# Syntheses and structures of two new lithium–heptamolybdates

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**SUPPLEMENTARY MATERIAL FOR ONLINE VERSION**

Table S1. List of structurally characterized heptamolybdate compounds.

| No | Compound | Space Group | Binding mode of $\{\text{Mo}_7\text{O}_{24}\}$ | Ref |
|----|----------|-------------|---------------------------------|-----|
| 1  | (H$_2$DABCO)$_2$[Mo$_3$O$_{24}$]-4H$_2$O | Cc | Counterion | 6 |
| 2  | (3-amp)$_2$[Co(H$_2$O)$_6$Mo$_5$O$_{23}$]-9H$_2$O | Pnma | Monodentate | 9 |
| 3  | [Zn(3-ampy)[H$_2$O]$_5$]Mo$_5$O$_{23}$]-4H$_2$O | Cc | Monodentate | 15 |
| 4  | [Zn(3-ampy)[H$_2$O]$_5$]Mo$_5$O$_{23}$]-4H$_2$O | Cc | Monodentate | 15 |
| 5  | Na(NH$_2$)$_2$(bppy)$_2$[Mo$_5$O$_{23}$]-8H$_2$O | P2$_1$/m | Tridentate | 8 |
| 6  | Na$_2$(Ru(DMSO)$_2$)Mo$_5$O$_{23}$]-6.5H$_2$O | C2/c | Tridentate | 14 |
| 7  | Na$_2$(Ox(DMSO)$_2$)Mo$_5$O$_{23}$]-4.8H$_2$O | C2/c | Tridentate | 14 |
| 8  | (Im)$_3$[Ca(H$_2$O)$_6$][Mo$_5$O$_{23}$]-2 (Im)-3H$_2$O | C2/m | $\mu_2$-bidentate | 17 |
| 9  | (NH$_4$)$_2$[Cu$_2$C$_4$I$_4$][Mo$_5$O$_{23}$]-9H$_2$O | P2$_1$/c | $\mu_2$-bidentate | 18 |
| 10 | hmH$_2$[Mg(H$_2$O)$_6$][Mo$_5$O$_{23}$]-3H$_2$O | C2/c | $\mu_2$-bidentate | 10 |
| 11 | hmH$_2$[Zn(H$_2$O)$_6$][Zn(H$_2$O)$_6$][Mo$_5$O$_{23}$]-2H$_2$O | C2/c | $\mu_2$-tridentate | 11 |
| 12 | hmH$_2$_[Nm$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-2H$_2$O | C2/c | $\mu_2$-tridentate | 12 |
| 13 | hmH$_2$_[Fe$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-2H$_2$O | C2/c | $\mu_2$-tridentate | 12 |
| 14 | (NH$_4$)$_2$[Cu(en)$_2$][Na(en)Cu(en)$_2$][H$_2$O]Mo$_5$O$_{23}$]-4H$_2$O | P1 | $\mu_2$-tridentate | 19 |
| 15 | (GuaNH$_2$)$_2$NaCo[Co(H$_2$O)$_6$][Mo$_5$O$_{23}$]-8H$_2$O | P2$_1$/c | $\mu_2$-tetradeinate | 13 |
| 16 | [(CH$_3$_)$_3$N][NH$_4$H$_2$][Mo$_4$(H$_2$O)$_6$(Mo$_5$O$_{23}$)$_1$]-12H$_2$O | T$_{3d}$ | $\mu_2$-tetradenate | 21 |
| 17 | [NH$_4$]$_2$[Cr$_2$(Mo$_5$O$_{23}$)-3H$_2$O] | P1 | $\mu_2$-tetradenate | 21 |
| 18 | [NH$_4$]$_2$[Pr$_4$(Mo$_5$O$_{23}$)-29H$_2$O] | C2/c | $\mu_2$-tetradenate | 21 |
