Supplementary Materials: $M[B_2(SO_4)_4]$ (M = Mn, Zn)—Syntheses and Crystal Structures of Two New Phyllosilicate Analogue Borosulfates

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Table S1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Mn[B_2(SO_4)_4]$. U_{eq} is defined as 1/3rd of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U_{eq}
Mn1	5000	0	5000	6.08(3)
B1	6399(1)	4753(1)	3606.1(9)	6.4(1)
S1	7903.4(2)	1706.6(2)	3503.9(2)	6.31(3)
S2	3102.7(2)	4120.2(2)	3554.5(2)	4.65(3)
O111	6540.4(8)	3128.5(8)	2956.2(7)	9.86(9)
O121	4465.3(8)	5113.0(7)	3104.4(7)	7.52(9)
O122	2719.2(8)	5291.9(7)	4694.5(7)	7.72(9)
O11	7153(1)	441.6(9)	4209.0(9)	14.5(1)
O12	9630.6(9)	2285(1)	4380.1(9)	17.2(1)
O21	3832.1(8)	2549.2(7)	4268.4(7)	8.28(9)
O22	1510.0(8)	4014.7(8)	2226.4(7)	10.4(1)
O112	7756.8(9)	1108.1(8)	1908.3(7)	10.7(1)

Table S2. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Mn[B_2(SO_4)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	6.89(6)	6.07(6)	5.01(6)	0.01(4)	1.79(5)	−0.07(4)
B1	8.1(3)	5.8(3)	6.4(3)	0.0(2)	4.3(2)	−0.2(2)
S1	6.26(7)	7.59(7)	6.04(7)	−1.04(5)	3.38(5)	0.38(5)
S2	5.65(6)	4.37(6)	3.80(6)	0.46(5)	1.53(5)	0.27(5)
O111	10.8(2)	8.1(2)	10.2(2)	−3.0(2)	3.2 (2)	3.1(2)
O121	7.7(2)	7.0(2)	9.6(2)	2.6(2)	5.1(2)	0.5(2)
O122	10.7(2)	7.6(2)	5.9(2)	0.2(2)	4.3(2)	2.9(2)
O11	17.2(3)	13.9(3)	18.0(3)	5.9(2)	13.1(2)	2.1(2)
O12	8.3(2)	21.1(3)	18.3(3)	−5.1(2)	0.0(2)	−2.4(2)
O21	11.0(2)	4.4(2)	9.6(2)	2.2(2)	3.8(2)	1.8(2)
O22	9.3(2)	12.4(2)	6.3(2)	1.5(2)	−1.2(2)	−1.7(2)
O112	14.4(2)	11.9(2)	7.2(2)	−1.0(2)	5.5(2)	6.1(2)

Table S3. Bond lengths for $Mn[B_2(SO_4)_4]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Mn1	O11[1]	2.1388(7)	S1	O11	1.4427(7)
Mn1	O22[2]	2.1400(6)	S1	O112	1.5229(6)
Mn1	O21[1]	2.2276(6)	S1	O111	1.5263(6)
B1	O112[3]	1.440(1)	S2	O22	1.4298(6)
B1	O111	1.443(1)	S2	O21	1.4333(6)
B1	O121	1.483(1)	S2	O122	1.5218(6)
B1	O122[4]	1.485(1)	S2	O121	1.5240(6)
S1	O12	1.4125(7)			

