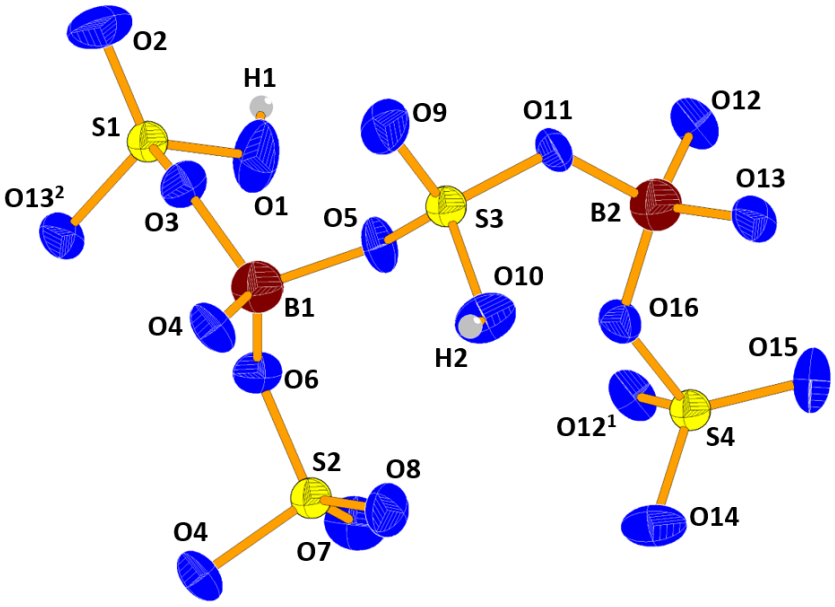

Figure S7. Asymmetric unit of $H_2[B_2(SO_4)_4]$. The thermal ellipsoids are set on 90% probability level. (Symmetry operators: [1]1-*x*,1-*y*,-*z*; [2]+*x*,1+*y*,+*z*).

Table S8. Crystal data and structure refinement for $Cd[B_2(SO_4)_4]$ determined from single-crystal XRD.

Formula weight	518.25	
Temperature/K	173(2)	250(2)
Crystal system	monoclinic	
Space group	$P2_1/n$ (no. 14)	
a/ Å	8.061(1)	8.076(1)
b/ Å	7.9599(5)	7.975(19
c/ Å	9.405(1)	9.395(1)
β/ °	109.96(1)	110.01(1)
Volume/ Å^3	567.2(1)	568.6(2)
Z	2	
ρ_{calc}/ g cm^{-3}	3.035	3.027
Absorption coefficient/ mm^{-1}	2.765	2.76
F(000)	500	500
Crystal size/ mm^3	0.172 × 0.06 × 0.06	0.05 × 0.04 × 0.02
2θ range for data collection	5.8 - 82.6°	5.8-67.0°
Index range $h\|k\|l$	±14|±14|±17	±11|±11|±12
Reflections collected	56664	23626
Independent reflections	3799	2230
Completeness to θ	100%	
Absorption correction	multi-scan	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3799 / 0 / 107	2230 / 0 / 106
Goodness-of-fit on F^2	1.138	1.11
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0143; wR_2 = 0.0379	R_1 = 0.030; wR_2 = 0.064
Final R indexes [all data]	R_1 = 0.0163; wR_2 = 0.0386	R_1 = 0.043; wR_2 = 0.067
Largest diff. peak/hole/ e$^-$/Å^{-3}	0.705 / -0.448	0.87 / -0.86
CSD number	2176209	2171676

