Syntheses and structures of two new lithium–heptamolybdates

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Table S1. List of structurally characterized heptamolybdate compounds.

No	Compound	Space Group	Binding mode of {Mo ₇ O ₂₄ } ⁻⁶	Ref
1	(H ₂ DABCO) ₃ [Mo ₇ O ₂₄]·4H ₂ O	<i>Cc</i>	Counterion	26
2	(2-ampH) ₄ [Co(H ₂ O) ₅ Mo ₇ O ₂₄]·9H ₂ O	<i>Pna2₁</i>	Monodentate	9
3	[3-ampH] ₄ [{Zn(3-ampy)(H ₂ O) ₄ }Mo ₇ O ₂₄]·4H ₂ O	<i>Cc</i>	Monodentate	15
4	[3-ampH] ₄ [{Co(3-ampy)(H ₂ O) ₄ }Mo ₇ O ₂₄]·4H ₂ O	<i>Cc</i>	Monodentate	15
5	[2-ampH] ₄ [{Zn(H ₂ O) ₅ }Mo ₇ O ₂₄]·9H ₂ O	<i>Pnma</i>	Monodentate	15
6	Na(NH ₄)[bppH ₂] ₂ [Mo ₇ O ₂₄]·8H ₂ O	<i>P2₁/m</i>	Tridentate	8
7	(NH ₄) ₄ [Ru(DMSO) ₃ Mo ₇ O ₂₄]·6.5H ₂ O	<i>C2/c</i>	Tridentate	14
8	(NH ₄) ₄ [Os(DMSO) ₃ Mo ₇ O ₂₄]·4.5H ₂ O	<i>C2/c</i>	Tridentate	14
9	(ImH) ₄ [Ca(H ₂ O) ₆ (μ-O) ₂ {Mo ₇ O ₂₄ }]·2 (Im)·3H ₂ O	<i>C2/m</i>	μ ₂ -bidentate	17
10	(NH ₄) ₆ H ₂ [Cu(C ₂ O ₄) ₂ (Mo ₇ O ₂₄)]·9H ₂ O	<i>P2₁/m</i>	μ ₂ -bidentate	18
11	(hmtH) ₂ [{Mg(H ₂ O) ₅ } ₂ {Mo ₇ O ₂₄ }]·3H ₂ O	<i>C2/c</i>	μ ₂ -bidentate	10
12	(hmtH) ₂ [{(Zn(H ₂ O) ₅ } ₂ {Mo ₇ O ₂₄ }]·2H ₂ O	<i>C2/c</i>	μ ₂ -tridentate	11
13	(hmtH) ₂ [Mn ₂ (H ₂ O) ₉ Mo ₇ O ₂₄]·2H ₂ O	<i>C2/c</i>	μ ₂ -tridentate	12
14	(hmtH) ₂ [Fe ₂ (H ₂ O) ₉ Mo ₇ O ₂₄]·2H ₂ O	<i>C2/c</i>	μ ₂ -tridentate	12
15	(NH ₄)[Cu(en) ₂][Na(en)Cu(en) ₂ (H ₂ O)(Mo ₇ O ₂₄)]·4H ₂ O	<i>P1̄</i>	μ ₃ -tridentate	19
16	(GuaNH ₂) ₇ Na[Co(H ₂ O) ₅ {Mo ₇ O ₂₄ }] ₂ ·8H ₂ O	<i>P2₁/c</i>	μ ₂ -tetradentate	13
17	[(CH ₃) ₄ N] _{1.33} [NH ₄] _{12.67} [La ₄ (MoO ₄)(H ₂ O) ₁₆ (Mo ₇ O ₂₄) ₄]·12H ₂ O	<i>I4̄3d</i>	μ ₃ -tetradentate	21
18	[NH ₄] ₁₄ [Ce ₄ (MoO ₄)(H ₂ O) ₁₆ (Mo ₇ O ₂₄) ₄]·36H ₂ O	<i>P1̄</i>	μ ₃ -tetradentate	21
19	[NH ₄] ₁₄ [Pr ₄ (MoO ₄)(H ₂ O) ₁₆ (Mo ₇ O ₂₄) ₄]·29H ₂ O	<i>C2/c</i>	μ ₃ -tetradentate	21
20	[(CH ₃) ₄ N] _{3.33} [NH ₄] _{10.67} [Sm ₄ (MoO ₄)(H ₂ O) ₁₆ (Mo ₇ O ₂₄) ₄]·22H ₂ O	<i>I4̄3d</i>	μ ₃ -tetradentate	21
21	[(CH ₃) ₄ N] _{3.33} [NH ₄] _{10.67} [Gd ₄ (MoO ₄)(H ₂ O) ₁₆ (Mo ₇ O ₂₄) ₄]·16H ₂ O	<i>I4̄3d</i>	μ ₃ -tetradentate	21
22	Na ₂ (hmtH) ₂ [Mo ₇ O ₂₄]·9H ₂ O	<i>Pnma</i>	μ ₂ -pentadentate	16
23	[(hmtH) ₂] _{1.5} [(ahmtH) ₂] _{0.5} [Na ₂ (H ₂ O) ₅ Mo ₇ O ₂₄]·4H ₂ O	<i>Pnma</i>	μ ₂ -pentadentate	12
24	(NH ₄) ₂₈ [Ce ₈ (MoO ₄) ₂ (H ₂ O) ₃₁ (Mo ₇ O ₂₄) ₈]·74H ₂ O	<i>P1̄</i>	μ ₃ -tetradentate, μ ₄ -pentadentate	20
25	(NH ₄) ₂₆ [CoPr ₈ (MoO ₄) ₂ (H ₂ O) ₃₃ (Mo ₇ O ₂₄) ₈]·54H ₂ O	<i>P1̄</i>	μ ₃ -tetradentate, μ ₄ -pentadentate, μ ₄ -hexadentate	20
26	(NH ₄) _{11.9} [Nd _{4.7} (MoO ₄)(H ₂ O) ₂₃ (Mo ₇ O ₂₄) ₄]·19H ₂ O	<i>P1̄</i>	μ ₃ -tetradentate, μ ₄ -hexadentate	20
27	(NH ₄) _{11.9} [Pr _{4.7} (MoO ₄)(H ₂ O) ₂₃ (Mo ₇ O ₂₄) ₄]·34H ₂ O	<i>P1̄</i>	μ ₃ -tetradentate, μ ₄ -hexadentate	20
28	Na ₇ [Mo ₇ O ₂₄](OH)·21H ₂ O	<i>P2₁/n</i>	μ ₆ -hexadentate	7
29	Na ₆ [Mo ₇ O ₂₄]·14H ₂ O	<i>Pca2₁</i>	μ ₁₁ -pentadecadentate	5
30	NaCs ₅ [Mo ₇ O ₂₄]·5H ₂ O	<i>P1̄</i>	μ ₁₆ -hentriacontadentate	25
31	Cs ₆ [Mo ₇ O ₂₄]·7H ₂ O	<i>P1̄</i>	μ ₁₈ -tritetracontadentate	6
32	K ₆ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/c</i>	---	23
33	(NH ₄) ₃ [Li ₃ (H ₂ O) ₄ (μ ₆ -Mo ₇ O ₂₄)]·2H ₂ O 2	<i>Pnma</i>	μ ₆ -hexadentate	This work
34	(NH ₄) ₄ [Li ₂ (H ₂ O) ₇][Mo ₇ O ₂₄]·H ₂ O 1	<i>P2₁/n</i>	Counterion	This work

