Supporting Information

Structure directing effect of aqueous alkali metal ion (Li^+, Na^+ and K^+) clusters on polyoxoanion configuration in vanadium-molybdenum polyoxometalate solid solutions

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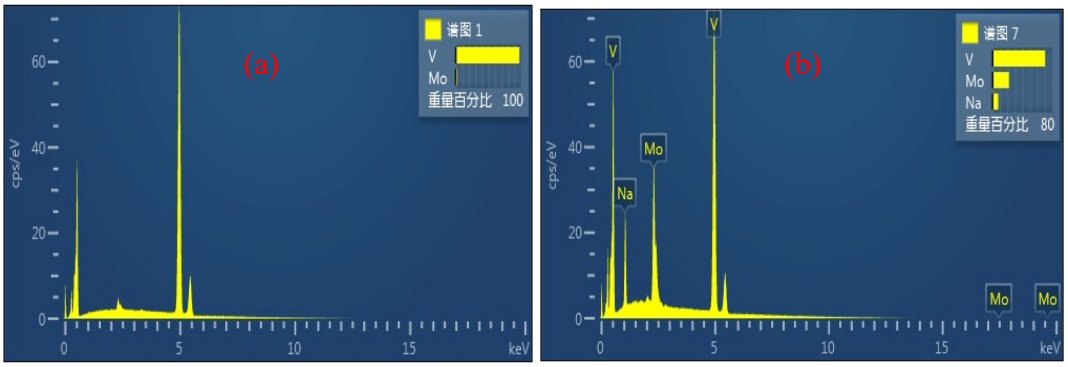

Figure S1. EDS of (a) **1** and (b) **2**.

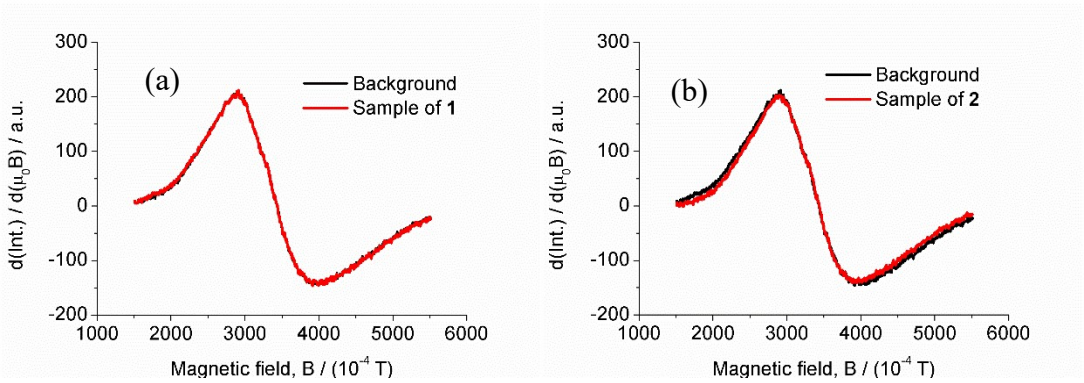

Figure S2. EPR spectra of (a) **1** and (b) **2** at room temperature.

