Electronic Supplementary Information

$K_2[B_4O_5(OH)_4]\cdot H_2O$ and $K_2[B_4O_5(OH)_4]$: Two New Hydrated Potassium Borates with Isolated $[B_4O_5(OH)_4]^{2-}$ Units and Different Structural Frameworks

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Table S1 Hydrated tetraborates with isolated $[B_4O_5(OH)_4]^{2-}$ FBBs.

Formula	Space group	Two-fold axis in FBB	Reference
$Na_2[B_4O_5(OH)_4]\cdot 3H_2O$	*R*32	Yes	[28a]
$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	$C2/_C$	Yes	[28b]
$K_2[B_4O_5(OH)_4]\cdot 2H_2O$	$P2_12_12_1$	No	[15]
$Rb_2[B_4O_5(OH)_4]\cdot 3.6H_2O$	*P*bcn	No	[28c]
$Rb_4[B_4O_5(OH)_4]_2\cdot 3H_2O$	*P*bcn	No	[28d]
$Cs_2[B_4O_5(OH)_4]\cdot 3H_2O$	$P2_1/c$	No	[27]
$Rb_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$	$P2_12_12_1$	No	[9]
$NaCs[B_4O_5(OH)_4]\cdot 4H_2O$	$P2_1/c$	No	[11]
$K_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$	$P2_12_12_1$	No	[28e]
$K_2Sr[B_4O_5(OH)_4]_2\cdot 10H_2O$	$Pna2_1$	No	[28f]
$K_{1.67}Na_{0.33}[B_4O_5(OH)_4]\cdot 3H_2O$	$P\bar{6}2c$	Yes	[28g]
$Cs_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$	$P2_12_12_1$	No	[10]
$(NH_4)_2[B_4O_5(OH)_4]\cdot 2H_2O$	$P2_1$	No	[28h]
$(NH4)_2Ca[B_4O_5(OH)_4]_2\cdot 8H_2O$	$P2_12_12_1$	No	[28f]
$Mg(H_2O)_5B_4O_5(OH)_4\cdot 2H_2O$	$P\bar{1}$	No	[28i]
$NH_4[Co(NH_3)_5(H_2O)][B_4O_5(OH)_4]_2\cdot 6H_2O$	*Pnma*	No	[28j]
$Na_6[B_4O_5(OH)_4]_3\cdot 8H_2O$	*R32*	Yes	[28k]
$K_2B_4O_5(OH)_4\cdot H_2O$ (**I**)	$P\bar{1}$	No	Tittle compound
$K_2B_4O_5(OH)_4$ (**II**)	*Pbcn*	Yse	Tittle compound

Table S2 Atomic coordinates (× 10^4), equivalent isotropic displacement parameters ($Å^2$ × 10^3), and bond valence sums (BVS) for **I** and **II**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Compounds	Atoms	x	y	z	U_{eq}	BVS
I	K(1)	2068(1)	5901(1)	1999(1)	24(1)	1.1
	K(2)	927(1)	1178(1)	1995(1)	27(1)	1.1
	B(1)	1485(3)	2378(4)	5679(3)	20(1)	3.1
	B(2)	2580(3)	1168(3)	8513(3)	16(1)	3.0
	B(3)	2905(3)	4305(3)	8280(3)	17(1)	3.0
	B(4)	4565(3)	2672(3)	6529(3)	16(1)	3.0
	O(1)	4101(2)	4334(2)	7052(2)	19(1)	1.9
	O(2)	2571(2)	5775(2)	8844(2)	24(1)	1.2
	O(3)	2509(2)	-517(2)	9855(2)	21(1)	1.2
	O(4)	2026(2)	2895(2)	8963(2)	18(1)	2.0
	O(5)	6456(2)	2478(2)	5873(2)	21(1)	1.0
	O(6)	4520(2)	996(2)	7895(2)	15(1)	1.6
	O(7)	3059(2)	3030(2)	5243(2)	20(1)	1.9
	O(8)	189(2)	2654(3)	4438(2)	33(1)	1.2
	O(9)	1120(2)	1477(2)	7221(2)	21(1)	2.1
	O(10)	4579(3)	2334(2)	2489(2)	31(1)	0.2
II	K(1)	6396(1)	6684(1)	674(1)	26(1)	1.1
	B(1)	9540(3)	6396(5)	1589(2)	15(1)	3.0
	B(2)	6666(3)	9746(5)	3088(3)	18(1)	3.1
	O(1)	5859(2)	2623(3)	658(2)	18(1)	1.3
	O(2)	6604(2)	10172(3)	1983(2)	18(1)	2.1
	O(3)	7231(2)	6031(3)	-1438(2)	25(1)	1.2
	O(4)	4391(2)	10001(3)	1232(2)	19(1)	1.9
	O(5)	10000	7678(4)	2500	13(1)	1.5