35	(NH ₄) ₆ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/c</i>	Counterion	22, 23
36	(2-ampH) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	Counterion	24
37	(BuNH ₃) ₈ [(Mo ₇ O ₂₄)(MoO ₄)]·3H ₂ O	<i>P1⁻</i>	Counterion	4
38	(BuNH ₃) ₆ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/c</i>	Counterion	To be published
39	(BuNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	Counterion	27
40	(PyrNH ₃) ₆ [(Mo ₇ O ₂₄)·2H ₂ O	<i>P1⁻</i>	Counterion	4
41	(PrNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P1⁻</i>	Counterion	4, 27
42	(PentNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	Counterion	4, 27
43	(HexNH ₃) ₆ [Mo ₇ O ₂₄]·3H ₂ O	<i>P2₁/n</i>	Counterion	27
44	(<i>t</i> -BuNH ₃) ₆ [Mo ₇ O ₂₄]·7H ₂ O	<i>P2₁/n</i>	Counterion	28
45	(TemedH ₂) ₃ [Mo ₇ O ₂₄]·4H ₂ O	<i>C2/c</i>	Counterion	29
46	(GuaNH ₂) ₆ [Mo ₇ O ₂₄]·H ₂ O	<i>C2/c</i>	Counterion	30
47	(GuaNH ₂) ₆ [Mo ₇ O ₂₄]·H ₂ O	<i>P2₁/c</i>	Counterion	31
48	(4-apH) ₆ [Mo ₇ O ₂₄]·6H ₂ O	<i>P2₁/c</i>	Counterion	32
49	[UreaH] ₃ (NH ₄) ₉ [Mo ₇ O ₂₄] ₂ ·5[Urea]·4H ₂ O	<i>Fddd</i>	Counterion	17
50	(dienH ₃) ₂ [Mo ₇ O ₂₄]·4H ₂ O	<i>C2/c</i>	Counterion	33
51	(dienH ₃) ₂ [Mo ₇ O ₂₄]·4H ₂ O	<i>P2₁/a</i>	Counterion	33
52	(NMe ₄) ₂ (NH ₄) ₈ [(Mo ₇ O ₂₂)(μ ₂ -O) ₂ (Mo ₇ O ₂₂)]·4H ₂ O	<i>P1⁻</i>	Counterion	34
53	(BuNH ₃) ₁₀ [(Mo ₇ O ₂₂)(μ ₂ -O) ₂ (Mo ₇ O ₂₂)]·5.5H ₂ O	<i>P2₁/n</i>	Counterion	4
54	[2,3-diampH] ₄ [Co(H ₂ O) ₆][Mo ₇ O ₂₄]·6H ₂ O	<i>C2/c</i>	Counterion	15

Abbreviations used: DABCO = 1,4-diazabicyclo[2.2.2]octane; 2-amp = 2-aminopyridine; 3-amp = 3-aminopyridine; bpp = 1,3-bis(4pyridyl)propane; DMSO = dimethylsulfoxide; Im = imidazole; hmt = hexamethylenetetramine; en = ethylenediamine; GuaNH₂ = guanidinium; ahmt = *N*-(aminomethylene)-hexamethylenetetramine; BuNH₂=butan-1-amine; PyrNH₂ = pyrrolidinium; PrNH₂= propan-1-amine; PentNH₂ = pentan-1-amine; HexNH₂ = hexan-1-amine; *t*-BuNH₂ = *tert*-butylamine; Temed = *N,N,N,N*-tetramethylethylenediamine; 4-ap = 4-aminopyridine; dien = diethylenetriamine.; 2,3-diamp = 2,3 diaminopyridine.

