Electronic Supplementary Material (ESI) for Dalton Transactions.
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$A_6Mo_2P_4O_{19}$ (A = Rb, Cs) and $Rb_2MoP_2O_9$: New molybdophosphates with distinct polyanionic configurations

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Table S1. The final coordinates ($\times 10^4$), Wyck. and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) of non-hydrogen atoms for $Rb_2MoP_2O_9$, $Cs_2MoP_2O_9$, $Rb_6Mo_2P_4O_{19}$ and $Cs_6Mo_2P_4O_{19}$. ***U*eq** is defined as one-third of the trace of the orthogonalized Uij tensor, and the Bond Valence Sum (BVS) for each atom in the asymmetric unit.

Atom	Wyck.	*x*	*y*	*z*	*Ueq*	*BVS*
			$Rb_2MoP_2O_9$			
Rb(1)	8f	6669(1)	2752(1)	6786(1)	18(1)	1.29
Rb(2)	8f	1847(1)	2476(1)	6432(1)	21(1)	1.07
Rb(3)	8f	44(1)	2586(1)	4729(1)	25(1)	0.97
Mo(1)	4e	0	5095(1)	2500	11(1)	6.20
Mo(2)	8f	3416(1)	5382(1)	5893(1)	11(1)	6.14
P(1)	8f	1664(1)	5781(1)	3339(1)	11(1)	5.03
P(2)	8f	5131(1)	6090(1)	6686(1)	12(1)	5.03
P(3)	8f	1726(1)	5783(1)	5023(1)	11(1)	5.00
O(1)	8f	1781(1)	7614(2)	3345(1)	16(1)	2.01
O(2)	8f	1645(1)	7622(2)	4947(1)	17(1)	1.96
O(3)	8f	5360(1)	7842(2)	6864(1)	16(1)	1.92
O(4)	8f	2361(1)	5360(2)	5657(1)	15(1)	2.22
O(5)	8f	2066(1)	4919(3)	2782(1)	19(1)	1.99
O(6)	8f	1960(1)	5109(2)	4213(1)	14(1)	2.07
O(7)	4e	5000	5245(3)	7500	18(1)	2.08
O(8)	8f	1091(1)	4930(3)	5212(1)	21(1)	1.92
O(9)	8f	877(1)	5391(3)	3252(1)	19(1)	2.10
O(10)	8f	5654(1)	5116(3)	6327(1)	20(1)	2.00
O(11)	8f	4416(1)	6063(3)	6143(1)	20(1)	2.06
O(12)	8f	362(1)	3819(3)	1888(1)	22(1)	2.15
O(13)	8f	3539(1)	4110(3)	5141(1)	22(1)	2.05
O(14)	8f	3417(1)	4082(3)	6666(1)	22(1)	2.03
			$Cs_2MoP_2O_9$			
Cs(1)	8c	1439(1)	6504(1)	4435(1)	26(1)	1.15
Cs(2)	8c	1482(1)	9768(1)	2850(1)	32(1)	0.92
Mo(1)	8c	3111(1)	4847(1)	5744(1)	16(1)	6.08
P(1)	8c	-1956(2)	7622(2)	3311(1)	18(1)	5.04
P(2)	8c	-144(2)	3018(2)	3844(1)	17(1)	4.99
O(1)	8c	4253(6)	5934(5)	5373(2)	28(1)	2.07
O(2)	8c	2229(6)	3820(5)	5274(2)	27(1)	2.06
O(3)	8c	-1808(6)	6286(5)	3643(2)	25(1)	1.88
O(4)	8c	-1235(6)	8914(5)	3583(2)	24(1)	2.02
O(5)	8c	-3874(6)	7974(5)	3306(2)	20(1)	2.07
O(6)	8c	-1451(6)	7488(5)	2756(2)	29(1)	1.94
O(7)	8c	1473(6)	3563(5)	3751(2)	24(1)	1.91
O(8)	8c	-119(5)	1453(4)	4047(2)	19(1)	2.12
O(9)	8c	-1132(5)	3892(4)	4240(2)	17(1)	2.11
			$Rb_6Mo_2P_4O_{19}$			
Rb(1)	4e	2339(1)	3365(1)	5537(1)	13(1)	1.20

Rb(2)	4e	4844(1)	8420(1)	6367(1)	36(1)	0.98
Rb(3)	4e	8903(1)	-722(1)	2094(1)	24(1)	0.99
Mo(1)	4e	8622(1)	1586(1)	4901(1)	23(1)	6.16
P(1)	4e	7965(2)	592(2)	6764(1)	32(1)	4.95
P(2)	4e	6099(2)	3149(2)	6113(1)	23(1)	5.00
O(1)	4e	4860(5)	2327(8)	5824(4)	66(3)	1.96
O(2)	4e	6112(6)	4992(7)	6533(4)	40(2)	1.84
O(3)	4e	6711(5)	1817(7)	6946(3)	41(2)	2.10
O(4)	4e	8232(5)	-512(7)	7627(4)	34(2)	1.95
O(5)	4e	9012(5)	1927(6)	6461(3)	36(1)	1.94
O(6)	4e	7646(5)	-449(6)	5839(3)	32(2)	1.95
O(7)	2c	10000	0	5000	38(2)	2.35
O(8)	4e	9455(5)	3419(8)	4529(4)	36(1)	2.13
O(9)	4e	7914(5)	700(8)	3893(4)	14(6)	2.11
O(10)	4e	7067(5)	3050(7)	5279(4)	48(2)	2.15
			$Cs_6Mo_2P_4O_{19}$			
Cs(1)	4e	4835(1)	1648(1)	8610(1)	27(1)	0.96
Cs(2)	4e	7655(1)	1583(1)	5550(1)	27(1)	1.16
Cs(3)	4e	8916(1)	733(1)	2923(1)	27(1)	1.02
Mo(1)	4e	1352(1)	1532(1)	9928(1)	17(1)	6.09
P(1)	4e	7980(1)	-626(1)	8279(1)	18(1)	4.90
P(2)	4e	3841(1)	1930(1)	6084(1)	18(1)	4.97
O(1)	4e	8217(3)	413(4)	7440(2)	29(1)	1.92
O(2)	4e	2886(3)	2069(4)	5281(2)	26(1)	2.13
O(3)	4e	7700(3)	396(3)	9166(2)	21(1)	1.92
O(4)	4e	2029(3)	732(4)	8947(2)	33(1)	2.07
O(5)	4e	6762(3)	-1816(4)	8105(2)	24(1)	2.10
O(6)	4e	550(3)	3331(4)	9599(2)	33(1)	2.12
O(7)	2a	0	0	10000	36(1)	2.27
O(8)	4e	3833(3)	158(4)	6468(2)	36(1)	1.87
O(9)	4e	9019(3)	-1892(4)	8577(2)	22(1)	1.91
O(10)	4e	5055(3)	2720(4)	5823(2)	36(1)	1.92

Table S2a. Selected bond distances (Å) and bond angles (deg.) for $Rb_2MoP_2O_9$.