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

Table S4. Bond angles for $Mn[B_2(SO_4)_4]$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11[1]	Mn1	O11	180	O12	S1	O11	116.59(5)
O11[1]	Mn1	O22[2]	88.59(3)	O12	S1	O112	112.42(4)
O11	Mn1	O22[2]	91.41(3)	O11	S1	O112	109.18(4)
O22[2]	Mn1	O22[3]	180	O12	S1	O111	113.24(4)
O11[1]	Mn1	O21[1]	92.95(2)	O11	S1	O111	107.26(4)
O11	Mn1	O21[1]	87.05(2)	O112	S1	O111	96.18(3)
O22[2]	Mn1	O21[1]	90.16(2)	O22	S2	O21	116.23(4)
O22[3]	Mn1	O21[1]	89.84(2)	O22	S2	O122	107.23(4)
O21[1]	Mn1	O21	180	O21	S2	O122	110.92(3)
O112[4]	B1	O111	114.05(7)	O22	S2	O121	107.61(4)
O112[4]	B1	O121	108.55(6)	O21	S2	O121	111.08(3)
O111	B1	O121	105.67(6)	O122	S2	O121	102.84(3)
O112[4]	B1	O122[4]	105.64(6)	B1	O111	S1	132.23(6)
O111	B1	O122[4]	110.25(6)	B1	O121	S2	126.20(5)
O121	B1	O122[4]	112.82(6)	B1[4]	O122	S2	126.13(5)
S1	O11	Mn1	142.37(5)	B1[6]	O112	S1	132.43(6)
S2	O21	Mn1	170.41(4)				
S2	O22	Mn1[5]	147.04(4)				

[1]1-*x*,-*y*,1-*z*; [2]1/2+*x*,1/2-*y*,1/2+*z*; [3]1/2-*x*,-1/2+*y*,1/2-*z*; [4]1-*x*,1-*y*,1-*z*; [5]1/2-*x*,1/2+*y*,1/2-*z*; [6]3/2-*x*,-1/2+*y*,1/2-*z*

Table S5. Fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for $Zn[B_2(SO_4)_4]$. U_{eq} is defined as 1/3rd of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U_{eq}
Zn1	5000	0	5000	4.97(3)
B1	6521(1)	4479(1)	3710.7(9)	4.8(1)
S1	7783.9(2)	1490.2(2)	3325.1(2)	4.50(3)
S2	6649.1(2)	3761.6(2)	6662.0(2)	3.29(3)
O11	7007.8(1)	332.7(8)	4122.7(9)	11.8(1)
O12	9631.9(9)	1937.1(9)	4144.8(8)	11.9(1)
O21	5567.6(8)	2293.6(7)	6177.8(7)	7.74(9)
O22	8148.8(8)	3661.3(7)	8142.8(7)	7.08(9)
O111	6508.1(8)	2976.4(7)	2817.7(7)	6.90(9)
O112	7478.5(8)	818.7(7)	1664.6(7)	6.84(9)
O211	7466.4(8)	4271.0(8)	5440.3(7)	6.60(9)
O212	5467.9(8)	5213.5(7)	6732.5(7)	6.03(8)

Table S6. Anisotropic displacement parameters (Å^2×10^3) for $Zn[B_2(SO_4)_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn1	5.95(5)	4.37(5)	4.86(5)	0.13(3)	2.26(4)	−0.32(3)
B1	6.1(3)	4.0(3)	5.6(3)	0.6(2)	3.5(2)	0.5(2)
S1	5.25(7)	4.26(6)	4.99(6)	−0.25(5)	3.04(5)	0.86(5)
S2	4.11(6)	2.97(6)	2.82(6)	−0.26(4)	1.30(5)	0.25(4)
O11	15.7(3)	9.2(2)	16.3(3)	5.6(2)	13.0(2)	3.4(2)
O12	6.2(2)	15.1(3)	12.2(2)	−3.8(2)	0.8(2)	−0.3(2)
O21	9.7(2)	4.7(2)	8.9(2)	−3.0(2)	3.5(2)	−2.9(2)
O22	7.0(2)	8.2(2)	3.9(2)	−0.5(2)	−0.6(2)	1.1(2)
O111	8.8(2)	4.3(2)	7.5(2)	−1.2(2)	2.8(2)	2.8(2)
O112	8.6(2)	6.6(2)	5.9(2)	−1.7(2)	3.4(2)	2.7(2)
O211	6.1(2)	10.1(2)	4.8(2)	1.2(2)	3.4(2)	0.13(2)
O212	5.3(2)	4.2(2)	9.1(2)	−0.8(2)	3.3(2)	1.3(2)

