Electronic supplementary information (ESI)

Syntheses and characterization of phosphonates and diphosphonates of molybdenum, $A_4[(MoO_3)_5(O_3PR)_2]\cdot xH_2O$, $A_2[Mo_2O_5(O_3PR)_2]$ and $A_2[Mo_2O_5(O_3P\text{-}R\text{-}PO_3)]$ (A = K, Rb, Cs, Tl, NH_4).

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Table S1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 8H_2O$(**1**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Rb(1)	7746(2)	1056(1)	4517(1)	63(1)
Rb(2)	2609(1)	1608(1)	6866(1)	36(1)
Mo(1)	276(1)	7629(1)	6711(1)	21(1)
Mo(2)	55(1)	9802(1)	6221(1)	21(1)
Mo(3)	0	1124(1)	7500	20(1)
P	8505(2)	9174(2)	7169(1)	18(1)
O(1)	0	7323(7)	7500	25(3)
O(2)	9141(6)	7203(6)	6180(4)	28(2)
O(3)	1207(6)	6853(6)	6677(4)	30(2)
O(4)	1664(5)	8344(5)	7465(4)	19(2)
O(5)	9262(6)	8934(5)	6770(4)	19(2)
O(6)	1607(6)	8589(5)	6218(4)	23(2)
O(7)	9469(6)	769(5)	6624(4)	24(2)
O(8)	1099(6)	337(6)	6072(4)	29(2)
O(9)	1047(6)	9954(5)	7361(4)	23(2)
O(10)	9077(7)	9816(6)	5498(4)	35(2)
O(11)	8992(6)	1838(6)	7512(4)	30(2)
O(12)	7602(9)	1718(8)	5785(6)	61(3)
O(13)	4080(9)	114(8)	6991(6)	68(4)
O(14)	6850(8)	1573(6)	3212(6)	56(3)
O(15)	6039(13)	9630(12)	4291(8)	97(5)
C(1)	6629(8)	8785(8)	6217(6)	27(3)
C(2)	6916(10)	8412(10)	5713(6)	34(3)
C(3)	6345(12)	7717(11)	5354(7)	47(4)
C(4)	5480(13)	7370(11)	5479(8)	53(4)
C(5)	5167(11)	7741(11)	5981(8)	50(4)
C(6)	5726(10)	8450(10)	6351(7)	41(3)
C(7)	7247(9)	9531(8)	6620(6)	23(2)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$(**2**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Cs(1)	8797(2)	7294(1)	6098(1)	49(1)
Cs(2)	2933(1)	1277(1)	7905(1)	36(1)
Cs(3)	4867(1)	7229(1)	9183(1)	43(1)
Cs(4)	0	0	0	63(1)
Cs(5)	7230(1)	4994(1)	4070(1)	107(1)
Mo(1)	6394(1)	847(1)	8938(1)	19(1)
Mo(2)	8996(1)	572(1)	7534(1)	21(1)
Mo(3)	9194(1)	3390(1)	6518(1)	25(1)
Mo(4)	6391(1)	5431(1)	6970(1)	24(1)
Mo(5)	4402(1)	3957(1)	8243(1)	21(1)
P(1)	7801(2)	3196(2)	8602(1)	19(1)
P(2)	6175(2)	2500(2)	6717(1)	20(1)
O(1)	5005(5)	2290(4)	8798(3)	22(1)
O(2)	5664(5)	9862(5)	8541(4)	29(1)
O(3)	6414(6)	353(5)	35(3)	29(1)
O(4)	7407(5)	2269(4)	9307(3)	23(1)
O(5)	6918(5)	1524(4)	7431(3)	23(1)
O(6)	8174(5)	189(4)	8642(3)	22(1)
O(7)	9182(5)	1711(5)	6512(3)	27(1)
O(8)	553(5)	186(5)	7919(4)	35(1)
O(9)	8810(5)	2582(4)	7954(3)	23(1)
O(10)	8876(6)	9382(5)	7032(4)	38(1)
O(11)	746(6)	3313(6)	6799(4)	40(1)
O(12)	9227(6)	3827(6)	5414(4)	43(2)
O(13)	8280(5)	4855(5)	6918(4)	30(1)
O(14)	6075(7)	6078(6)	5917(4)	41(2)
O(15)	6447(6)	6618(5)	7499(4)	39(1)
O(16)	6893(5)	3532(5)	6426(3)	24(1)
O(17)	6575(5)	3983(4)	8113(3)	24(1)

Table S2continued

Atom	*x*	*y*	*z*	*U(eq)*
O(18)	4671(5)	5247(5)	7330(4)	29(1)
O(19)	4300(6)	4679(5)	9145(4)	34(1)
O(20)	2814(5)	4019(5)	8064(4)	32(1)
O(21)	4803(5)	2986(5)	7057(3)	24(1)
O(22)	591(11)	8795(12)	5203(6)	97(4)
O(23)	1610(30)	7180(30)	6580(20)	136(11)
O(24)	2419(17)	2009(16)	8062(14)	78(6)
O(25)	9548(19)	6950(18)	6467(14)	162(7)
C(1)	9477(7)	3671(6)	9738(5)	23(1)
C(2)	733(9)	3197(9)	9474(6)	38(2)
C(3)	1691(10)	2648(9)	78(8)	50(3)
C(4)	1406(11)	2576(9)	949(7)	52(3)
C(5)	1169(12)	3073(11)	1225(7)	55(3)
C(6)	9204(10)	3617(10)	622(6)	45(2)
C(7)	8446(8)	4258(6)	9091(5)	27(2)
C(8)	5072(8)	987(8)	5922(5)	31(2)
C(9)	5378(10)	9813(8)	6390(6)	42(2)
C(10)	4457(12)	9113(9)	6513(7)	54(3)
C(11)	3235(12)	9564(11)	6180(8)	57(3)
C(12)	2921(11)	726(12)	5721(8)	57(3)
C(13)	3847(10)	1426(9)	5581(6)	46(2)
C(14)	6052(9)	1774(8)	5787(5)	33(2)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Cs_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**3**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Cs(1)	8918(1)	1195(1)	8576(1)	63(1)
Cs(2)	5622(1)	9517(1)	9673(1)	47(1)
Mo(1)	2386(1)	2386(1)	0	23(1)
Mo(2)	180(1)	1930(1)	717(1)	19(1)
Mo(3)	8449(1)	9270(1)	507(1)	18(1)
P	9259(2)	1491(2)	9758(1)	16(1)
O(1)	630(5)	1728(4)	9614(1)	20(1)
O(2)	9224(5)	1103(4)	194(1)	19(1)
O(3)	8574(5)	479(5)	9518(1)	22(1)
O(4)	2530(6)	3686(6)	9703(2)	39(2)
O(5)	1008(5)	2969(5)	329(1)	23(1)
O(6)	9050(5)	3031(6)	844(2)	33(1)
O(7)	9300(5)	387(5)	878(1)	23(1)
O(8)	8124(5)	7988(5)	802(2)	31(1)
O(9)	6986(5)	38(5)	474(2)	28(1)
O(10)	8486(5)	8486(5)	0	23(2)
O(11)	1292(6)	1993(6)	1085(2)	32(1)
O(12)	9823(9)	8025(9)	8384(2)	84(3)
O(13)	6535(9)	9237(9)	8566(3)	87(3)
O(14)	5692(13)	1443(12)	8953(3)	126(5)
C(1)	8347(7)	2924(7)	9710(2)	21(2)
C(2)	8685(9)	3875(7)	9441(2)	29(2)
C(3)	7880(10)	4912(7)	9381(2)	37(2)
C(4)	6752(10)	5003(9)	9597(3)	46(2)
C(5)	6424(10)	4081(10)	9859(3)	50(3)
C(6)	7230(8)	3029(7)	9923(2)	31(2)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**4**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
N(1)	2798(2)	994(2)	4553(2)	39(1)
N(2)	8498(2)	3518(2)	5314(2)	38(1)
Mo(1)	92(1)	4403(1)	3638(1)	17(1)
Mo(2)	459(1)	2265(1)	4181(1)	17(1)
Mo(3)	0	957(1)	2500	19(1)
P	8770(1)	2906(1)	2650(1)	15(1)
O(1)	0	4744(2)	2500	20(1)
O(2)	9428(1)	5158(1)	4076(1)	30(1)
O(3)	1172(1)	4785(1)	3931(1)	28(1)
O(4)	8755(1)	3731(1)	3178(1)	20(1)
O(5)	9204(1)	3139(1)	1844(1)	17(1)
O(6)	6(1)	3429(1)	4407(1)	21(1)
O(7)	775(1)	1343(1)	3432(1)	21(1)
O(8)	9819(1)	1675(1)	4824(1)	31(1)
O(9)	9270(1)	2141(1)	3117(1)	18(1)
O(10)	1502(1)	2339(1)	4716(1)	27(1)
O(11)	9261(1)	260(1)	2941(1)	31(1)
O(12)	7205(2)	4724(2)	3303(2)	41(1)
O(13)	8639(3)	9928(3)	4593(3)	105(2)
O(14)	6768(2)	3344(2)	4343(2)	75(1)
C(1)	7629(2)	2562(2)	2357(2)	19(1)
C(2)	7073(2)	3112(2)	1843(2)	28(1)
C(3)	6184(2)	2866(3)	1606(2)	39(1)
C(4)	5854(2)	2074(3)	1874(2)	44(1)
C(5)	6401(2)	1520(3)	2380(2)	43(1)
C(6)	7291(2)	1768(2)	2631(2)	29(1)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S5. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(K)_{1.5}(H_3O)_{0.5}([(Mo_2O_5)(O_3PPh)_2]$(**5**) compound

Atom	*x*	*y*	*z*	*U(eq)*
Mo(1)	3803(1)	9129(1)	3732(1)	9(1)
Mo(2)	1776(1)	4123(1)	3740(1)	9(1)
Mo(3)	6781(1)	1505(1)	3731(1)	9(1)
Mo(4)	8795(1)	6507(1)	3733(1)	9(1)
P(1)	4066(3)	2227(3)	2824(2)	11(1)
P(2)	1931(3)	7217(3)	2832(2)	9(1)
P(3)	6923(3)	8866(3)	2817(2)	9(1)
P(4)	9074(3)	13859(3)	2828(2)	9(1)
K(1)	359(3)	10380(3)	3457(2)	30(1)
K(2)	5366(3)	5390(3)	3410(2)	32(1)
K(3)	3359(6)	11789(5)	5003(3)	26(3)
O(3W)	3359(6)	11789(5)	5003(3)	130(60)
K(4)	1653(6)	6779(6)	5000(3)	26(4)
O(4W)	1653(6)	6779(6)	5000(3)	160(80)
O(1)	3381(8)	3368(8)	3182(4)	13(2)
O(2)	223(8)	5248(8)	3992(4)	15(2)
O(3)	2457(8)	9569(9)	4286(4)	18(2)
O(4)	7582(9)	49(8)	3065(4)	16(2)
O(5)	8419(8)	2520(8)	3187(4)	14(2)
O(6)	8293(8)	5064(8)	3073(4)	14(2)
O(7)	5645(8)	12180(8)	2898(4)	12(2)
O(8)	7456(9)	7544(8)	3164(4)	18(2)
O(9)	335(8)	7184(8)	2906(4)	15(2)
O(10)	5318(8)	8856(8)	2896(4)	13(2)
O(11)	1112(9)	2612(8)	4128(4)	19(2)
O(12)	648(8)	3861(8)	2906(4)	14(2)
O(13)	2430(8)	8392(8)	3180(4)	17(2)
O(14)	4305(9)	7607(9)	4118(4)	21(2)
O(15)	2592(8)	5895(8)	3082(4)	16(2)

Table S5 continued

O(16)	9278(9)	7810(9)	4128(4)	22(2)
O(17)	3304(9)	925(8)	3060(4)	17(2)
O(18)	7885(9)	803(9)	4280(4)	17(2)
O(19)	2887(9)	4548(8)	4282(4)	15(2)
O(20)	5229(8)	263(8)	3986(4)	16(2)
O(21)	7441(9)	5826(9)	4274(4)	18(2)
O(22)	6134(9)	2816(9)	4120(4)	19(2)
C(1)	3911(13)	2655(12)	1950(6)	15(3)
C(2)	5070(20)	2990(30)	1510(9)	68(7)
C(3)	4950(20)	3390(30)	845(9)	74(7)
C(4)	3696(18)	3355(19)	601(8)	44(4)
C(5)	2520(20)	3057(16)	1021(8)	46(5)
C(6)	2609(17)	2662(17)	1708(8)	37(4)
C(7)	2517(14)	7631(13)	1972(6)	18(3)
C(8)	2665(19)	6599(19)	1565(9)	47(4)
C(9)	3090(20)	6950(20)	882(10)	65(6)
C(10)	3316(18)	8269(19)	616(9)	46(4)
C(11)	3117(18)	9250(20)	1009(9)	50(5)
C(12)	2741(15)	8973(15)	1691(8)	31(4)
C(13)	7493(12)	8892(11)	1942(6)	11(2)
C(14)	8867(17)	8901(18)	1697(8)	42(4)
C(15)	9310(20)	8860(20)	1029(9)	60(6)
C(16)	8344(18)	8885(17)	594(7)	38(4)
C(17)	6930(20)	8930(30)	830(9)	80(8)
C(18)	6500(20)	8910(30)	1494(10)	73(7)
C(19)	8881(13)	3866(12)	1969(6)	15(3)
C(2O)	8920(20)	5073(19)	1561(8)	49(5)
C(21)	8860(20)	5030(20)	875(9)	60(6)
C(22)	8745(18)	3884(18)	618(9)	44(4)
C(23)	8671(18)	2700(20)	1009(9)	51(5)
C(24)	8729(16)	2659(18)	1701(8)	38(4)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2[(Mo_2O_5)(O_3PC_6H_4PO_3)]$(**11**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Rb(1)	1626(3)	1787(2)	5000	28(1)
Rb(2)	5000	0	2794(2)	37(1)
Mo	3560(1)	3784(1)	3306(1)	7(1)
P(1)	1451(4)	1661(3)	2091(2)	6(1)
O(1)	4098(10)	2397(10)	3875(6)	17(2)
O(2)	5000	5000	3652(8)	11(3)
O(3)	2307(11)	4362(11)	3991(6)	16(2)
O(4)	2174(11)	2870(9)	2510(6)	13(2)
O(5)	2065(10)	360(9)	2390(6)	11(2)
O(6)	4924(9)	3226(9)	2251(6)	9(2)
C(1)	1625(14)	1777(13)	923(8)	14(3)
C(2A)	1770(30)	2940(20)	448(17)	13(5)
C(3A)	1820(30)	580(30)	444(18)	15(5)
C(2B)	2870(40)	1740(50)	490(40)	13(6)
C(3B)	440(40)	2060(60)	450(30)	21(7)
C(2C)	2770(60)	2060(80)	410(60)	13(7)
C(3C)	400(50)	1490(70)	480(50)	15(7)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(NH_4)_2[(Mo_2O_5)(O_3PC_6H_4PO_3)]$(**13**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
N(1)	1622(6)	1778(6)	5000	30(1)
N(2)	5000	0	2806(4)	30(1)
Mo	3545(1)	3786(1)	3305(1)	11(1)
P(1)	1453(1)	1665(1)	2086(1)	10(1)
O(1)	4101(3)	2391(3)	3852(2)	24(1)
O(2)	5000	5000	3648(2)	16(1)
O(3)	2300(3)	4360(3)	4016(2)	22(1)
O(4)	2144(3)	2872(2)	2525(2)	19(1)
O(5)	2103(2)	371(2)	2400(2)	18(1)
O(6)	9891(3)	1726(3)	2234(2)	18(1)
C(1)	1673(4)	1776(4)	916(2)	19(1)
C(2A)	1830(14)	2908(9)	458(5)	41(2)
C(3A)	1624(14)	553(10)	450(6)	52(3)
C(2B)	2773(17)	1420(20)	450(10)	43(4)
C(3B)	652(18)	2552(18)	449(9)	43(3)
C(2C)	2710(20)	2280(30)	446(12)	28(4)
C(3C)	560(30)	1190(30)	455(13)	46(5)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2[(Mo_2O_5)(O_3PC_4H_8PO_3)]$(**16**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Rb(1)	1716(2)	3284(2)	0	41(1)
Rb(2)	5000	5000	1113(1)	29(1)
Mo	3673(1)	1327(1)	873(1)	18(1)
P	3454(3)	8454(3)	1494(2)	21(1)
O(1)	3090(9)	9906(13)	1398(3)	39(3)
O(2)	5000	0	714(4)	7(3)
O(3)	4275(10)	2624(9)	546(3)	32(2)
O(4)	2833(15)	2871(15)	1232(5)	17(3)
C(1)	3131(13)	8131(13)	2088(6)	19(4)
C(2)	1390(30)	1600(30)	2240(8)	22(6)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S9. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Rb_2[(Mo_2O_5)(O_3PC_3H_6PO_3)]$(**19**) compound.