Mo(1)-O(12)#1	1.694(2)	O(13)#4-Rb(2)-O(8)	69.21(6)
Mo(1)-O(12)	1.694(2)	O(10)#12-Rb(2)-O(8)	95.63(5)
Mo(1)-O(9)#1	1.9771(18)	O(3)#12-Rb(2)-O(8)	74.73(5)
Mo(1)-O(3)#2	2.171(2)	O(4)-Rb(2)-O(5)#13	76.53(5)
Mo(1)-O(3)#3	2.171(2)	O(13)#4-Rb(2)-O(5)#13	162.24(6)
Mo(1)-Rb(1)#4	4.2761(3)	O(10)#12-Rb(2)-O(5)#13	120.45(6)
Mo(1)-Rb(1)#5	4.2761(3)	O(5)#4-Rb(2)-O(5)#13	96.01(2)
Mo(1)-Rb(3)#1	4.3090(4)	O(3)#12-Rb(2)-O(5)#13	77.65(5)
Mo(1)-Rb(3)	4.3090(4)	O(8)-Rb(2)-O(5)#13	93.08(5)
Mo(2)-O(14)	1.694(2)	O(4)-Rb(2)-O(14)	50.78(5)
Mo(2)-O(13)	1.694(2)	O(13)#4-Rb(2)-O(14)	113.01(6)
Mo(2)-O(11)	1.9817(19)	O(10)#12-Rb(2)-O(14)	163.21(5)
Mo(2)-O(4)	2.0064(18)	O(5)#4-Rb(2)-O(14)	68.97(5)
Mo(2)-O(1)#2	2.1578(19)	O(3)#12-Rb(2)-O(14)	143.93(6)
Mo(2)-O(2)#2	2.163(2)	O(8)-Rb(2)-O(14)	98.96(5)
Mo(2)-Rb(2)	4.0442(4)	O(5)#13-Rb(2)-O(14)	67.13(5)
Mo(2)-Rb(3)#4	4.0794(4)	O(4)-Rb(2)-O(1)#13	121.90(5)
Mo(2)-Rb(3)#6	4.3281(4)	O(13)#4-Rb(2)-O(1)#13	147.74(6)
Mo(2)-Rb(1)#7	4.3339(4)	O(10)#12-Rb(2)-O(1)#13	84.57(5)
Rb(1)-O(10)	2.775(2)	O(5)#4-Rb(2)-O(1)#13	70.70(5)
Rb(1)-O(5)#8	2.803(2)	O(3)#12-Rb(2)-O(1)#13	65.89(5)
Rb(1)-O(12)#8	2.845(2)	O(8)-Rb(2)-O(1)#13	126.92(5)
Rb(1)-O(14)#9	2.882(2)	O(5)#13-Rb(2)-O(1)#13	45.78(5)
Rb(1)-O(1)#10	3.028(2)	O(14)-Rb(2)-O(1)#13	93.20(5)
Rb(1)-O(5)#10	3.088(2)	O(4)-Rb(2)-O(6)#4	93.84(5)
Rb(1)-O(2)#11	3.131(2)	O(13)#4-Rb(2)-O(6)#4	61.95(5)
Rb(1)-O(4)#11	3.167(2)	O(10)#12-Rb(2)-O(6)#4	97.15(5)
Rb(1)-P(3)#11	3.4254(8)	O(5)#4-Rb(2)-O(6)#4	44.87(5)
Rb(1)-P(1)#10	3.4496(7)	O(3)#12-Rb(2)-O(6)#4	146.06(5)
Rb(1)-O(8)#11	3.590(2)	O(8)-Rb(2)-O(6)#4	117.05(5)
Rb(1)-Rb(2)#9	3.8564(4)	O(5)#13-Rb(2)-O(6)#4	129.51(5)
Rb(2)-O(4)	2.942(2)	O(14)-Rb(2)-O(6)#4	68.77(5)
Rb(2)-O(13)#4	2.975(2)	O(1)#13-Rb(2)-O(6)#4	115.54(5)
Rb(2)-O(10)#12	2.979(2)	O(8)-Rb(3)-O(12)#1	97.02(6)
Rb(2)-O(5)#4	3.027(2)	O(8)-Rb(3)-O(8)#14	91.13(5)
Rb(2)-O(3)#12	3.0624(19)	O(12)#1-Rb(3)-O(8)#14	72.73(6)
Rb(2)-O(8)	3.095(2)	O(8)-Rb(3)-O(13)#4	72.26(6)
Rb(2)-O(5)#13	3.119(2)	O(12)#1-Rb(3)-O(13)#4	109.83(6)
Rb(2)-O(14)	3.255(2)	O(8)#14-Rb(3)-O(13)#4	163.34(6)

Rb(2)-O(1)#13	3.284(2)	O(8)-Rb(3)-O(10)#4	154.79(6)
Rb(2)-O(6)#4	3.4124(19)	O(12)#1-Rb(3)-O(10)#4	70.04(6)
Rb(2)-P(2)#12	3.5662(7)	O(8)#14-Rb(3)-O(10)#4	104.70(5)
Rb(2)-P(3)	3.6017(8)	O(13)#4-Rb(3)-O(10)#4	91.39(5)
Rb(3)-O(8)	2.811(2)	O(8)-Rb(3)-O(11)#12	112.72(6)
Rb(3)-O(12)#1	2.933(2)	O(12)#1-Rb(3)-O(11)#12	141.92(5)
Rb(3)-O(8)#14	2.989(2)	O(8)#14-Rb(3)-O(11)#12	83.08(6)
Rb(3)-O(13)#4	3.030(2)	O(13)#4-Rb(3)-O(11)#12	101.79(6)
Rb(3)-O(10)#4	3.035(2)	O(10)#4-Rb(3)-O(11)#12	88.94(6)
Rb(3)-O(11)#12	3.108(2)	O(8)-Rb(3)-O(2)#14	130.48(6)
Rb(3)-O(2)#14	3.368(2)	O(12)#1-Rb(3)-O(2)#14	92.37(5)
Rb(3)-O(10)#12	3.457(2)	O(8)#14-Rb(3)-O(2)#14	46.08(5)
Rb(3)-P(2)#12	3.5369(8)	O(13)#4-Rb(3)-O(2)#14	146.98(5)
Rb(3)-O(11)#4	3.553(2)	O(10)#4-Rb(3)-O(2)#14	73.08(5)
Rb(3)-O(3)#12	3.611(2)	O(11)#12-Rb(3)-O(2)#14	50.36(5)
Rb(3)-P(3)#14	3.7286(7)	O(8)-Rb(3)-O(10)#12	91.22(5)
P(1)-O(5)	1.485(2)	O(12)#1-Rb(3)-O(10)#12	162.81(6)
P(1)-O(1)	1.515(2)	O(8)#14-Rb(3)-O(10)#12	122.34(5)
P(1)-O(9)	1.5283(19)	O(13)#4-Rb(3)-O(10)#12	58.50(5)
P(1)-O(6)	1.613(2)	O(10)#4-Rb(3)-O(10)#12	96.44(5)
P(1)-Rb(1)#10	3.4497(7)	O(11)#12-Rb(3)-O(10)#12	43.88(5)
P(1)-Rb(2)#15	3.6140(8)	O(2)#14-Rb(3)-O(10)#12	93.70(5)
P(1)-Rb(2)#4	3.8824(7)	O(8)-Rb(3)-O(11)#4	117.09(5)
P(1)-Rb(1)#5	3.9199(8)	O(12)#1-Rb(3)-O(11)#4	87.08(6)
P(2)-O(10)	1.481(2)	O(8)#14-Rb(3)-O(11)#4	147.40(5)
P(2)-O(3)	1.516(2)	O(13)#4-Rb(3)-O(11)#4	48.22(5)
P(2)-O(11)	1.5408(19)	O(10)#4-Rb(3)-O(11)#4	43.23(5)
P(2)-O(7)	1.6023(14)	O(11)#12-Rb(3)-O(11)#4	99.08(5)
P(2)-Rb(3)#6	3.5369(8)	O(2)#14-Rb(3)-O(11)#4	111.86(5)
P(2)-Rb(2)#6	3.5661(7)	O(10)#12-Rb(3)-O(11)#4	75.73(5)
P(2)-Rb(3)#4	3.8380(8)	P(2)#12-Rb(3)-O(11)#4	97.35(4)
P(3)-O(8)	1.480(2)	O(8)-Rb(3)-O(3)#12	69.91(5)
P(3)-O(2)	1.515(2)	O(12)#1-Rb(3)-O(3)#12	155.67(6)
P(3)-O(4)	1.5448(19)	O(8)#14-Rb(3)-O(3)#12	86.73(5)
P(3)-O(6)	1.611(2)	O(13)#4-Rb(3)-O(3)#12	86.27(5)
P(3)-Rb(1)#7	3.4254(8)	O(10)#4-Rb(3)-O(3)#12	129.46(5)
P(3)-Rb(3)#14	3.7286(7)	O(11)#12-Rb(3)-O(3)#12	42.92(5)
O(1)-Mo(2)#2	2.1578(19)	O(2)#14-Rb(3)-O(3)#12	82.06(5)
O(1)-Rb(1)#10	3.028(2)	O(10)#12-Rb(3)-O(3)#12	41.45(5)
O(1)-Rb(2)#15	3.284(2)	P(2)#12-Rb(3)-O(3)#12	24.45(3)
O(2)-Mo(2)#2	2.163(2)	O(11)#4-Rb(3)-O(3)#12	117.01(5)