Table S3 Bond lengths (Å) and angles (°) for **I** and **II**.

I

K(1)-O(10)	2.7897(17)	K(2)-O(9)#5	2.7309(16)	B(1)-O(7)	1.348(3)
K(1)-O(1)#1	2.8386(14)	K(2)-O(4)#3	2.7553(15)	B(1)-O(9)	1.358(3)
K(1)-O(3)#2	2.8601(16)	K(2)-O(3)#3	2.7746(15)	B(1)-O(8)	1.389(3)
K(1)-O(2)#3	2.8773(15)	K(2)-O(8)	2.8097(17)	B(2)-O(3)	1.439(3)
K(1)-O(4)#4	2.8907(14)	K(2)-O(2)#4	2.8690(16)	B(2)-O(6)	1.474(3)
K(1)-O(9)#4	2.9069(14)	K(2)-O(3)#5	3.2597(15)	B(2)-O(9)	1.493(2)
K(1)-O(7)	2.9242(15)	K(2)-O(5)#6	2.9664(16)	B(2)-O(4)	1.505(3)
K(1)-O(5)#1	2.9962(16)	K(2)-O(10)	3.0779(19)		
K(1)-O(8)	3.263(2)	K(2)-O(6)#6	3.2502(13)		
B(4)-O(6)	1.441(3)	B(3)-O(4)	1.358(3)		
B(4)-O(1)	1.498(3)	B(3)-O(1)	1.373(3)		
B(4)-O(5)	1.456(3)	B(3)-O(2)	1.385(3)		
B(4)-O(7)	1.501(2)				
O(10)-K(1)-O(1)#1	68.36(5)	O(1)#1-K(1)-O(3)#2	78.85(4)	O(1)#1-K(1)-O(2)#3	100.92(4)
O(10)-K(1)-O(3)#2	126.38(5)	O(10)-K(1)-O(4)#4	126.24(5)	O(3)#2-K(1)-O(2)#3	71.16(4)
O(10)-K(1)-O(2)#3	74.81(5)	O(1)#1-K(1)-O(4)#4	165.40(4)	O(10)-K(1)-O(9)#4	154.24(5)
O(2)#3-K(1)-O(9)#4	124.30(4)	O(3)#2-K(1)-O(4)#4	90.56(4)	O(1)#1-K(1)-O(9)#4	118.08(4)
O(4)#4-K(1)-O(9)#4	49.13(4)	O(2)#3-K(1)-O(4)#4	84.87(4)	O(3)#2-K(1)-O(9)#4	78.83(4)
O(10)-K(1)-O(7)	59.74(4)	O(1)#1-K(1)-O(7)	72.12(4)	O(3)#2-K(1)-O(7)	144.57(4)
O(2)#3-K(1)-O(7)	133.56(4)	O(1)#1-K(1)-O(5)#1	48.80(4)	O(9)#4-K(1)-O(5)#1	69.85(4)
O(4)#4-K(1)-O(7)	113.55(4)	O(3)#2-K(1)-O(5)#1	75.54(4)	O(7)-K(1)-O(5)#1	70.18(4)
O(9)#4-K(1)-O(7)	97.17(4)	O(2)#3-K(1)-O(5)#1	139.02(5)	O(10)-K(1)-O(8)	71.37(5)
O(10)-K(1)-O(5)#1	108.30(5)	O(4)#4-K(1)-O(5)#1	118.98(4)	O(1)#1-K(1)-O(8)	115.08(4)