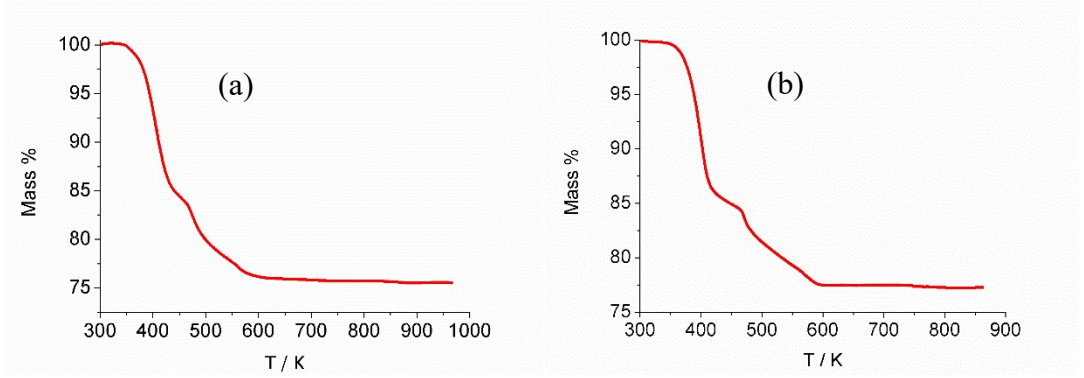

Figure S3. TG plots of (a) **1** and (b) **2** in the range of 303−1068 K.

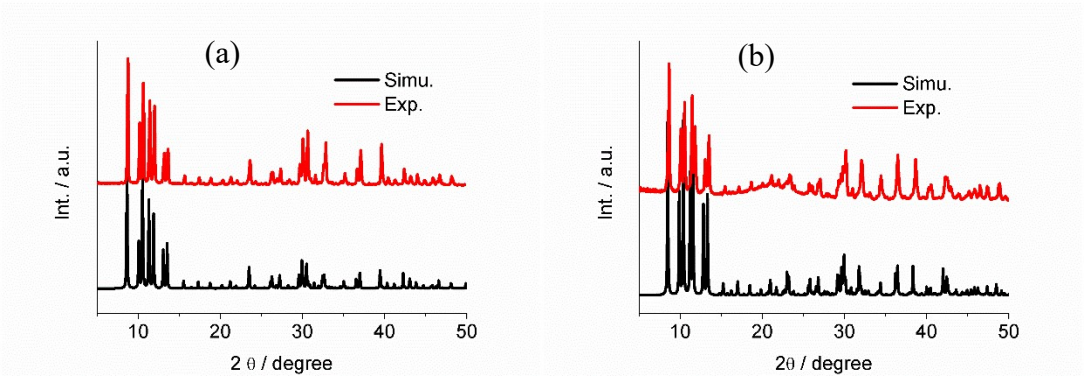

Figure S4. Experimental and simulated PXRD patterns of (a) **1** and (b) **2**.