O(2)-Rb(1)#7	3.132(2)	O(5)-P(1)-O(1)	112.55(12)
O(2)-Rb(3)#14	3.368(2)	O(5)-P(1)-O(9)	115.84(12)
O(3)-Mo(1)#2	2.171(2)	O(1)-P(1)-O(9)	110.44(12)
O(3)-Rb(2)#6	3.0624(19)	O(5)-P(1)-O(6)	106.49(11)
O(3)-Rb(3)#6	3.611(2)	O(1)-P(1)-O(6)	107.39(11)
O(4)-Rb(1)#7	3.167(2)	O(9)-P(1)-O(6)	103.28(11)
O(5)-Rb(1)#5	2.803(2)	O(10)-P(2)-O(3)	113.41(12)
O(5)-Rb(2)#4	3.027(2)	O(10)-P(2)-O(11)	109.89(12)
O(5)-Rb(1)#10	3.088(2)	O(3)-P(2)-O(11)	109.92(12)
O(5)-Rb(2)#15	3.119(2)	O(10)-P(2)-O(7)	109.13(12)
O(6)-Rb(2)#4	3.4124(19)	O(3)-P(2)-O(7)	108.14(12)
O(7)-P(2)#9	1.6022(14)	O(11)-P(2)-O(7)	106.08(9)
O(8)-Rb(3)#14	2.989(2)	O(8)-P(3)-O(2)	114.08(12)
O(8)-Rb(1)#7	3.590(2)	O(8)-P(3)-O(4)	109.42(12)
O(10)-Rb(2)#6	2.979(2)	O(2)-P(3)-O(4)	110.09(11)
O(10)-Rb(3)#4	3.035(2)	O(8)-P(3)-O(6)	111.49(12)
O(10)-Rb(3)#6	3.456(2)	O(2)-P(3)-O(6)	107.69(11)
O(11)-Rb(3)#6	3.108(2)	O(4)-P(3)-O(6)	103.54(11)
O(11)-Rb(3)#4	3.553(2)	O(5)#10-Rb(1)-O(4)#11	98.16(5)
O(12)-Rb(1)#5	2.845(2)	O(2)#11-Rb(1)-O(4)#11	46.92(5)
O(12)-Rb(3)#1	2.933(2)	O(10)-Rb(1)-O(8)#11	96.21(5)
O(13)-Rb(2)#4	2.975(2)	O(5)#8-Rb(1)-O(8)#11	88.86(5)
O(13)-Rb(3)#4	3.030(2)	O(12)#8-Rb(1)-O(8)#11	64.93(6)
O(14)-Rb(1)#9	2.882(2)	O(14)#9-Rb(1)-O(8)#11	151.00(5)
O(12)#1-Mo(1)-O(12)	104.01(15)	O(1)#10-Rb(1)-O(8)#11	94.68(5)
O(12)#1-Mo(1)-O(9)	93.57(9)	O(5)#10-Rb(1)-O(8)#11	136.16(5)
O(12)-Mo(1)-O(9)	95.08(9)	O(2)#11-Rb(1)-O(8)#11	43.23(5)
O(12)#1-Mo(1)-O(9)#1	95.08(9)	O(4)#11-Rb(1)-O(8)#11	42.28(5)
O(12)-Mo(1)-O(9)#1	93.57(9)	O(4)-Rb(2)-O(13)#4	89.97(6)
O(9)-Mo(1)-O(9)#1	165.92(12)	O(4)-Rb(2)-O(10)#12	142.78(6)
O(12)#1-Mo(1)-O(3)#2	88.96(9)	O(13)#4-Rb(2)-O(10)#12	64.83(6)
O(12)-Mo(1)-O(3)#2	167.01(9)	O(4)-Rb(2)-O(5)#4	117.57(5)
O(9)-Mo(1)-O(3)#2	83.29(8)	O(13)#4-Rb(2)-O(5)#4	100.50(6)
O(9)#1-Mo(1)-O(3)#2	85.78(8)	O(10)#12-Rb(2)-O(5)#4	94.69(6)
O(12)#1-Mo(1)-O(3)#3	167.01(9)	O(4)-Rb(2)-O(3)#12	114.49(5)
O(12)-Mo(1)-O(3)#3	88.96(9)	O(13)#4-Rb(2)-O(3)#12	98.10(6)
O(9)-Mo(1)-O(3)#3	85.78(8)	O(10)#12-Rb(2)-O(3)#12	48.97(5)
O(9)#1-Mo(1)-O(3)#3	83.29(8)	O(5)#4-Rb(2)-O(3)#12	124.24(6)
O(3)#2-Mo(1)-O(3)#3	78.07(11)	O(4)-Rb(2)-O(8)	48.20(5)
O(14)-Mo(2)-O(13)	102.73(11)	O(10)-Rb(1)-O(1)#10	134.79(6)
O(14)-Mo(2)-O(11)	96.78(9)	O(5)#8-Rb(1)-O(1)#10	77.58(6)

O(13)-Mo(2)-O(11)	95.67(10)	O(12)#8-Rb(1)-O(1)#10	147.49(6)
O(14)-Mo(2)-O(4)	92.09(9)	O(14)#9-Rb(1)-O(1)#10	106.99(6)
O(13)-Mo(2)-O(4)	95.13(9)	O(10)-Rb(1)-O(5)#10	97.64(6)
O(11)-Mo(2)-O(4)	164.16(9)	O(5)#8-Rb(1)-O(5)#10	101.60(2)
O(14)-Mo(2)-O(1)#2	89.28(9)	O(12)#8-Rb(1)-O(5)#10	158.86(6)
O(13)-Mo(2)-O(1)#2	167.84(9)	O(14)#9-Rb(1)-O(5)#10	72.32(6)
O(11)-Mo(2)-O(1)#2	84.61(8)	O(1)#10-Rb(1)-O(5)#10	48.15(5)
O(4)-Mo(2)-O(1)#2	82.40(8)	O(10)-Rb(1)-O(2)#11	80.40(6)
O(14)-Mo(2)-O(2)#2	169.35(9)	O(5)#8-Rb(1)-O(2)#11	122.96(6)
O(13)-Mo(2)-O(2)#2	87.80(9)	O(12)#8-Rb(1)-O(2)#11	99.25(6)
O(11)-Mo(2)-O(2)#2	83.59(8)	O(14)#9-Rb(1)-O(2)#11	159.34(6)
O(4)-Mo(2)-O(2)#2	85.29(8)	O(1)#10-Rb(1)-O(2)#11	78.17(5)
O(1)#2-Mo(2)-O(2)#2	80.15(8)	O(5)#10-Rb(1)-O(2)#11	99.03(5)
O(10)-Rb(1)-O(12)#8	75.10(6)	O(10)-Rb(1)-O(4)#11	126.67(6)
O(5)#8-Rb(1)-O(12)#8	77.00(6)	O(5)#8-Rb(1)-O(4)#11	77.70(6)
O(10)-Rb(1)-O(14)#9	82.22(6)	O(12)#8-Rb(1)-O(4)#11	102.07(6)
O(5)#8-Rb(1)-O(14)#9	77.59(6)	O(14)#9-Rb(1)-O(4)#11	150.99(5)
O(12)#8-Rb(1)-O(14)#9	86.91(6)	O(1)#10-Rb(1)-O(4)#11	52.55(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,-z+1/2 #2 -x+1/2,-y+3/2,-z+1 #3 x-1/2,-y+3/2,z-1/2 #4 -x+1/2,-y+1/2,-z+1

#5 x-1/2,-y+1/2,z-1/2 #6 x+1/2,y+1/2,z #7 x-1/2,y+1/2,z #8 x+1/2,-y+1/2,z+1/2

#9 -x+1,y,-z+3/2 #10 -x+1,-y+1,-z+1 #11 x+1/2,y-1/2,z #12 x-1/2,y-1/2,z

#13 x,-y+1,z+1/2 #14 -x,-y+1,-z+1 #15 x,-y+1,z-1/2

Table S2b. Selected bond distances (Å) and bond angles (deg.) for $Cs_2MoP_2O_9$.

Cs(1)-O(1)#1	3.062(5)	O(8)#2-Cs(1)-O(9)#3	111.82(11)
Cs(1)-O(7)#2	3.131(5)	O(7)-Cs(1)-O(9)#3	115.78(11)
Cs(1)-O(2)#3	3.180(6)	O(9)-Cs(1)-O(9)#3	91.00(11)
Cs(1)-O(2)#2	3.235(5)	O(2)-Cs(1)-O(9)#3	46.09(11)
Cs(1)-O(8)#2	3.242(5)	O(1)#1-Cs(1)-O(3)	70.07(13)
Cs(1)-O(7)	3.257(5)	O(7)#2-Cs(1)-O(3)	99.18(13)
Cs(1)-O(9)	3.301(5)	O(2)#3-Cs(1)-O(3)	49.70(13)
Cs(1)-O(2)	3.358(5)	O(2)#2-Cs(1)-O(3)	134.95(12)
Cs(1)-O(9)#3	3.385(5)	O(8)#2-Cs(1)-O(3)	125.83(13)
Cs(1)-O(3)	3.391(5)	O(7)-Cs(1)-O(3)	68.97(12)
Cs(1)-O(1)	3.391(6)	O(9)-Cs(1)-O(3)	48.78(11)
Cs(1)-P(2)#2	3.732(3)	O(2)-Cs(1)-O(3)	119.17(12)
Cs(2)-O(6)#4	2.976(5)	O(9)#3-Cs(1)-O(3)	121.24(12)
Cs(2)-O(4)	3.049(5)	O(1)#1-Cs(1)-O(1)	115.50(7)
Cs(2)-O(7)#2	3.069(5)	O(7)#2-Cs(1)-O(1)	95.45(13)
Cs(2)-O(6)#5	3.152(5)	O(2)#3-Cs(1)-O(1)	119.80(13)
Cs(2)-O(6)	3.270(5)	O(2)#2-Cs(1)-O(1)	53.56(12)
Cs(2)-O(5)#5	3.389(5)	O(8)#2-Cs(1)-O(1)	63.04(13)
Cs(2)-O(8)#6	3.672(5)	O(7)-Cs(1)-O(1)	103.46(12)
Cs(2)-P(1)	3.707(3)	O(9)-Cs(1)-O(1)	116.32(12)
Cs(2)-P(1)#5	3.796(3)	O(2)-Cs(1)-O(1)	45.73(12)
Cs(2)-P(1)#4	3.994(3)	O(9)#3-Cs(1)-O(1)	48.85(12)
Cs(2)-P(2)#6	4.181(3)	O(3)-Cs(1)-O(1)	164.71(11)
Cs(2)-Cs(2)#7	4.556(3)	O(6)#4-Cs(2)-O(4)	122.18(13)
Mo(1)-O(1)	1.684(5)	O(6)#4-Cs(2)-O(7)#2	134.70(14)
Mo(1)-O(2)	1.701(5)	O(4)-Cs(2)-O(7)#2	82.49(15)
Mo(1)-O(8)#8	1.994(4)	O(6)#4-Cs(2)-O(6)#5	109.57(14)
Mo(1)-O(9)#3	2.039(4)	O(4)-Cs(2)-O(6)#5	122.01(13)
Mo(1)-O(4)#9	2.133(5)	O(7)#2-Cs(2)-O(6)#5	78.72(13)
Mo(1)-O(3)#3	2.176(5)	O(6)#4-Cs(2)-O(6)	121.07(7)
Mo(1)-Cs(1)#3	4.050(3)	O(4)-Cs(2)-O(6)	46.28(13)
Mo(1)-Cs(1)#9	4.440(3)	O(7)#2-Cs(2)-O(6)	103.56(13)
P(1)-O(6)	1.472(5)	O(6)#5-Cs(2)-O(6)	86.30(13)
P(1)-O(3)	1.513(5)	O(6)#4-Cs(2)-O(5)#5	88.81(14)
P(1)-O(4)	1.520(5)	O(4)-Cs(2)-O(5)#5	109.23(12)
P(1)-O(5)	1.643(5)	O(7)#2-Cs(2)-O(5)#5	120.54(13)
P(1)-Cs(2)#7	3.796(3)	O(6)#5-Cs(2)-O(5)#5	44.87(12)
P(1)-Cs(2)#10	3.994(3)	O(6)-Cs(2)-O(5)#5	63.01(12)
P(2)-O(7)	1.469(5)	O(6)#4-Cs(2)-O(8)#6	93.07(13)