Table S7. Bond lengths for $Zn[B_2(SO_4)_4]$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O11	2.0199(6)	S1	O12	1.4135(7)
Zn1	O22[2]	2.0811(6)	S1	O11	1.4442(7)
Zn1	O21	2.1063(6)	S1	O111	1.5247(6)
Zn1	O21[1]	2.1063(6)	S1	O112	1.5315(6)
B1	O112[3]	1.449(1)	S2	O22	1.4277(6)
B1	O111	1.458(1)	S2	O21	1.4329(6)
B1	O211	1.477(1)	S2	O212	1.5116(6)
B1	O212[4]	1.482(1)	S2	O211	1.5208(6)

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

Table S8. Bond angles for $Zn[B_2(SO_4)_4]$.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O11	Zn1	O11[1]	180	O211	B1	O212[5]	112.32(6)
O11	Zn1	O22[2]	91.60(3)	O12	S1	O11	116.16(4)
O11[1]	Zn1	O22[2]	88.40(3)	O12	S1	O111	113.00(4)
O22[2]	Zn1	O22[3]	180	O11	S1	O111	108.28(4)
O11	Zn1	O21	91.67(3)	O12	S1	O112	111.78(4)
O22[2]	Zn1	O21	84.62(2)	O11	S1	O112	108.34(4)
O22[3]	Zn1	O21	95.38(2)	O111	S1	O112	97.64(3)
O11	Zn1	O21[1]	88.33(3)	O22	S2	O21	115.70(4)
O21	Zn1	O21[1]	180	O22	S2	O212	108.23(3)
O112[4]	B1	O111	113.00(6)	O21	S2	O212	110.78(4)
O112[4]	B1	O211	103.12(6)	O22	S2	O211	106.04(4)
O111	B1	O211	113.02(6)	O21	S2	O211	111.17(3)
O112[4]	B1	O212[5]	114.58(6)	O212	S2	O211	104.18(3)
O111	B1	O212[5]	101.24(6)	S1	O11	Zn1	144.22(4)
B1	O111	S1	128.31(5)	S2	O21	Zn1	151.50(4)
B1[6]	O112	S1	126.14(5)	S2	O22	Zn1[7]	145.35(4)
B1	O211	S2	128.18(5)				
B1[5]	O212	S2	135.95(5)				

[1]1-*x*,-*y*,1-*z*; [2]-1/2+*x*,1/2-*y*,-1/2+*z*; [3]3/2-*x*,-1/2+*y*,3/2-*z*; [4]3/2-*x*,1/2+*y*,1/2-*z*; [5]1-*x*,1-*y*,1-*z*; [6]3/2-*x*,-1/2+*y*,1/2-*z*; [7]3/2-*x*,1/2+*y*,3/2-*z*