Table S9. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cd[B_2(SO_4)_4]$ at 173 K. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

atom	*x*	*y*	*z*	U_{eq}
Cd1	5000	0	5000	6.68(2)
B1	6370(2)	4713(2)	3582.6(9)	7.1(2)
S1	7930.0(2)	1735.3(2)	3463.0(2)	6.84(3)
S2	3099.2(2)	4184.0(2)	3600.0(2)	5.49(3)
O111	6500.1(8)	3088.9(7)	2926.9(6)	10.16(8)
O121	4457.4(8)	5103.6(7)	3087.5(7)	8.12(8)
O122	2799.1(8)	5387.4(7)	4747.4(6)	8.46(8)
O11	7308.9(9)	474.9(9)	4265.3(8)	15.0(2)
O12	9621.7(8)	2406.2(9)	4229.3(8)	16.9(2)
O21	3788.7(8)	2618.7(7)	4306.4(6)	9.58(8)
O22	1496.6(8)	4105.1(8)	2337.2(6)	12.26(9)
O112	7744.0(8)	1061.4(8)	1897.8(6)	11.13(9)

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Cd[B_2(SO_4)_4]$ at 173 K. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+...+2hka\times b\times U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	7.92(3)	6.34(3)	5.52(3)	0.19(2)	1.96(2)	0.51(2)
B1	9.1(3)	6.5(2)	7.3(2)	0.1(2)	4.9(2)	0.0(2)
S1	7.06(6)	8.05(6)	6.70(6)	-1.02(5)	4.03(5)	0.20(5)
S2	6.68(6)	5.28(6)	4.50(5)	0.59(4)	1.92(4)	0.19(4)
O111	10.9(2)	8.8(2)	10.8(2)	-2.9(2)	3.6(2)	2.8(2)
O121	8.9(2)	7.8(2)	9.5(2)	2.7(2)	5.4(2)	1.0(2)
O122	12.2(2)	8.2(2)	6.5(2)	0.5(2)	5.0(2)	3.1(2)
O11	17.1(2)	15.3(3)	17.5(3)	6.4(2)	12.2(2)	2.2(2)
O12	8.8(2)	20.3(3)	19.3(3)	-5.2(2)	2.1(2)	-3.1(2)
O21	13.1(2)	5.2(2)	11.0(2)	2.4(2)	4.7(2)	1.7(2)
O22	10.4(2)	16.2(2)	7.0(2)	2.3(2)	-1.2(2)	-2.8(2)
O112	14.6(2)	12.7(2)	7.3(2)	-1.6(2)	5.2(2)	5.5(2)

Table S11. Wyckoff symbol, atomic coordinates *x*; *y*; *z* and equivalent isotropic displacement parameters U_{eq} in Å^2 for Cd[$B_2(SO_4)_4$] at 250 K.

Atom	**Wyckoff symbol**	***x***	***y***	***z***	U_{eq}
Cd1	2*a*	0	0	0	0.00981(7)
S1	4*e*	0.18967(7)	0.41774(7)	0.14024(6)	0.00795(11)
S2	4*e*	-0.29299(8)	0.17394(7)	0.15331(7)	0.01002(11)
O11	4*e*	0.1507(2)	-0.0900(3)	0.2337(2)	0.0170(4)
O12	4*e*	0.1211(2)	0.2612(2)	0.0700(2)	0.0134(3)
O13	4*e*	0.2190(2)	0.5381(2)	0.0247(2)	0.0118(3)
O14	4*e*	0.0544(2)	0.5097(2)	0.1916(2)	0.0116(3)
O21	4*e*	-0.4611(3)	0.2402(3)	0.0757(2)	0.0241(4)
O22	4*e*	-0.2297(3)	0.0485(3)	0.0745(3)	0.0213(4)
O23	4*e*	-0.2759(2)	0.1071(2)	0.3100(2)	0.0153(4)
O24	4*e*	-0.1515(2)	0.3096(2)	0.2069(2)	0.0144(4)
B1	4*e*	-0.1375(4)	0.4715(3)	0.1417(3)	0.0101(5)