Table S2. Metric parameters (Å, °) of (Mo₇O₂₄)⁶⁻ unit in (NH₄)₄[Li₂(H₂O)₇][Mo₇O₂₄]·H₂O **1**.

Bond lengths

Mo(1)-O(2)	1.721(3)	Mo(4)-O(20)	1.897(3)
Mo(1)-O(4)	1.733(3)	Mo(4)-O(5)	1.899(3)
Mo(1)-O(6)	1.931(3)	Mo(4)-O(3)	2.267(3)
Mo(1)-O(1)	1.990(3)	Mo(4)-O(8)	2.282(3)
Mo(1)-O(3)	2.158(3)	Mo(5)-O(16)	1.722(3)
Mo(1)-O(5)	2.244(3)	Mo(5)-O(15)	1.742(3)
Mo(1)-Mo(3)	3.2110(5)	Mo(5)-O(10)	1.913(3)
Mo(2)-O(7)	1.713(3)	Mo(5)-O(23)	1.917(3)
Mo(2)-O(9)	1.721(3)	Mo(5)-O(8)	2.152(3)
Mo(2)-O(6)	1.944(3)	Mo(6)-O(18)	1.716(3)
Mo(2)-O(10)	1.991(3)	Mo(6)-O(19)	1.737(3)
Mo(2)-O(8)	2.149(3)	Mo(6)-O(21)	1.936(3)
Mo(2)-O(5)	2.284(3)	Mo(6)-O(17)	1.949(3)
Mo(3)-O(11)	1.722(3)	Mo(6)-O(3)	2.156(3)
Mo(3)-O(12)	1.728(3)	Mo(6)-O(20)	2.272(3)
Mo(3)-O(17)	1.924(3)	Mo(7)-O(24)	1.706(3)
Mo(3)-O(1)	1.926(3)	Mo(7)-O(22)	1.730(3)
Mo(3)-O(3)	2.159(3)	Mo(7)-O(21)	1.929(3)
Mo(3)-O(11)	1.722(3)	Mo(7)-O(23)	1.985(3)
Mo(4)-O(14)	1.740(3)	Mo(7)-O(8)	2.146(3)
Mo(4)-O(13)	1.757(3)	Mo(7)-O(20)	2.277(3)

Bond angles

O(2)-Mo(1)-O(4)	105.19(17)	O(16)-Mo(5)-O(23)	97.74(15)
O(2)-Mo(1)-O(6)	96.99(15)	O(15)-Mo(5)-O(23)	102.34(15)
O(4)-Mo(1)-O(6)	100.94(15)	O(10)-Mo(5)-O(23)	147.09(13)
O(2)-Mo(1)-O(1)	98.83(15)	O(16)-Mo(5)-O(8)	106.04(14)
O(4)-Mo(1)-O(1)	92.52(15)	O(15)-Mo(5)-O(8)	147.79(14)