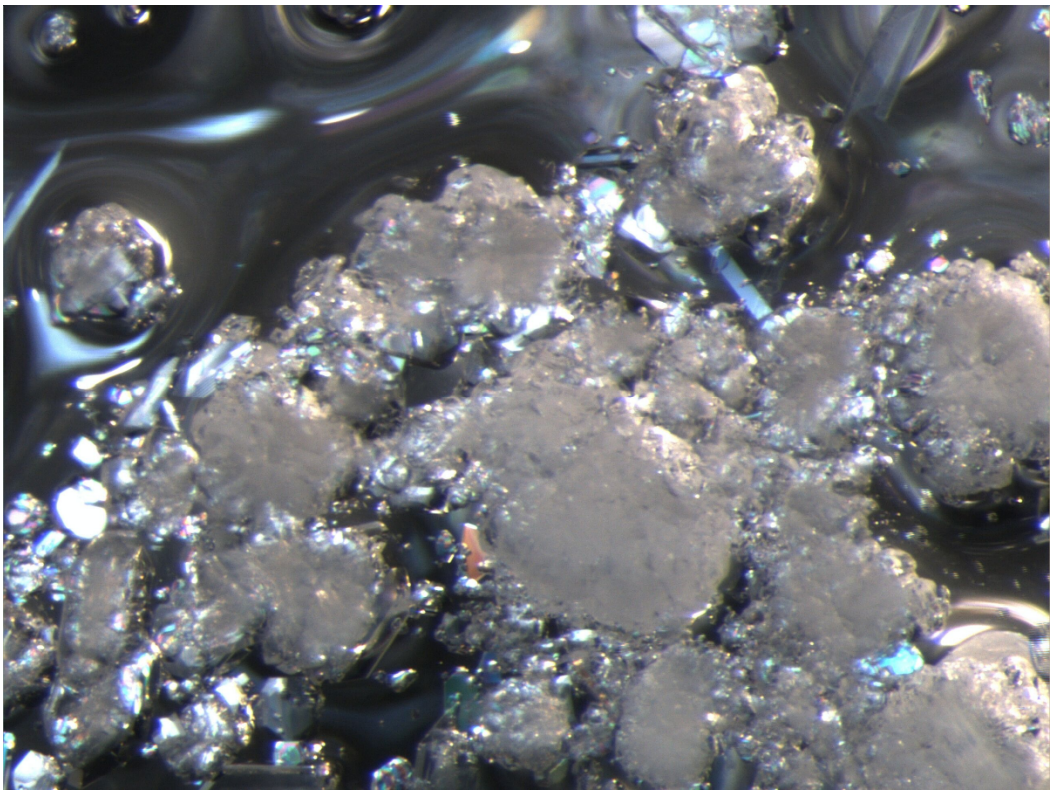

Figure S1. Crystals of $Zn[B_2(SO_4)_4]$ under a polarization microscope.

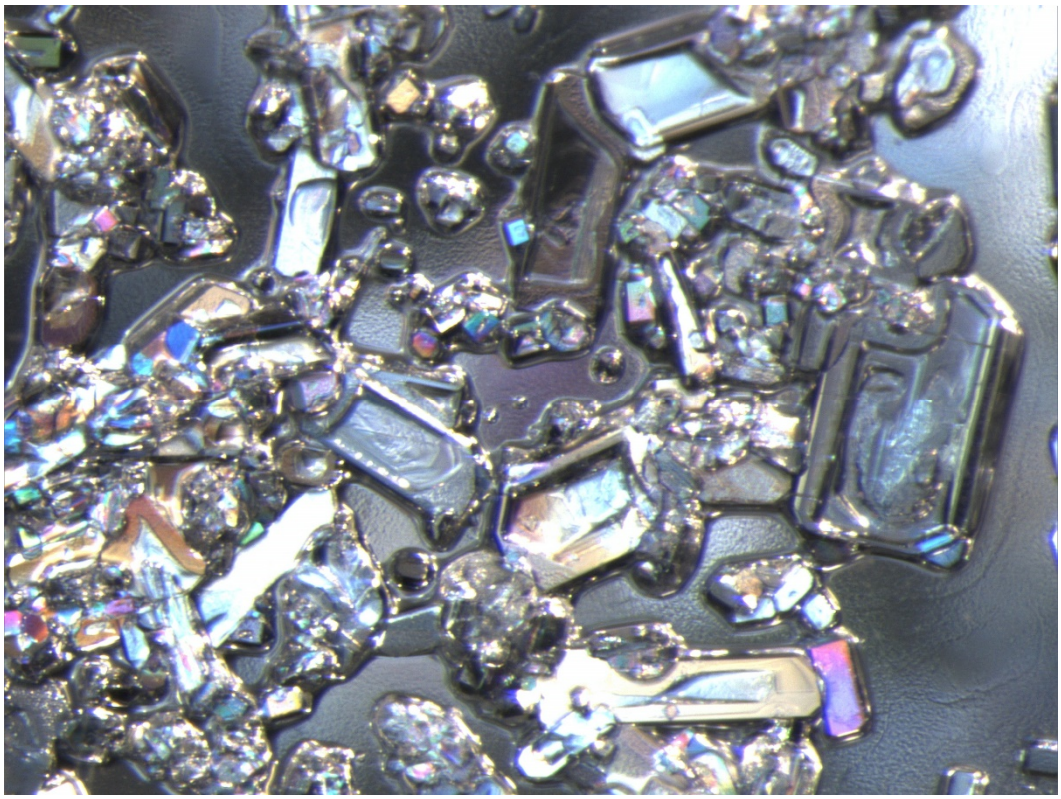

Figure S2. Crystals of $Mn[B_2(SO_4)_4]$ under a polarization microscope.