| 19 | [NH$_4$]$_2$[Cr$_3$(Mo$_5$O$_{23}$)-16H$_2$O] | C2/c | $\mu_2$-hexadentate | 21 |
| 20 | [nh$_2$(hmt)$_2$[Cu$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-16H$_2$O | Pnma | $\mu_2$-pentadentate | 16 |
| 21 | [hmH$_2$_[hmH$_2$_[hmH$_2$]$_{1.5}$][Na$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-4H$_2$O | Pnma | $\mu_2$-pentadentate | 12 |
| 22 | (NH$_4$)$_2$[Ca$_2$(Mo$_5$O$_{23}$)-74H$_2$O | P1 | $\mu_2$-pentadentate, $\mu_4$-pentadentate, $\mu_6$-pentadentate | 20 |
| 23 | (NH$_4$)$_2$[Co$_2$(Mo$_5$O$_{23}$)-54H$_2$O | P1 | $\mu_2$-pentadentate, $\mu_4$-pentadentate, $\mu_6$-pentadentate | 20 |
| 24 | (NH$_4$)$_2$[Nd$_2$(Mo$_5$O$_{23}$)-19H$_2$O | P1 | $\mu_2$-pentadentate, $\mu_4$-pentadentate, $\mu_6$-pentadentate | 20 |
| 25 | (NH$_4$)$_2$[Pr$_2$(Mo$_5$O$_{23}$)-3H$_2$O] | P1 | $\mu_2$-pentadentate, $\mu_4$-pentadentate, $\mu_6$-pentadentate | 20 |
| 26 | Na$_2$[Mo$_6$O$_{24}$]-7H$_2$O | P2/n | $\mu_6$-pentadentate | 7 |
| 27 | [K$_2$(Mo$_5$O$_{23}$)-14H$_2$O | P2/n | $\mu_6$-pentadentate | 5 |
| 28 | Na$_2$(Mo$_5$O$_{23}$)-OH] | P2/n | $\mu_6$-pentadentate | 23 |
| 29 | (NH$_4$)$_2$[Li$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-2H$_2$O | Pnma | $\mu_6$-hexadentate | This work |
| 30 | (NH$_4$)$_2$[Li$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-H$_2$O | Pnma | $\mu_6$-hexadentate | This work |
| 31 | (NH$_4$)$_2$[Li$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-H$_2$O | Pnma | $\mu_6$-hexadentate | This work |
| 32 | (NH$_4$)$_2$[Li$_2$(H$_2$O)$_6$][Mo$_5$O$_{23}$]-H$_2$O | Pnma | $\mu_6$-hexadentate | This work |
Abbreviations used: DABCO = 1,4-diazabicyclo[2.2.2]octane; 2-amp = 2-aminopyridine; 3-amp = 3-aminopyridine; bpp = 1,3-bis(4-pyridyl)propane; DMSO = dimethylsulfoxide; Im = imidazole; hmt = hexamethylenetetramine; en = ethylenediamine; GuaNH = guanidinium; hex = hexamethylenetetramine; PyrNH = pyrrolidinium; PrNH = propan-1-amine; PentNH = pentan-1-amine; HexNH = hexan-1-amine; tert-ButNH = tert-butylamine; Temed = N,N,N',N-tetramethylethylenediamine; 4-ap = 4-aminopyridine; dien = diethylentriamine; 2,3-diamp = 2,3 diaminoypyridine.