O(6)-Mo(1)-O(1)	155.75(14)	O(10)-Mo(5)-O(8)	74.14(12)
O(2)-Mo(1)-O(3)	95.73(14)	O(23)-Mo(5)-O(8)	73.95(12)
O(4)-Mo(1)-O(3)	156.38(15)	O(18)-Mo(6)-O(19)	104.19(17)
O(6)-Mo(1)-O(3)	87.01(12)	O(18)-Mo(6)-O(21)	96.72(14)
O(1)-Mo(1)-O(3)	73.24(12)	O(19)-Mo(6)-O(21)	98.90(14)
O(2)-Mo(1)-O(5)	165.72(14)	O(18)-Mo(6)-O(17)	100.86(15)
O(4)-Mo(1)-O(5)	87.96(14)	O(19)-Mo(6)-O(17)	94.05(14)
O(6)-Mo(1)-O(5)	74.66(12)	O(21)-Mo(6)-O(17)	154.88(13)
O(1)-Mo(1)-O(5)	85.88(13)	O(18)-Mo(6)-O(3)	95.14(14)
O(3)-Mo(1)-O(5)	72.60(11)	O(19)-Mo(6)-O(3)	158.76(14)
O(7)-Mo(2)-O(9)	105.20(16)	O(21)-Mo(6)-O(3)	87.32(12)
O(7)-Mo(2)-O(6)	100.42(15)	O(17)-Mo(6)-O(3)	73.43(11)
O(9)-Mo(2)-O(6)	97.25(14)	O(18)-Mo(6)-O(20)	164.12(14)
O(7)-Mo(2)-O(10)	91.16(15)	O(20)-Mo(4)-O(3)	77.29(12)
O(9)-Mo(2)-O(10)	101.09(15)	O(5)-Mo(4)-O(3)	76.90(12)
O(6)-Mo(2)-O(10)	154.92(13)	O(14)-Mo(4)-O(8)	82.91(14)
O(7)-Mo(2)-O(8)	155.21(14)	O(13)-Mo(4)-O(8)	171.88(13)
O(9)-Mo(2)-O(8)	96.50(14)	O(20)-Mo(4)-O(8)	76.92(12)
O(6)-Mo(2)-O(8)	88.38(12)	O(5)-Mo(4)-O(8)	75.98(12)
O(10)-Mo(2)-O(8)	72.74(12)	O(3)-Mo(4)-O(8)	88.30(10)
O(7)-Mo(2)-O(5)	88.73(14)	O(16)-Mo(5)-O(15)	106.17(17)
O(9)-Mo(2)-O(5)	164.66(14)	O(16)-Mo(5)-O(10)	98.55(15)
O(6)-Mo(2)-O(5)	73.49(12)	O(15)-Mo(5)-O(10)	100.28(15)
O(10)-Mo(2)-O(5)	84.72(12)	O(19)-Mo(6)-O(20)	89.86(14)
O(8)-Mo(2)-O(5)	71.48(11)	O(21)-Mo(6)-O(20)	73.45(12)
O(11)-Mo(3)-O(12)	105.71(16)	O(17)-Mo(6)-O(20)	85.22(12)
O(11)-Mo(3)-O(17)	99.50(15)	O(3)-Mo(6)-O(20)	72.37(11)
O(12)-Mo(3)-O(17)	97.60(15)	O(24)-Mo(7)-O(22)	105.35(17)
O(11)-Mo(3)-O(1)	98.17(16)	O(24)-Mo(7)-O(21)	97.53(15)
O(12)-Mo(3)-O(1)	104.64(15)	O(22)-Mo(7)-O(21)	100.14(15)
O(17)-Mo(3)-O(1)	146.53(13)	O(24)-Mo(7)-O(23)	100.38(15)
O(11)-Mo(3)-O(3)	104.01(14)	O(22)-Mo(7)-O(23)	92.72(15)
O(12)-Mo(3)-O(3)	150.05(15)	O(21)-Mo(7)-O(23)	154.31(13)
O(17)-Mo(3)-O(3)	73.83(12)	O(24)-Mo(7)-O(8)	93.34(14)
O(1)-Mo(3)-O(3)	74.43(12)	O(22)-Mo(7)-O(8)	158.30(14)
O(14)-Mo(4)-O(13)	105.19(16)	O(21)-Mo(7)-O(8)	87.99(12)
O(14)-Mo(4)-O(20)	100.26(15)	O(23)-Mo(7)-O(8)	72.78(12)
O(13)-Mo(4)-O(20)	101.77(15)	O(24)-Mo(7)-O(20)	163.13(14)
O(14)-Mo(4)-O(5)	101.16(15)	O(22)-Mo(7)-O(20)	90.47(14)
O(13)-Mo(4)-O(5)	101.48(15)	O(21)-Mo(7)-O(20)	73.46(12)
O(20)-Mo(4)-O(5)	142.80(13)	O(23)-Mo(7)-O(20)	84.37(12)
O(14)-Mo(4)-O(3)	171.20(13)	O(8)-Mo(7)-O(20)	72.47(11)
O(13)-Mo(4)-O(3)	83.60(13)		

Table S3. Geometric parameters of the O–H···O, O–H···N and N–H···O hydrogen bonds length (Å) and (°) in the crystal structure of (NH₄)₄[Li₂(H₂O)₇][Mo₇O₂₄]·H₂O **1**.

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A	Symmetry codes
O31-H1O	0.850	1.948	156.47	2.749	O4	[x-1/2, -y+3/2, z+1/2]
O32-H3O	0.850	1.865	163.66	2.691	O6	[-x+3/2, y-1/2, -z+3/2]
O32-H4O	0.850	1.989	145.03	2.729	O22	
O34-H7O	0.850	2.096	147.56	2.850	O18	[-x+1/2, y-1/2, -z+3/2]
O34-H8O	0.850	2.148	153.73	2.934	O9	[-x+3/2, y-1/2, -z+3/2]
O35-H9O	0.850	2.009	147.14	2.762	O5	[-x+1, -y+1, -z+1]
O35-H10O	0.850	2.355	2.896	O15		[x-1, y, z]
O36-H11O	0.850	2.029	161.32	2.847	O13	[-x+1, -y+1, -z+1]
O36-H12O	0.850	2.196	130.31	2.821	O20	
O37-H13O	0.850	2.023	168.83	2.861	O9	[-x+3/2, y-1/2, -z+3/2]
O37-H14O	0.850	2.205	144.83	2.941	N3	
N1-H1N1	0.900	2.222	155.45	3.064	O16	
N1-H2N1	0.900	2.075	160.67	2.939	O2	[-x+3/2, y-1/2, -z+3/2]
N1-H3N1	0.900	2.340	174.59	3.237	O1	[x+1/2, -y+3/2, z+1/2]
N1-H4N1	0.900	2.209	137.86	2.939	O11	[-x+3/2, y-1/2, -z+3/2]
N2-H2N2	0.900	2.394	123.46	2.986	O4	
N2-H2N2	0.900	2.623	136.08	3.330	O35	[-x+1, -y+1, -z+1]
N2-H3N2	0.900	2.280	143.19	3.049	O15	[-x+2, -y+1, -z+1]
N2-H4N2	0.900	2.130	147.77	2.931	O19	[x+1/2, -y+3/2, z-1/2]
N2-H1N2	0.900	2.107	150.51	2.925	O38	[x+1, y, z]
N3-H1N3	0.900	1.848	164.90	2.727	O21	[-x+3/2, y-1/2, -z+3/2]
N3-H3N3	0.900	1.952	157.88	2.806	O12	[-x+1, -y+1, -z+1]
N3-H4N3	0.900	1.886	162.86	2.759	O23	
N4-H1N4	0.900	2.140	165.00	3.019	O36	
N4-H3N4	0.900	2.209	129.81	2.870	O10	[x-1, y, z]
N4-H4N4	0.900	2.570	135.27	3.271	O15	[-x+1, -y+1, -z+1]
N4-H4N4	0.900	2.587	140.11	3.328	O12	

Table S4. Metric parameters (Å, °) of (Mo₇O₂₄)⁶⁻ unit in (NH₄)₃[Li₃(H₂O)₄(μ₆-Mo₇O₂₄)]·2H₂O **2**.