Table S12. Anisotropic displacement parameters U_{ij} in Å^2 for β-Cu[$B_2(SO_4)_4$] at 250 K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cd1	0.01152(11)	0.00943(10)	0.00798(11)	-0.00031(9)	0.00269(8)	-0.00072(9)
S1	0.0096(2)	0.0078(2)	0.0064(3)	-0.00082(19)	0.0027(2)	-0.00035(18)
S2	0.0103(2)	0.0118(2)	0.0100(3)	0.0015(2)	0.0060(2)	-0.00038(19)
O11	0.0156(9)	0.0214(9)	0.0104(9)	0.0037(7)	-0.0004(7)	-0.0024(7)
O12	0.0175(8)	0.0077(7)	0.0157(9)	-0.0021(7)	0.0065(7)	-0.0018(6)
O13	0.0168(8)	0.0099(7)	0.0100(8)	-0.0011(6)	0.0064(7)	-0.0042(6)
O14	0.0139(8)	0.0106(7)	0.0124(8)	-0.0038(7)	0.0073(7)	-0.0009(6)
O21	0.0150(9)	0.0285(11)	0.0255(12)	0.0067(9)	0.0029(8)	0.0033(8)
O22	0.0247(10)	0.0208(9)	0.0254(11)	-0.0083(8)	0.0178(9)	-0.0038(8)
O23	0.0182(9)	0.0188(9)	0.0098(9)	0.0014(7)	0.0061(7)	-0.0084(7)
O24	0.0161(8)	0.0126(8)	0.0142(9)	0.0049(7)	0.0049(7)	-0.0029(7)
B1	0.0122(11)	0.0095(12)	0.0106(12)	0.0011(9)	0.0064(10)	-0.0004(8)

Table S13. Selected interatomic distances /pm and angles /deg in $Cd[B_2(SO_4)_4]$ at 173 K, 250 K and 300 K determined by single crystal XRD and Rietveld refinement, respectively; the respective standard deviations are given in parentheses.

Distance / angle	173 K (SC-XRD)	250 K (SC-XRD)	300 K (Rietveld)
Cd-O	222.77(6)-229.98(6)	222.9(2)-230.0(2)	222.7(6)-228.4(5)
$\sum IR(Cd\text{-}O)^3$	220	220	220
S-O	141.19(7)-153.19(6)	140.6(2)-152.8(2)	1.37(1)-154(1)
$\sum IR(S\text{-}O)^3$	147	147	147
B-O	144.5(2)-148.4(2)	144.3(3)-148.9(3)	141(1)-151(1)
$\sum IR(B\text{-}O)^3$	146	146	146
O-S-O	96.59(3)-116.46(4)	96.8(1)-116.4(1)	97.7(3)-117.2(3)
O-B-O	105.75(6)-114.45(6)	105.8(2)-114.7(2)	103.7(6)-114.1(9)

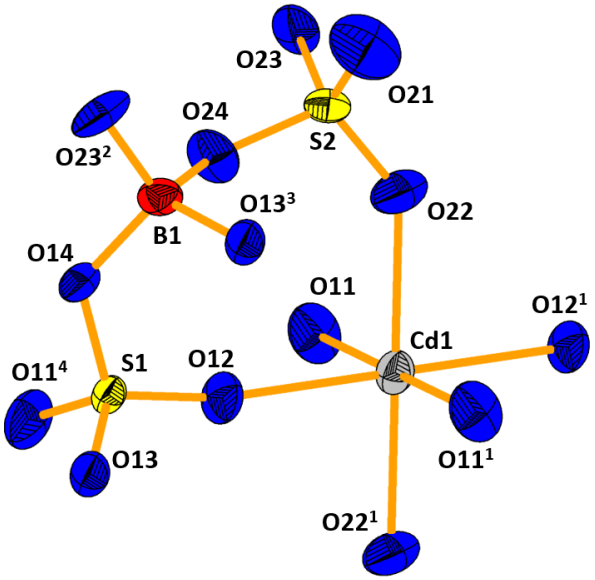

Figure S8. Extended asymmetric unit of $Cd[B_2(SO_4)_4]$. The thermal ellipsoids are set on 90% probability level. (Symmetry operators: [1]-*x*, -*y*,-*z*; [2]-1/2-*x*,1/2+*y*,1/2-*z*; [2]--*x*,1-*y*, *z*; ½-x, ½+y, ½-z)