O(3)#2-K(1)-O(8)	161.80(5)	O(9)#5-K(2)-O(3)#3	83.38(4)	O(3)#3-K(2)-O(2)#4	121.79(4)
O(2)#3-K(1)-O(8)	114.87(5)	O(4)#3-K(2)-O(3)#3	52.09(4)	O(8)-K(2)-O(2)#4	69.67(5)
O(4)#4-K(1)-O(8)	73.48(4)	O(9)#5-K(2)-O(8)	103.00(5)	O(9)#5-K(2)-O(5)#6	72.66(4)
O(9)#4-K(1)-O(8)	84.01(4)	O(4)#3-K(2)-O(8)	127.86(5)	O(4)#3-K(2)-O(5)#6	117.97(4)
O(7)-K(1)-O(8)	43.70(4)	O(3)#3-K(2)-O(8)	167.16(5)	O(3)#3-K(2)-O(5)#6	77.29(4)
O(5)#1-K(1)-O(8)	104.22(4)	O(9)#5-K(2)-O(2)#4	91.57(5)	O(8)-K(2)-O(5)#6	93.82(5)
O(9)#5-K(2)-O(4)#3	124.61(4)	O(4)#3-K(2)-O(2)#4	87.55(4)	O(2)#4-K(2)-O(5)#6	154.38(5)
O(9)#5-K(2)-O(10)	149.76(5)	O(4)#3-K(2)-O(6)#6	75.17(4)	O(4)#3-K(2)-O(3)#5	85.15(4)
O(4)#3-K(2)-O(10)	74.22(4)	O(3)#3-K(2)-O(6)#6	55.45(4)	O(3)#3-K(2)-O(3)#5	70.36(5)
O(3)#3-K(2)-O(10)	94.78(5)	O(8)-K(2)-O(6)#6	111.72(4)	O(8)-K(2)-O(3)#5	122.05(4)
O(8)-K(2)-O(10)	74.04(5)	O(2)#4-K(2)-O(6)#6	158.98(5)	O(2)#4-K(2)-O(3)#5	65.65(4)
O(2)#4-K(2)-O(10)	114.36(5)	O(5)#6-K(2)-O(6)#6	45.01(4)	O(5)#6-K(2)-O(3)#5	111.64(4)
O(5)#6-K(2)-O(10)	77.48(4)	O(10)-K(2)-O(6)#6	49.80(4)	O(10)-K(2)-O(3)#5	159.28(4)
O(9)#5-K(2)-O(6)#6	107.98(4)	O(9)#5-K(2)-O(3)#5	45.70(4)	O(6)#6-K(2)-O(3)#5	123.28(4)
O(7)-B(1)-O(9)	124.36(18)	O(3)-B(2)-O(9)	108.28(16)	O(6)-B(4)-O(5)	111.44(16)
O(7)-B(1)-O(8)	116.2(2)	O(9)-B(2)-O(4)	107.00(16)	O(6)-B(4)-O(1)	108.36(16)
O(9)-B(1)-O(8)	119.4(2)	O(4)-B(3)-O(1)	122.67(19)	O(5)-B(4)-O(1)	109.65(17)
O(3)-B(2)-O(6)	111.57(17)	O(4)-B(3)-O(2)	118.42(19)	O(6)-B(4)-O(7)	109.92(16)
O(6)-B(2)-O(9)	109.70(16)	O(1)-B(3)-O(2)	118.9(2)		