P(2)-O(9)	1.537(5)	O(4)-Cs(2)-O(8)#6	48.44(11)
P(2)-O(8)	1.554(4)	O(7)#2-Cs(2)-O(8)#6	75.53(13)
P(2)-O(5)#11	1.593(5)	O(6)#5-Cs(2)-O(8)#6	153.52(11)
P(2)-Cs(1)#12	3.732(3)	O(6)-Cs(2)-O(8)#6	93.76(11)
P(2)-Cs(2)#13	4.181(3)	O(5)#5-Cs(2)-O(8)#6	153.37(11)
O(1)-Cs(1)#9	3.062(5)	O(1)-Mo(1)-O(2)	101.6(3)
O(2)-Cs(1)#3	3.180(6)	O(1)-Mo(1)-O(8)#8	95.4(2)
O(2)-Cs(1)#12	3.235(5)	O(2)-Mo(1)-O(8)#8	99.4(2)
O(3)-Mo(1)#3	2.176(5)	O(1)-Mo(1)-O(9)#3	97.2(2)
O(4)-Mo(1)#1	2.133(5)	O(2)-Mo(1)-O(9)#3	89.3(2)
O(5)-P(2)#14	1.593(5)	O(8)#8-Mo(1)-O(9)#3	162.98(19)
O(5)-Cs(2)#7	3.389(5)	O(1)-Mo(1)-O(4)#9	88.2(2)
O(6)-Cs(2)#10	2.976(5)	O(2)-Mo(1)-O(4)#9	168.3(2)
O(6)-Cs(2)#7	3.152(5)	O(8)#8-Mo(1)-O(4)#9	85.96(18)
O(7)-Cs(2)#12	3.069(5)	O(9)#3-Mo(1)-O(4)#9	82.97(18)
O(7)-Cs(1)#12	3.131(5)	O(1)-Mo(1)-O(3)#3	168.2(2)
O(8)-Mo(1)#15	1.994(4)	O(2)-Mo(1)-O(3)#3	90.2(2)
O(8)-Cs(1)#12	3.242(5)	O(8)#8-Mo(1)-O(3)#3	83.49(19)
O(8)-Cs(2)#13	3.672(5)	O(9)#3-Mo(1)-O(3)#3	81.89(19)
O(9)-Mo(1)#3	2.039(4)	O(4)#9-Mo(1)-O(3)#3	80.0(2)
O(9)-Cs(1)#3	3.385(5)	O(6)-P(1)-O(3)	115.8(3)
O(1)#1-Cs(1)-O(7)#2	86.51(14)	O(6)-P(1)-O(4)	112.7(3)
O(1)#1-Cs(1)-O(2)#3	57.18(13)	O(3)-P(1)-O(4)	112.0(3)
O(7)#2-Cs(1)-O(2)#3	136.81(12)	O(6)-P(1)-O(5)	106.9(3)
O(1)#1-Cs(1)-O(2)#2	64.97(13)	O(3)-P(1)-O(5)	104.5(3)
O(7)#2-Cs(1)-O(2)#2	75.86(14)	O(4)-P(1)-O(5)	103.5(3)
O(2)#3-Cs(1)-O(2)#2	104.29(9)	O(7)-P(2)-O(9)	114.7(3)
O(1)#1-Cs(1)-O(8)#2	129.10(12)	O(7)-P(2)-O(8)	111.7(3)
O(7)#2-Cs(1)-O(8)#2	46.20(12)	O(9)-P(2)-O(8)	107.2(3)
O(2)#3-Cs(1)-O(8)#2	172.41(11)	O(7)-P(2)-O(5)#11	110.5(3)
O(2)#2-Cs(1)-O(8)#2	83.08(12)	O(9)-P(2)-O(5)#11	106.9(3)
O(1)#1-Cs(1)-O(7)	138.91(13)	O(8)-P(2)-O(5)#11	105.4(3)
O(7)#2-Cs(1)-O(7)	102.87(14)	O(7)#2-Cs(1)-O(2)	134.55(13)
O(2)#3-Cs(1)-O(7)	92.91(12)	O(2)#3-Cs(1)-O(2)	88.46(13)
O(2)#2-Cs(1)-O(7)	156.08(12)	O(2)#2-Cs(1)-O(2)	91.17(13)
O(8)#2-Cs(1)-O(7)	79.50(11)	O(8)#2-Cs(1)-O(2)	89.58(12)
O(1)#1-Cs(1)-O(9)	102.35(13)	O(7)-Cs(1)-O(2)	72.53(13)
O(7)#2-Cs(1)-O(9)	137.74(13)	O(9)-Cs(1)-O(2)	70.60(12)
O(2)#3-Cs(1)-O(9)	48.02(11)	O(1)#1-Cs(1)-O(9)#3	83.33(12)
O(2)#2-Cs(1)-O(9)	145.31(12)	O(7)#2-Cs(1)-O(9)#3	131.23(12)
O(8)#2-Cs(1)-O(9)	124.49(11)	O(2)#3-Cs(1)-O(9)#3	71.70(12)

O(7)-Cs(1)-O(9)	45.40(12)	O(2)#2-Cs(1)-O(9)#3	56.64(12)
O(1)#1-Cs(1)-O(2)	127.34(13)		

Symmetry transformations used to generate equivalent atoms:

#1 x-1/2,-y+3/2,-z+1 #2 -x+1/2,y+1/2,z #3 -x,-y+1,-z+1 #4 -x,y+1/2,-z+1/2

#5 x+1/2,y,-z+1/2 #6 x,y+1,z #7 x-1/2,y,-z+1/2 #8 x+1/2,-y+1/2,-z+1

#9 x+1/2,-y+3/2,-z+1 #10 -x,y-1/2,-z+1/2 #11 -x-1/2,y-1/2,z

#12 -x+1/2,y-1/2,z #13 x,y-1,z #14 -x-1/2,y+1/2,z #15 x-1/2,-y+1/2,-z+1

Table S2c. Selected bond distances (Å) and bond angles (deg.) for $Rb_6Mo_2P_4O_{19}$