Atom	*x*	*y*	*z*	*U(eq)*
Rb(1)	4989(1)	1617(1)	8160(1)	21(1)
Rb(2)	2651(1)	24(1)	4593(1)	24(1)
Mo(1)	3163(1)	3574(1)	5898(1)	8(1)
Mo(2)	6901(1)	3543(1)	6543(1)	8(1)
P(1)	1832(1)	3540(1)	2783(1)	7(1)
P(2)	1777(1)	1386(1)	1137(1)	7(1)
O(1)	2035(3)	2970(4)	4222(3)	12(1)
O(2)	2326(3)	2109(4)	2387(3)	13(1)
O(3)	2522(3)	2111(3)	6861(4)	14(1)
O(4)	3923(3)	2376(4)	5351(4)	15(1)
O(5)	3455(3)	5004(3)	4710(3)	11(1)
O(6)	3827(3)	4177(4)	7352(4)	16(1)
O(7)	1947(3)	4845(3)	6298(4)	12(1)
O(8)	6118(3)	2352(4)	5754(4)	17(1)
O(9)	6286(3)	4089(4)	7826(4)	17(1)
O(10)	1903(3)	99(3)	7693(3)	11(1)
O(11)	2050(3)	3002(4)	4840(3)	13(1)
C(1)	668(4)	3052(6)	1983(6)	13(1)
C(2)	232(4)	3740(6)	2384(6)	17(1)
C(3)	529(4)	1730(6)	1259(6)	17(1)

*U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table S10. Bond lengths (Å) for $Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 8H_2O$(**1**) compound.

Bond	Length	Bond	Length	Bond	Length
Rb(1)-O(6)	3.106(8)	Rb(2)-O(13)	2.906(12)	Mo(2)-O(9)	2.433(8)
Rb(1)-O(8)	3.067(9)	Rb(2)-O(9)	3.573(8)	Mo(2)-O(10)	1.702(9)
Rb(1)-O(10)	2.957(9)	**BVS**	**1.059**	**BVS**	**5.924**
Rb(1)-O(12)	2.978(12)	Mo(1)-O(1)	1.907(3)	Mo(3)-O(7) X2	1.890(8)
Rb(1)-O(12)	3.370(12)	Mo(1)-O(2)	1.713(8)	Mo(3)-O(9) X2	2.296(7)
Rb(1)-O(14)	2.822(13)	Mo(1)-O(3)	1.702(8)	Mo(3)-O(11) X 2	1.709(8)
Rb(1)-O(15)	3.023(17)	Mo(1)-O(4)	2.312(7)	**BVS**	**6.208**
BVS	**0.913**	Mo(1)-O(5)	2.378(7)	P-C(7)	1.808(12)
Rb(2)-O(1)	3.221(4)	Mo(1)-O(6)	1.908(8)	P-O(4)	1.517(8)
Rb(2)-O(2)	2.983(8)	**BVS**	**6.042**	P-O(5)	1.549(8)
Rb(2)-O(3)	3.093(9)	Mo(2)-O(5)	2.220(7)	P-O(9)	1.536(8)
Rb(2)-O(4)	2.969(8)	Mo(2)-O(6)	1.942(8)		
Rb(2)-O(8)	2.902(8)	Mo(2)-O(7)	1.955(8)		
Rb(2)-O(11)	2.852(8)	Mo(2)-O(8)	1.705(8)		

Table S11. Bond lengths (Å) for $Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$(**2**) compound.

Bond	Length	Bond	Length	Bond	Length
Cs(1)-O(10)	2.995(6)	Cs(4)-O(4)X2	3.389(5)	Mo(3)-O(9)	2.324(5)
Cs(1)-O(12)	3.252(7)	Cs(4)-O(3)X2	3.719(6)	Mo(3)-O(11)	1.704(6)
Cs(1)-O(13)	3.031(5)	**BVS**	**0.914**	Mo(3)-O(12)	1.707(6)
Cs(1)-O(14)	3.527(7)	Cs(5)-O(11)	3.308(6)	Mo(3)-O(13)	1.896(6)
Cs(1)-O(15)	3.351(7)	Cs(5)-O(12)	2.986(6)	Mo(3)-O(16)	2.414(5)
Cs(1)-O(22)	2.991(10)	Cs(5)-O(14)	3.346(7)	**BVS**	**6.021**
Cs(1)-O(23)	3.09(3)	Cs(5)-O(16)	3.804(5)	Mo(4)-O(13)	1.951(6)
Cs(1)-O(25)	0.97(2)	Cs(5)-O(18)	3.135(5)	Mo(4)-O(14)	1.702(6)
BVS	**1.033**	Cs(5)-O(21)	3.135(5)	Mo(4)-O(15)	1.703(6)
Cs(2)-O(1)	3.186(5)	Cs(5)-O(20)	3.325(6)	Mo(4)-O(16)	2.378(5)
Cs(2)-O(2)	3.093(6)	Cs(5)-O(23)	2.80(3)	Mo(4)-O(17)	2.208(5)
Cs(2)-O(3)	3.455(5)	Cs(5)-O(25)	3.725(19)	Mo(4)-O(18)	1.921(6)
Cs(2)-O(8)	3.062(6)	**BVS**	**1.168**	**BVS**	**6.050**
Cs(2)-O(11)	3.221(6)	Mo(1)-O(1)	1.922(5)	Mo(5)-O(1)	1.934(5)
Cs(2)-O(20)	3.148(6)	Mo(1)-O(2)	1.711(5)	Mo(5)-O(17)	2.304(5)
Cs(2)-O(21)	3.188(5)	Mo(1)-O(3)	1.706(5)	Mo(5)-O(18)	1.936(5)
BVS	**0.908**	Mo(1)-O(4)	2.302(5)	Mo(5)-O(19)	1.717(6)
Cs(3)-O(1)	3.279(5)	Mo(1)-O(5)	2.418(5)	Mo(5)-O(20)	1.703(6)
Cs(3)-O(2)	3.299(5)	Mo(1)-O(6)	1.911(5)	Mo(5)-O(21)	2.261(5)
Cs(3)-O(3)	3.159(6)	**BVS**	**5.964**	**BVS**	**5.988**
Cs(3)-O(4)	3.269(5)	Mo(2)-O(5)	2.212(5)	P(1)-O(4)	1.510(5)
Cs(3)-O(15)	3.097(7)	Mo(2)-O(6)	1.914(5)	P(1)-O(9)	1.540(6)
Cs(3)-O(19)	3.118(6)	Mo(2)-O(7)	1.917(5)	P(1)-O(17)	1.555(5)
Cs(3)-O(19)	3.137(6)	Mo(2)-O(8)	1.720(6)	P(1)-C(7)	1.805(7)
Cs(3)-O(24)	3.083(17)	Mo(2)-O(9)	2.440(5)	P(2)-O(5)	1.545(5)
BVS	**1.041**	Mo(2)-O(10)	1.700(6)	P(2)-O(16)	1.544(5)
Cs(4)-O(6)X2	2.895(5)	**BVS**	**6.038**	P(2)-O(21)	1.520(6)
Cs(4)-O(8)X2	3.229(6)	Mo(3)-O(7)	1.920(5)	P(2)-C(14)	1.797(8)

Table S12. Bond lengths (Å) for $A_4[(MoO_3)_5(O_3PC_6H_5)_2]\cdot 6H_2O$ (*A* = Cs(**3**), NH_4(**4**)) compounds.

A	Bond	Length	Bond	Length	Bond	Length
Cs(3)	Cs(1)-O(3)	3.333(5)	Cs(2)-O(9)	3.140(5)	Mo(2)-O(11)	1.713(6)
	Cs(1)-O(4)	3.039(6)	Cs(2)-O(10)	3.366(3)	**BVS**	**6.028**
	Cs(1)-O(7)	3.121(5)	Cs(2)-O(12)	3.370(9)	Mo(3)-O(3)	2.239(5)
	Cs(1)-O(11)	3.302(6)	Cs(2)-O(14)	3.180(10)	Mo(3)-O(2)	2.335(5)
	Cs(1)-O(11)	3.412(6)	**BVS**	**0.902**	Mo(3)-O(7)	1.940(5)
	Cs(1)-O(12)	3.499(10)	Mo(1)-O(1) X2	2.361(5)	Mo(3)-O(8)	1.710(5)
	Cs(1)-O(13)	3.216(9)	Mo(1)-O(4) X2	1.701(6)	Mo(3)-O(9)	1.726(5)
	Cs(1)-O(14)	3.613(13)	Mo(1)-O(5) X2	1.925(5)	Mo(3)-O(10)	1.919(2)
	Cs(1)-O(14)	3.082(12)	**BVS**	**5.982**	**BVS**	**5.940**
	BVS	**0.952**	Mo(2)-O(1)	2.392(4)	P-C(1)	1.780(7)
	Cs(2)-O(3)	3.280(5)	Mo(2)-O(2)	2.223(5)	P-O(1)	1.531(5)
	Cs(2)-O(5)	3.174(5)	Mo(2)-O(5)	1.918(5)	P-O(2)	1.549(5)
	Cs(2)-O(6)	3.266(6)	Mo(2)-O(6)	1.702(5)	P-O(3)	1.515(5)
	Cs(2)-O(8)	3.291(6)	Mo(2)-O(7)	1.933(5)		
$(NH_4)_4$(4)	Mo(1)-O(1)	1.9044(7)	Mo(2)-O(6)	1.9287(17)	Mo(3)-O(11) X2	1.7165(19)
	Mo(1)-O(2)	1.699(18)	Mo(2)-O(7)	1.9310(17)	**BVS**	**5.966**
	Mo(1)-O(3)	1.7231(18)	Mo(2)-O(8)	1.7159(19)	P-O(4)	1.5122(18)
	Mo(1)-O(4)	2.2882(16)	Mo(2)-O(9)	2.3560(17)	P-O(5)	1.5439(17)
	Mo(1)-O(5)	2.3425(16)	Mo(2)-O(10)	1.7044(18)	P-O(9)	1.5336(17)
	Mo(1)-O(6)	1.9377(18)	**BVS**	**6.022**	P-C(1)	1.788(2)
	BVS	**5.990**	Mo(3)-O(7) X2	1.9018(17)		
	Mo(2)-O(5)	2.2105(16)	Mo(3)-O(9) X2	2.3573(17)		

Table S13. Bond lengths (Å) for $(K)_{1.5}(H_3O)_{0.5}[(Mo_2O_5)(O_3PPh)_2]$(**5**) compound.

Bond	Length	Bond	Length	Bond	Length
K(1)-O(4)	2.871(9)	K(4)-O(2)	3.114(11)	Mo(3)-O(18)	1.705(8)
K(1)-O(5)	2.859(10)	K(4)-O(2)	3.126(10)	Mo(3)-O(20)	1.912(8)
K(1)-O(11)	2.883(10)	K(4)-O(3)	3.046(11)	Mo(3)-O(22)	1.693(9)
K(1)-O(13)	2.859(10)	K(4)-O(11)	3.114(11)	**BVS**	**6.229**
K(1)-O(16)	2.893(10)	K(4)-O(14)	2.996(11)	Mo(4)-O(2)	1.920(8)
K(1)-O(17)	2.866(9)	K(4)-O(16)	3.121(11)	Mo(4)-O(6)	2.174(8)
K(1)-O(18)	2.801(10)	K(4)-O(18)	3.037(11)	Mo(4)-O(8)	2.017(9)
BVS	**1.137**	K(4)-O(19)	2.982(10)	Mo(4)-O(9)	2.157(9)
K(2)-O(1)	2.874(9)	K(4)-O(21)	3.001(11)	Mo(4)-O(16)	1.697(9)
K(2)-O(6)	2.820(9)	K(4)-O(22)	2.971(11)	Mo(4)-O(21)	1.688(9)
K(2)-O(8)	2.894(10)	**BVS**	**0.846**	**BVS**	**6.274**
K(2)-O(14)	2.912(10)	Mo(1)-O(3)	1.703(9)	P(1)-C(1)	1.801(14)
K(2)-O(15)	2.819(9)	Mo(1)-O(10)	2.157(8)	P(2)-C(7)	1.779(14)
K(2)-O(19)	2.858(9)	Mo(1)-O(13)	2.011(8)	P(3)-C(13)	1.803(13)
K(2)-O(21)	2.853(10)	Mo(1)-O(14)	1.715(9)	P(4)-C(19)	1.777(13)
K(2)-O(22)	2.924(10)	Mo(1)-O(17)	2.205(9)	P(1)-O(1)	1.537(9)
BVS	**1.097**	Mo(1)-O(20)	1.922(8)	P(1)-O(7)	1.532(9)
K(3)-O(3)	2.977(11)	**BVS**	**6.087**	P(1)-O(17)	1.488(9)
K(3)-O(11)	2.987(10)	Mo(2)-O(1)	2.008(9)	P(2)-O(9)	1.512(9)
K(3)-O(14)	3.101(11)	Mo(2)-O(2)	1.917(9)	P(2)-O(13)	1.543(9)
K(3)-O(16)	2.972(11)	Mo(2)-O(11)	1.703(9)	P(2)-O(15)	1.515(9)
K(3)-O(18)	2.989(11)	Mo(2)-O(12)	2.151(8)	P(3)-O(4)	1.502(9)
K(3)-O(19)	3.022(10)	Mo(2)-O(15)	2.177(9)	P(3)-O(8)	1.530(9)
K(3)-O(20)	3.123(11)	Mo(2)-O(19)	1.703(9)	P(3)-O(10)	1.521(9)
K(3)-O(20)	3.124(11)	**BVS**	**6.205**	P(4)-O(5)	1.541(9)
K(3)-O(21)	3.012(10)	Mo(3)-O(4)	2.194(9)	P(4)-O(6)	1.528(9)
K(3)-O(22)	3.129(11)	Mo(3)-O(5)	2.012(8)	P(4)-O(12)	1.524(9)
BVS	**0.864**	Mo(3)-O(7)	2.149(8)		

Table S14. Bond lengths (Å) for $A_2[(Mo_2O_5)(O_3PC_6H_4PO_3)]$)] ($A$ = Rb(**11**), NH_4(**13**)) compounds.

A	Bond	Length	Bond	Length	Bond	Length
	Rb(1)-O(1)	3.008(10)	Rb(2)-O(4)X 2	3.026(10)	Mo-O(5)	2.188(9)
	Rb(1)-O(3)X 2	3.047(10)	Rb(2)-O(5)X 2	2.936(10)	Mo-O(6)	2.152(9)
	Rb(1)-O(3)X 2	3.066(11)	Rb(2)-O(6)X 2	3.326(9)	**BVS**	**6.087**
Rb(11)	Rb(1)-O(1)X 2	3.100(10)	**BVS**	**1.250**	P(1)-O(4)	1.535(10)
	Rb(1)-O(2)X 2	3.143(8)	Mo-O(1)	1.714(10)	P(1)-O(5)	1.499(9)
	BVS	**0.996**	Mo-O(2)	1.925(4)	P(1)-O(6)	1.506(10)
	Rb(2)-O(1)X 2	3.033(10)	Mo-O(3)	1.702(10)	P(1)-C(1)	1.789(13)
	Rb(2)-O(3)X 2	2.956(10)	Mo-O(4)	2.026(10)		
	N(1)-H(1B)	0.90(2)	Mo-O(2)	1.9247(9)	P(1)-C(1)	1.793(4)
	N(1)-H(1C)	0.90(2)	Mo-O(3)	1.711(2)	P(1)-O(4)	1.532(3)
NH_4(13)	N(1)-H(1A)	0.90(2)	Mo-O(4)	2.014(2)	P(1)-O(5)	1.514(3)
	N(2)-H(2C)	0.91(2)	Mo-O(5)	2.190(2)	P(1)-O(6)	1.519(2)
	N(2)-H(2D)	0.90(2)	Mo-O(6)	2.142(2)		
	Mo-O(1)	1.710(3)	**BVS**	**6.098**		

Table S15. Bond lengths (Å) for $Rb_2[(Mo_2O_5)(O_3PC_4H_8PO_3)]$(**16**)compound.

Bond	Length	Bond	Length	Bond	Length
Rb(1)-O(2) X 2	3.189(9)	Rb(2)-O(3) X 3	2.965(9)	Mo-O(4) X 2	2.031(15)
Rb(1)-O(3) X 4	3.028(10)	Rb(2)-O(4) X 3	3.006(14)	**BVS**	**5.846**
Rb(1)-O(3) X 4	3.061(9)	**BVS**	**1.050**	P-O(1) X 2	1.499(12)
BVS	**1.132**	Mo-O(1) X2	2.170(9)	P-O(4) X 2	1.591(15)
Rb(2)-O(1) X 2	3.154(9)	Mo-O(3) X 2	1.707(9)	P-C(1)	1.819(17)

Table S16. Bond lengths (Å) for $Rb_2[(Mo_2O_5)(O_3PC_3H_6PO_3)]$(**19**) compound.