O(3)-B(2)-O(4)	111.09(16)	O(5)-B(4)-O(7)	108.90(16)		
O(6)-B(2)-O(4)	109.08(17)	O(1)-B(4)-O(7)	108.52(15)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, -y+1, -z+1	#2 x, y+1, z-1	#3 x, y, z-1
#4 -x, -y+1, -z+1	#5 -x, -y, -z+1	#6 -x+1, -y, -z+1
#7 -x, -y+1, -z	#8 x, y, z+1	#9 x, y-1, z+1

II

K(1)-O(3)	2.718(3)	K(1)-O(4)#4	3.278(3)	B(1)-O(5)	1.466(3)
K(1)-O(1)	2.748(3)	K(1)-O(1)#3	2.870(3)	B(1)-O(4)#1	1.493(4)
K(1)-O(2)#1	2.768(3)	K(1)-O(4)	3.078(3)	B(2)-O(4)#8	1.365(4)
K(1)-O(2)	2.807(3)	B(1)-O(2)#1	1.499(4)	B(2)-O(2)	1.362(4)
K(1)-O(1)#2	2.843(3)	B(1)-O(1)#3	1.443(4)	B(2)-O(3)#7	1.363(4)
O(3)-K(1)-O(1)	84.24(7)	O(3)-K(1)-O(2)#1	104.13(8)	O(1)-K(1)-O(2)#1	78.24(7)
O(3)-K(1)-O(2)	129.30(7)	O(2)#1-K(1)-O(1)#2	167.77(6)	O(2)-K(1)-O(1)#3	75.62(6)
O(1)-K(1)-O(2)	145.73(7)	O(2)-K(1)-O(1)#2	104.19(7)	O(1)#2-K(1)-O(1)#3	138.70(5)
O(2)#1-K(1)-O(2)	85.56(7)	O(3)-K(1)-O(1)#3	73.85(6)	O(3)-K(1)-O(4)	121.77(6)
O(3)-K(1)-O(1)#2	75.60(8)	O(1)-K(1)-O(1)#3	114.01(6)	O(1)-K(1)-O(4)	124.69(8)
O(1)-K(1)-O(1)#2	89.60(6)	O(2)#1-K(1)-O(1)#3	50.37(7)	O(2)#1-K(1)-O(4)	128.68(7)
O(2)-K(1)-O(4)	48.63(6)	O(1)#2-K(1)-O(4)	57.96(7)	O(1)#3-K(1)-O(4)	119.72(7)
O(3)-K(1)-O(4)#4	61.83(7)	O(4)-K(1)-O(4)#4	60.73(7)	O(5)-B(1)-O(2)#1	109.0(2)
O(1)-K(1)-O(4)#4	127.09(7)	O(1)#3-B(1)-O(5)	110.2(2)	O(4)#1-B(1)-O(2)#1	109.0(2)
O(2)#1-K(1)-O(4)#4	145.33(6)	O(1)#3-B(1)-O(4)#1	109.4(2)	O(2)-B(2)-O(3)#7	121.8(3)
O(2)-K(1)-O(4)#4	81.94(8)	O(5)-B(1)-O(4)#1	109.9(2)	O(2)-B(2)-O(4)#8	121.6(2)
O(1)#2-K(1)-O(4)#4	45.41(5)	O(1)#3-B(1)-O(2)#1	109.4(2)	O(3)#7-B(2)-O(4)#8	116.6(3)
O(1)#3-K(1)-O(4)#4	95.10(6)				

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2, y-1/2, z	#2 -x+1, -y+1, -z	#3 -x+3/2, y+1/2, z	
#4 -x+1, -y+2, -z	#5 x-1/2, -y+3/2, -z	#6 x+1/2, -y+3/2, -z	
#7 -x+3/2, -y+3/2, z+1/2	#8 -x+1, y, -z+1/2	#9 -x+3/2, -y+3/2, z-1/2	#10 -x+2, y, -z+1/2

Table S4 Hydrogen bond lengths (Å) and angles (°) for **I** and **II**. D, hydrogen bond

donor; A, hydrogen bond acceptor.