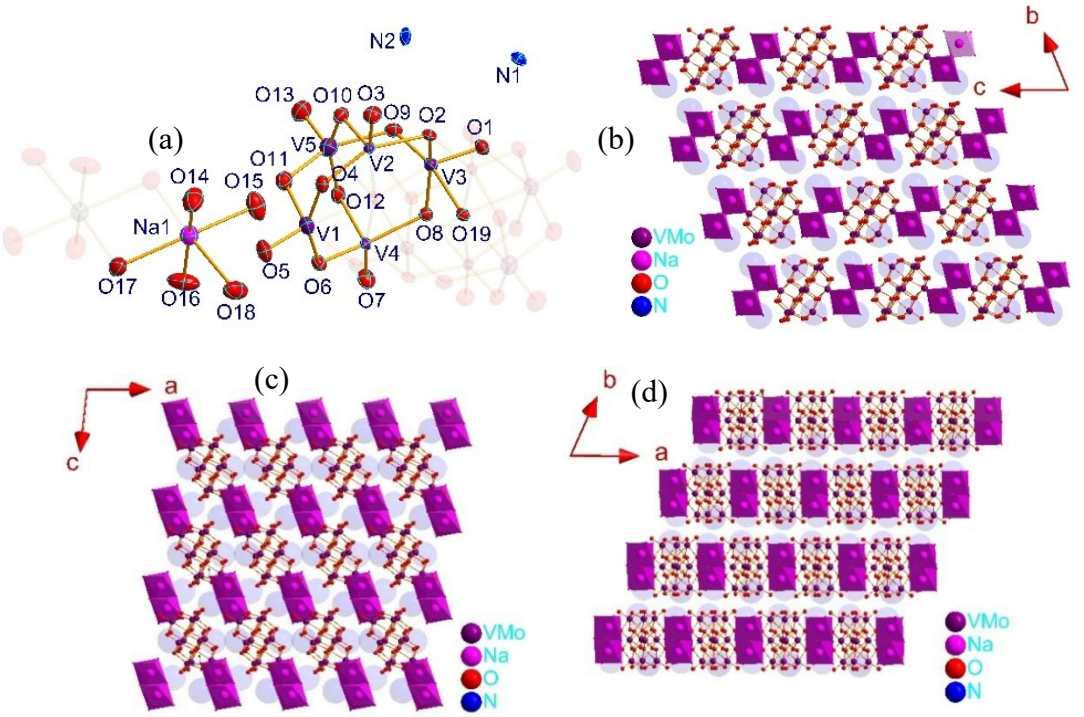

Figure S5. (a) An asymmetric unit of **2**, wherein the non-hydrogen atoms are labeled and the thermal ellipsoids are drawn at 50% probability level, the hydrogen atoms are omitted for clarity and (b–d) packing diagrams of **2** viewed along *a*-, *b*- and *c*-axes, respectively.

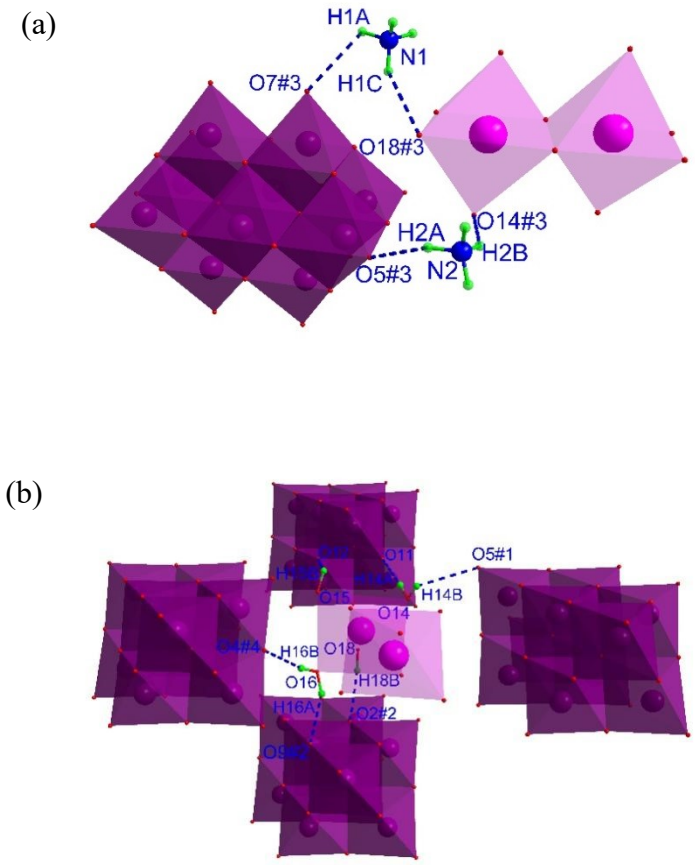

Figure S6. H-bonds (a) between NH_4^+ ion with polyoxoanion and $\{M_2(H_2O)_{10}\}^{2+}$ cluster as well as (b) between polyoxoanion and $\{M_2(H_2O)_{10}\}^{2+}$ cluster in **2**. Herein, the symmetric codes: #1=-x+2, -y+1, -z+2; #2=x+1, y-1, z; #3=x-1, y+1, z; #4= x, y-1, z.