Bond	Length	Bond	Length	Bond	Length
Rb(1)-O(4)	3.073(4)	Rb(2)-O(4)	2.933(4)	Mo(2)-O(9)	1.709(4)
Rb(1)-O(4)	2.955(4)	Rb(2)-O(6)	3.031(4)	Mo(2)-O(2)	1.984(3)
Rb(1)-O(5)	3.207(4)	Rb(2)-O(8)	2.926(4)	Mo(2)-O(5)	1.903(3)
Rb(1)-O(5)	3.234(4)	Rb(2)-O(9)	2.932(4)	Mo(2)-O(11)	2.197(4)
Rb(1)-O(6)	2.972(4)	Rb(2)-O(10)	3.375(4)	Mo(2)-O(10)	2.186(3)
Rb(1)-O(6)	3.020(4)	Rb(2)-O(11)	3.075(4)	**BVS**	**6.145**
Rb(1)-O(8)	3.010(4)	**BVS**	**1.234**	P(1)-O(1)	1.523(4)
Rb(1)-O(8)	3.108(4)	Mo(1)-O(1)	2.217(3)	P(1)-O(3)	1.547(4)
Rb(1)-O(9)	3.052(4)	Mo(1)-O(3)	1.989(4)	P(1)-O(10)	1.521(3)
Rb(1)-O(9)	3.117(4)	Mo(1)-O(4)	1.710(4)	P(1)-C(1)	1.779(6)
BVS	**1.145**	Mo(1)-O(5)	1.900(3)	P(2)-O(2)	1.540(3)
Rb(2)-O(1)	2.998(4)	Mo(1)-O(6)	1.714(3)	P(2)-O(7)	1.521(3)
Rb(2)-O(2)	3.005(3)	Mo(1)-O(7)	2.177(4)	P(2)-O(11)	1.511(4)
Rb(2)-O(3)	3.051(4)	**BVS**	**6.123**	P(2)-C(3)	1.793(6)
Rb(2)-O(7)	3.291(4)	Mo(2)-O(8)	1.710(4)		

Table S17. Unit cell parameters of compounds **6, 10, 12, 14, 15, 17, 18 and 20**

Sl. No	Composition	Space group	Volume	Unit Cell					
				a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	α (°)	β (°)	γ (°)
1	$Rb_2[(Mo_2O_5)(O_3PPh)_2]$(**6**)	$P\bar{1}$	2003.08	9.7497	10.0044	20.8846	82.004	83.241	89.805
2	$K_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**10**)	*Pbam*	1428.55	9.4106	10.0157	15.1564			
3	$Cs_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**12**)	*Pbam*	1540.28	9.9724	9.9694	15.5131			
4	$Tl_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**14**)	*P*222	1431.28	9.5700	9.8799	15.1378			
5	$K_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**15**)	*I*4/*mcm*	2777.15	9.7359	9.7359	29.2984			
6	$Cs_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**17**)	*I*4/*mcm*	2975.10	9.9150	9.9150	30.2792			
7	$(NH_4)_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**18**)	*I*4/*mcm*	2854.96	9.8069	9.8069	29.6847			
8	$Cs_2[(Mo_2O_5)(O_3P(CH_2)_3PO_3)]$(**20**)	$P2_1/c$	1399.99	14.3051	9.9134	9.9511	90	97.223	90

Table S18. CHN analysis of compounds **1**-**20**

Sl. No	Composition	C %		H %		N %	
		Calc	Obs	Calc	Obs	Calc	Obs
1	$Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2].8H_2O$(**1**)	10.88	10.65	1.96	1.17	-	-
2	$Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2].3H_2O$(**2**)	10.22	10.15	1.23	0.88	-	-
3	$Cs_4[(MoO_3)_5(O_3PPh)_2].6H_2O$(**3**)	8.62	8.66	1.33	0.43	-	-
4	$(NH_4)_4[(MoO_3)_5(O_3PPh)_2].6H_2O$(**4**)	11.89	14.96	3.16	1.89	4.62	4.72
5	$K_{1.5}(H_3O)_{0.5}[(Mo_2O_5)(O_3PPh)_2]$(**5**)	22.09	22.45	1.78	1.51	-	-
6	$Rb_2[(Mo_2O_5)(O_3PPh)_2]$(**6**)	19.09	19.43	1.34	0.83	-	-
7	$Cs_2[(Mo_2O_5)(O_3PPh)_2]$(**7**)	16.61	16.53	1.19	0.84	-	-
8	$(NH_4)_2[(Mo_2O_5)(O_3PPh)_2]$(**8**)	23.24	23.49	2.93	1.86	4.52	6.07
9	$Tl_2[(Mo_2O_5)(O_3PPh)_{2]}]$(**9**)	14.52	14.10	1.02	1.51	-	-
10	$K_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**10**)	12.34	12.58	0.690	0.85	-	-
11	$Rb_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**11**)	10.64	10.73	0.596	0.37	-	-
12	$Cs_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**12**)	9.34	9.48	0.522	0.24	-	-
13	$(NH_4)_2[(Mo_2O_5)(O_3P(C_6H_4)\,PO_3)]$(**13**)	13.29	13.37	2.23	1.13	5.17	5.31
14	$Tl_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**14**)	7.88	7.03	0.441	0.13	-	-
15	$K_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**15**)	8.52	9.07	1.43	0.94	-	-
16	$Rb_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**16**)	7.31	7.24	1.23	0.85	-	-
17	$Cs_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**17**)	6.39	6.74	1.07	0.24	-	-
18	$(NH_4)_2[(Mo_2O_5)(O_3P(CH_2)_4PO_3)]$(**18**)	9.20	9.14	3.09	2.08	5.37	5.27
19	$Rb_2[(Mo_2O_5)(O_3P(CH_2)_3PO_3)]$(**19**)	5.61	5.59	0.94	0.57	-	-
20	$Cs_2[(Mo_2O_5)(O_3P(CH_2)_3PO_3)]$(**20**)	4.88	5.16	0.82	0.42	-	-

The carbon contents of all compounds except **4** agree with the calculated values. The hydrogen contents of all compounds except **4** reasonably agree with the calculated values.

Table S19. Compilation of molecular and non-molecular molybdoorganophosphonates

Molecular molybdoorganophosphonates		
Sl.No	**Compound**	**Reference**
1	$[Cu(bpy)(MoO_2)(H_2O)(O_3PCH_2PO_3)]$	42
2	$[\{Cu_2(bpyr)\}(MoO_2)(HO_3PCH_2PO_3)_2]\cdot 2H_2O$	65
3	$[Cu(bpy)(Mo_2O_5)(O_3PCH_2CH_2CH_2PO_3)]$	42
4	$[Cu(bpy)(Mo_2O_5)(H_2O)(O_3PCH_2PO_3)]\cdot H_2O$	42
5	$[Cu(o\text{-}phen)(Mo_2O_5)(O_3PCH_2PO_3)(H_2O)]$	43
6	$[Cu(terpy)(Mo_2O_5)(O_3PCH_2PO_3)]$	42
7	$[\{Ni(tpyprz)(H_2O)_2\}(Mo_3O_8)_2\ (O_3PCH_2PO_3)_2]$	39
8	$[\{Cu_2(tpypyz)(H_2O)\}Mo_3O_8\ (HO_3PCH_2PO_3)_2]\cdot 8H_2O$	37
9	$[\{Cu_2(tpypyz)(H_2O)\}_2(Mo_3O_8)_2(O_3PCH_2PO_3)_3]\cdot 16.9H_2O$	37
10	$[Co(H_2tpyprz)_2][(Mo_3O_8)_3(O_3PCH_2PO_3)_3]\cdot 7H_2O\cdot C_5H_5N\cdot py)$	36
11	$[\{Co(1,10\text{-}phen)_2\}_2\{(Mo_4O_{12})(O_3PCH_2CH_2PO_3)\}\cdot(H_2O)]$	53
12	$[\{Co(1,10\text{-}phen)_2\}_2\{(Mo_4O_{12})(O_3PCH_2CH_2CH_2PO_3)\}\cdot(1.5H_2O)]$	53
13	$[\{Cu(bpy)\}_2(Mo_4O_{12})(H_2O)_2(O_3PCH_2CH_2PO_3)]\cdot 2H_2O$	42
14	$[\{Cu(o\text{-}phen)\}_2(Mo_4O_{12})(H_2O)_2(O_3PCH_2CH_2PO_3)]\cdot\ 2H_2O$	42
15	$[C(NH_2)_3]_4.(\ Mo_5O_{21}(PhP)_2)$	44
16	$((CH_3CH_2CH_2)_3NH)_4[Mo_5O_{15}(CH_3PO_3)_2]$	64
17	$(C_4H_{12}N_2)_2[Mo_5O_{15}(C_6H_5O_3P)_2].2H_2O$	45
18	$[\{Cu_2(L7)(H_2O)_2\}Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}]\cdot 2H_2O$	25
19	$(4,4'\text{-}H_2dpa)_2[Mo_5O_{15}(1,2\text{-}O_3PC_8H_8PO_3)]\cdot H_2O$	35
20	$(4,4'\text{-}H_2dpa)_2[Mo_5O_{15}(1,3\text{-}O_3PC_8H_8PO_3)]$	35
21	$[(HOOCC_5H_9NCH_2PO_3)_2Mo_5O_{15}]^{4-}$	51
22	$[\{Co_4(tpyprz)_3\}(Mo_5O_{15})_2(O_3PCH_2CH_2PO_3)_2]\cdot 18H_2O$	36
23	$[\{Co(H_2tpyprz)\}Mo_5O_{15}\{O_3PCH_2CH_2PO_3\}]$	36

Sl.No	Compound	Reference
24	$[\{Co_2(tpyprz)_2\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]\cdot 5H_2O$	36
25	$[\{Co_2(tpyprz)(H_2O)_3\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]\cdot 7H_2O$	36
26	$[\{Co_2(tpyprz)(H_2O)_3\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]\cdot H_2O$	36
27	$[H_3O]_2[\{Co_3(tpyprz)_2(H_2O)_3\}(Mo_5O_{15})_2\{O_3P(CH_2)_3PO_3\}_2]\cdot 21.4H_2O$	36
28	$[\{Co_2(tpyprz)(H_2O)_2\}Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}]\cdot 2H_2O$	36
29	$[\{Co_2(tpyprz)(H_2O)_3\}Mo_5O_{15}\{O_3P(CH_2)_5PO_3\}]\cdot 2.5H_2O$	36
30	$[\{Co_2(tpyprz)(H_2O)_3\}Mo_5O_{15}\{O_3P(CH_2)_9PO_3\}]\cdot 2.5H_2O$	36
31	$[Co(bpy)_3][Mo_5O_{14}(OH)\{HO_3P(CH_2)_3PO_3\}]\cdot H_2O$	36
32	$[Co(terpy)_2][Mo_5O_{14}(OH)\{HO_3P(CH_2)_3PO_3\}]\cdot H_2O$	36
33	$[\{Co_2(phen)_3(H_2O)\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]$	36
34	$[\{Co_3(tpyprz)_2(H_2O)_3\}[Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]_2]$	36
35	$[\{Co(1,10\text{-}phen)_2(H_2O)\}_2\ \{(Mo_5O_{15})(4,4'\text{-}dbp)\}\cdot(5.5H_2O)]$	70
36	$[Ni(H_2O)(bipy))_2(C_6H_5PO_3)_2Mo_5O_{15}]_n$	68
37	$[Co(H_2O)(bipy))_2(C_6H_5PO_3)_2Mo_5O_{15}]_n$	68
38	$[\{Ni(1,10\text{-}phen)_2(H_2O)\}_2\ \{(Mo_5O_{15})(4,4'\text{-}dbp)\}\cdot(5.75H_2O)]$ $(4,4'\text{-}dbp = O_3PCH_2C_6H_4C_6H_4CH_2PO_3)$	70
39	$\{[Ni(2,2'\text{-}bpy)_2]_2[(C_6H_5P)_2Mo_5O_{21}]\ H_2O\}\ .2H_2O$ (bpy = bipyridine)	70
40	$[\{Ni_4(tpypyz)_3\}\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}_2]$	37
41	$[\{Ni_2(bpyr)(H_2O)_4\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]\cdot 9H_2O$	65
42	$[\{Ni_2(tpyprz)_2\}Mo_5O_{15}\{O_3P(CH_2)_4PO_3\}]\cdot 6.5H_2O$	38
43	$[\{Ni_2(tpyprz)_2\}Mo_5O_{15}\{O_3P(CH_2)_5PO_3\}]\cdot 3.5H_2O$	38
44	$[\{Ni_4(tpyprz)_3\}\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}_2]\cdot 23H_2O$	38
45	$[\{Ni_3(tpyprz)_2(H_2O)_2\}(Mo_5O_{15})(Mo_2O_4F_2)\{O_3P(CH_2)_3PO_3\}_2]\cdot 8H_2O$	38
46	$[\{Ni_2(tpyprz)(H_2O)_3]Mo_5O_{15}\{O_3P(CH_2)_3PO_3)\}]\cdot H_2O$	38
47	$[\{Ni_2(tpyprz)(H_2O)_2\}Mo_5O_{15}\ \{O_3P(CH_2)_4PO_3\}]\cdot 2.25H_2O$	38
48	$[\{Cu(terpy)\}_2(Mo_5O_{15})\ (O_3PCH_2CH_2CH_2PO_3)]$	42
49	$[Ni(H_2O)_4(4,4'\text{-}Hbpy)\}Mo_5O_{15}(1,2\text{-}O_3PC_8H_8PO_3)]\cdot 4H_2O$	35
50	$[Ni(phen)_2(H_2O)_2][Ni(phen)_2Mo_5O_{15}\{HO_2CC_6H_4PO_3\}_2]\cdot 2H_2O$	33

Sl.No	Compound	Reference
51	$[\{Ni(H_2O)(2,2'\text{-dpa})\}_2Mo_5O_{15}(1,4\text{-}O_3PC_8H_8PO_3)]\cdot 2H_2O$	35
52	$[Ni(2,2'\text{-bpy})_3]_2[\ Mo_5O_{21}(C_6H_5P)_2]\cdot 2H_2O$	34
53	$\{[Ni(2,2'\text{-bpy})_2]_2[\ Mo_5O_{21}(C_6H_5P)_{21}]\cdot H_2O\}\cdot 2H_2O$	34
54	$\{Cu_2(L5)\}Mo_6O_{18}(H_2O)\{O_3P(CH_2)_4PO_3\}]\cdot 14H_2O$	25
55	$\{[Cu(2,2'\text{-bpy})_2]_2[\ Mo_5O_{21}(C_6H_5P)_{21}]\}\cdot H_2O$	34
56	$[\{Ni(2,2'\text{-bpy})_3\}\{Ni(2,2'\text{-bpy})_2(H_2O)\}\ \{(Mo_5O_{15})(4,4'\text{-dbp})\}\cdot(4.75H_2O)]$	70
57	$[Cu(terpy)_2](H_3O)[Mo_5O_{15}(1,4\text{-}O_3PC_8H_8PO_3)]\cdot H_2O$	35
58	$[\{Cu(2,2'\text{-bpy})_2\}_2Mo_5O_{15}(1,4\text{-}O_3PC_8H_8PO_3)]\cdot 6H_2O$	35
59	$[\{Cu(H_2O)_2(o\text{-phen})\}_2Mo_5O_{15}(1,4\text{-}HO_3PC_8H_8PO_3)]\cdot 4H_2O$	35
60	$[(Cu(H_2O))_2(\mu\text{-bipy})_2\ Mo_5O_{15}(C_6H_5PO_3)_2]_n$	46
61	$\{[Cu(2,2'\text{-bpy})_2]_2[(C_6H_5P)_2Mo_5O_{21}]\}\cdot H_2O$	34
62	$[\{Cu(bpy)(H_2O)\}_3\{O_2CC_6H_4PO_3\}_2Mo_5O_{15}]\cdot 4.5H_2O$	33
63	$[\{Cu_2(bpyr)_2\}Mo_5O_{15}(O_3PCH_3)_2]\cdot 2.5H_2O$	65
64	$[\{Cu_2(bpyr)(H_2O)\}Mo_5O_{15}(O_3PCH_2CH_3)_2]$	65
65	$\{\{Cu_2(bpyr)\}[Mo_5O_{15}\{O_3P(CH_2)_nPO_3\}]$ .xH2O $n = 2-6$	65
66	$[\{Cu_2(bpyr)(H_2O)_4\}Mo_5O_{15}\{O_3P(CH_2)_3PO_3\}]\cdot 3H_2O$	65
67	$[\{Cu_2(tpypyz)(H_2O)_3\}Mo_5O_{15}(HPO_4)(O_3PCH_2CO_2H)]\cdot H_2O$	37
68	$[\{Cu_2(tpypyz)(H_2O)\}Mo_5O_{15}(O_3PC_6H_5)_2]\cdot 2H_2O$	37
69	$[\{Cu_2(tpypyz)(H_2O)_2\}Mo_5O_{15}\{O_3P(CH_2)_nPO_3\}]\cdot xH_2O$	37
70	$[\{Co(1,10\text{-phen})_2(H_2O)_2\}\{Co(1,10\text{-phen})_2(H_2O)\}\{(Mo_5O_{15})(O_3PCH_2CH_2CH_2CH_2PO_3)\}\cdot(6H_2O)]$	53
71	$[\{Cu2(tpypyz)(H_2O)_2\}(Mo_5O_{15})(HOPO_3)_2]\cdot nH_2O$	40
72	$[\{Cu(H_2O)_2(o\text{-phen})\}\{Cu(o\text{-phen})_2\}(Mo_5O_{15})(O_3PCH_2CH_2CH_2PO_3)]\cdot 2.5H_2O$	43
73	$[\{Cu(bpy)_2\}\{Cu(bpy)(H_2O)\}(MO_5O_{15})(O_3PCH_2CH_2CH_2CH_2PO_3)]\cdot H_2O$	42
74	$[\{Cu(terpy)(H_2O)\}_2(Mo_5O_{15})(O_3PCH_2CH_2PO_3)]\cdot 3H_2O$	42
75	$\{[Cu(2,20\text{-bpy})_2]_2[\ Mo_5O_{21}(C_6H_5P)_{21}]\}.\ H_2O$	43
76	$[(Zn(bipy)(\mu\text{-}OH))_2(Zn(bipy)_2\ Mo_5O_{15}\ (C_6H_5PO_3)_2)_2]\cdot 3H_2O$	42
77	$[(Cu(bipy)_2)_2\ Mo_5O_{15}(C_6H_5PO_3)_2]\cdot 2H_2O$	42