Mo(1)-Rb(2)#1	3.9994(9)	O(1)#1-Rb(2)-O(2)#4	163.85(14)
Mo(1)-Rb(3)	4.2920(10)	O(1)#5-Rb(2)-O(2)#4	83.65(15)
Mo(1)-Rb(1)#2	3.8408(10)	O(2)-Rb(2)-O(6)#5	79.96(16)
Mo(1)-Rb(1)#1	3.9097(10)	O(2)-Rb(2)-O(10)#1	92.24(14)
Mo(1)-Rb(1)#3	4.1732(10)	O(2)-Rb(2)-O(3)#4	81.12(16)
Mo(1)-P(1)	2.8001(19)	O(2)-Rb(2)-O(3)#5	112.78(15)
Mo(1)-O(5)	2.228(5)	O(2)-Rb(2)-O(9)#1	130.45(18)
Mo(1)-O(6)	2.247(5)	O(2)-Rb(2)-O(1)#5	150.67(17)
Mo(1)-O(10)	2.023(5)	O(2)-Rb(2)-O(1)#1	82.65(15)
Mo(1)-O(9)	1.712(5)	O(2)-Rb(2)-O(2)#4	112.37(13)
Mo(1)-O(7)	1.8568(6)	O(5)#6-Rb(3)-O(5)#7	116.32(12)
Mo(1)-O(8)	1.694(6)	O(5)#6-Rb(3)-O(4)#7	73.73(13)
Rb(2)-P(2)#4	3.676(2)	O(5)#7-Rb(3)-O(4)#7	48.84(12)
Rb(2)-P(2)#5	3.750(2)	O(5)#6-Rb(3)-O(4)#8	168.37(14)
Rb(2)-P(1)#5	3.6604(19)	O(5)#7-Rb(3)-O(6)#8	110.12(12)
Rb(2)-O(6)#5	3.132(5)	O(5)#6-Rb(3)-O(6)#8	128.53(12)
Rb(2)-O(10)#1	3.212(6)	O(5)#6-Rb(3)-O(2)#6	78.15(13)
Rb(2)-O(3)#4	3.114(5)	O(4)#8-Rb(3)-O(5)#7	74.33(13)
Rb(2)-O(3)#5	3.270(5)	O(4)#8-Rb(3)-O(4)#7	117.90(13)
Rb(2)-O(9)#1	2.962(5)	O(4)#8-Rb(3)-O(6)#8	45.07(12)
Rb(2)-O(1)#1	3.132(6)	O(4)#7-Rb(3)-O(6)#8	129.26(13)
Rb(2)-O(1)#5	2.985(6)	O(4)#8-Rb(3)-O(2)#6	90.22(14)
Rb(2)-O(2)#4	3.323(6)	O(9)-Rb(3)-O(5)#6	86.08(15)
Rb(2)-O(2)	2.865(5)	O(9)-Rb(3)-O(5)#7	78.08(14)
Rb(3)-P(2)#6	3.7298(19)	O(9)-Rb(3)-O(4)#7	97.72(14)
Rb(3)-P(1)#7	3.6128(18)	O(9)-Rb(3)-O(4)#8	91.98(16)
Rb(3)-P(1)#6	3.941(2)	O(9)-Rb(3)-O(6)#8	125.21(14)
Rb(3)-P(1)#8	3.756(2)	O(9)-Rb(3)-O(2)#6	79.17(15)
Rb(3)-O(5)#6	2.944(5)	O(9)-Rb(3)-O(8)#9	163.67(15)
Rb(3)-O(5)#7	3.077(5)	O(2)#6-Rb(3)-O(5)#7	151.90(14)
Rb(3)-O(4)#7	3.139(5)	O(2)#6-Rb(3)-O(4)#7	151.86(14)
Rb(3)-O(4)#8	2.967(5)	O(2)#6-Rb(3)-O(6)#8	70.83(13)
Rb(3)-O(6)#8	3.570(5)	O(8)#9-Rb(3)-O(5)#6	87.02(15)
Rb(3)-O(9)	2.925(5)	O(8)#9-Rb(3)-O(5)#7	91.81(14)
Rb(3)-O(2)#6	3.048(6)	O(8)#9-Rb(3)-O(4)#7	66.12(15)
Rb(3)-O(8)#9	2.930(6)	O(8)#9-Rb(3)-O(4)#8	97.65(16)
Rb(1)-Mo(1)#2	3.8408(10)	O(8)#9-Rb(3)-O(6)#8	70.20(14)
Rb(1)-Mo(1)#1	3.9097(10)	O(8)#9-Rb(3)-O(2)#6	113.78(16)
Rb(1)-P(2)#1	3.835(2)	O(4)#4-Rb(1)-O(6)#2	147.54(15)

Rb(1)-O(4)#4	2.769(5)	O(4)#4-Rb(1)-O(10)#1	97.94(15)
Rb(1)-O(6)#2	2.890(5)	O(4)#4-Rb(1)-O(9)#2	91.83(15)
Rb(1)-O(10)#1	2.954(5)	O(4)#4-Rb(1)-O(7)#10	104.50(11)
Rb(1)-O(9)#2	3.121(6)	O(4)#4-Rb(1)-O(2)#1	139.41(14)
Rb(1)-O(1)	2.759(6)	O(4)#4-Rb(1)-O(8)#1	69.67(16)
Rb(1)-O(7)#10	3.5547(8)	O(4)#4-Rb(1)-O(8)#10	100.75(15)
Rb(1)-O(2)#1	3.547(6)	O(6)#2-Rb(1)-O(10)#1	114.12(14)
Rb(1)-O(8)#10	3.301(6)	O(6)#2-Rb(1)-O(9)#2	56.84(14)
Rb(1)-O(8)#1	3.024(6)	O(6)#2-Rb(1)-O(7)#10	49.25(10)
P(2)-Rb(2)#1	3.774(2)	O(6)#2-Rb(1)-O(2)#1	72.86(13)
P(2)-Rb(2)#11	3.7499(19)	O(6)#2-Rb(1)-O(8)#1	125.08(15)
P(2)-Rb(2)#12	3.676(2)	O(6)#2-Rb(1)-O(8)#10	74.79(14)
P(2)-Rb(3)#13	3.7298(19)	O(10)#1-Rb(1)-O(9)#2	168.88(14)
P(2)-Rb(1)#1	3.835(2)	O(10)#1-Rb(1)-O(7)#10	133.81(11)
P(2)-O(10)	1.553(5)	O(10)#1-Rb(1)-O(2)#1	43.75(13)
P(2)-O(3)	1.647(5)	O(10)#1-Rb(1)-O(8)#1	54.23(14)
P(2)-O(1)	1.477(6)	O(10)#1-Rb(1)-O(8)#10	91.03(14)
P(2)-O(2)	1.483(5)	O(9)#2-Rb(1)-O(7)#10	47.18(9)
P(1)-Rb(2)#11	3.6604(19)	O(9)#2-Rb(1)-O(2)#1	125.38(13)
P(1)-Rb(3)#7	3.6128(18)	O(9)#2-Rb(1)-O(8)#10	92.36(13)
P(1)-Rb(3)#14	3.756(2)	O(1)-Rb(1)-O(4)#4	99.47(17)
P(1)-O(5)	1.535(5)	O(1)-Rb(1)-O(6)#2	82.85(16)
P(1)-O(4)	1.480(5)	O(1)-Rb(1)-O(10)#1	95.86(15)
P(1)-O(6)	1.537(5)	O(1)-Rb(1)-O(9)#2	77.21(15)
P(1)-O(3)	1.612(5)	O(1)-Rb(1)-O(7)#10	118.95(12)
O(5)-Rb(3)#7	3.077(5)	O(1)-Rb(1)-O(2)#1	76.79(15)
O(5)-Rb(3)#13	2.944(5)	O(1)-Rb(1)-O(8)#1	144.03(17)
O(4)-Rb(3)#7	3.139(5)	O(1)-Rb(1)-O(8)#10	157.50(17)
O(4)-Rb(3)#14	2.967(5)	O(2)#1-Rb(1)-O(7)#10	112.64(10)
O(4)-Rb(1)#12	2.769(5)	O(8)#1-Rb(1)-O(9)#2	135.26(14)
O(6)-Rb(2)#11	3.132(5)	O(8)#10-Rb(1)-O(7)#10	45.66(10)
O(6)-Rb(3)#14	3.570(5)	O(8)#1-Rb(1)-O(7)#10	97.01(11)
O(6)-Rb(1)#2	2.890(5)	O(8)#10-Rb(1)-O(2)#1	93.93(14)
O(10)-Rb(2)#1	3.212(6)	O(8)#1-Rb(1)-O(2)#1	89.63(14)
O(10)-Rb(1)#1	2.954(5)	O(8)#1-Rb(1)-O(8)#10	54.48(19)
O(3)-Rb(2)#12	3.114(5)	O(10)-P(2)-O(3)	104.7(3)
O(3)-Rb(2)#11	3.270(5)	O(1)-P(2)-O(10)	110.4(3)
O(9)-Rb(2)#1	2.962(5)	O(1)-P(2)-O(3)	106.0(3)
O(9)-Rb(1)#2	3.121(6)	O(1)-P(2)-O(2)	119.3(4)
O(1)-Rb(2)#11	2.985(6)	O(2)-P(2)-O(10)	109.8(3)
O(1)-Rb(2)#1	3.132(6)	O(2)-P(2)-O(3)	105.6(3)