Table S1: Selected bond lengths (Å) in **1**

V1(Mo1)–O4	1.8912(17)	V3(Mo3)-O19	2.1021(16)	V5(Mo5) –O19#1	2.3584(16)
V1(Mo1)–O19#1	2.2926(16)	V3(Mo3)–O19#1	2.1238(15)	V5(Mo5)–O9	2.0286(17)
V1(Mo1)–O1#1	2.0709(18)	V3(Mo3)–O2	1.9267(16)	V5(Mo5)–O12	1.8735(17)
V1(Mo1)–O6	1.8771(18)	V3(Mo3)–O8	1.9073(16)	V5(Mo5)–O10	1.8964(17)
V1(Mo1)–O11	1.8226(18)	V3(Mo3)–O9	1.7031(17)	V5(Mo5)–O11	1.8537(18)
V1(Mo1)–O5	1.6080(18)	V3(Mo3)–O1	1.6867(17)	V5(Mo5)–O13	1.6002(19)
V2(Mo2)–O3	1.6234(18)	V4(Mo4)–O19#1	2.2463(15)	Li–O17#2	2.269(5)
V2(Mo2)–O19#1	2.2263(15)	V4(Mo4)–O2#1	2.0111(17)	Li –O17	2.216(5)
V2(Mo2)–O2	1.9994(17)	V4(Mo4)–O8	1.9998(16)	Li –O14	2.143(5)
V2(Mo2)–O8#1	2.0394(16)	V4(Mo4)–O6	1.8250(18)	Li –O18	2.077(7)
V2(Mo2)–O10	1.8068(17)	V4(Mo4)–O12	1.8257(17)	Li –O15	2.210(5)
V2(Mo2)–O4	1.8183(17)	V4(Mo4)–O7	1.6146(18)	Li –O16	2.137(5)

Symmetry codes: #1 =1-x, -y, 1-z; #2 = 2-x, 2-y, -z

Table S2: Selected bond lengths (Å) in **2**

V1(Mo1)-O4	1.909(5)	V3(Mo3)–O19	2.130(4)	V5(Mo5)–O19#1	2.365(4)
V1(Mo1)–O19#1	2.303(4)	V3(Mo3)–O19#1	2.131(4)	V5(Mo5)–O9	2.058(5)
V1(Mo1)–O1#1	2.109(5)	V3(Mo3)–O2	1.925(4)	V5(Mo5)–O12	1.916(5)
V1(Mo1)–O6	1.886(19)	V3(Mo3)–O8	1.914(4)	V5(Mo5)–O10	1.915(5)
V1(Mo1)–O11	1.813(18)	V3(Mo3)–O9	1.699(5)	V5(Mo5)–O11	1.873(5)
V1(Mo1)–O5	1.611 (19)	V3(Mo3)–O1	1.682(5)	V5(Mo5)–O13	1.617(6)
V2(Mo2)–O3	1.636(5)	V4(Mo4)–O19#1	2.267(4)	Na–O17#2	2.440(6)
V2(Mo2)–O19#1	2.236(4)	V4(Mo4)–O2#1	2.508(4)	Na–O17	2.412(6)
V2(Mo2)–O2	2.012(4)	V4(Mo4)–O2	2.019(4)	Na–O14	2.347(7)
V2(Mo2)–O8#1	2.075(4)	V4(Mo4)–O6	1.820(5)	Na–O18	2.360(7)
V2(Mo2)–O10	1.793(5)	V4(Mo4)–O12	1.804(5)	Na–O15	2.360(7)
V2(Mo2)–O4	1.823(5)	V4(Mo4)–O7	1.619(5)	Na–O16	2.345(7)

