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$NaKB_6O_9F_2$: a new complex alkali metal fluorooxoborate with $^{2}_{\infty}[B_6O_9F_2]^{2-}$ puckered layers

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Table S1. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sums (BVS) for $NaKB_6O_9F_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atoms	Wyck.	x/a	y/b	z/c	U(eq)	BVS
K(1)	e	-2959(1)	7019(1)	2073(1)	29(1)	0.93
Na(1)	e	1841(1)	6410(1)	8872(1)	21(1)	1.12
B(1)	e	408(3)	7988(2)	6029(3)	14(1)	3.09
B(2)	e	6590(3)	10906(2)	9157(3)	14(1)	3.07
B(3)	e	2594(4)	9599(2)	6516(3)	17(1)	3.07
B(4)	e	8178(4)	10643(2)	11778(3)	15(1)	3.03
B(5)	e	8651(4)	9118(2)	10371(3)	16(1)	3.07
B(6)	e	4790(3)	11136(2)	6530(3)	15(1)	3.06
O(1)	e	1270(2)	8677(1)	5582(2)	17(1)	2.16
O(2)	e	6997(2)	11346(1)	10422(2)	17(1)	2.03
O(3)	e	499(2)	8352(1)	7186(2)	18(1)	2.01
O(4)	e	2819(2)	9946(2)	7735(2)	19(1)	1.93
O(5)	e	3490(2)	10080(2)	6026(2)	24(1)	2.04
O(6)	e	-557(2)	6926(1)	5184(2)	20(1)	2.15
O(7)	e	5506(2)	11620(1)	7942(2)	15(1)	2.10
O(8)	e	7359(2)	9744(2)	9120(2)	21(1)	2.13
O(9)	e	9162(2)	9545(1)	11669(2)	19(1)	1.96
F(1)	e	3985(2)	12198(1)	5562(2)	30(1)	0.91
F(2)	e	6181(2)	10668(1)	6454(2)	25(1)	1.03

Table S2. Bond lengths [Å] and angles [°] for $NaKB_6O_9F_2$.

K(1)-F(1)#1	2.611(2)	O(6)-K(1)-O(4)#2	88.48(4)
K(1)-O(7)#2	2.722(2)	F(1)#1-K(1)-O(3)#4	73.11(6)
K(1)-F(2)#3	2.788(2)	O(7)#2-K(1)-O(3)#4	156.53(5)
K(1)-O(8)#3	2.8344(18)	F(2)#3-K(1)-O(3)#4	91.37(5)