Bond lengths			
Mo(1)-O(1)	1.720(3)	Mo(3)-O(13)	2.477(4)
Mo(1)-O(3)	1.721(3)	Mo(3)-O(12)	1.753(4)
Mo(1)-O(5)	1.939(2)	Mo(3)-O(2)#1	1.919(3)
Mo(1)-O(2)	1.965(2)	Mo(4)-O(14)	1.735(4)
Mo(1)-O(4)	2.2207(7)	Mo(4)-O(13)	1.745(4)
Mo(1)-O(6)	2.237(2)	Mo(4)-O(6)#1	1.900(3)
Mo(2)-O(9)	1.723(3)	Mo(4)-O(6)	1.900(3)
Mo(2)-O(7)	1.725(3)	Mo(4)-O(8)	2.259(3)
Mo(2)-O(5)	1.932(2)	Mo(4)-O(4)	2.280(3)
Mo(2)-O(10)	1.972(2)	Mo(5)-O(15)	1.709(4)
Mo(2)-O(8)	2.1457(9)	Mo(5)-O(16)	1.748(4)
Mo(2)-O(6)	2.249(2)	Mo(5)-O(10)	1.907(3)
Mo(2)-Mo(5)	3.1851(4)	Mo(5)-O(10)#1	1.907(3)
Mo(3)-O(11)	1.715(4)	Mo(5)-O(8)	2.158(3)
Mo(3)-O(2)	1.919(3)	Mo(2)#1-O(8)	2.1457(9)
Mo(3)-O(4)	2.118(3)		
Bond angles			
O(1)-Mo(1)-O(3)	104.38(14)	O(11)-Mo(3)-O(12)	105.81(17)
O(1)-Mo(1)-O(5)	96.35(12)	O(11)-Mo(3)-O(2)#1	99.64(8)
O(3)-Mo(1)-O(5)	101.68(12)	O(12)-Mo(3)-O(2)#1	99.60(8)
O(1)-Mo(1)-O(2)	99.91(12)	O(11)-Mo(3)-O(2)	99.64(8)
O(3)-Mo(1)-O(2)	94.63(12)	O(12)-Mo(3)-O(2)	99.60(8)
O(5)-Mo(1)-O(2)	153.30(11)	O(2)#1-Mo(3)-O(2)	147.82(15)
O(1)-Mo(1)-O(4)	95.11(13)	Mo(2)#1-O(8)-Mo(2)	151.62(18)
O(3)-Mo(1)-O(4)	158.29(12)	Mo(2)#1-O(8)-Mo(5)	95.48(9)
O(5)-Mo(1)-O(4)	85.29(12)	Mo(2)#1-O(8)-Mo(4)	101.56(9)
O(2)-Mo(1)-O(4)	72.34(12)	Mo(2)-O(8)-Mo(4)	101.56(9)
O(1)-Mo(1)-O(6)	164.51(12)	Mo(5)-O(8)-Mo(4)	102.22(14)
O(3)-Mo(1)-O(6)	89.63(11)	Mo(5)-O(10)-Mo(2)	110.36(12)
O(5)-Mo(1)-O(6)	73.99(9)	Mo(4)-O(13)-Mo(3)	105.04(16)
O(2)-Mo(1)-O(6)	85.23(10)	O(2)-Mo(3)-O(13)	78.77(8)
O(4)-Mo(1)-O(6)	72.38(11)	O(4)-Mo(3)-O(13)	71.45(12)
O(1)-Mo(1)-Mo(3)	88.62(10)	O(11)-Mo(3)-Mo(1)#1	91.45(10)
O(3)-Mo(1)-Mo(3)	128.60(9)	O(12)-Mo(3)-Mo(1)#1	134.23(4)
O(5)-Mo(1)-Mo(3)	126.45(8)	O(2)#1-Mo(3)-Mo(1)#1	34.93(7)
O(2)-Mo(1)-Mo(3)	33.99(8)	O(2)-Mo(3)-Mo(1)#1	119.22(7)
O(4)-Mo(1)-Mo(3)	41.19(8)	O(4)-Mo(3)-Mo(1)#1	43.669(17)
O(6)-Mo(1)-Mo(3)	87.66(7)	O(2)-Mo(3)-O(13)	78.77(8)
O(9)-Mo(2)-O(7)	107.37(14)	O(13)-Mo(3)-Mo(1)#1	83.11(6)
O(9)-Mo(2)-O(5)	96.05(12)	O(11)-Mo(3)-Mo(1)	91.45(10)
O(7)-Mo(2)-O(5)	100.30(12)	O(12)-Mo(3)-Mo(1)	134.23(4)
O(9)-Mo(2)-O(10)	101.60(11)	O(2)#1-Mo(3)-Mo(1)	119.22(7)
O(7)-Mo(2)-O(10)	91.96(13)	O(2)-Mo(3)-Mo(1)	34.93(7)
O(5)-Mo(2)-O(10)	154.45(11)	O(4)-Mo(3)-Mo(1)	43.669(17)
O(9)-Mo(2)-O(8)	91.27(14)	O(13)-Mo(3)-Mo(1)	83.11(6)