O(7)-Mo(1)#7	1.8568(6)	O(9)#1-Rb(2)-O(6)#5	144.80(15)
O(7)-Rb(1)#3	3.5547(8)	O(9)#1-Rb(2)-O(10)#1	52.85(13)
O(7)-Rb(1)#2	3.5547(8)	O(9)#1-Rb(2)-O(3)#4	70.30(14)
O(2)-Rb(2)#12	3.323(6)	O(9)#1-Rb(2)-O(3)#5	115.73(14)
O(2)-Rb(3)#13	3.048(6)	O(9)#1-Rb(2)-O(1)#5	76.44(16)
O(2)-Rb(1)#1	3.547(6)	O(9)#1-Rb(2)-O(1)#1	91.54(14)
O(8)-Rb(3)#15	2.930(6)	O(9)#1-Rb(2)-O(2)#4	74.34(15)
O(8)-Rb(1)#1	3.024(6)	O(1)#5-Rb(2)-O(6)#5	70.95(14)
O(8)-Rb(1)#3	3.301(6)	O(1)#1-Rb(2)-O(6)#5	73.29(13)
O(5)-Mo(1)-O(6)	65.32(17)	O(1)#5-Rb(2)-O(10)#1	98.67(14)
O(10)-Mo(1)-O(5)	79.6(2)	O(1)#1-Rb(2)-O(10)#1	46.18(13)
O(10)-Mo(1)-O(6)	80.53(19)	O(1)#5-Rb(2)-O(3)#4	124.44(15)
O(9)-Mo(1)-O(5)	157.0(2)	O(1)#5-Rb(2)-O(3)#5	46.78(13)
O(9)-Mo(1)-O(6)	91.8(2)	O(1)#1-Rb(2)-O(3)#5	108.16(13)
O(9)-Mo(1)-O(10)	94.7(2)	O(1)#5-Rb(2)-O(1)#1	85.47(17)
O(9)-Mo(1)-O(7)	98.27(19)	O(5)-P(1)-O(6)	103.7(3)
O(7)-Mo(1)-O(5)	82.40(13)	O(5)-P(1)-O(3)	105.2(3)
O(7)-Mo(1)-O(6)	83.65(13)	O(4)-P(1)-O(5)	117.0(3)
O(7)-Mo(1)-O(10)	159.77(14)	O(4)-P(1)-O(6)	116.5(3)
O(8)-Mo(1)-O(5)	97.0(2)	O(4)-P(1)-O(3)	108.9(3)
O(8)-Mo(1)-O(6)	162.1(2)	O(6)-P(1)-O(3)	104.3(3)
O(8)-Mo(1)-O(10)	93.9(2)	O(3)#4-Rb(2)-O(6)#5	140.87(13)
O(8)-Mo(1)-O(9)	105.6(3)	O(3)#4-Rb(2)-O(10)#1	95.19(13)
O(8)-Mo(1)-O(7)	97.4(2)	O(3)#4-Rb(2)-O(3)#5	114.72(9)
O(6)#5-Rb(2)-O(10)#1	119.44(13)	O(3)#4-Rb(2)-O(1)#1	137.12(14)
O(6)#5-Rb(2)-O(3)#5	45.66(12)	O(3)#4-Rb(2)-O(2)#4	45.46(13)
O(6)#5-Rb(2)-O(2)#4	113.96(13)	O(3)#5-Rb(2)-O(2)#4	72.37(13)
O(10)#1-Rb(2)-O(3)#5	142.92(12)	O(10)#1-Rb(2)-O(2)#4	124.15(14)

Symmetry transformations used to generate equivalent atoms:

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

#8 -x,y+1/2,-z+1/2 #9 x+2,y-1,z #10+0 #11 1 #12 x+1,y-1,z+1

#13 -x,y+3/2,-z+3/2 #14 -x,y+1/2,-z+3/2 #15 x+2,y,z

Table S2d. Selected bond distances (Å) and bond angles (deg) for $Cs_6Mo_2P_4O_{19}$.

Cs(1)-P(1)	3.8234(11)	O(7)-Mo(1)-O(2)#1	161.16(8)
Cs(1)-P(2)	3.8338(12)	O(7)-Mo(1)-O(3)#7	84.03(7)
Cs(1)-P(2)#1	3.9127(12)	O(7)-Mo(1)-O(9)#7	83.44(7)
Cs(1)-O(2)#1	3.354(3)	O(9)#7-Mo(1)-O(3)#7	65.59(10)
Cs(1)-O(3)	3.311(3)	O(1)-P(1)-O(3)	116.52(17)
Cs(1)-O(4)	3.122(3)	O(1)-P(1)-O(5)	108.51(17)
Cs(1)-O(5)	3.454(3)	O(1)-P(1)-O(9)	116.82(17)
Cs(1)-O(5)#2	3.248(3)	O(3)-P(1)-O(5)	105.33(16)
Cs(1)-O(8)#2	3.061(3)	O(9)-P(1)-O(3)	103.22(16)
Cs(1)-O(8)	3.491(3)	O(9)-P(1)-O(5)	105.34(15)
Cs(1)-O(10)#3	3.142(3)	O(2)-P(2)-O(5)#2	103.88(15)
Cs(1)-O(10)#1	3.267(3)	O(8)-P(2)-O(2)	110.17(19)
Cs(2)-Mo(1)#3	4.0984(5)	O(8)-P(2)-O(5)#2	105.55(17)
Cs(2)-Mo(1)#2	4.0235(5)	O(8)-P(2)-O(10)	118.82(19)
Cs(2)-P(2)#4	3.9436(12)	O(10)-P(2)-O(2)	110.70(19)
Cs(2)-O(1)	2.957(3)	O(10)-P(2)-O(5)#2	106.46(18)
Cs(2)-O(2)#4	3.120(3)	O(1)#5-Cs(3)-O(1)#10	116.55(7)
Cs(2)-O(3)#5	3.081(3)	O(1)#5-Cs(3)-O(3)#5	42.94(7)
Cs(2)-O(4)#2	3.300(3)	O(1)#10-Cs(3)-O(3)#5	129.02(7)
Cs(2)-O(6)#6	3.393(3)	O(1)#5-Cs(3)-O(5)#11	128.46(7)
Cs(2)-O(6)#3	3.166(3)	O(1)#10-Cs(3)-O(5)#11	111.59(7)
Cs(2)-O(7)#2	3.7254(4)	O(1)#5-Cs(3)-O(8)#4	92.71(8)
Cs(2)-O(8)#4	3.600(3)	O(1)#5-Cs(3)-O(9)#10	75.52(7)
Cs(2)-O(10)	2.943(3)	O(3)#5-Cs(3)-O(5)#11	112.99(6)
Mo(1)-P(1)#7	2.7955(12)	O(4)#4-Cs(3)-O(1)#5	94.06(8)
Mo(1)-Cs(3)#8	4.4425(8)	O(4)#4-Cs(3)-O(1)#10	93.71(8)
Mo(1)-O(2)#1	2.029(3)	O(4)#4-Cs(3)-O(3)#5	127.01(7)
Mo(1)-O(3)#7	2.232(3)	O(4)#4-Cs(3)-O(5)#11	65.02(7)
Mo(1)-O(4)	1.716(3)	O(4)#4-Cs(3)-O(8)#4	82.24(8)
Mo(1)-O(6)	1.700(3)	O(4)#4-Cs(3)-O(9)#10	74.41(8)
Mo(1)-O(7)	1.8697(3)	O(6)#6-Cs(3)-O(1)#10	69.95(8)
Mo(1)-O(9)#7	2.231(3)	O(6)#6-Cs(3)-O(1)#5	95.14(8)
P(1)-Cs(3)#1	3.9396(11)	O(6)#6-Cs(3)-O(3)#5	68.03(7)
P(1)-Cs(3)#9	4.0978(11)	O(6)#6-Cs(3)-O(4)#4	163.54(8)
P(1)-Cs(3)#10	3.7533(12)	O(6)#6-Cs(3)-O(5)#11	118.19(7)
P(1)-O(1)	1.482(3)	O(6)#6-Cs(3)-O(8)#4	110.88(9)
P(1)-O(3)	1.543(3)	O(6)#6-Cs(3)-O(9)#10	94.75(8)
P(1)-O(5)	1.613(3)	O(6)#6-Cs(3)-O(9)#11	87.77(8)
P(1)-O(9)	1.541(3)	O(8)#4-Cs(3)-O(1)#10	150.71(8)