K(1)-O(6)	2.902(2)	O(8)#3-K(1)-O(3)#4	107.16(5)
K(1)-O(4)#2	3.060(2)	O(6)-K(1)-O(3)#4	86.33(6)
K(1)-O(3)#4	3.153(2)	O(4)#2-K(1)-O(3)#4	96.74(4)
Na(1)-F(2)#6	2.2112(19)	F(2)#6-Na(1)-O(1)#7	139.58(7)
Na(1)-O(1)#7	2.3391(18)	F(2)#6-Na(1)-O(2)#8	97.21(7)
Na(1)-O(2)#8	2.425(2)	O(1)#7-Na(1)-O(2)#8	91.60(6)
Na(1)-O(9)#3	2.463(2)	F(2)#6-Na(1)-O(9)#3	96.79(8)
Na(1)-O(5)#7	2.506(2)	O(1)#7-Na(1)-O(9)#3	105.49(8)
Na(1)-O(3)	2.509(2)	O(2)#8-Na(1)-O(9)#3	133.22(6)
B(1)-O(3)	1.344(3)	F(2)#6-Na(1)-O(5)#7	83.81(7)
B(1)-O(6)	1.363(3)	O(1)#7-Na(1)-O(5)#7	56.21(6)
B(1)-O(1)	1.372(3)	O(2)#8-Na(1)-O(5)#7	109.61(8)
B(2)-O(7)	1.352(3)	O(9)#3-Na(1)-O(5)#7	116.15(8)
B(2)-O(2)	1.353(3)	F(2)#6-Na(1)-O(3)	101.96(6)
B(2)-O(8)	1.383(3)	O(1)#7-Na(1)-O(3)	115.63(6)
B(3)-O(5)	1.345(3)	O(2)#8-Na(1)-O(3)	56.80(7)
B(3)-O(4)	1.346(3)	O(9)#3-Na(1)-O(3)	76.67(7)
B(3)-O(1)	1.399(3)	O(5)#7-Na(1)-O(3)	165.54(7)
B(4)-O(2)	1.457(3)	O(3)-B(1)-O(6)	123.7(2)
B(4)-O(4)#8	1.466(3)	O(3)-B(1)-O(1)	122.3(2)
B(4)-O(9)	1.486(3)	O(6)-B(1)-O(1)	113.96(19)
B(4)-O(3)#8	1.489(3)	O(7)-B(2)-O(2)	120.72(19)
B(5)-O(9)	1.351(3)	O(7)-B(2)-O(8)	119.56(19)
B(5)-O(8)	1.367(3)	O(2)-B(2)-O(8)	119.6(2)
B(5)-O(6)#11	1.371(3)	O(5)-B(3)-O(4)	127.0(2)
B(6)-F(1)	1.401(3)	O(5)-B(3)-O(1)	112.90(19)
B(6)-F(2)	1.425(3)	O(4)-B(3)-O(1)	120.1(2)
B(6)-O(7)	1.437(3)	O(2)-B(4)-O(4)#8	111.79(19)
B(6)-O(5)	1.444(3)	O(2)-B(4)-O(9)	111.97(17)
F(1)#1-K(1)-O(7)#2	104.35(6)	O(4)#8-B(4)-O(9)	107.03(18)
F(1)#1-K(1)-F(2)#3	85.21(5)	O(2)-B(4)-O(3)#8	105.70(17)
O(7)#2-K(1)-F(2)#3	111.84(6)	O(4)#8-B(4)-O(3)#8	111.65(17)
F(1)#1-K(1)-O(8)#3	143.83(5)	O(9)-B(4)-O(3)#8	108.73(19)
O(7)#2-K(1)-O(8)#3	88.71(6)	O(9)-B(5)-O(8)	122.8(2)
F(2)#3-K(1)-O(8)#3	58.69(5)	O(9)-B(5)-O(6)#11	123.7(2)
F(1)#1-K(1)-O(6)	158.89(6)	O(8)-B(5)-O(6)#11	113.46(19)
O(7)#2-K(1)-O(6)	92.56(6)	F(1)-B(6)-F(2)	105.83(18)
F(2)#3-K(1)-O(6)	100.33(4)	F(1)-B(6)-O(7)	108.57(18)
O(8)#3-K(1)-O(6)	47.03(5)	F(2)-B(6)-O(7)	111.20(19)
F(1)#1-K(1)-O(4)#2	89.23(4)	F(1)-B(6)-O(5)	108.6(2)
O(7)#2-K(1)-O(4)#2	59.80(5)	F(2)-B(6)-O(5)	107.46(18)
F(2)#3-K(1)-O(4)#2	168.41(5)	O(7)-B(6)-O(5)	114.79(18)
O(8)#3-K(1)-O(4)#2	125.79(5)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+1/2 #2 -x,-y+2,-z+1 #3 x-1,-y+3/2,z-1/2 #4 x,-y+3/2,z-1/2
#5 x-1,y,z-1 #6 -x+1,y-1/2,-z+3/2 #7 x,-y+3/2,z+1/2 #8 -x+1,-y+2,-z+2
#9 -x,-y+1,-z+1. #10 x+1,y,z+1 #11 x+1,-y+3/2,z+1/2 #12 -x,y+1/2,-z+1/2
#13 -x+1,y+1/2,-z+3/2