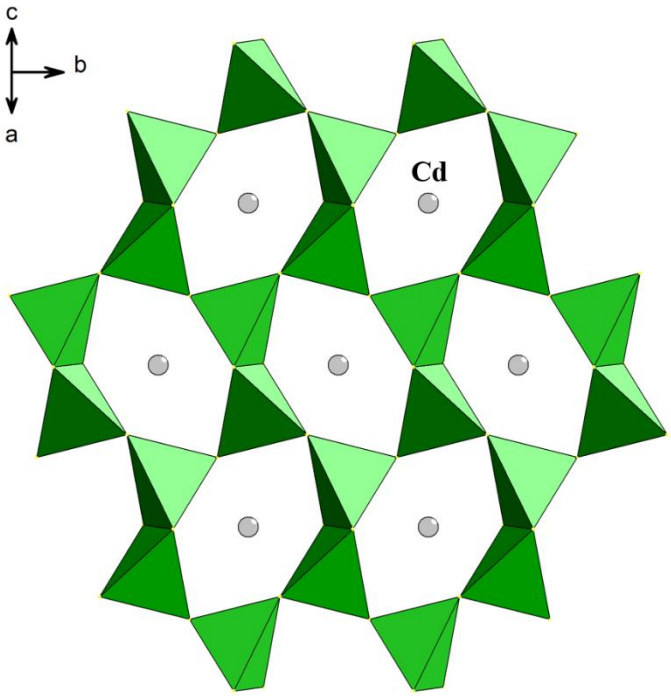

Figure S9. Layers in $Cd[B_2(SO_4)_2]$ formed by corner and edge sharing supertetrahedra $B(SO_4)_4$ resulting in *sechser* rings with the cations located inside and corner sharing dimers of supertetrahedra; supertetrahedra light green, cadmium atoms grey, sulfur atoms yellow; oxygen atoms are omitted.

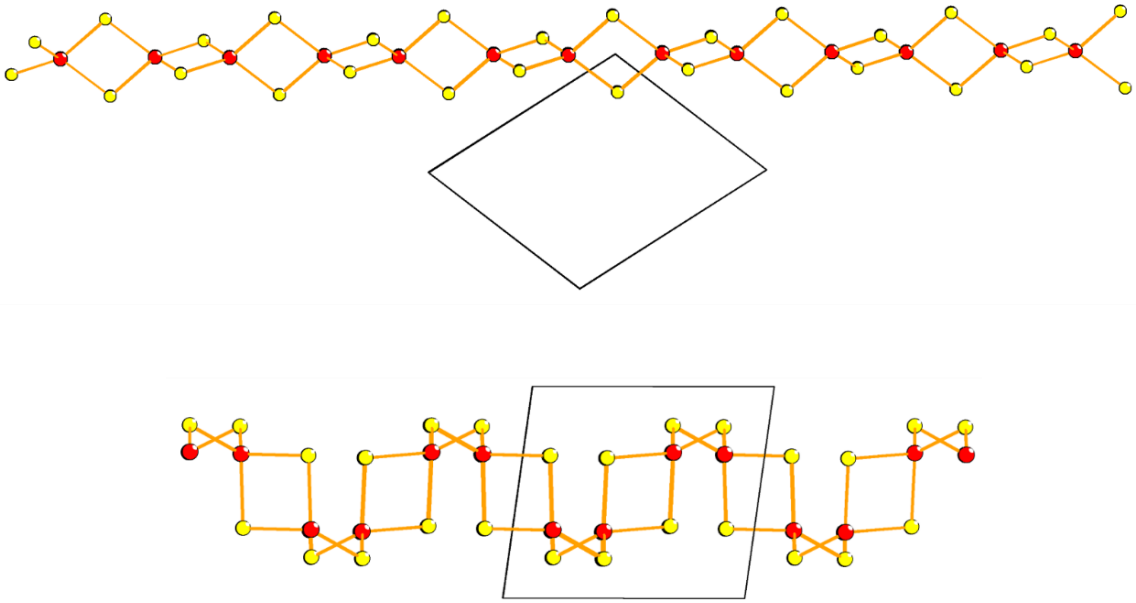

Figure S10. Comparison of both anionic networks just displaying the B (red) and S atoms (yellow) for better clarity viewed along the *vierer* rings; $Cd[B_2(SO_4)_2]$ (top) and $H_2[B_2(SO_4)_2]$ (bottom) show the same topology but very different conformations, thus preventing a simple and reasonable group-subgroup relationship according to a Bärnighausen scheme.