Sl.No	Compound	Reference
78	$[(Ni(H_2O)(bipy))_2\ Mo_5O_{15}(C_6H_5PO_3)_2]_n$	68
79	$[(Co(H_2O)(bipy))_2\ Mo_5O_{15}(C_6H_5PO_3)_2]_n$	68
80	$[(Cu(bipy)_2)_2\ Mo_5O_{15}\ (C_6H_5PO_3)_2]\cdot 2H_2O$ (bipy = 2,2'-bipyridine)	68
81	$[(Zn(bipy)(\mu\text{-}OH))_2(Zn(bipy)_2(C_6H_5PO_3)_2Mo_5O_{15})_2]\cdot 3H_2O$ (bipy = 2,2'-bipyridine)	68
82	$[(nC_4H_9)_4N]_2[(\ Mo_5O_{15}NH_2CH_2PO_3)_2]\cdot(CH_3NHCH_3)_2\cdot H_2O$	47
83	$[H_4tphz]_3[\{Zn_2(tphz)(H_2O)_4\}\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}_4]\cdot 14H_2O$	39
84	$[Ni_x(4\text{-}Hpt)_y(H_2O)_z\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}]\cdot n$hydrate (x = 2, y = 2, z = 6)	32
85	$[Co_x(4\text{-}Hpt)_y(H_2O)_z\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}]\cdot n$hydrate (x = 2, y = 2, z = 6)	32
86	$[Cu_x(4\text{-}Hpt)_y(H_2O)_z\{Mo_5O_{15}(O_3PCH_2CH_2PO_3)\}]\cdot n$hydrate (x = 4, y = 3, z = 1)	32
87	$[NEt_4]_2Na_3(H_3O)_4\{Na[Mo_6O_{15}(O_3PPh)(HO_3PPh)_3]_2\}.nH_2O$	31
88	$[\{Co_2(tpyprz)(H_2O)_2\}Mo_6O_{18}\{O_3P(CH_2)_5PO_3\}]\cdot 2H_2O$	36
89	$[Ni_2(tpyprz)_2][Mo_7O_{21}(O_3PCH_2PO_3)]\cdot 3.5H_2O$	39
90	$\{[Ni(1,10\text{-}phen)_3][Ni(1,10\text{-}phen)_2(Mo_6O_{18})(O_3P(CH_2)_4PO_3)]\cdot 6H_2O\}_n$	55
92	$\{[Ni(1,10\text{-}phen)_2(H_2O)_2][Ni(1,10\text{-}phen)_2(H_2O)(Mo_5O_{15})(O_3P(CH_2)_4PO_3)]\cdot 6H_2O\}_n$	55
91	$(Et_3NH)_2[Mo_2O_5\{(C_6H_5)_2]\cdot CH_3CN$	37
93	$(NH_4)_4[\ Mo_5O_{21}(CH_3P)_2].5H_2O$	57
94	$(PhNMe_3)_4[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]$	54
95	$(ppzH_2)_4[Mo_7O_{16}(O_3PCH_2PO_3)_3]\cdot 8H_2O$	30
96	$(Et_3NH)_4[Mo_6O_{18}(BuPO_3)_2]$	64
97	$((enH_2)_4[Mo_7O_{16}(O_3\ PCH_2PO_3)_3]\cdot 7H_2O$	30
98	$Na_8[(Mo_3O_8)\{O_3PC(O)(CH_2\text{-}3\text{-}C_5NH_5)PO_3\}]_4\cdot 30H_2O$	28
99	$Rb_4KNa[\ Mo_5O_{15}(O_2CCH_2PO_3)_2]\cdot H_2O$	26
100	$(NH_4)_2[Mo_5O_{21}(PCH_2C_6H_4NH_3)_2]$	28
101	$Cs_4[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]\cdot 7H_2O$	27
102	$Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$	**Present work**
103	$Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$	**Present work**
104	$(NH_4)_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$	**Present work**
105	$Cs_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$	**Present work**

Non-molecular molybdoorganophosphonates		
Sl.No	**Compound**	**Reference**
106	$Cs_2(MoO_3)_3PO_3CH_3$	56
107	$Rb_2(MoO_3)_3PO_3CH_3$	56
108	$Tl_2(MoO_3)_3PO_3CH_3$	50
109	$Rb[MoO_2(O_3PCH_2PO_3H)]$	59
110	$Cs[MoO_2(O_3PCH_2PO_3H)]$	48
111	NH4$[MoO_2(O_3PCH_2PO_3H)]$	59
112	$Tl[MoO_2(O_3PCH_2PO_3H)]$	59
113	$NH_4[Mo_2O_5(O_3PCH_2CH_2PO_3)]$	60
114	$K(H_3O)[Mo_2O_5(O_3PCH_2CH_2PO_3)]$	60
115	$(K)_{1.5}(H_3O)_{0.5}([(Mo_2O_5)(O_3PPh)_2]$	**Present work**
116	$Rb_2[(Mo_2O_5)(O_3PC_6H_4PO_3)]$	**Present work**
117	$(NH_4)_2[(Mo_2O_5)(O_3PC_6H_4PO_3)]$	**Present work**
118	$Rb_2[(Mo_2O_5)(O_3PC_4H_8PO_3)]$	**Present work**
119	$Rb_2[(Mo_2O_5)(O_3PC_3H_6PO_3)]$	**Present work**

Table S20. Red-ox potentials (V) for compounds **1**-**5**, **11**, **16** and **20**.

Compound	KNO_3		KNO_3		NaOAc-AcOH	
	Reduction I	Oxidation I	Reduction II	Oxidation II	Reduction II	Oxidation II
1	-0.39	-0.49	-1.04	-0.93	-0.55	-0.32
2	-0.44	-0.47	-0.77	-0.91	-0.58	-0.34
3	-	-	-0.90	0.40	-0.69	-0.36
4	-	-	-0.92	-0.33	-0.93	-0.52
5	-	-	-0.84	-0.33	-0.93	-0.29
11	-	-	-0.82	-	-0.80	-
16	-	-	-0.78	-	-0.73	-
20	-	-	-0.70	-	-0.73	-

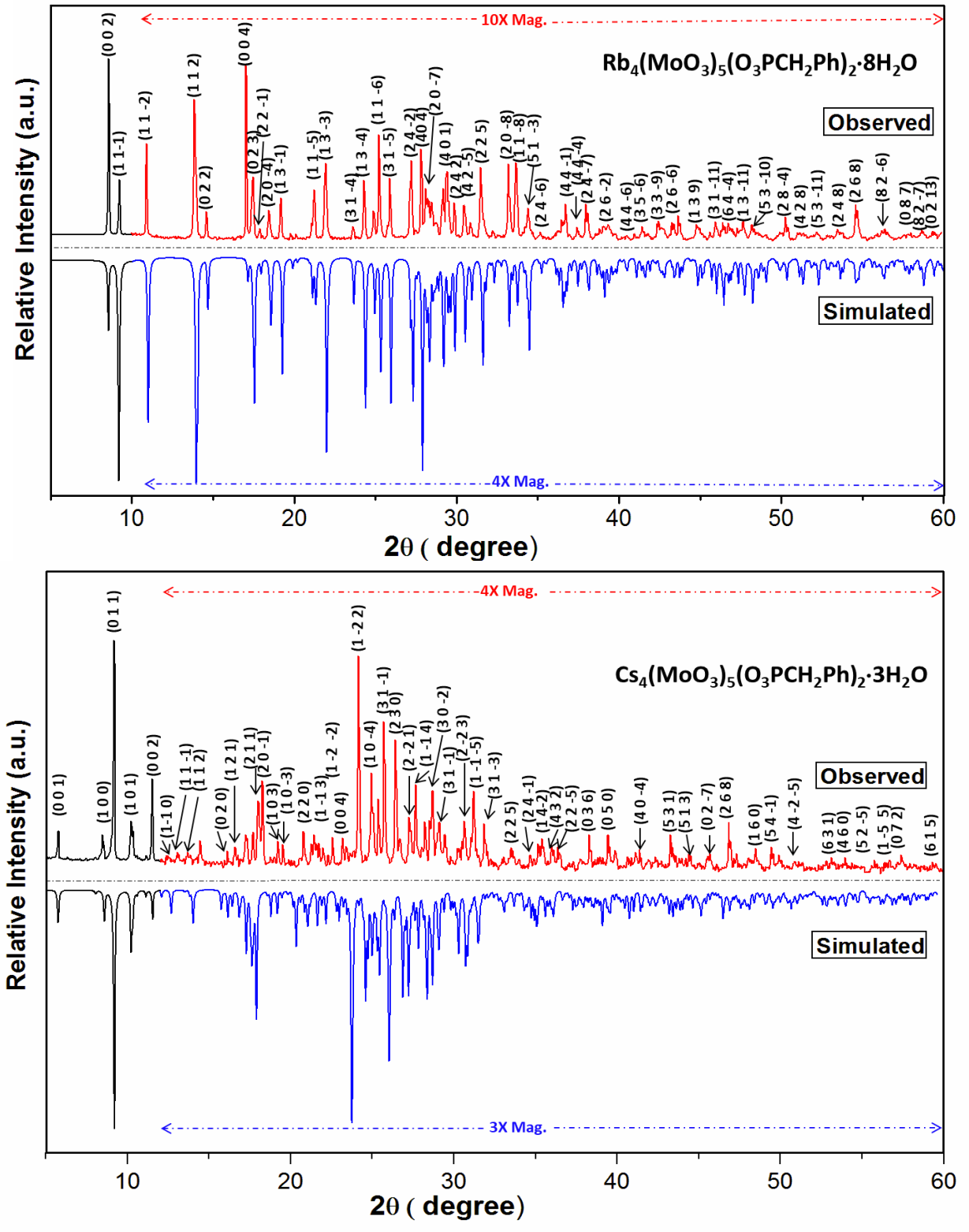

Figure S1. Simulated and observed powder XRD patterns of (top) $Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 8H_2O$(**1**) and (bottom) $Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$(**2**).

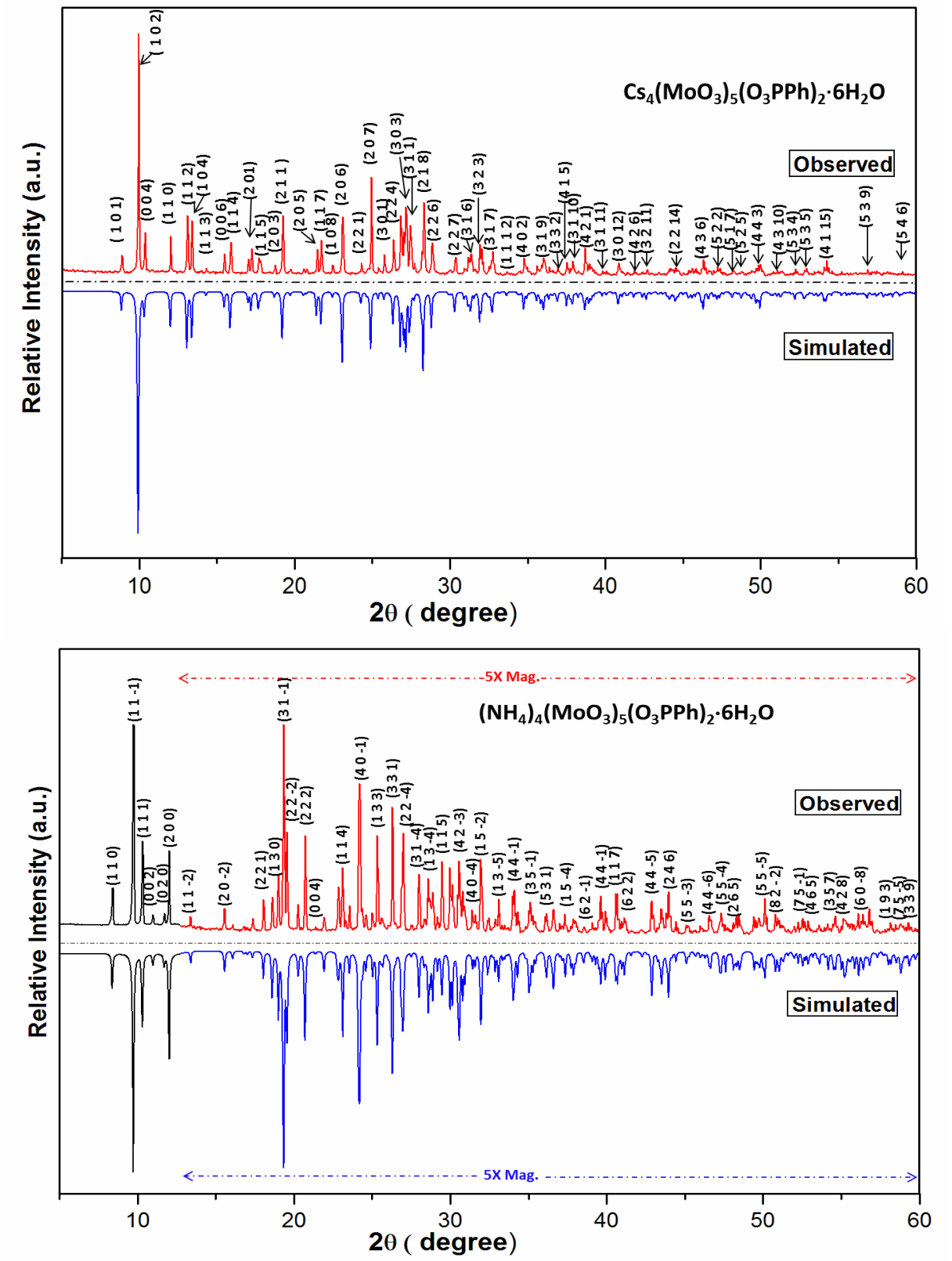

Figure S2. Simulated and observed powder XRD patterns of (top) $Cs_4(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**3**) and (bottom) $(NH_4)_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**4**).