Table S3. The investigation of the reported inorganic fluorooxoborate

	Compounds	Space groups		FBB	Anionic framework	Rfes
1	$Na_3B_3O_3F_6$	*C*2/*c*	BO_2F_2	$B_3O_3F_6$	$[B_3O_3F_6]$ cluster	[1]
2	$K_3B_3O_3F_6$	$P2_1/n$	BO_2F_2	$B_3O_3F_6$	$[B_3O_3F_6]$ cluster	[2]
3	$K_{0.42}Rb_{2.58}B_3O_3F_6$	*Pbcn*	BO_2F_2	$B_3O_3F_6$	$[B_3O_3F_6]$ cluster	[3]
4	$Cs_{1.29}Rb_{1.71}B_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3]
5	$Na_{0.76}Rb_{2.24}B_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3]
6	$K_{2.64}Cs_{0.36}B_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3]
7	$K_{1.66}Rb_{1.34}B_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3]
8	$KCs_2B_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3
9	$Rb_3B_3O_3F_6$	*Pbcn*	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3
10	$K_2RbB_3O_3F_6$	$P2_1/c$	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[3]
11	$Cs_3B_3O_3F_6$	*Pbcn*	BO_2F_2	$B_3O_3F_6$	$B_3O_3F_6$ cluster	[4]
12	$K_{10}B_{13}O_{15}F_{19}$	*R*3*m*	BO_3, BO_2F_2 BO_3F	$B_{10}O_{12}F_{13}$ and $B_3O_3F_6$	$B_{10}O_{12}F_{13}$ and $B_{10}O_{12}F_{13}$ cluster	[5]
13	$Rb_{10}B_{13}O_{15}F_{19}$	*R*3*m*	BO_3, BO_2F_2 BO_3F	$B_{10}O_{12}F_{13}$ and $B_3O_3F_6$	$B_{10}O_{12}F_{13}$ and $B_{10}O_{12}F_{13}$ cluster	[5]
14	$Ba(B_2OF_3(OH)_2)_2$	*C*2/*m*	BOF_2 $BO(OH)_2$	$B_2OF_3(OH)_2$	$[B_2OF_3(OH)]$ cluster	[6]
15	$BaBO_3F$	*Pnma*	BO_2F_2	BO_2F_2	$[BOF_3]$ chain	[7]
16	$Li_2B_3O_4F_3$	$P2_12_12_1$	BO_3,BO_3F, BO_2F_2	$B_3O_5F_3$	$[B_3O_4F_3]$ chain	[8]
17	BiB_2O_4F	$P3_2$	BO_4, BO_3F	B_2O_6F	$[B_2O_4F]$ chain	[9]
18	$K_3B_6O_9F_3$	$P2_1/c$	BO_3, BO_4 BO_2F_2 BO_3F	$B_6O_{11}F_3$	$[B_6O_9F_3]$ layer	[10]
19	$Li_2Na_{0.9}K_{0.1}B_5O_8F_2$	*Pbca*	BO_3, BO_2F_2 BO_3F	$B_5O_{10}F_2$	$[B_5O_8F_2]$ layer	[11]
20	$BaB_2O_3F_2$	$P2_1$	BO_4, BO_3F	B_2O_6F	$[B_2O_3F]$ layer	[12]
21	$SnB_2O_3F_2$	$P3_1m$	BO_3F	$B_2O_5F_2$	$[B_2O_3F]$ layer	[13, 14]
22	$PbB_2O_3F_2$	$P3_1m$	BO_3F	$B_2O_5F_2$	$[B_6O_{12}F_6]$ layer	[14]
23	$KNiB_4O_6F_3$	$P2_1/c$	BO_3,BO_3F	$B_4O_6F_4$	$[B_3O_6F_3]$ layer	[15]
24	$Na_2B_6O_9F_2$	$P2_1/c$	BO_3,BO_3F	$B_6O_{11}F_2$	$[B_6O_9F_2]$ layer	[16]
25	$NaKB_6O_9F_2$	$P2_1/n$	BO_3,BO_4, BO_2F_2	$B_6O_{11}F_2$	$[B_6O_9F_2]$ layer	
26	$NaRbB_6O_9F_2$	$P2_1/n$	BO_3,BO_4,	$B_6O_{11}F_2$	$[B_6O_9F_2]$ layer	[17]