O(7)-Mo(2)-O(8)	158.31(13)	O(14)-Mo(4)-O(13)	105.55(17)
O(5)-Mo(2)-O(8)	88.35(12)	O(14)-Mo(4)-O(6)#1	100.34(8)
O(10)-Mo(2)-O(8)	73.04(12)	O(13)-Mo(4)-O(6)#1	101.77(8)
O(9)-Mo(2)-O(6)	160.14(12)	O(14)-Mo(4)-O(6)	100.34(8)
O(7)-Mo(2)-O(6)	91.45(11)	O(13)-Mo(4)-O(6)	101.77(8)
O(5)-Mo(2)-O(6)	73.84(9)	O(6)#1-Mo(4)-O(6)	143.00(14)
O(10)-Mo(2)-O(6)	83.60(10)	O(14)-Mo(4)-O(8)	84.11(15)
O(8)-Mo(2)-O(6)	71.74(11)	O(13)-Mo(4)-O(8)	170.33(15)
O(9)-Mo(2)-Mo(5)	86.49(10)	O(6)#1-Mo(4)-O(8)	76.00(7)
O(7)-Mo(2)-Mo(5)	125.87(9)	O(6)-Mo(4)-O(8)	76.00(7)
O(5)-Mo(2)-Mo(5)	130.75(8)	O(14)-Mo(4)-O(4)	171.36(15)
O(10)-Mo(2)-Mo(5)	34.15(8)	O(13)-Mo(4)-O(4)	83.09(14)
O(8)-Mo(2)-Mo(5)	42.41(9)	O(6)#1-Mo(4)-O(4)	77.48(7)
O(6)-Mo(2)-Mo(5)	87.53(6)	O(6)-Mo(4)-O(4)	77.48(7)
O(11)-Mo(3)-O(4)	101.10(16)	O(8)-Mo(4)-O(4)	87.25(12)
O(12)-Mo(3)-O(4)	153.09(15)	O(15)-Mo(5)-O(16)	106.44(17)
O(2)#1-Mo(3)-O(4)	75.59(7)	O(15)-Mo(5)-O(10)	99.06(9)
O(2)-Mo(3)-O(4)	75.59(7)	O(16)-Mo(5)-O(10)	101.04(8)
O(11)-Mo(3)-O(13)	172.55(16)	O(15)-Mo(5)-O(10)#1	99.06(8)
O(12)-Mo(3)-O(13)	81.64(14)	O(16)-Mo(5)-O(10)#1	101.04(8)
O(15)-Mo(5)-Mo(2)#1	91.21(10)	O(10)-Mo(5)-Mo(2)#1	115.79(7)
O(16)-Mo(5)-Mo(2)#1	136.06(4)	O(8)-Mo(5)-Mo(2)#1	42.11(2)

Symmetry transformations used to generate equivalent atoms.

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

Table S5. Geometric parameters of the N–H···O and O–H···O, hydrogen bonds length (Å) and (°) in the crystal structure of (NH₄)₃[Li₃(H₂O)₄(μ₆-Mo₇O₂₄)]·2H₂O **2**.

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A	Symmetry codes
N1-H1N1	0.840	2.049	178.60	2.889	O16	
N1-H2N1	0.840	2.361	134.82	3.012	O3	[$-x+1/2, -y+1, z-1/2$]
N1-H2N1	0.840	2.361	134.82	3.012	O3	[$-x+1/2, y-1/2, z-1/2$]
N1-H3N1	0.840	2.018	163.48	2.833	O5	[$x-1/2, -y+1/2, -z+3/2$]
N2-H1N2	0.840	2.146	168.02	2.973	O9	[$-x+1, y-1/2, -z+1$]
N2-H2N2	0.840	2.175	130.25	2.792	O10	[$-x+1/2, y-1/2, z-1/2$]
N2-H3N2	0.840	2.292	141.54	2.995	O11	[$x, y, z-1$]
N2-H3N2	0.840	2.362	123.42	2.910	O1	[$x, -y+1/2, z-1$]
N2-H4N2	0.840	2.182	148.31	2.930	O12	[$x+1/2, y, -z+3/2$]
O21-H21A	0.880	1.998	144.79	2.764	O2	[$-x+1/2, -y+1, z-1/2$]
O21-H21B	0.880	2.470	121.86	3.028	O14	[$x+1/2, y, -z+3/2$]
O22-H22A	0.880	1.865	176.60	2.744	O1	[$-x+1, y+1/2, -z+2$]

Figure S1. Calculated and experimental powder patterns of **1**(top) & **2** (bottom).

Figure S2. Coordination sphere of $\{\text{LiO}_4\}$ tetrahedra around Li1 and Li2 showing μ_2 -bridging bidentate coordination of O34 resulting in a water bridged dinuclear cationic unit $[\text{Li}_2(\text{H}_2\text{O})_7]^{2+}$ in **1**.