Table S14. Electrostatic calculations $H_2[B_2(SO_4)_4]$ and $Cd[B_2(SO_4)_4]$.[1-4]

$H_2[B_2(SO_4)_4]$	$H_2O + B_2O_3 + 4\ SO_3$
MAPLE = 147036 kJ mol^{-1}	MAPLE = 146662 kJ mol^{-1}
(Δ = 0.25%)	
$Cd[B_2(SO_4)_4]$	$CdSO_4 + B_2O_3 + 3\ SO_3$
MAPLE = 146705 kJ mol^{-1}	MAPLE = 146270 kJ mol^{-1}
(Δ**Fehler! Textmarke nicht definiert.** = 0.30%)	

Table S15. ECon derived by MAPLE-calculations for cadmium atoms in $Cd[B_2(SO_4)_4]$ using our data at 250 K

Atom	***x***	***y***	***z***	**Distance / pm**	**Econ(1)**	**Econ(2)**
Central atom						
Cd1	0	0	0			
Ligand						
O22	0.2297	-0.0485	-0.0745	222.932	1.059	1.059
O22	-0.2297	0.0485	0.0745	222.932	1.059	1.059
O11	-0.1507	0.09	-0.2337	223.352	1.047	1.048
O11	0.1507	-0.09	0.2337	223.352	1.047	1.048
O12	-0.1211	-0.2612	-0.07	229.949	0.873	0.873
O12	0.1211	0.2612	0.07	229.949	0.873	0.873
Next Ligand						
O24	0.1515	-0.3096	-0.2069	360.545	0	0

Table S16. ECon derived by MAPLE-calculations for cadmium atoms in $Mn[B_2(SO_4)_4]$ using the data from [5].

Atom	*x*	*y*	*z*	Distance / pm	Econ(1)	Econ(2)
Central atom						
Cd1	½	0	½			
Ligand						
O4	0.2847	-0.0442	0.5791	213.878	1.069	1.07
O4	0.7153	0.0442	0.4209	213.878	1.069	1.07
O7	0.651	0.0985	0.7226	213.996	1.066	1.067
O7	0.349	-0.0985	0.2774	213.996	1.066	1.067
O6	0.6168	-0.2549	0.5732	222.767	0.826	0.827
O6	0.3832	0.2549	0.4268	222.767	0.826	0.827
Next Ligand						
O1	0.654	0.3129	0.2956	360.2	0	0

Table 17. Comparison of CShM values of the coordination polyhedra surrounding B, S and M atoms in all currently know phyllosilicate analogous borosulfates with the general composition $M[B_2(SO_4)_4]$ with *M* = 2 H, Mn, Ni, Mg, Zn, Co, Cd and Ca.

M^{x+}	$2\ H^+$	Mn^{2+}	Ni^{2+}	$^{\alpha}Mg^{2+}$	$^{\beta}Mg^{2+}$	Zn^{2+}	$^{\alpha}Co^{2+}$	$^{\beta}Co^{2+}$	Cd^{2+}	Ca^{2+}
S1	0.161	0.354	0.176	0.107	0.108	0.270	0.168	0.268	0.325	0.130
S2	0.193	0.116	0.114	0.278	0.165	0.103	0.111	0.103	0.112	0.172
S3	0.174	-	-	-	-	-	-	-	-	0.133
S4	0.234	-	-	-	-	-	-	-	-	0.155
B1	0.099	0.168	0.065	0.107	0.060	0.416	0.063	0.419	0.162	0.173
B2	0.091	-	-	-	-	-	-	-	-	0.154
M^{2+}	-	0.091	0.176	0.094	0.100	0.205	0.158	0.226	0.141	1.839**

** All coordination spheres of the metal cations except Ca^{2+} may be described as idealized octahedra and their CShM deviation is given. For Ca^{2+} the deviation of an ideal trigonal dodecahedron is given.