Symmetry codes: #1 =1-x, -y, 1-z; #2 = 2-x, 2-y, -z

Table S3: Selected bond angles (°) in **1**

O2–V2(Mo2)–O19#1	76.41(6)	O11–V1(Mo1)–O4	91.45(8)
O2–V2(Mo2)–O8#1	75.68(7)	O11–V1(Mo1)–O1#1	157.41(7)
O8#1–V2(Mo2)–O19#1	75.21(6)	O11–V1(Mo1)–O6	92.95(8)
O10–V2(Mo2)–O2	91.19(8)	O4–V1(Mo1)–O19#1	77.32(7)
O10–V2(Mo2)–O19#1	82.23(7)	O4–V1(Mo1)–O1#1	82.26(7)
O10–V2(Mo2)–O8#1	155.96(7)	O1#1–V1(Mo1)–O19#1	74.21(6)
O10–V2(Mo2)–O4	95.46(8)	O6–V1(Mo1)–O19#1	78.62(7)
O4–V2(Mo2)–O2	154.87(7)	O6–V1(Mo1)–O4	154.83(8)
O4–V2(Mo2)–O19#1	80.52(7)	O6–V1(Mo1)–O1#1	83.61(8)
O4–V2(Mo2)–O8#1	88.97(7)	O5–V1(Mo1)–O19#1	117.74(9)
O3–V2(Mo2)–O2	99.95(9)	O5–V1(Mo1)–O11	105.03(9)
O3–V2(Mo2)–O19#1	173.35(8)	O5–V1(Mo1)–O4	101.62(9)
O3–V2(Mo2)–O8#1	98.58(8)	O5–V1(Mo1)–O1#1	97.54(9)
O3–V2(Mo2)–O10	103.54(9)	O5–V1(Mo1)–O6	101.12(10)
O3–V2(Mo2)–O4	101.98(9)	O10–V5(Mo5)–O19#1	76.92(6)
O2–V3(Mo3)–O19	80.94(7)	O10–V5(Mo5)–O9	93.64(7)
O2–V3(Mo3)–O19#1	80.42(7)	O11–V5(Mo5)–O19#1	80.74(7)
O19–V3(Mo3)–O19#1	78.57(7)	O11–V5(Mo5)–O10	90.11(8)
O8– V3(Mo3)–O19	80.96(7)	O11–V5(Mo5)–O9	154.78(7)
O8– V3(Mo3)–O19#1	80.81(7)	O11–V5(Mo5)–O12	90.94(8)
O9– V3(Mo3)–O2	96.48(8)	O9–V5(Mo5)–O19#1	74.05(6)
O9– V3(Mo3)–O19#1	87.11(7)	O12–V5(Mo5)–O19#1	77.09(6)
O9– V3(Mo3)–O19	165.67(7)	O12–V5(Mo5)–O10	153.46(8)
O9– V3(Mo3)–O8	97.20(8)	O12–V5(Mo5)–O9	84.19(7)
O1– V3(Mo3)–O19	87.53(7)	O13–V5(Mo5)–O19#1	174.62(8)
O1– V3(Mo3)–O19#1	166.09(8)	O13–V5(Mo5)–O10	103.30(9)
O1– V3(Mo3)–O8	97.52(8)	O13–V5(Mo5)–O11	104.61(9)
O1– V3(Mo3)–O9	106.79(9)	O13–V5(Mo5)–O9	100.60(9)
O2–V4(Mo4)–O19	75.67(6)	O13–V5(Mo5)–O12	102.08(9)
O8–V4(Mo4)–O2#1	76.29(7)	O17–Li1–O17#2	85.52(19)
O8–V4(Mo4)–O19#1	75.89(6)	O18–Li1–O17#2	97.32(2)
O6–V4(Mo4)–O2#1	89.65(7)	O18–Li1–O17	91.3(2)
O6–V4(Mo4)–O19#1	80.90(7)	O18–Li1–O16	87.1(2)
O6–V4(Mo4)–O8	155.18(7)	O18–Li1–O15	93.9(2)
O6–V4(Mo4)–O12	95.03(8)	O18–Li1–O14	172.4(3)
O12–V4(Mo4)–O2#1	155.116(7)	O16–Li1–O17	98.4(2)
O12–V4(Mo4)–O19#1	81.00(7)	O16–Li1–O17#2	174.1(3)
O12–V4(Mo4)–O8	89.96(7)	O16–Li1–O15	88.1(2)
O7–V4(Mo4)–O2#1	98.30(8)	O16–Li1–O14	89.9(2)
O7–V4(Mo4)–O19#1	172.76(8)	O15–Li1–O17	171.9(3)
O7–V4(Mo4)–O8	98.95(9)	O15–Li1–O17#2	87.7(2)
O7–V4(Mo4)–O6	103.31(9)	O14–Li1–O17	85.66(19)
O7–V4(Mo4)–O12	104.28(9)	O14–Li1–O15	89.5(2)