Figure S3. The hydrogen bonding situation around ammonium cations 'N1' (**left**) and 'N2' (**right**) showing intramolecular and intermolecular N–H $\cdots$ O interactions (black dotted lines). Symmetry codes: iii) $3/2-x, 1/2+y, 3/2-z$ iv) $1-x, 1-y, 1-z$ vi) $-1/2+x, 3/2-y, 1/2+z$ vii) $1+x, y, z$ viii) $1-x, 1-y, 1-z$.

Figure S4. A view along 'a' axis of the unit cell packing showing only heptamolybdate anions (**top left**), ammonium cations (**top right**), $[\text{Li}_2(\text{H}_2\text{O})_7]^{2+}$ cationic unit (bottom left) and $[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]^{4-}$ unit (**bottom right**) in compound **1**. Colour codes: Mo, maroon; Li, pink; O, red; N, blue; H, medium grey; heptamolybdate anions are shown as polyhedra.

Figure S5. The coordination sphere of Li1 (**left**) and Li2, Li3 (**right**) in compound **2**. Symmetry codes: i) $x, 1/2-y, z$ ii) $x, 3/2-y, z$ iii) $-1/2+x, 1/2-y, 3/2-z$ iv) $1/2-x, 1-y, -1/2+z$ v) $1/2-x, -1/2+y, -1/2+z$ vi) $-1/2+x, 3/2-y, 1/2+z$.

Figure S6. The hydrogen bonding situation around Li1 (**left**) and Li2, Li3 (**right**) showing O–H···O interactions (black dotted lines). Symmetry codes: iii) $-1/2+x, 1/2-y, 3/2-z$ iv) $1/2-x, 1-y, -1/2+z$ vi) $1/2-x, 1/2+y, 1/2+z$ xii) $1-x, -1/2+y, 2-z$.

Figure S7. The hydrogen bonding situation around ammonium cations 'N1' (**left**) and 'N2' (**right**) shown by black dotted lines. Symmetry codes: iii) $-1/2+x, 1/2-y, 3/2-z$ iv) $1/2-x, 1-y, -1/2+z$ v) $1/2-x, -1/2+y, -1/2+z$ vii) $1/2+x, y, 3/2-z$ ix) $1-x, 1/2+y, 1-z$ x) $x, 1/2-y, -1+z$ xi) $x, y, 1+z$.

μ_{18} -tritetracontadentate

μ_{16} -hentriacontadentate

Figure S8. The binding modes of heptamolybdate in $\text{Cs}_6[\text{Mo}_7\text{O}_{24}] \cdot 7\text{H}_2\text{O}$ (**top**), $\text{NaCs}_5[\text{Mo}_7\text{O}_{24}] \cdot 5\text{H}_2\text{O}$ (**bottom**)

Figure S9. IR (**top**) and Raman spectra (**bottom**) of $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ (1), $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})]\cdot 2\text{H}_2\text{O}$ (2) and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$ (3).

Figure S10. IR and Raman spectra of $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ **1** (top) and $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})]\cdot 2\text{H}_2\text{O}$ **2** (bottom).

Figure S11. IR spectra of the residue obtained after heating $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ (1), $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})]\cdot 2\text{H}_2\text{O}$ (2) at 600 °C.

Figure S12. UV-Vis spectra of compound 1, 2 and $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot 4\text{H}_2\text{O}$.

checkCIF/PLATON report (NH₄)₄[Li₂(H₂O)₇][Mo₇O₂₄].H₂O 1

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: srini903

Bond precision: Mo- O = 0.0030 A Wavelength=0.71073

Cell: a=10.5894(8) b=15.8542(8) c=18.7820(14)
 alpha=90 beta=101.473(9) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	3090.2(4)	3090.2(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	Mo7 O24, 7(H2 O), O, 4(H4 N), 2(Li)	Mo7 O24, 7(H2 O), O, 4(H4 N), 2(Li)
Sum formula	H30 Li2 Mo7 N4 O32	H32 Li2 Mo7 N4 O32
Mr	1283.74	1285.76
Dx,g cm-3	2.759	2.764
Z	4	4
Mu (mm-1)	2.866	2.866
F000	2456.0	2464.0
F000'	2409.00	
h,k,lmax	13,20,24	13,20,24
Nref	7442	7408
Tmin,Tmax	0.696,0.818	
Tmin'	0.682	

Correction method= Not given

Data completeness= 0.995 Theta(max)= 28.000

R(reflections)= 0.0427(6720) wR2(reflections)= 0.1143(7408)

S = 1.059 Npar= 416

The following ALERTS were generated. Each ALERT has the format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT430_ALERT_2_B Short Inter D...A Contact	011	.. 038	..	2.74 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact	011	.. 038'	..	2.80 Ang.

Alert level C

PLAT041_ALERT_1_C Calc. and Reported SumFormula	Strings Differ	Please Check
PLAT043_ALERT_1_C Calculated and Reported Mol. Weight	Differ by ..	2.02 Check
PLAT052_ALERT_1_C Info on Absorption Correction Method	Not Given	Please Do !
PLAT057_ALERT_3_C Correction for Absorption Required	RT(exp) ...	1.18 Do !
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...		Please Check

Alert level G

FORMU01_ALERT_1_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and _chemical_formula_moiety. This is
usually due to the moiety formula being in the wrong format.
Atom count from _chemical_formula_sum: H32 Li2 Mo7 N4 O32 Atom
count from _chemical_formula_moiety:H30 Li2 Mo7 N4 O32

FORMU01_ALERT_2_G There is a discrepancy between the atom counts in the
_chemical_formula_sum and the formula from the _atom_site*
data. Atom count from _chemical_formula_sum:H32 Li2 Mo7 N4 O32
Atom count from the _atom_site data: H30 Li2 Mo7 N4 O32 CELLZ01_ALERT_1_G
Difference between formula and atom_site contents detected. CELLZ01_ALERT_1_G WARNING:
H atoms missing from atom site list. Is this intentional?