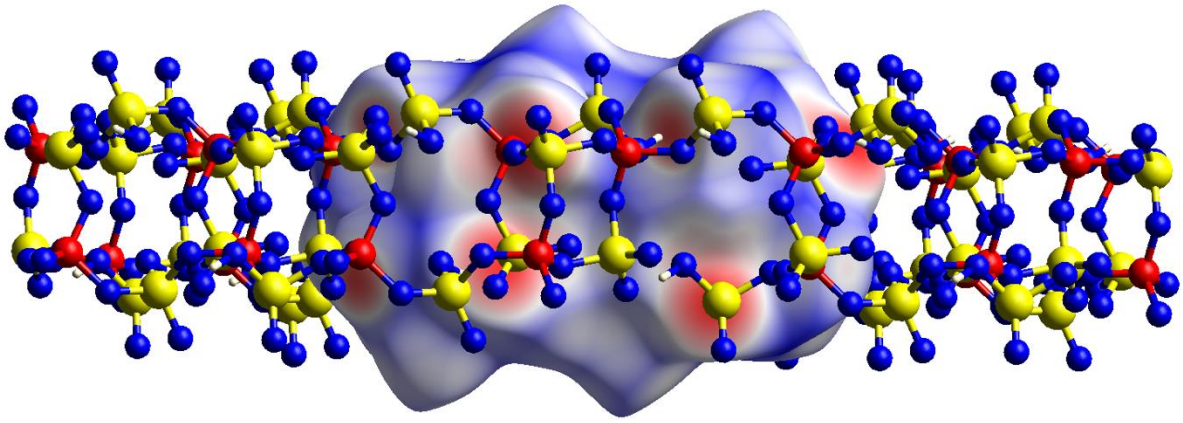

Figure S11. Excerpt of a single layer of $H_2[B_2(SO_4)_2]$ viewed along the layer with the Hirshfeld-surface around one *zwölfer*-ring in the d_{norm}-mapping.