O11–V1(Mo1)–O19#1	83.22(7)	O14–Li1–O17#2	85.93(19)

Symmetry codes: #1 =1-x, -y, 1-z; #2 = -x, 2-y, -z

Table S4. Selected bond angles (°) in **2**

O2–V2(Mo2)–O19#1	75.89(16)	O11–V1(Mo1)–O19#1	83.7(2)
O2–V2(Mo2)–O8#1	75.17(18)	O11–V1(Mo1)–O4	91.5(2)
O8#1–V2(Mo2)–O19#1	74.74(17)	O11–V1(Mo1)–O1#1	157.6(2)
O10–V2(Mo2)–O2	91.6(2)	O11–V1(Mo1)–O6	93.6(2)
O10–V2(Mo2)–O19#1	83.00(19)	O4–V1(Mo1)–O19#1	77.09(17)
O10–V2(Mo2)–O8#1	156.2(2)	O4–V1(Mo1)–O1#1	82.4(2)
O10–V2(Mo2)–O4	96.4(2)	O1#1–V1(Mo1)–O19#1	74.01(17)
O4–V2(Mo2)–O2	154.0(2)	O6–V1(Mo1)–O19#1	78.46(18)
O4–V2(Mo2)–O19#1	80.59(19)	O6–V1(Mo1)–O4	154.3(2)
O4–V2(Mo2)–O8#1	88.2(2)	O6–V1(Mo1)–O1#1	83.4(2)
O3–V2(Mo2)–O2	99.3(2)	O5–V1(Mo1)–O19#1	169.8(2)
O3–V2(Mo2)–O19#1	171.6(2)	O5–V1(Mo1)–O11	106.5(3)
O3–V2(Mo2)–O8#1	97.5(2)	O5–V1(Mo1)–O4	101.6(3)
O3–V2(Mo2)–O10	104.2(2)	O5–V1(Mo1)–O1#1	97.54(9)
O3–V2(Mo2)–O4	102.6(2)	O5–V1(Mo1)–O6	101.0(3)
O2–V3(Mo3)–O19	80.73(17)	O10–V5(Mo5)–O19#1	77.07(18)
O2–V3(Mo3)–O19#1	80.24(17)	O10–V5(Mo5)–O9	83.9(2)
O19–V3(Mo3)–O19#1	78.33(18)	O11–V5(Mo5)–O19#1	80.70(19)
O8–V3(Mo3)–O19	80.57(17)	O11–V5(Mo5)–O10	90.4(2)
O8–V3(Mo3)–O19#1	80.81(7)	O11–V5(Mo5)–O9	154.8(2)
O9–V3(Mo3)–O2	97.20(2)	O11–V5(Mo5)–O12	91.2(2)
O9–V3(Mo3)–O19#1	87.9(2)	O9–V5(Mo5)–O19#1	74.08(17)
O9–V3(Mo3)–O19	166.2(2)	O12–V5(Mo5)–O19#1	77.29(18)
O9–V3(Mo3)–O8	97.20(2)	O12–V5(Mo5)–O9	83.5(2)
O1–V3(Mo3)–O19	87.7(2)	O13–V5(Mo5)–O19#1	174.4(3)
O1–V3(Mo3)–O19#1	166.0(2)	O13–V5(Mo5)–O10	103.7(3)
O1–V3(Mo3)–O8	97.2(2)	O13–V5(Mo5)–O11	104.8(3)
O1–V3(Mo3)–O9	106.1(2)	O13–V5(Mo5)–O9	100.4(3)
O2–V4(Mo4)–O19#1	74.75(16)	O13–V5(Mo5)–O12	101.3(3)
O8–V4(Mo4)–O2#1	75.42(17)	O17–Na1–O17#2	90.0(2)
O8–V4(Mo4)–O19#1	75.38(16)	O14–Na1–O17	89.6(2)
O6–V4(Mo4)–O2#1	88.4(2)	O14–Na1–O17#2	104.2(3)
O6–V4(Mo4)–O19#1	80.72(18)	O14–Na1–O18	85.0(3)
O6–V4(Mo4)–O8	153.9(2)	O14–Na1–O15	97.4(3)
O6–V4(Mo4)–O12	96.09(8)	O18–Na1–O17	97.9(2)
O12–V4(Mo4)–O2#1	155.1 (7)	O18–Na1–O17#2	168.0(3)
O12–V4(Mo4)–O19#1	81.11(19)	O18–Na1–O15	85.5(3)
O12–V4(Mo4)–O8	90.2(2)	O16–Na1–O17#2	83.8(2)
O12–V4(Mo4)–O6	96.09(8)	O16–Na1–O17	84.8(3)
O7–V4(Mo4)–O2#1	97.9(2)	O16–Na1–O14	170.3(3)
O7–V4(Mo4)–O19#1	171.8(2)	O16–Na1–O18	87.9(3)
O7–V4(Mo4)–O8	99.4(2)	O16–Na1–O15	88.6(2)
O7–V4(Mo4)–O6	103.1(2)	O15–Na1–O17#2	85.7(2)