			BO_2F_2			
27	$Ba_3B_{10}O_{17}F_2$ 0.1KF	$P\bar{1}$	BO_3, BO_4 BO_3F	$B_{10}O_{22}F$	$B_{10}O_{16}F$ layer	[18]
28	NaB_4O_6F	$C2$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[19]
29	RbB_4O_6F	$Pna2_1$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[20]
30	CsB_4O_6F	$Pna2_1$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[21]
31	$NH_4B_4O_6F$	$Pna2_1$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[22]
32	$CaB_4O_6F_2$	$P\bar{1}$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F_2]$ layer	[23]
33	$SrB_4O_6F_2$	$P\bar{1}$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F_2]$ layer	[24]
34	$BaB_4O_6F_2$	$P2_1/n$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F_2]$ layer	[23]
35	$CsRbB_8O_{12}F_2$	$P\bar{6}2c$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[20]
36	$CsKB_8O_{12}F_2$	$P321$	BO_3, BO_3F	B_4O_8F	$[B_4O_6F]$ layer	[20]
37	$CaB_5O_7F_3$	$Cmc2_1$	BO_3, BO_3F	$B_5O_9F_3$	$[B_5O_7F_3]$ layer	[24,25]
38	$SrB_5O_7F_3$	$Cmc2_1$	BO_3, BO_3F	$B_5O_9F_3$	$[B_5O_7F_3]$ layer	[25,26]
39	$PbB_5O_7F_3$	$Cmc2_1$	BO_3, BO_3F	$B_5O_9F_3$	$[B_5O_7F_3]$ layer	[27]
40	LiB_6O_9F	$Pna2_1$	BO_3, BO_3F	$B_6O_{11}F$	$[B_6O_9F]$ layer	[28]
41	$BaB_8O_{18}F_2$	$R\bar{3}c$	BO_3, BO_3F	B_4O_8F	$[B_6O_6F_2]$ layer	[29]
42	$Na_3B_7O_{11}F_2$	$Pnma$	BO_3,BO_4, BO_2F_2	$B_7O_{13}F_2$	$[B_7O_{13}F_2]$ network	[30]
43	$Li_2B_6O_9F_2$	Cc	BO_3,BO_4, BO_2F_2	$B_6O_{11}F_2$	$[B_6O_9F_2]$ network	[31]
44	PbB_5O_8F	$Pbca$	BO_3, BO_4, BO_3F	$B_5O_{10}F$	$[B_5O_8F_3]$ network	[32]
45	$BaB_5O_8F \cdot xH_2O$	$Pbca$	BO_3, BO_4, BO_3F	$B_5O_{10}F$	$[B_5O_8F_3]$ network	[33]

Table S4. The birefringence of some borates and fluorooxoborates with fixed 3D B-O/F network structures.

1	LBO	0.040 @ 1064 nm	[34]
2	CBO	0.059 @ 1064 nm	[34]
3	CLBO	0.049 @ 1064 nm	[34]
4	$K_3B_6O_{10}Cl$	0.048 @ 589.3 nm	[35]
5	$K_3B_6O_{10}Br$	0.046 @ 1064 nm	[36]
6	$NaKB_6O_9F_2$	0.096 @ 193 nm 0.053 @ 1064 nm	—
7	$Na_3B_7O_{11}F_2$	0.083 @ 193 nm	[30]
8	$Li_2B_6O_9F_2$	0.07 @ 1064 nm	[31,37]
9	PbB_5O_8F	0.0685 @ 1064 nm	[32]
10	$BaB_5O_8F \cdot xH_2O$	0.093 @ 193 nm	[33]

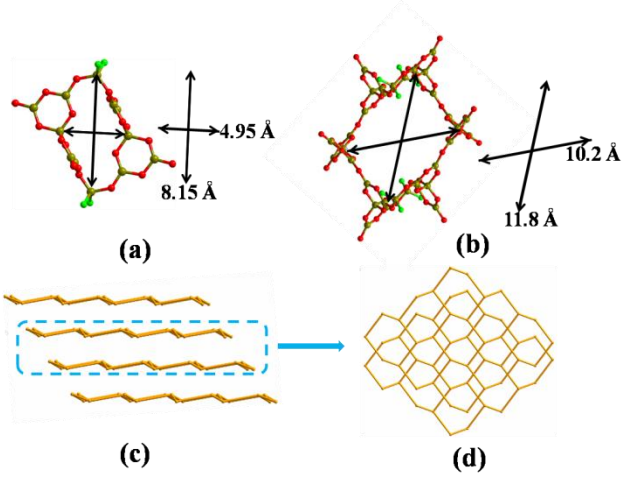

Figure S1. The 16-member ring(a) and super large rectangular ring in the puckered layers; (c), (d) is the topological model of $NaKB_6O_9F_2$(The Schläfli symbol, as analyzed by the TOPOS 4.0 program, is {6^3}).

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