Compounds	D−H···A	$d_{(D-H)}$	$d_{(H\cdots A)}$	$d_{(D\cdots A)}$	$<_{(D-H\cdots A)}$
I	O(10)-H(1)...O(6) #6	0.861(16)	1.812(16)	2.669(2)	173(2)
	O(10)-H(2)...O(7)	0.848(15)	2.116(18)	2.848(2)	144(2)
	O(2)-H(3)...O(10) #1	0.817(16)	2.016(17)	2.821(2)	168(2)
	O(5)-H(5)...O(1) #1	0.823(17)	2.037(18)	2.837(2)	164(2)
	O(3)-H(6)...O(6) #10	0.811(17)	2.043(18)	2.8345(18)	165(3)
	Symmetry transformations used to generate equivalent atoms:				
	#1 -x+1, -y+1, -z+1	#2 x, y+1, z-1	#3 x, y, z-1		
	#4 -x, -y+1, -z+1	#5 -x, -y, -z+1	#6 -x+1, -y, -z+1		
	#7 -x, -y+1, -z	#8 x, y, z+1	#9 x, y-1, z+1	#10 -x+1, -y, -z+2	
II	O(3)-H(2)...O(5) #9	0.850(19)	1.94(2)	2.748(3)	159(4)
	O(1)-H(1)...O(4) #2	0.841(19)	2.04(2)	2.876(3)	170(4)
	Symmetry transformations used to generate equivalent atoms:				
	#1 -x+3/2, y-1/2, z	#2 -x+1, -y+1, -z	#3 -x+3/2, y+1/2, z	#4 -x+1, -y+2, -z	
	#5 x-1/2, -y+3/2, -z	#6 x+1/2, -y+3/2, -z	#7 -x+3/2, -y+3/2, z+1/2	#8 -x+1, y, -z+1/2	
	#9 -x+3/2, -y+3/2, z-1/2	#10 -x+2, y, -z+1/2			

Table S5 Bonding electron density difference ($\Delta\rho$) of different units calculated by the REDA method in **I** and **II**.

Compounds	Units	$\Delta\rho$
I	$[BO_3]^{3-}$	0.01047
	$[BO_4]^{5-}$	0.0008379
	$[OH]^-$	0.003361
II	$[BO_3]^{3-}$	0.01294
	$[BO_4]^{5-}$	0.0002131
	$[OH]^-$	0.007358

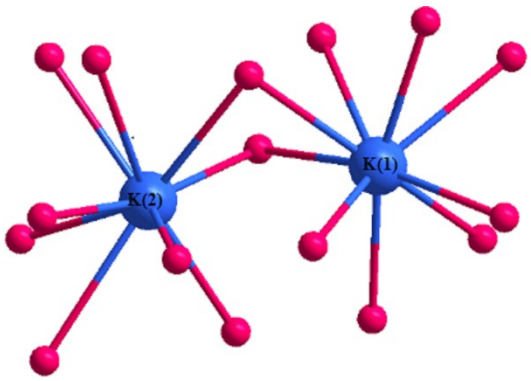

Figure S1. Coordination environments of the K(1) and K(2) cations for **I**.

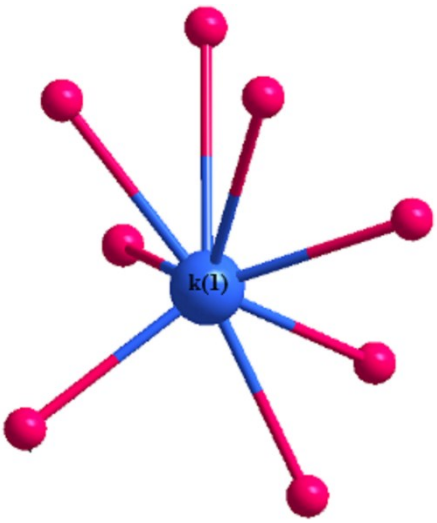

Figure S2. Coordination environment of the K(1) cation for **II**.