O7–V4(Mo4)–O12	104.4(3)	O15–Na1–O17	172.4(2)

Symmetry codes: #1 =1-x, 2-y, 1-z; #2 = 2-x, -y, 2-z

Table S5: H-bond parameters in **2**

D…A	Distance / Å	∠D-H…A	Angle / °
O14...O11	2.820	O14-H14A...O11	172.74
O14...O5#1	2.987	O14-H14B...O5#1	115.89
O18...O2#2	2.940	O18-H18B...O2#2	171.99
O16...O9#2	2.845	O16-H16A...O9#2	146.57
O16...O4#4	2.857	O16-H16B...O4	170.69
N1...O7#3	2.927	N1-H1A...O7#3	117.76
N1...O18#3	3.041	N1-H1C...O18#3	146.22
N2...O5#3	2.884	N2-H2A...O5#3	150.49
N2...O14#3	3.044	N2-H2B...O14#3	143.40
N2...O3	2.919	N2-H2D...O3	164.90
O15-O12	2.821	O15-H15B...O12	123.89

#1=-x+2, -y+1, -z+2; #2=x+1, y-1, z; #3=x-1, y+1, z; #4= x, y-1, z.

Table S6: Coordination number and effective ionic radius of ions [1]

Ion	Coordination Number	Effective Ionic Radius / Å
Li^+	4	0.59
	6	0.76
	8	0.92
Na^+	4	0.99
	5	1.00
	6	1.02
	7	1.12
	8	1.18
	9	1.24
	12	1.39
K^+	4	1.37
	6	1.38
	7	1.46
	8	1.51
	9	1.55
	10	1.59
	12	1.64

Table S7: Summary of critical radius ratio values with corresponding coordination number and crystal structure types

Cation and anion ions radius ratio (r_+/r_-)	Coordination number	Crystal structure type
0.225 ~ 0.414	4	ZnS-type
0.414 ~ 0.732	6	NaCl-type, TiO_2-type, $CdCl_2$-type, CdI_2-type
0.732 ~ 1.000	8	CsCl-type, CaF_2-type

References

1. www.knowledgedoor.com