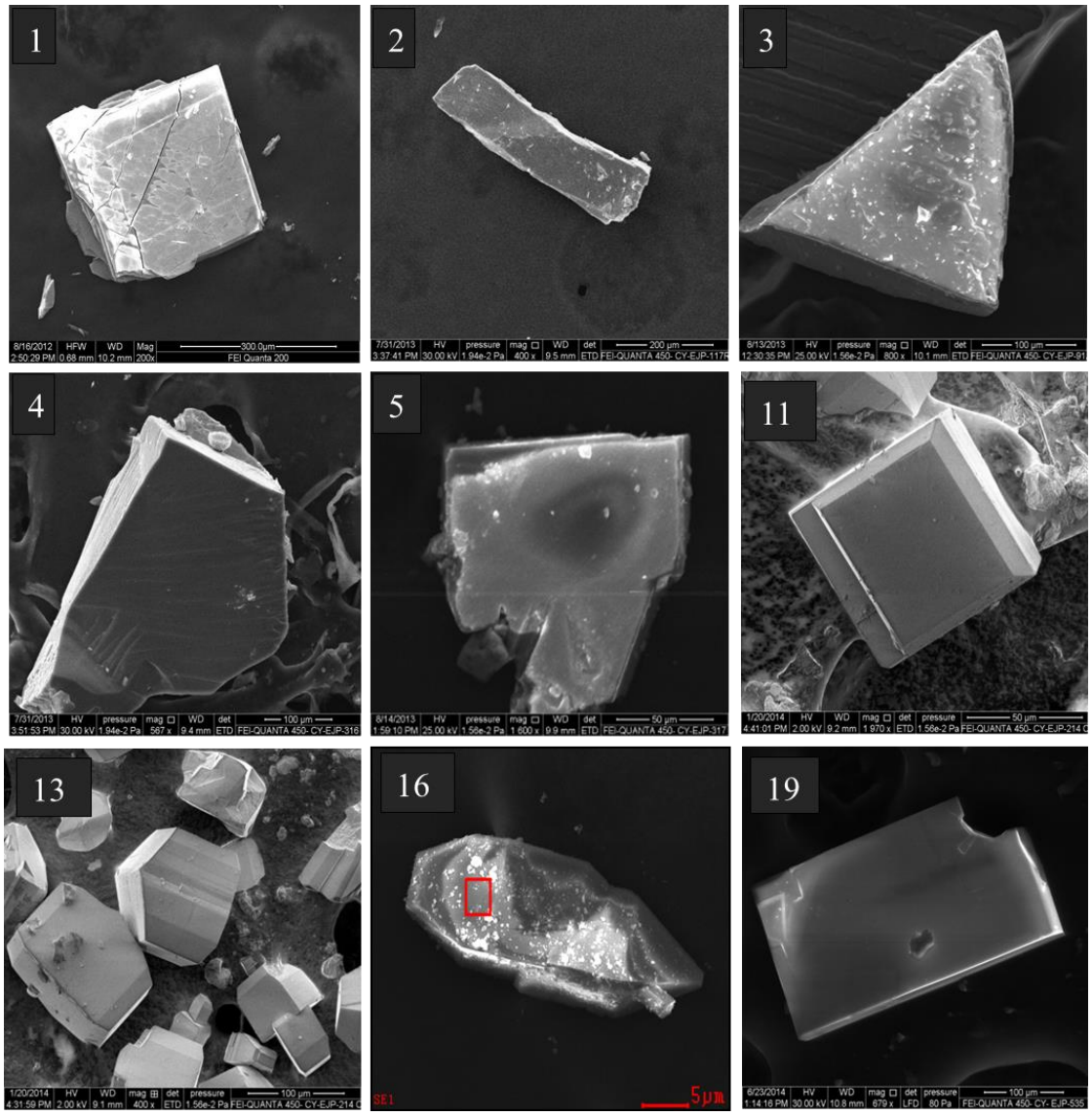

Figure S3. Scanning electron microscope (SEM) images of the crystals of nine compounds, **1- 4**, **5, 11, 13, 16** and **19**.

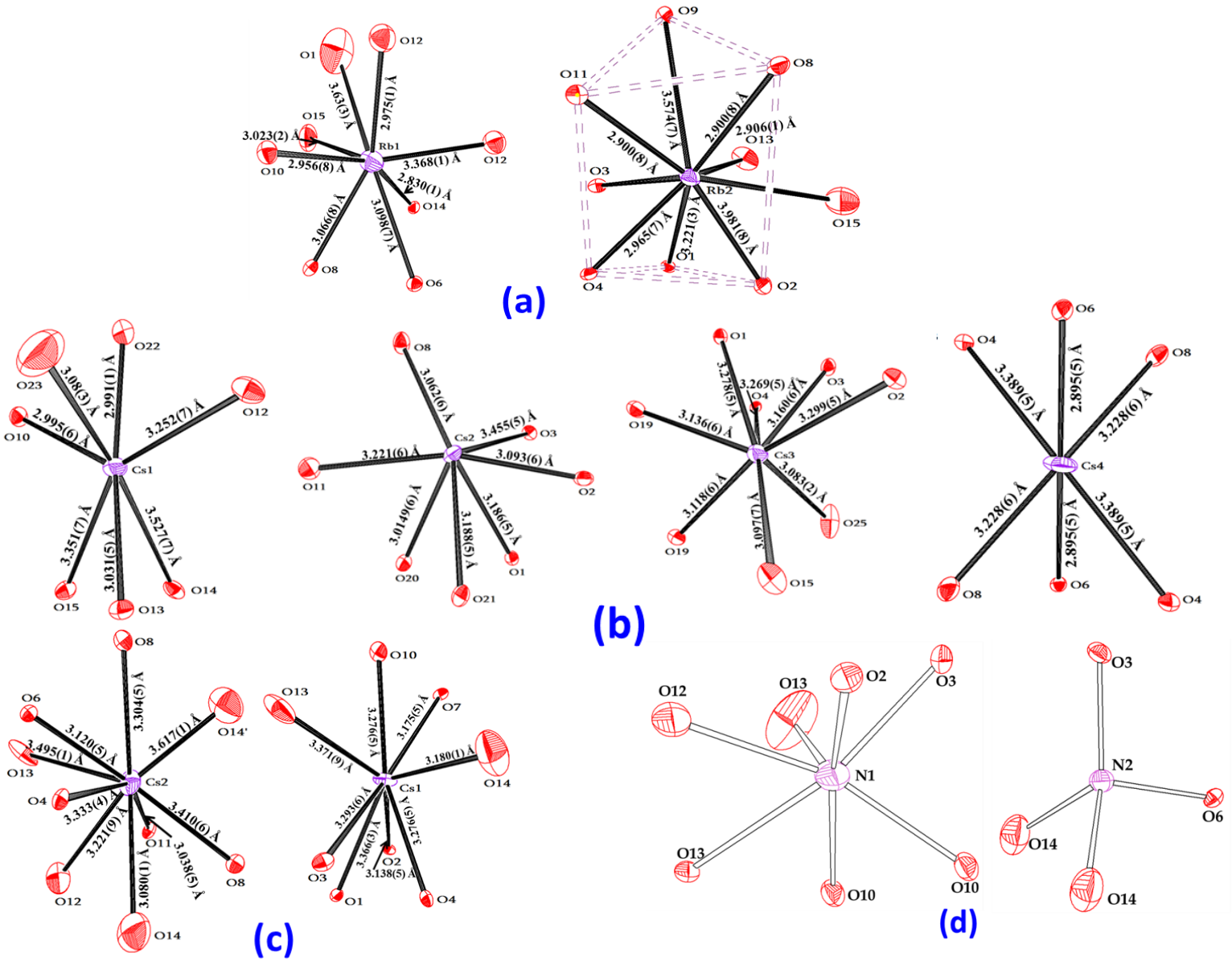

Figure S4. ORTEP diagram showing the atom labelling scheme and coordination of A^+ ions in (a) $Rb_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 8H_2O$(**1**), (b) $Cs_4[(MoO_3)_5(O_3PCH_2Ph)_2]\cdot 3H_2O$(**2**), (c) $Cs_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**3**) and (d) $(NH_4)_4[(MoO_3)_5(O_3PPh)_2]\cdot 6H_2O$(**4**) compounds.

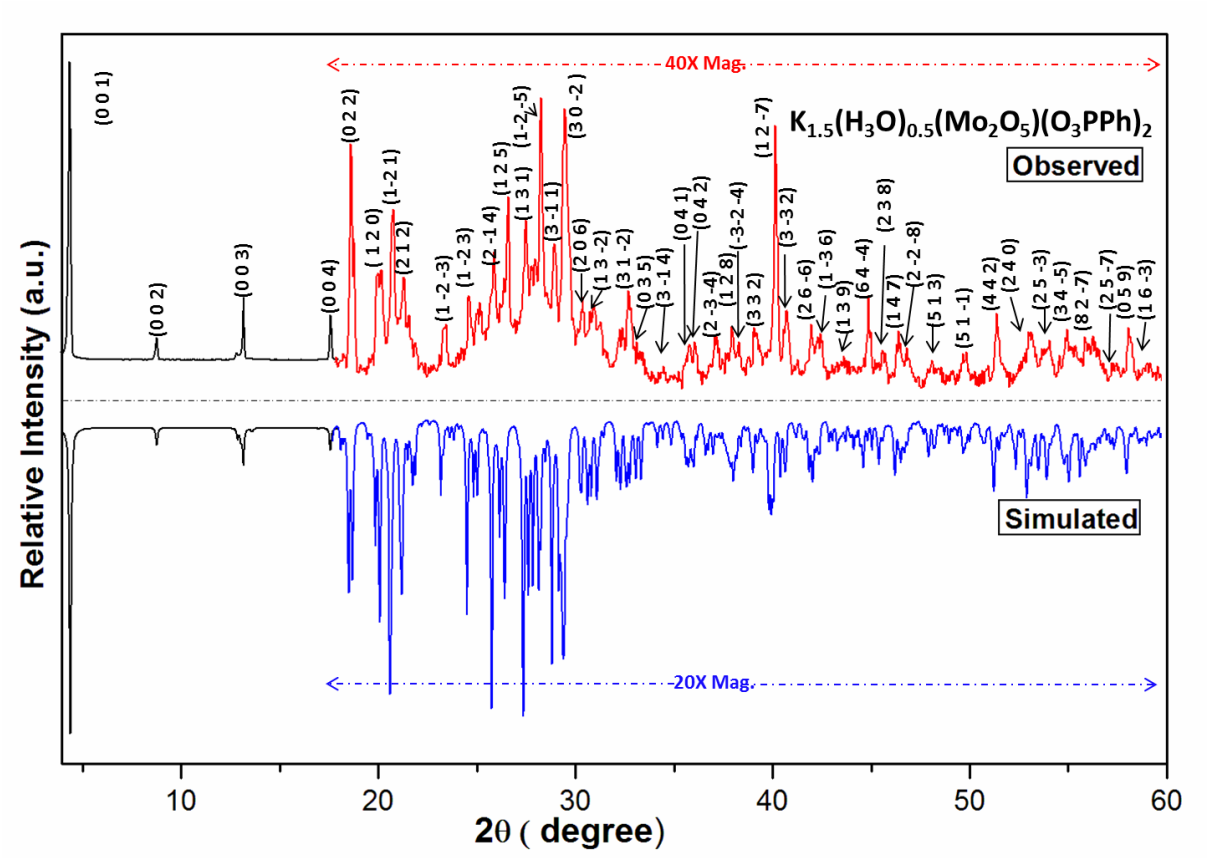

Figure S5. Simulated and observed powder XRD patterns of $K_{1.5}(H_3O)_{0.5}[(Mo_2O_5)(O_3PPh)_2]$(**5**)

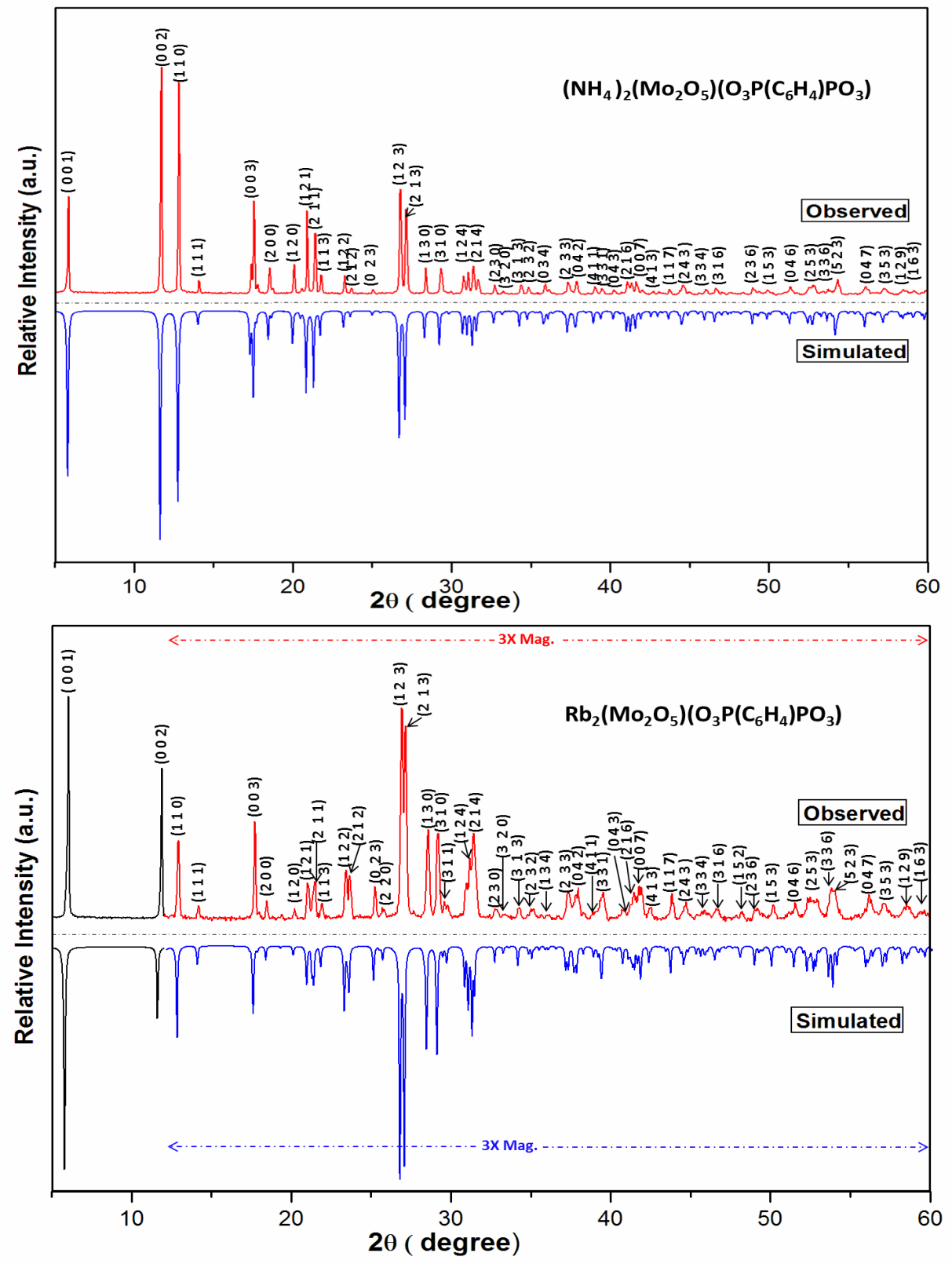

Figure S6. Simulated and observed powder XRD patterns of (top) $(NH_4)_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**11**) and (bottom) $Rb_2[(Mo_2O_5)(O_3P(C_6H_4)PO_3)]$(**13**).

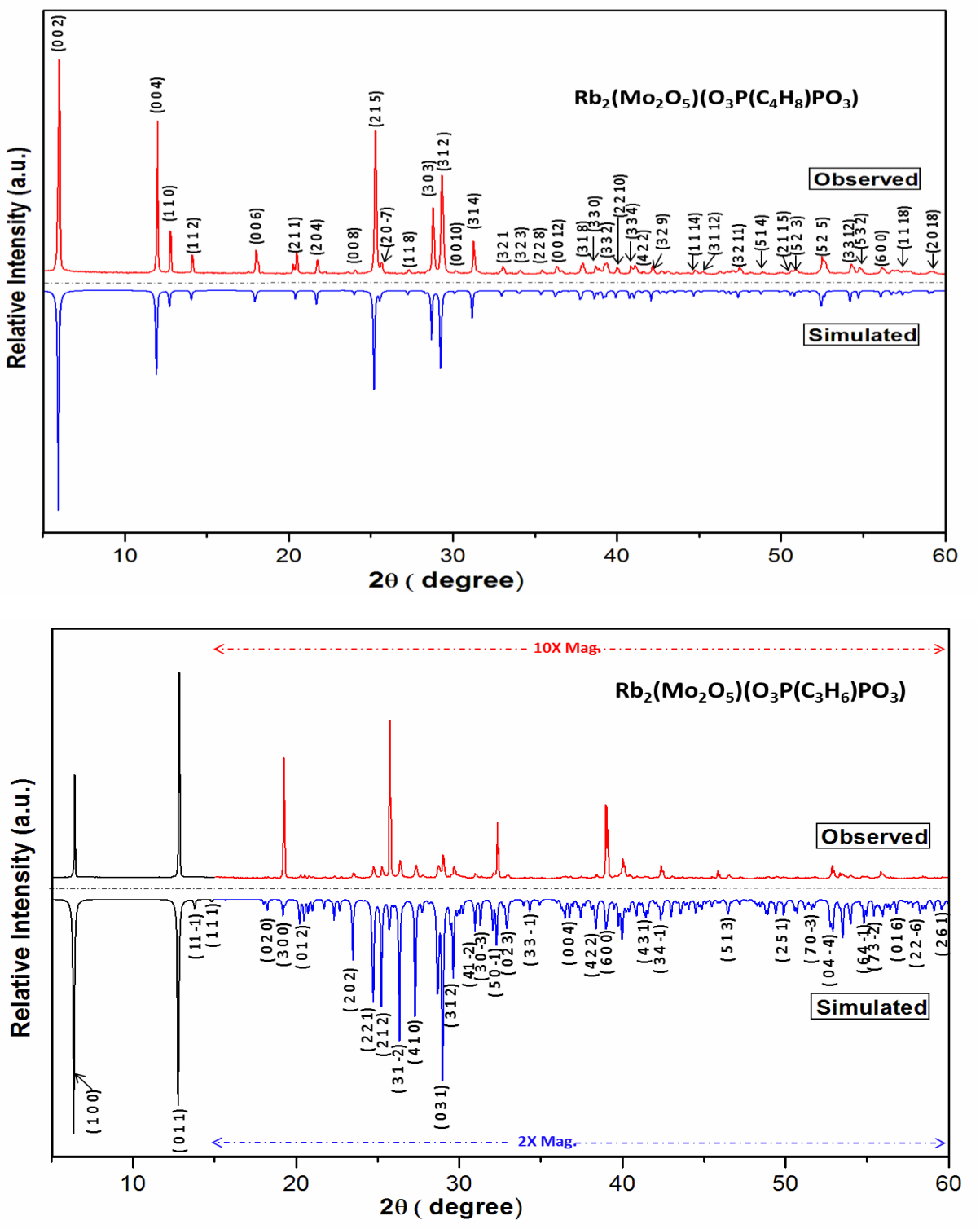

Figure S7. Simulated and observed powder XRD patterns of (top) $Rb_2[(Mo_2O_5)(O_3P(C_4H_8)PO_3]$(**16**) and (bottom) $Rb_2[(Mo_2O_5)(O_3P(C_3H_6)PO_3)]$(**19**).