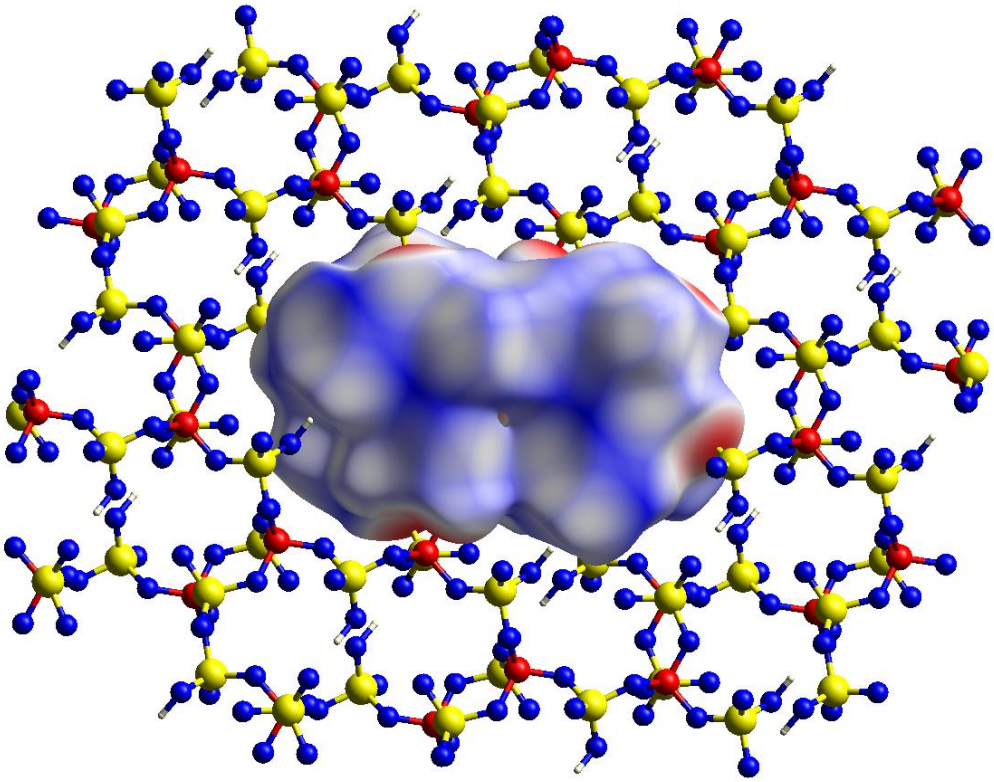

Figure S12. Excerpt of a single layer of $H_2[B_2(SO_4)_2]$ viewed perpendicular to the layer with the Hirshfeld-surface around one *zwölfer*-ring in the d_{norm}-mapping.

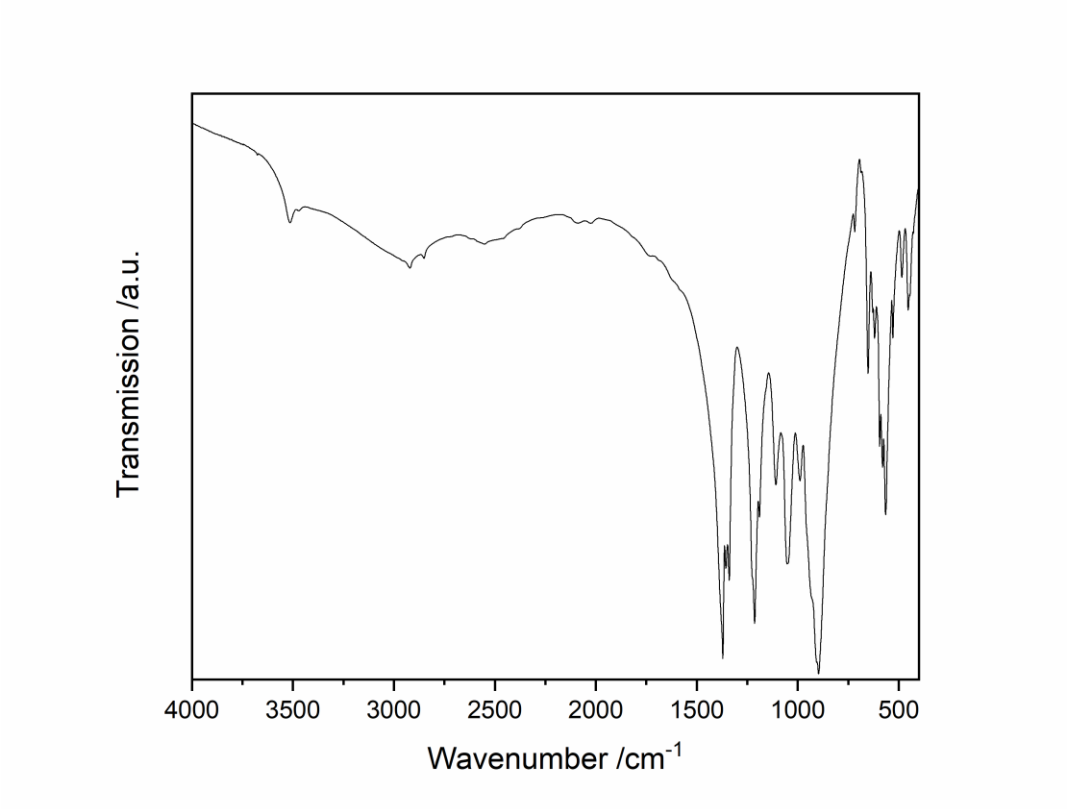

Figure S13. IR-spectrum of $Cd[B_2(SO_4)_2]$.