From the CIF: _cell_formula_units_Z 4
From the CIF: _chemical_formula_sum H32Li2 Mo7 N4 O32
TEST: Compare cell contents of formula and atom_site data

atom	Z*formula	cif sites	diff
H	128.00	120.00	8.00
Li	8.00	8.00	0.00
Mo	28.00	28.00	0.00
N	16.00	16.00	0.00
O	128.00	128.00	0.00

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 30 Report
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT232_ALERT_2_G Hirshfeld Test Diff (M-X) Mo5 -- O14 .. 5.3 s.u.
PLAT300_ALERT_4_G Atom Site Occupancy of >038 is Constrained at 0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <038' is Constrained at 0.25 Check
PLAT302_ALERT_4_G Anion/Solvent Disorder Percentage = 7 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (0.75) in Resd. # 9 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (0.25) in Resd. # 14 Check
PLAT311_ALERT_2_G Isolated Disordered Oxygen Atom (No H's ?) 038 Check
PLAT311_ALERT_2_G Isolated Disordered Oxygen Atom (No H's ?) 038' Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 16 Note
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

0 **ALERT level A** = Most likely a serious problem - resolve or explain 2

ALERT level B = A potentially serious problem, consider carefully

5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight 17

ALERT level G = General information/check it is not something unexpected

8 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

6 ALERT type 2 Indicator that the structure model may be wrong or deficient

1 ALERT type 3 Indicator that the structure quality may be low

7 ALERT type 4 Improvement, methodology, query or suggestion

2 ALERT type 5 Informative message, check

checkCIF/PLATON report of (NH₄)₃[Li₃(H₂O)₄(μ₆-Mo₇O₂₄)]·2H₂O 2

You have not supplied any structure factors. As a result the full set of tests cannot be run.

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: srini903

Bond precision: Mo- O = 0.0026 A Wavelength=0.71073

Cell: a=14.0745(10) b=10.8681(6) c=17.2459(11)
 alpha=90 beta=90 gamma=90

Temperature: 200 K

	Calculated	Reported
Volume	2638.0(3)	2638.0(3)
Space group	P n m a	P n m a
Hall group	-P 2ac 2n	-P 2ac 2n
Moiety formula	Mo7 O24, H4 O2, 4(H2 O), 3(H4 N), 3(Li)	Mo7 O24, H4 O2, 4(H2 O), 3(H4 N), 3(Li)
Sum formula	H24 Li3 Mo7 N3 O30	H24 Li3 Mo7 N3 O30
Mr	1238.62	1238.62
Dx, g cm-3	3.119	3.119
Z	4	4
Mu (mm-1)	3.344	3.344
F000	2352.0	2352.0
F000'	2304.92	
h,k,lmax	18,14,22	18,14,22
Nref	3352	3327
Tmin,Tmax	0.704,0.765	
Tmin'	0.685	

Correction method= Not given

Data completeness= 0.993 Theta(max)= 28.000

R(reflections)= 0.0309(2944) wR2(reflections)= 0.0768(3327)

S = 1.067 Npar= 229

The following ALERTS were generated. Each ALERT has the
format **test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT417_ALERT_2_A Short Inter D-H..H-D H23A .. H24A .. 1.35 Ang.

Alert level B

PLAT213_ALERT_2_B Atom Mo4 has ADP max/min Ratio 4.2
oblate

Alert level C

PLAT052_ALERT_1_C Info on Absorption Correction Method Not Given Please Do !
PLAT220_ALERT_2_C Large Non-Solvent O Ueq(max)/Ueq(min) Range 3.1 Ratio
PLAT417_ALERT_2_C Short Inter D-H..H-D H21B .. H24A .. 2.14 Ang.

Alert level G

PLAT005_ALERT_5_G No Embedded Refinement Details found in the CIF Please Do !
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms 13 Report
PLAT042_ALERT_1_G Calc. and Reported MoietyFormula Strings Differ Please Check
PLAT093_ALERT_1_G No s.u.'s on H-positions, Refinement Reported as mixed Check
PLAT300_ALERT_4_G Atom Site Occupancy of >024 is Constrained at 0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <024' is Constrained at 0.25 Check
PLAT302_ALERT_4_G Anion/Solvent Disorder Percentage = 20 Note
PLAT304_ALERT_4_G Non-Integer Number of Atoms (0.50) in Resd. # 8 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (0.50) in Resd. # 9 Check
PLAT304_ALERT_4_G Non-Integer Number of Atoms (0.50) in Resd. # 10 Check
PLAT720_ALERT_4_G Number of Unusual/Non-Standard Labels 7 Note
PLAT899_ALERT_4_G SHELXL97 is Deprecated and Succeeded by SHELXL 2014 Note

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- 3 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
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0 ALERT type 3 Indicator that the structure quality may be low
8 ALERT type 4 Improvement, methodology, query or suggestion
2 ALERT type 5 Informative message, check
-