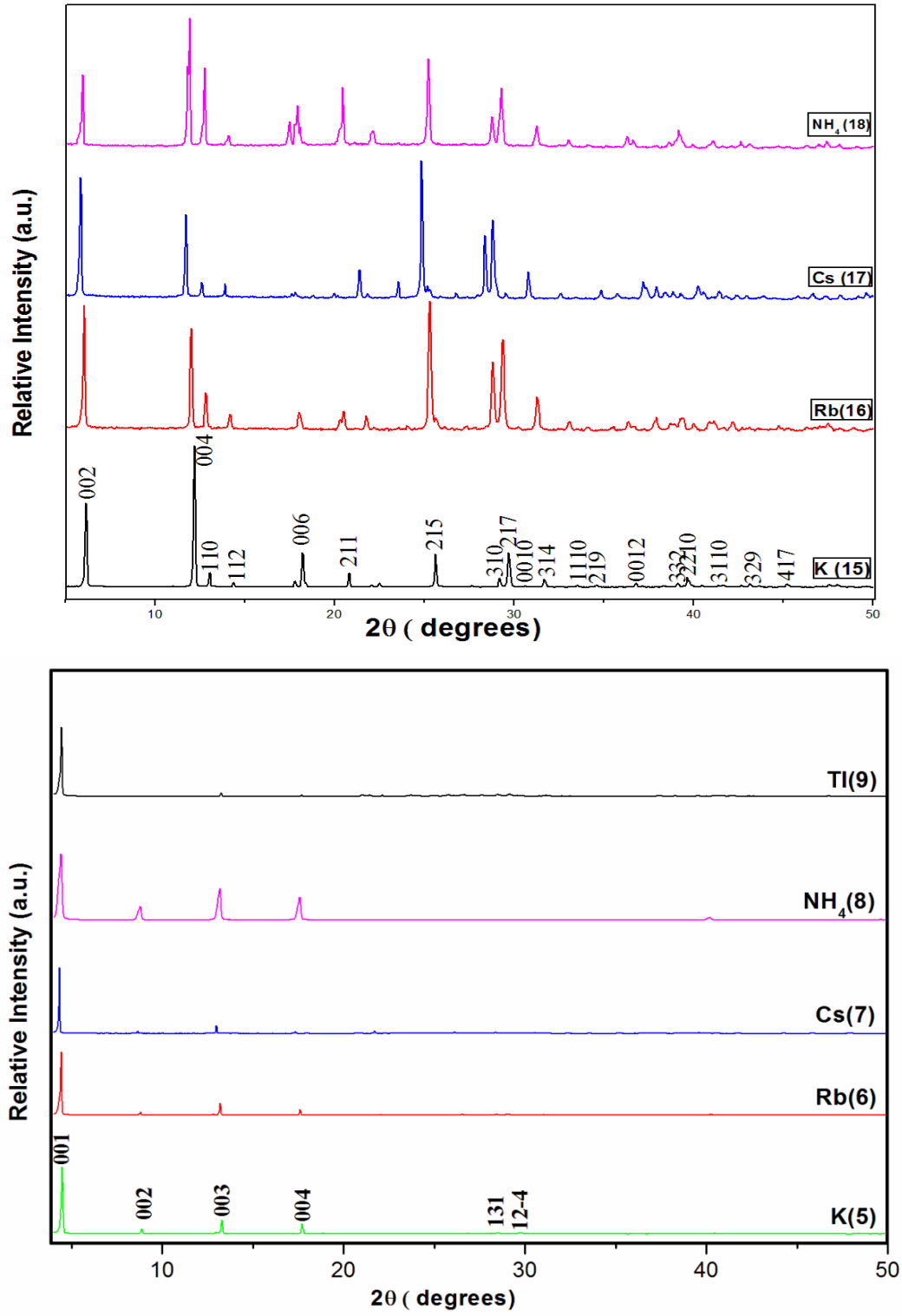

Figure S8. Powder XRD patterns of (top) butylenediphosphonates **15-18** and (bottom) phenylphosphonates **5-9**

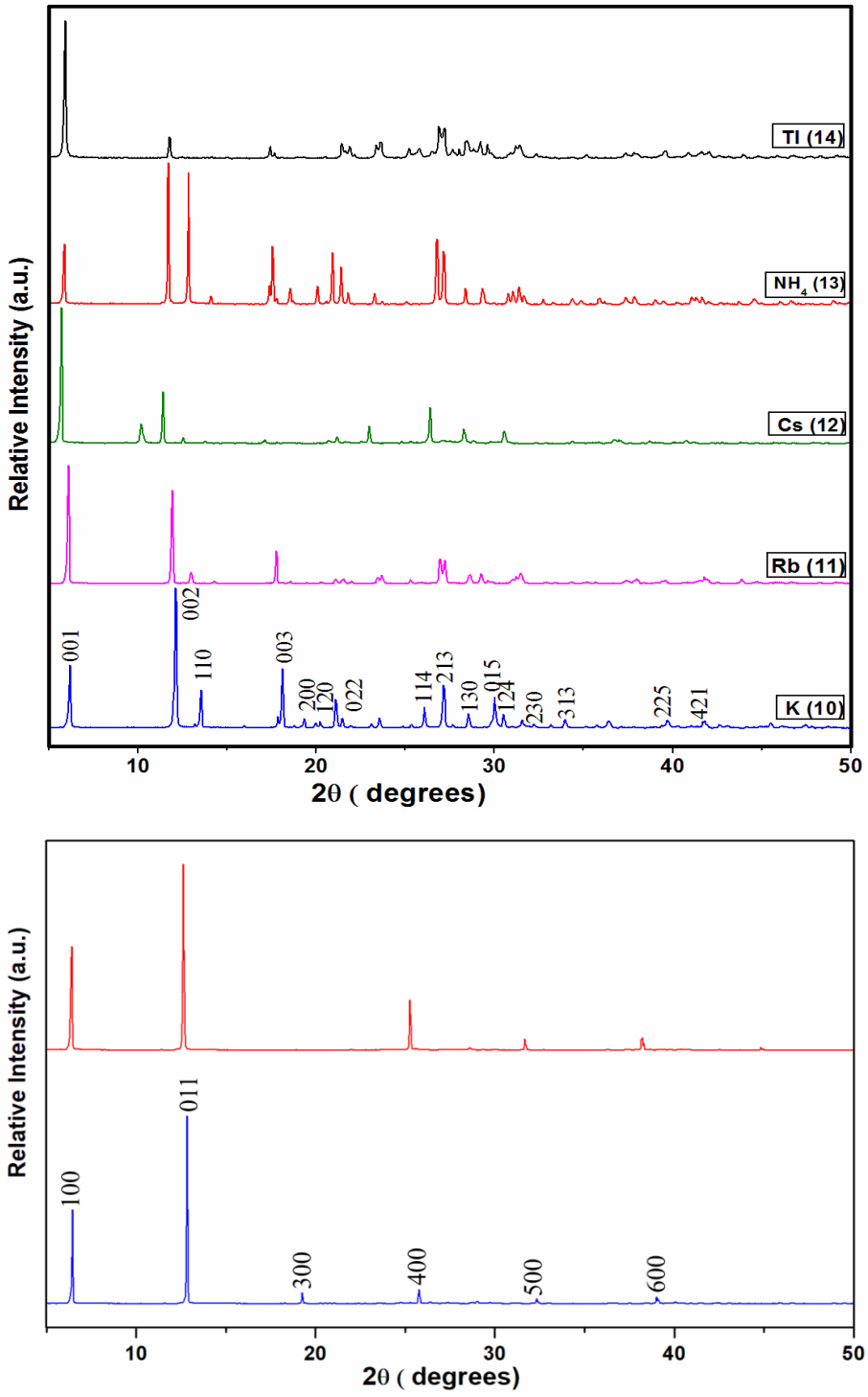

Figure S9. Powder XRD patterns of (top) phenylenediphosphonates **10**-**14** and (bottom) propylenediphosphonates **19** and **20**

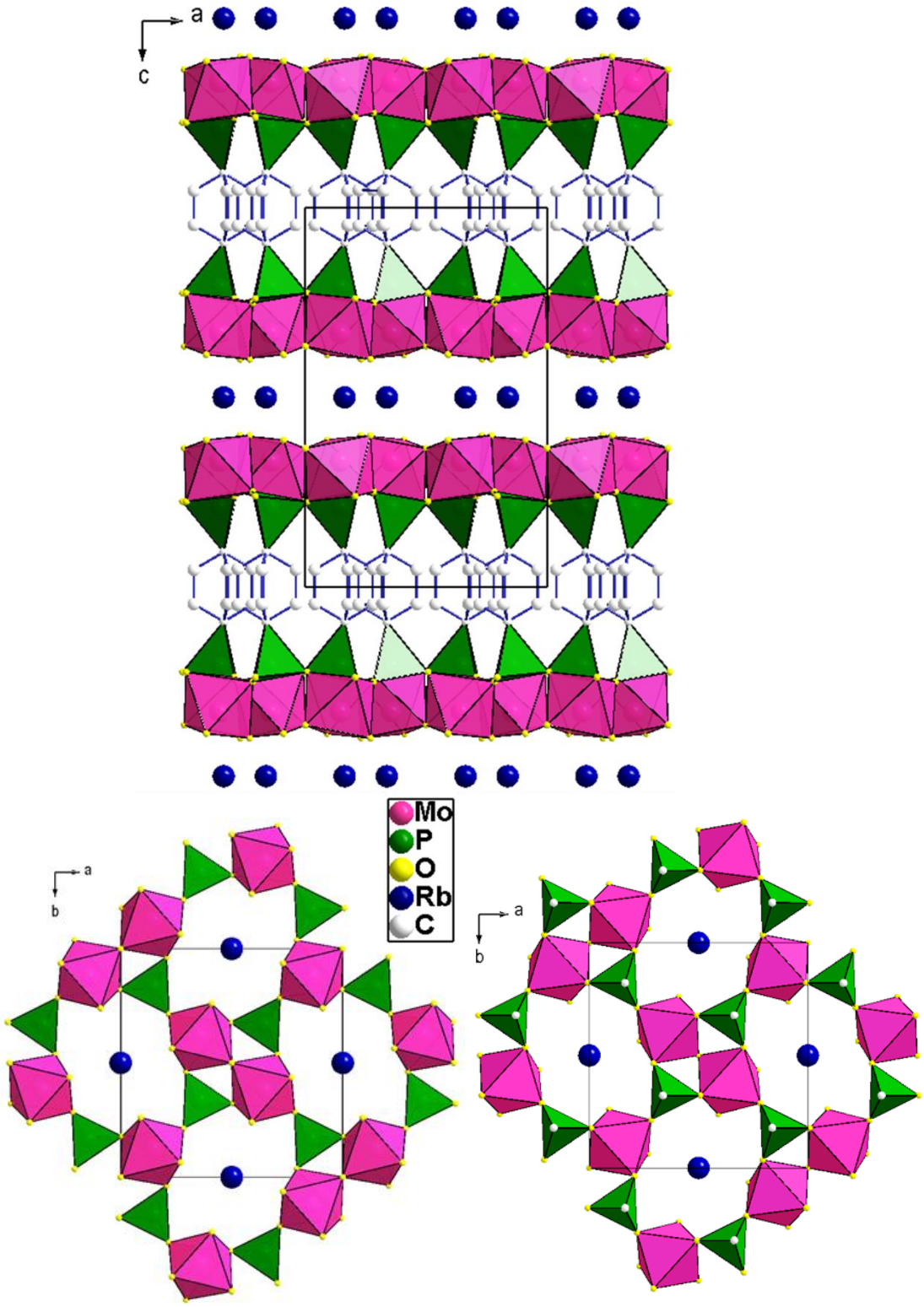

Figure S10. Polyhedral representation of (top) unit cell structure viewed along *a*-axis and (bottom) sublayers of $[Mo_2O_5(O3P(C_6H_4)PO_3)]^{2-}$ anion viewed along *c*-axis of $Rb_2[Mo_2O_5(O_3P(C_6H_4)PO_3)]$ (**13**).

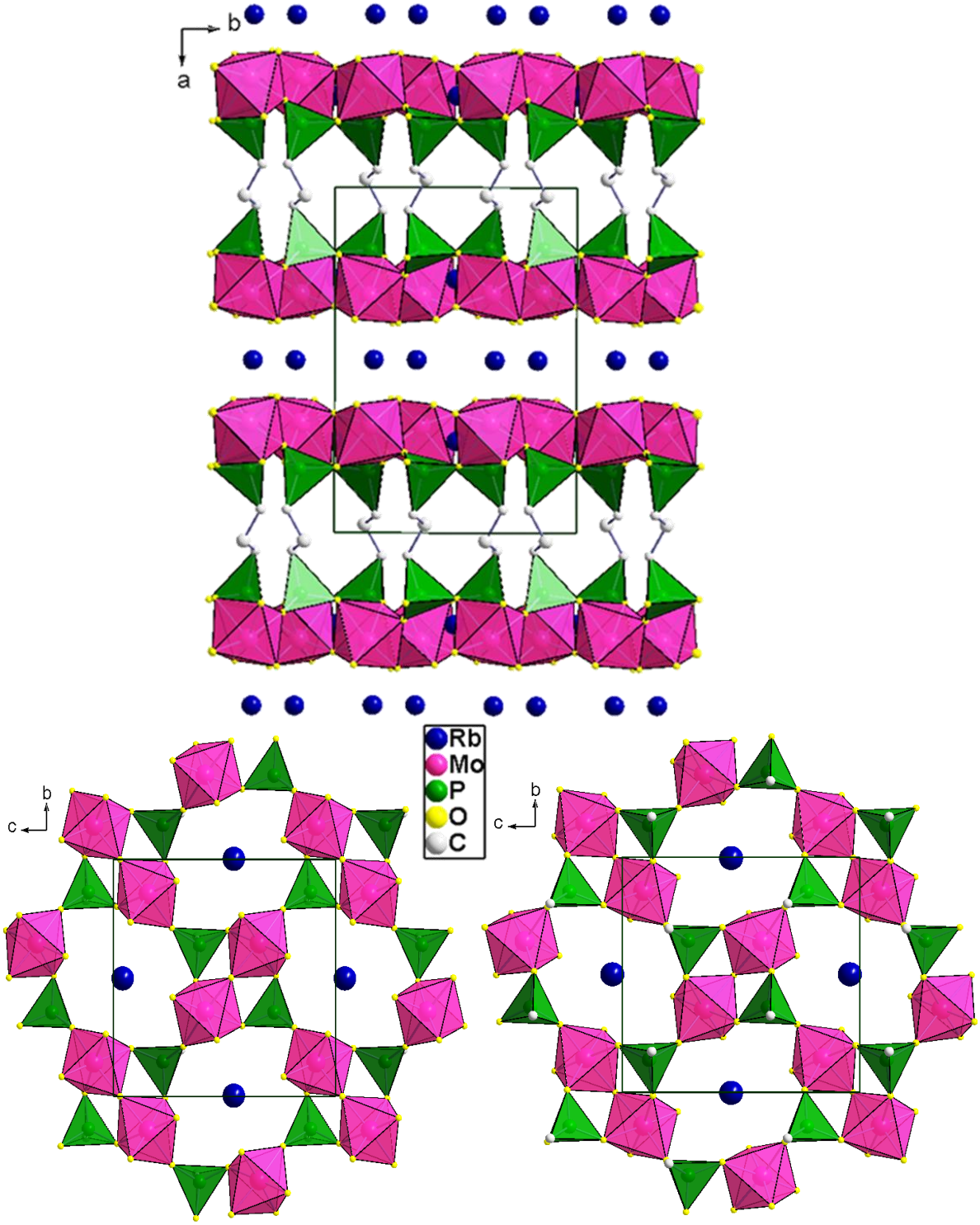

Figure S11. Polyhedral representation of (top) unit cell structure viewed along *c*-axis and (bottom) sublayers of $[Mo_2O_5(O_3P(CH_2)_3PO_3)]^{2-}$ anion viewed along *a*-axis, of $Rb_2[Mo_2O_5(O_3P(CH_2)_3PO_3)]$ (**19**).