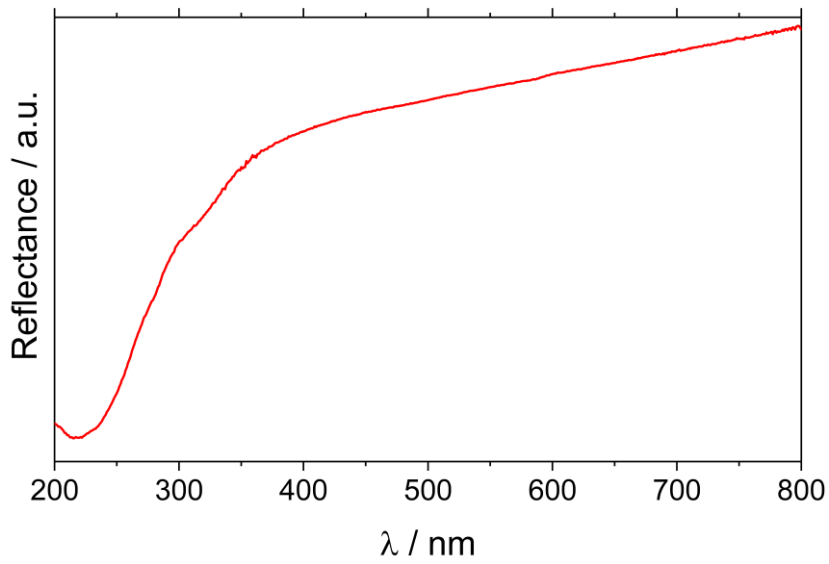

Figure S14. UV-Vis spectrum of $Cd[B_2(SO_4)_2]$.

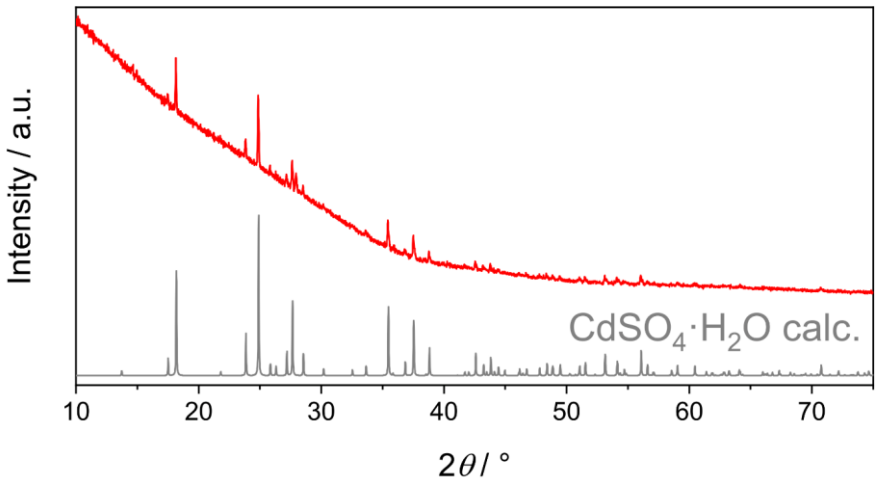

Figure S15. PXRD pattern of $Cd[B_2(SO_4)_2]$ decomposed due to the presence of moisture compared to a calculated pattern for $CdSO_4 \cdot H_2O$.[6]

References

[1] A. Goto, T. Hondoh, S. Mae, *J. Chem. Phys.* **1990**, *93*, 1412–1417.

[2] G. E. Gurr, P. W. Montgomery, C. D. Knutson, B. T. Gorres, *Acta Crystallogr. B* **1970**, *26*, 906-915.

[3] R. Pascard, C. Pascard-Billy, *Acta Crystallogr.* **1965**, *18*, 830-834.

[4] K. Aurivillius, C. Stålhandske, *Z. Kristallogr.* **1980**, *153*, 121-129.

[5] L. C. Pasqualini, H. Huppertz, J. Bruns, *Inorganics* **2019**, *7*, 145-154.

[6] C. Theppitak, K. Chainok, *Acta Crystallogr. E* **2015**, *71*, i8-i9.