P(2)-Cs(3)#4	3.8743(12)	O(8)#4-Cs(3)-O(3)#5	73.23(7)
P(2)-O(2)	1.555(3)	O(8)#4-Cs(3)-O(5)#11	40.73(7)
P(2)-O(5)#2	1.657(3)	O(8)#4-Cs(3)-O(9)#10	152.80(8)
P(2)-O(8)	1.478(3)	O(9)#10-Cs(3)-O(1)#10	46.94(7)
P(2)-O(10)	1.484(3)	O(9)#11-Cs(3)-O(1)#10	75.93(7)
Cs(3)-O(1)#5	3.145(3)	O(9)#11-Cs(3)-O(1)#5	167.44(8)
Cs(3)-O(1)#10	3.234(3)	O(9)#10-Cs(3)-O(3)#5	110.18(6)
Cs(3)-O(3)#5	3.727(3)	O(9)#11-Cs(3)-O(3)#5	128.77(7)
Cs(3)-O(4)#4	3.114(3)	O(9)#11-Cs(3)-O(4)#4	86.19(8)
Cs(3)-O(5)#11	3.809(3)	O(9)#11-Cs(3)-O(5)#11	40.97(6)
Cs(3)-O(6)#6	3.085(3)	O(9)#10-Cs(3)-O(5)#11	132.86(6)
Cs(3)-O(8)#4	3.147(3)	O(9)#11-Cs(3)-O(8)#4	74.86(7)
Cs(3)-O(9)#10	3.233(3)	O(9)#11-Cs(3)-O(9)#10	116.49(6)
Cs(3)-O(9)#11	3.114(3)	O(1)-Cs(2)-O(2)#4	97.03(8)
O(2)#1-Cs(1)-O(5)	138.92(7)	O(1)-Cs(2)-O(3)#5	146.75(8)
O(2)#1-Cs(1)-O(8)	123.69(7)	O(1)-Cs(2)-O(4)#2	93.95(8)
O(3)-Cs(1)-O(2)#1	118.96(7)	O(1)-Cs(2)-O(6)#3	72.50(9)
O(3)-Cs(1)-O(5)	43.48(7)	O(1)-Cs(2)-O(6)#6	101.62(8)
O(3)-Cs(1)-O(8)	113.90(7)	O(1)-Cs(2)-O(7)#2	106.26(6)
O(4)-Cs(1)-O(2)#1	49.82(7)	O(1)-Cs(2)-O(8)#4	137.29(7)
O(4)-Cs(1)-O(3)	141.68(8)	O(2)#4-Cs(2)-O(4)#2	168.70(8)
O(4)-Cs(1)-O(5)	115.59(8)	O(2)#4-Cs(2)-O(6)#3	50.94(8)
O(4)-Cs(1)-O(5)#2	72.47(8)	O(2)#4-Cs(2)-O(6)#6	91.62(7)
O(4)-Cs(1)-O(8)	76.81(8)	O(2)#4-Cs(2)-O(7)#2	132.86(6)
O(4)-Cs(1)-O(10)#1	86.96(8)	O(2)#4-Cs(2)-O(8)#4	42.71(7)
O(4)-Cs(1)-O(10)#3	77.07(8)	O(3)#5-Cs(2)-O(2)#4	115.62(8)
O(5)#2-Cs(1)-O(2)#1	97.08(7)	O(3)#5-Cs(2)-O(4)#2	53.85(7)
O(5)#2-Cs(1)-O(3)	141.24(7)	O(3)#5-Cs(2)-O(6)#6	72.74(8)
O(5)#2-Cs(1)-O(5)	115.60(5)	O(3)#5-Cs(2)-O(6)#3	122.99(8)
O(5)#2-Cs(1)-O(8)	43.34(7)	O(3)#5-Cs(2)-O(7)#2	46.63(5)
O(5)-Cs(1)-O(8)	74.80(7)	O(3)#5-Cs(2)-O(8)#4	75.84(7)
O(5)#2-Cs(1)-O(10)#1	137.83(7)	O(4)#2-Cs(2)-O(6)#6	88.76(7)
O(8)#2-Cs(1)-O(2)#1	93.17(7)	O(4)#2-Cs(2)-O(7)#2	44.99(5)
O(8)#2-Cs(1)-O(3)	80.61(8)	O(4)#2-Cs(2)-O(8)#4	126.01(7)
O(8)#2-Cs(1)-O(4)	130.78(8)	O(6)#3-Cs(2)-O(4)#2	136.19(8)
O(8)#2-Cs(1)-O(5)#2	83.86(8)	O(6)#3-Cs(2)-O(6)#6	55.55(10)
O(8)#2-Cs(1)-O(5)	113.51(8)	O(6)#3-Cs(2)-O(7)#2	97.93(6)
O(8)#2-Cs(1)-O(8)	113.61(7)	O(6)#6-Cs(2)-O(7)#2	44.28(5)
O(8)#2-Cs(1)-O(10)#3	147.69(9)	O(6)#3-Cs(2)-O(8)#4	85.18(7)
O(8)#2-Cs(1)-O(10)#1	82.62(8)	O(6)#6-Cs(2)-O(8)#4	94.41(7)
O(10)#1-Cs(1)-O(2)#1	44.34(7)	O(8)#4-Cs(2)-O(7)#2	112.67(5)

O(10)#3-Cs(1)-O(2)#1	96.73(7)	O(10)-Cs(2)-O(1)	98.99(9)
O(10)#3-Cs(1)-O(3)	67.68(7)	O(10)-Cs(2)-O(2)#4	98.44(8)
O(10)#1-Cs(1)-O(3)	74.75(7)	O(10)-Cs(2)-O(3)#5	83.01(8)
O(10)#3-Cs(1)-O(5)#2	124.98(8)	O(10)-Cs(2)-O(4)#2	77.14(8)
O(10)#3-Cs(1)-O(5)	44.58(7)	O(10)-Cs(2)-O(6)#3	144.91(9)
O(10)#1-Cs(1)-O(5)	106.43(7)	O(10)-Cs(2)-O(6)#6	155.74(9)
O(10)#1-Cs(1)-O(8)	162.14(8)	O(10)-Cs(2)-O(7)#2	117.01(6)
O(10)#3-Cs(1)-O(8)	85.90(8)	O(10)-Cs(2)-O(8)#4	78.73(8)
O(10)#3-Cs(1)-O(10)#1	83.23(9)	O(2)#1-Mo(1)-O(3)#7	80.68(11)
O(6)-Mo(1)-O(2)#1	92.53(14)	O(2)#1-Mo(1)-O(9)#7	80.26(11)
O(6)-Mo(1)-O(3)#7	159.96(13)	O(4)-Mo(1)-O(2)#1	93.46(14)
O(6)-Mo(1)-O(4)	105.80(16)	O(4)-Mo(1)-O(3)#7	93.47(13)
O(6)-Mo(1)-O(7)	98.21(11)	O(4)-Mo(1)-O(7)	98.41(11)
O(6)-Mo(1)-O(9)#7	94.77(14)	O(4)-Mo(1)-O(9)#7	158.78(13)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z+1/2 #2 -x+1,y+1/2,-z+3/2 #3 -x+1,y-1/2,-z+3/2 #4 -x+1,-y,-z+1

#5 x,-y+1/2,z-1/2 #6 x+1,-y+1/2,z-1/2 #7 -x+1,-y,-z+2 #8 x-1,-y+1/2,z+1/2

#9 x,-y-1/2,z+1/2 #10 -x+2,-y,-z+1 #11 x,-y-1/2,z-1/2 #12 -x,-y,-z+2

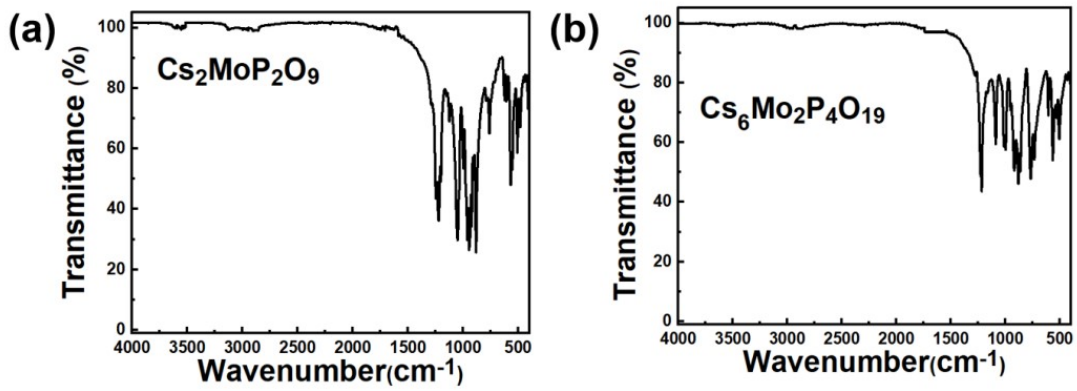

Figure S1. IR spectra of $Cs_2MoP_2O_9$ and $Cs_6Mo_2P_4O_{19}$

Table S3. Assignment of the absorption bands observed in the IR spectra for $Cs_2MoP_2O_9$ and $Cs_6Mo_2P_4O_{19}$.

Assignment	$Cs_2MoP_2O_9$	$Cs_6Mo_2P_4O_{19}$
ν_{as} (O-P-O)	1247, 1219	1219
ν_{s} (O-P-O)	1125,1049	1087, 1016
ν_{as} (P-O-P)	1002, 964, 945	997, 917
ν_{s} (P-O-P)	761, 624, 605	770, 737
δ_{as} (O-P-O)	605, 567	605, 563, 525
δ_{s} (O-P-O)	506, 482	506, 435
Mo−O vibration	879	883

Table S4. The anhydrous compounds of A-Mo-P-O (A:Rb, Cs) system, space group, Mo-P-O framework configuration, P-O framework configuration and A/P ratio.