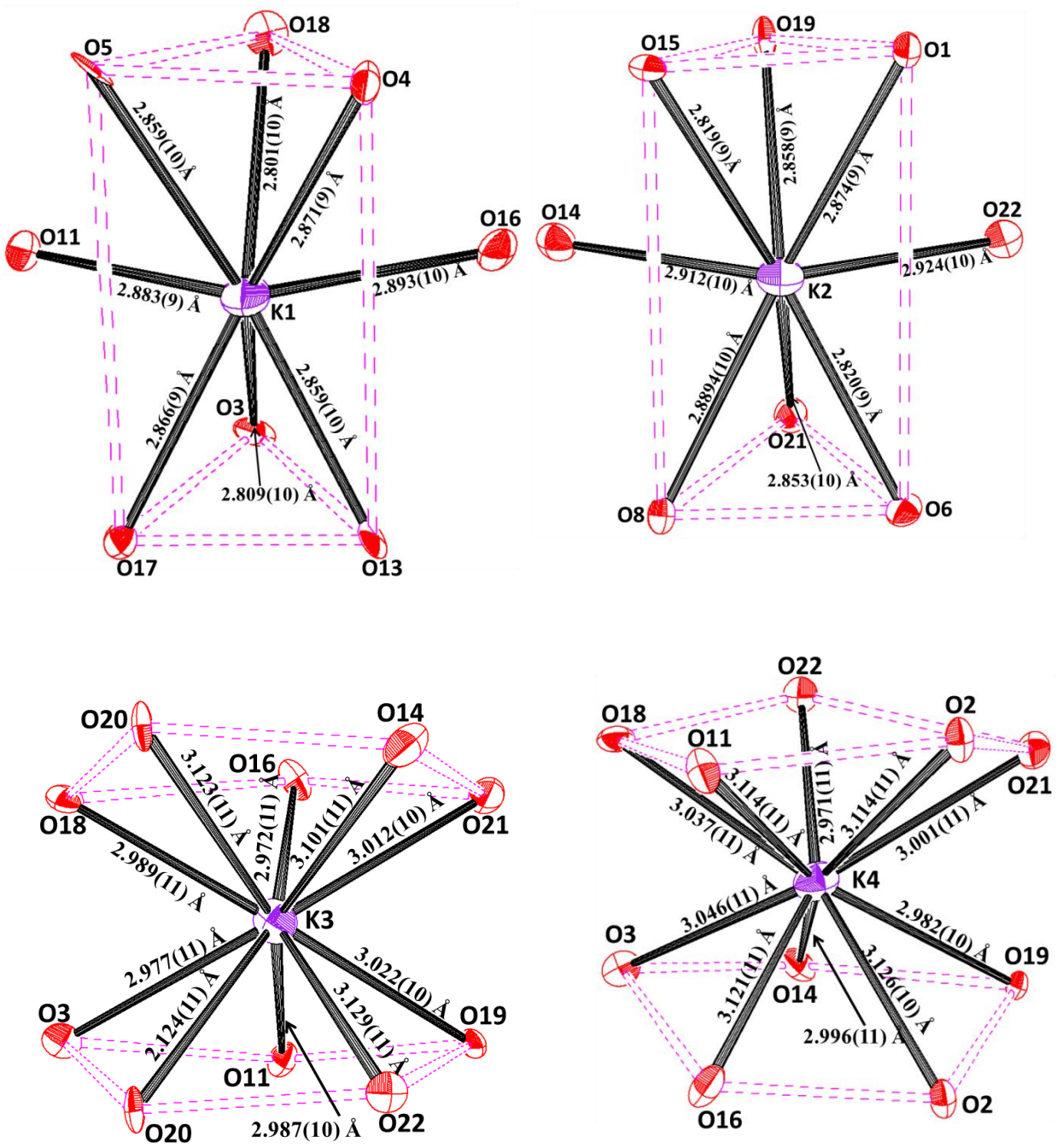

Figure S12. ORTEP digram showing the atom labelling scheme and coordination of K^+ ions in $K_{1.5}(H_3O)_{0.5}[Mo_2O_5(O_3PPh)_2]$(**5**).

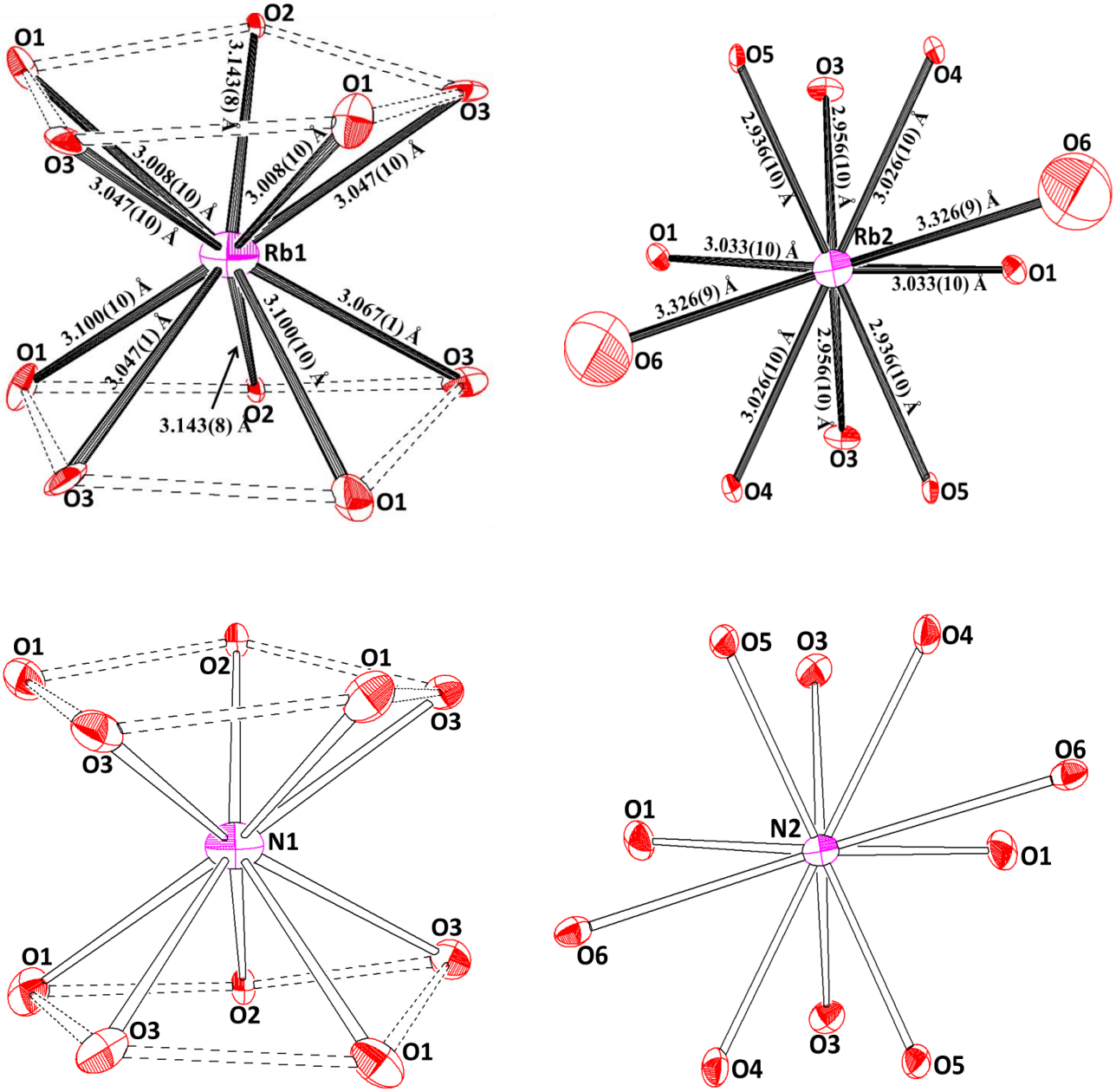

Figure S13. ORTEP digram showing the atom labelling scheme and coordination of A^+ ions in (top) $Rb_2[Mo_2O_5(O_3PC_6H_4PO_3)]$(**11**) and (bottom) $(NH_4)_2[Mo_2O_5(O_3PC_6H_4PO_3)]$(**13**),

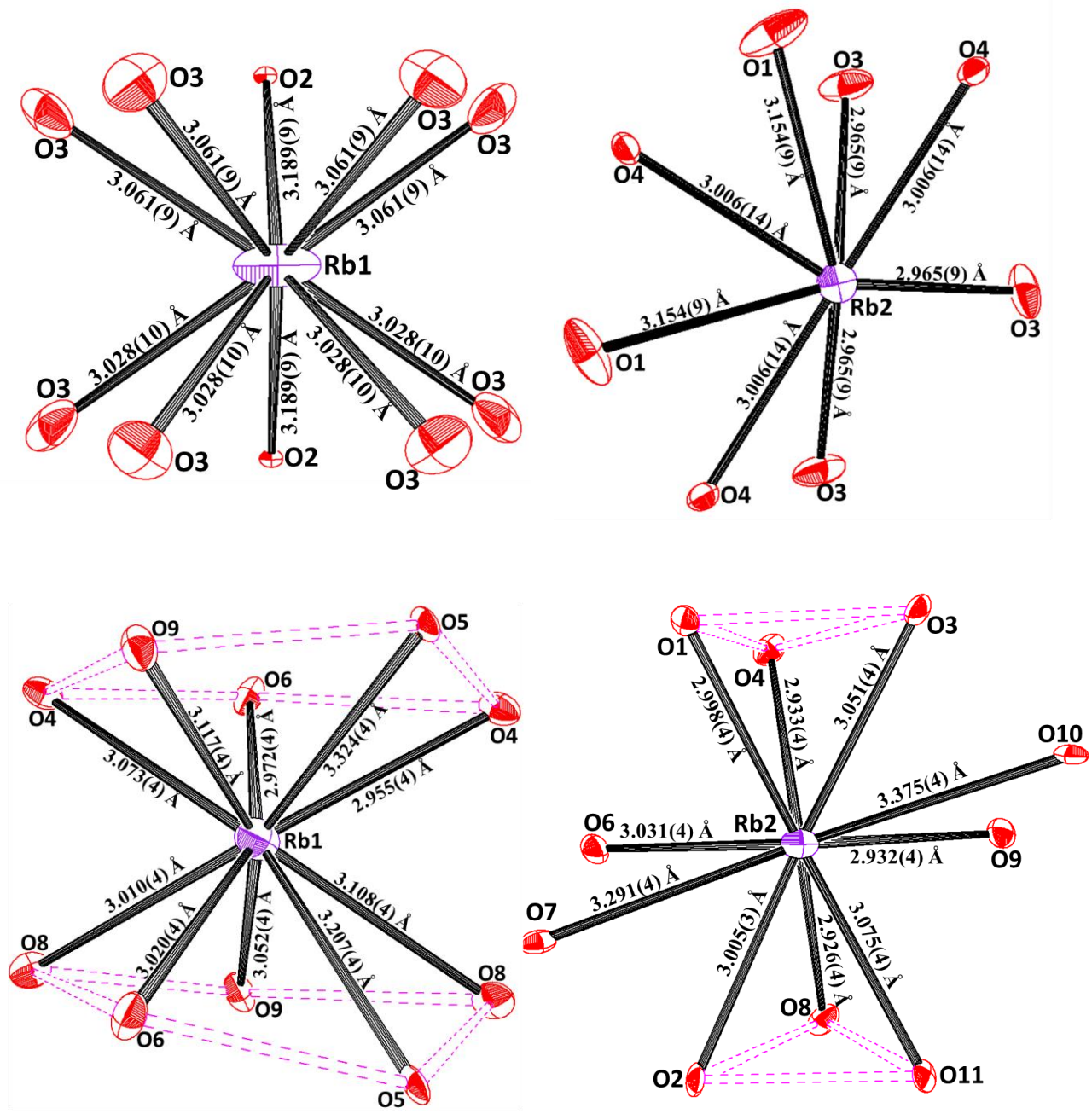

Figure S14 . ORTEP digram showing the atom labelling scheme and coordination of A^{+} ions in (top) $Rb_2[Mo_2O_5(O_3PC_4H_8PO_3)]$(**16**) and (bottom) $Rb_2[Mo_2O_5(O_3PC_3H_6PO_3)]$(**19**) compounds.

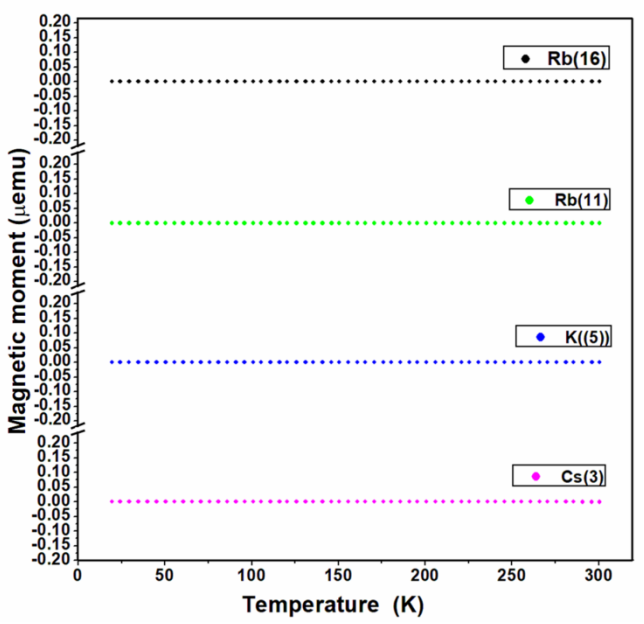

Figure **S15**. Magnetic moment versus temperature plots for compounds **3**, **5**, **11** and **16**.