Serial number	compounds	Space group (No.)	Mo-P-O framework	P-O framework	A/P (A = Cs, Rb)
1	$CsMo_4P_7O_{28}$[1]	*P*1 (2)	3d structure	P_3O_{10},P_2O_7	1:7 (0.14)
2	$Cs_4Mo_{10}P_{18}O_{66}$[2]	*P*1 (2)	3d structure	P_3O_{10},P_2O_7	2:9 (0.22)
3	$RbMoPO_6$[3]	*Fddd* (70)	3d structure	Isolated PO_4	1:4 (0.25)
4	$CsMo_8P_4O_{33}$[4]	$I\bar{4}2d$ (122)	3d structure	Isolated PO_4	1:4 (0.25)
5	$Rb_3Mo_{12}PO_{40}$[5]	$Pn\bar{3}m$ (224)	0 d structure	Isolated PO_4	1:4 (0.25)
6	$Cs_3(Mo_6P_{10}O_{38})$[6]	*P*1 (2)	3d structure	PO_4,P_2O_7 coexistence	3:10 (0.3)
7	$RbMo_2P_3O_{12}$[7]	*Pbcm* (57)	3d structure	PO_4,P_2O_7 coexistence	1:3 (0.33)
8	$Rb_4Mo_8P_{12}O_{52}$[8]	$P2_1$ (4)	3d structure	PO_4,P_2O_7 coexistence	1:3 (0.33)
9	$Cs_2Mo_4P_6O_{26}$[9]	*P*2/*c* (13)	1d chain	PO_4,P_2O_7 coexistence	1:3 (0.33)
10	$Cs_4Mo_8P_{12}O_{52}$[9]	$P2_1$ (4)	3d structure	PO_4,P_2O_7 coexistence	1:3 (0.33)
11	$Cs_3Mo_8P_8O_{43}$[10]	*C*2/*m* (12)	3d structure	Isolated PO_4	3:8 (0.38)
12	$Cs_4Mo_6P_{10}O_{38}$[11]	$P2_1/m$ (11)	3d structure	PO_4,P_2O_7 coexistence	2:5 (0.4)
13	$Cs_3(Mo_5P_7O_{24})$[12]	*P*31*c* (159)	3d structure	PO_4,P_2O_7 coexistence	3:7 (0.43)
14	$CsMoP_2O_7$[13]	$P2_1/c$ (14)	3d structure	Isolated P_2O_7	1:2 (0.5)
15	$Cs(MoO)(P_2O_7)$[14]	$P2_1/c$ (14)	3d structure	Isolated P_2O_7	1:2 (0.5)
16	$Cs(Mo_2P_2O_{10})$[15]	$P2_1/c$ (14)	3d structure	Isolated PO_4	1:2 (0.5)
17	$CsMo_2P_3O_{13}$[16]	*P*1 (2)	3d structure	PO_4,P_2O_7 coexistence	1:2 (0.5)
18	$Cs(Mo_2O_3(PO_4)_2)$[17]	$P2_1/c$ (14)	1d chain	Isolated PO_4	1:2 (0.5)
19	$Cs_3Mo_5P_6O_{25}$[18]	*P*31*c* (159)	3d structure	Isolated P_2O_7	1:2 (0.5)
20	$Cs_3(Mo_4P_4O_{22})$[19]	$P2_1/c$ (14)	3d structure	Isolated PO_4	3:4 (0.75)
21	$Rb_3Mo_4P_4O_{22}$[20]	$C222_1$ (20)	3d structure	Isolated PO_4	3:4 (0.75)
22	$Rb_3Mo_4P_4O_{22}$[21]	$P4_32_12$ (96)	3d structure	Isolated PO_4	3:4 (0.75)
23	$RbMo(P_2O_7)$[22]	$P2_1/c$ (14)	3d structure	Isolated P_2O_7	1:1 (1.0)
24	$Rb_2Mo_2P_2O_{11}$[23]	$P2_1/c$ (14)	3d structure	Isolated PO_4	1:1 (1.0)
25	$Cs(MoO_2(PO_4))$[24]	*Fddd* (70)	3d structure	Isolated PO_4	1:1 (1.0)
26	$Cs_3(Mo_4O_4)(PO_4)_3$[25]	$P\bar{4}3m$ (215)	3d structure	Isolated PO_4	1:1 (1.0)
27	$Rb_4Mo_5P_2O_{22}$[3]	$C222_1$ (20)	0 d structure	Isolated P_2O_7	2:1 (2.0)
28	$Cs_4Mo_5P_2O_{22}$[26]	$C222_1$	1d chain	Isolated PO_4	2:1 (2.0)
29	$Cs_3Mo_{12}PO_{40}$[27]	$Pn\bar{3}m$ (224)	0 d structure	Isolated PO_4	3:1 (3.0)

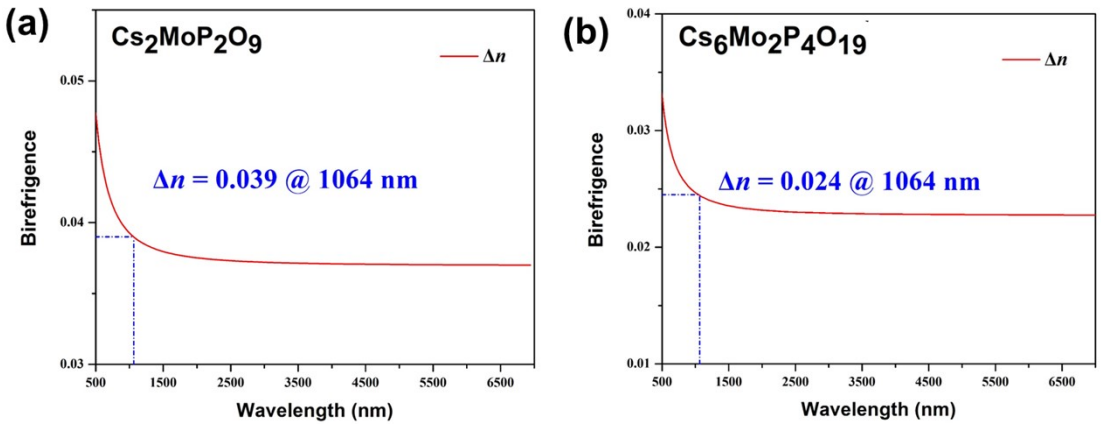

Figure S2. The calculated frequency-dependent birefringence of $Cs_2MoP_2O_9$ and $Cs_6Mo_2P_4O_{19}$.

Thermal behavior analysis

Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out with NETZSCH STA 449F3 simultaneous thermal analyzer instrument. The sample and reference (Al_2O_3) were enclosed in Pt crucibles, and heated from 40 to 900 ^oC at a heating rate of 5 ^oC/min under a nitrogen atmosphere.

As shown in Figure S3, there is only one big endothermic (exothermic) peak on the heating (cooling) curve at 626 ^oC (548 ^oC) for $Cs_2MoP_2O_9$, and 545 ^oC (432 ^oC) for $Cs_6Mo_2P_4O_{19}$, respectively. Remarkably, the XRD patterns for the residuals of $Cs_2MoP_2O_9$ after TG-DTA are distinct from that before melting. The decomposition products include $Cs_2MoP_2O_9$, $Cs_2Mo_4O_{13}$, $Cs_4P_2O_7$, $Mo_2P_2O_{11}$, $Cs_2Mo_5O_{16}$ and MoO_3 phase (PDF Card no. 39-0076, 53-0031, 38-0001, 15-0610, 28-0320 and 47-1320, respectively). For $Cs_6Mo_2P_4O_{19}$, XRD pattern after melting is consistent with before melting.

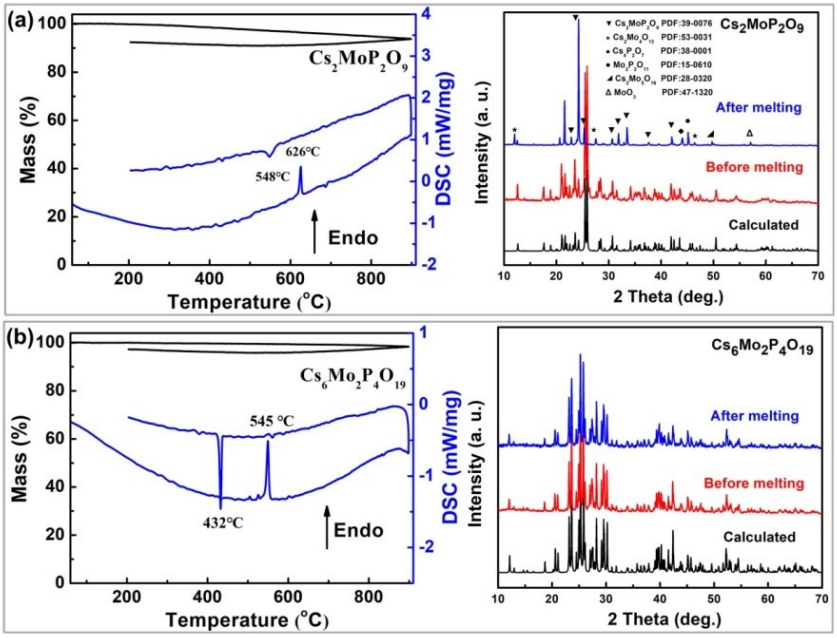

Figure S3 TGA - DSC curves and PXRD patterns of calculated, before melting and after melting for (a) $Cs_2MoP_2O_9$, (b) $Cs_6Mo_2P_4O_{19}$

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