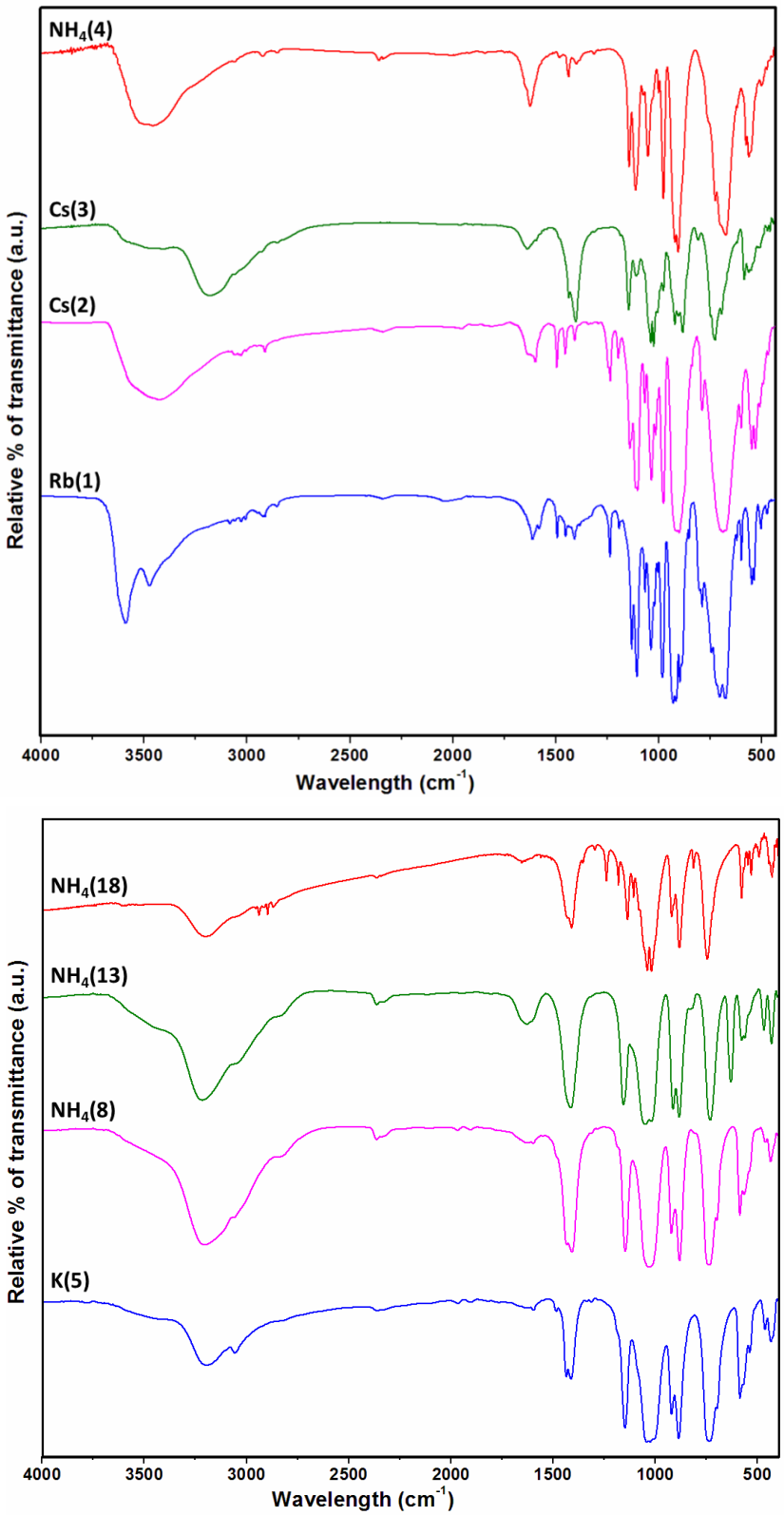

Figure S16. FT-IR spectra of compounds (top) **1 -4** and (bottom) **5, 8, 13, 18.**

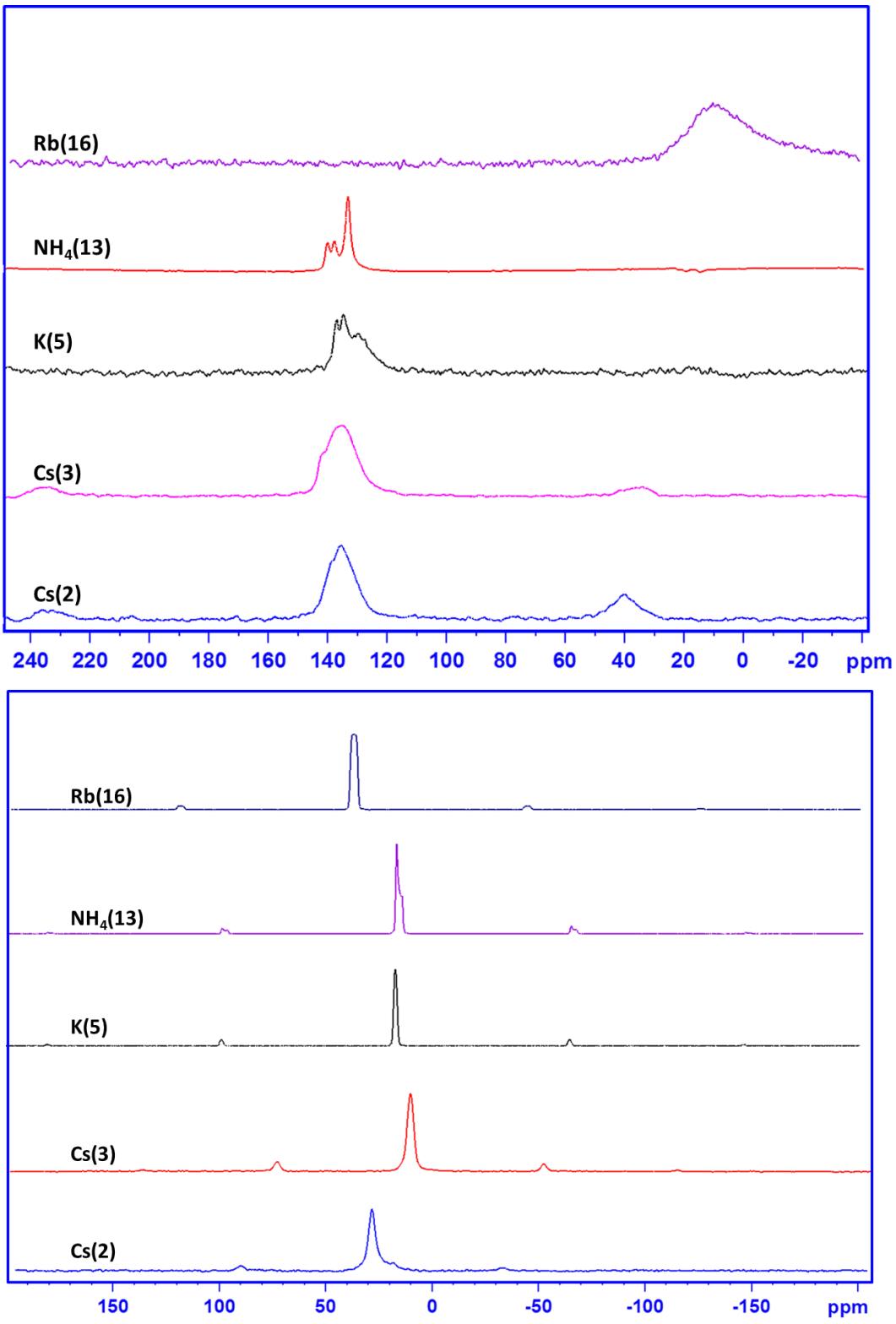

Figure S17. Solid state (top) ^{13}C and (bottom) ^{31}P nmr spectra of compounds **2**, **3**, **5**, **13** and **16**

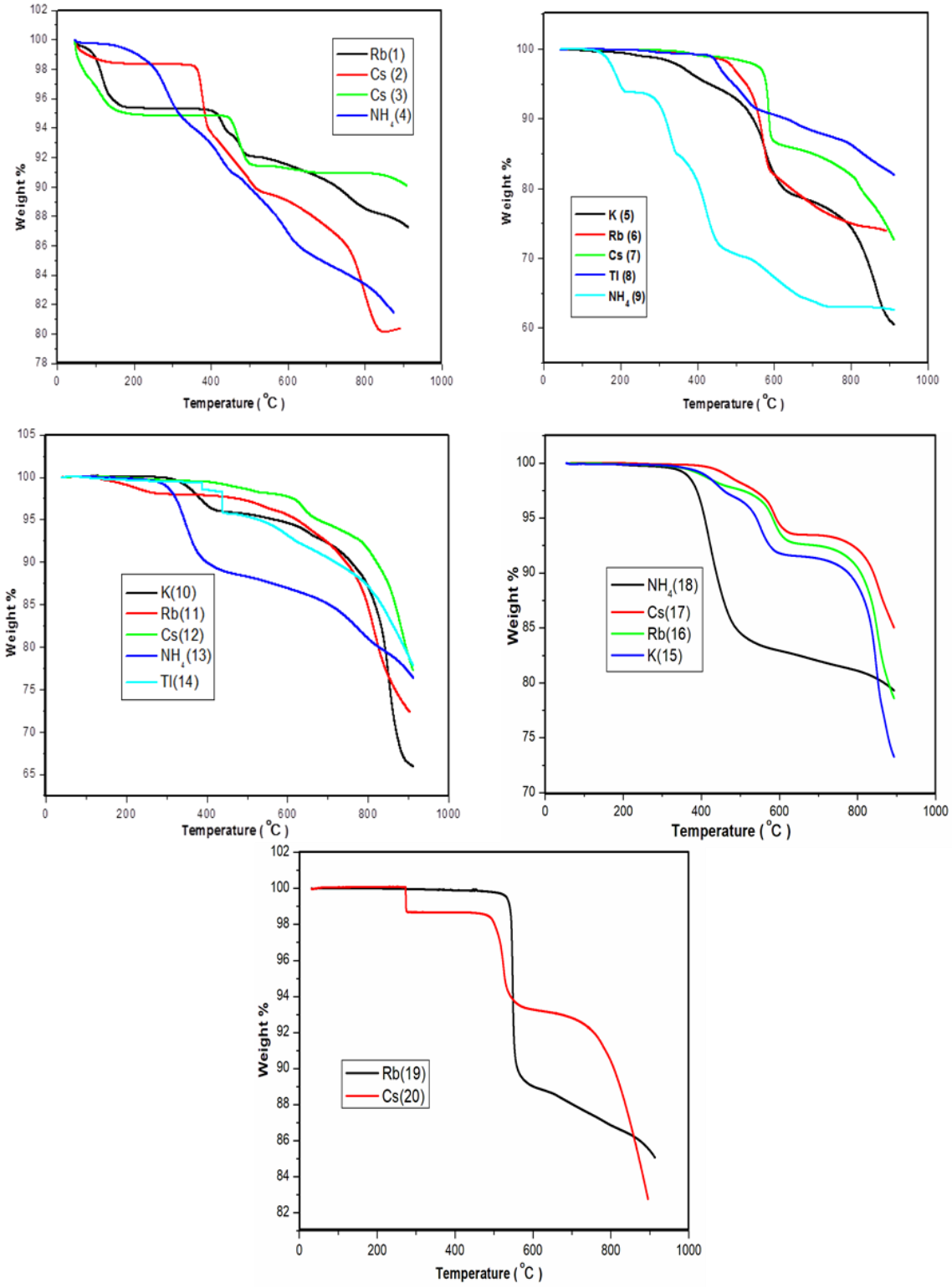

Figure S18. Thermogravimetric plots of compounds **1-20**.

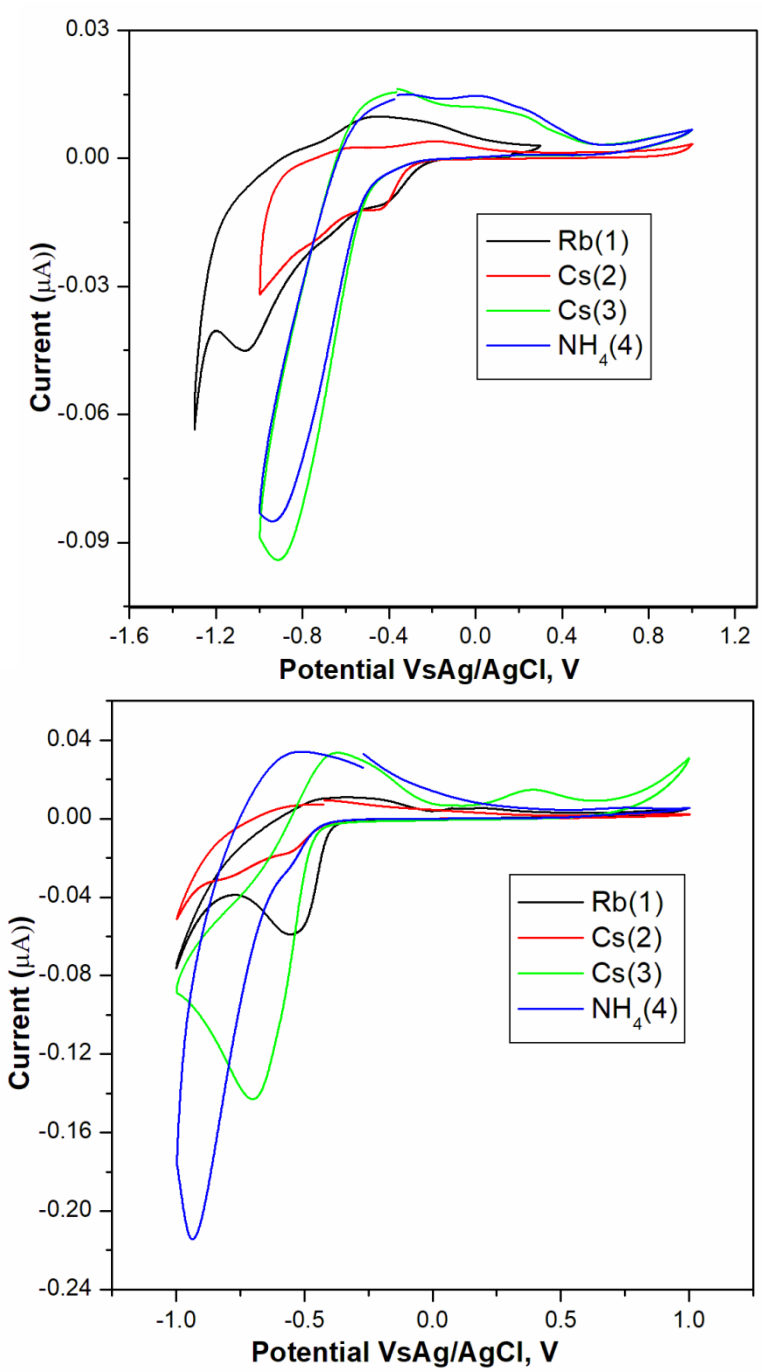

Figure **S19**. Cyclic voltammograms of molecular molybdoorganophosphonates **1**-**4**, in (top) 0.1N KNO_3 and (bottom) NaOAc-AcOH.

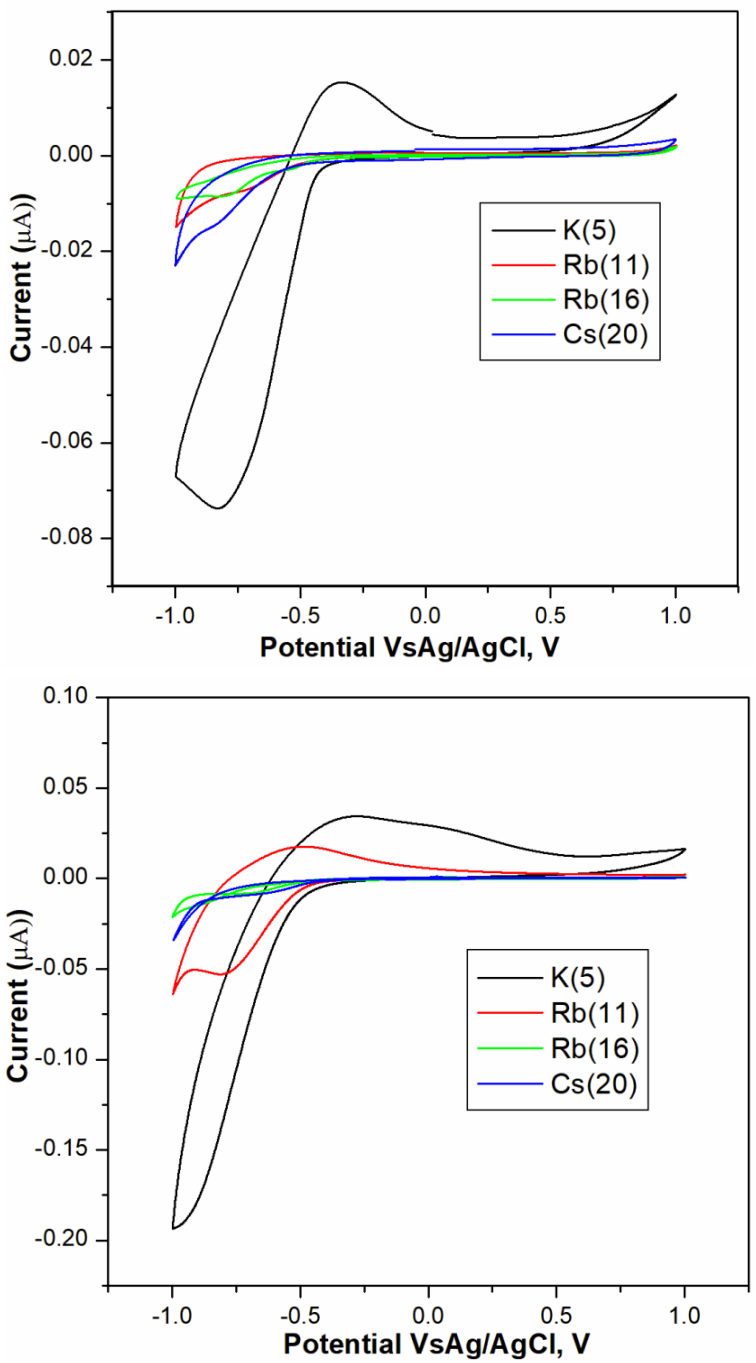

Figure **S20**. Cyclic voltammograms of non-molecular molybdoorganophosphonates **5**, **11**, **16** and **20**, in (top) 0.1N KNO_3 and (bottom) NaOAc-AcOH.