| Counterion | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|------------|---|---|---|---|---|---|---|---|---|----|
| P2/c       | 22, 23 | 24 | 4 | To be published | 27 | 4, 27 | 27 | 28 | 29 | 30 |
| C2/c       | 31 | 31 | 32 | 17 | 33 | 34 | 4 |
| P2/a       | 15 |

**Table S2.** Metric parameters (Å, °) of $(\text{Mo}_7\text{O}_{24})^{6-}$ unit in $(\text{NH}_4)_4[(\text{Li}_2(\text{H}_2\text{O})_2)][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$.  

**Bond lengths**

| Bond   | 1 Å | 2 Å | 3 Å | 4 Å | 5 Å | 6 Å | 7 Å | 8 Å | 9 Å | 10 Å |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| Mo(1)-O(2) | 1.721(3) | Mo(4)-O(20) | 1.897(3) |
| Mo(1)-O(3) | 1.733(3) | Mo(4)-O(5) | 1.899(3) |
| Mo(1)-O(4) | 1.931(3) | Mo(4)-O(3) | 2.267(3) |
| Mo(1)-O(5) | 1.990(3) | Mo(4)-O(8) | 2.282(3) |
| Mo(1)-O(6) | 2.158(3) | Mo(5)-O(16) | 1.722(3) |
| Mo(1)-O(7) | 2.244(3) | Mo(5)-O(15) | 1.742(3) |
| Mo(1)-O(8) | 3.2110(5) | Mo(5)-O(10) | 1.913(3) |
| Mo(2)-O(2) | 1.713(3) | Mo(5)-O(23) | 1.917(3) |
| Mo(2)-O(3) | 1.7213(3) | Mo(5)-O(8) | 2.152(3) |
| Mo(2)-O(4) | 1.944(3) | Mo(6)-O(18) | 1.716(3) |
| Mo(2)-O(5) | 1.9913(3) | Mo(6)-O(19) | 1.737(3) |
| Mo(2)-O(6) | 2.1493(3) | Mo(6)-O(21) | 1.936(3) |
| Mo(2)-O(7) | 2.284(3) | Mo(6)-O(17) | 1.949(3) |
| Mo(2)-O(8) | 1.7223(3) | Mo(6)-O(3) | 2.156(3) |
| Mo(3)-O(2) | 1.7283(3) | Mo(6)-O(20) | 2.272(3) |
| Mo(3)-O(3) | 1.924(3) | Mo(7)-O(24) | 1.706(3) |
| Mo(3)-O(4) | 1.926(3) | Mo(7)-O(22) | 1.730(3) |
| Mo(3)-O(5) | 2.159(3) | Mo(7)-O(21) | 1.929(3) |
| Mo(3)-O(6) | 1.722(3) | Mo(7)-O(23) | 1.985(3) |
| Mo(4)-O(1) | 1.740(3) | Mo(7)-O(8) | 2.146(3) |
| Mo(4)-O(2) | 1.757(3) | Mo(7)-O(20) | 2.277(3) |

**Bond angles**

| Bond | 1° | 2° | 3° | 4° | 5° | 6° | 7° | 8° | 9° | 10° |
|------|----|----|----|----|----|----|----|----|----|-----|
| 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-H2N3| 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-H4N4| 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 (Mo\textsubscript{7}O\textsubscript{24})\textsuperscript{6-} unit in (NH\textsubscript{4})\textsubscript{2}Li\textsubscript{3}(H\textsubscript{2}O)\textsubscript{4}(μ\textsubscript{6}-Mo\textsubscript{7}O\textsubscript{24})·2H\textsubscript{2}O 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(4)-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(5)-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 | 43.66(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) | 43.66(17) |
| O(9)-Mo(2)-O(8)       | 91.27(14) | O(13)-Mo(3)-Mo(1) | 83.11(6)  |
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.  

| 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-H2N2 | 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-H3N1 | 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 $\mu_2$-bridging bidentate coordination of O34 resulting in a water bridged dinuclear cationic unit [Li$_2$(H$_2$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···O interactions (black dotted lines). Symmetry codes: iii) 3/2-x, 1/2+y, 3/2- 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), [Li$_2$(H$_2$O)$_7$]$^{2+}$ cationic unit (bottom left) and [Li$_2$(H$_2$O)$_7$][Mo$_7$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.
Figure S8. The binding modes of heptamolybdate in Cs₆[Mo₇O₂₄]·7H₂O (top), NaCs₃[Mo₇O₂₄]·5H₂O (bottom)
Figure S9. IR (top) and Raman spectra (bottom) of $(\text{NH}_4)_4[\text{Li}_3(\text{H}_2\text{O})_2][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ (1), $(\text{NH}_4)_3[\text{Li}_4(\text{H}_2\text{O})_4(\mu_6-\text{Mo}_7\text{O}_{24})] \cdot 2\text{H}_2\text{O}$ (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 \((\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_3(\text{Mo}_7\text{O}_{24})] \cdot \text{H}_2\text{O}\) 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 $(\text{NH}_4)_2[\text{Li}_2(\text{H}_2\text{O})_2][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ (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 $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}]\cdot4\text{H}_2\text{O}$. 
checkCIF/PLATON report (NH₄)₄[Li₂(H₂O)₇][Mo₇O₂₄]·H₂O

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 Å | 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           |                   |
| Volume          | Calculated      | Reported          |
|                 | 3090.2(4)       | 3090.2(4)         |
| Space group     | P 21/n          | P 21/n            |
| Hall group      | -P 2yn          | -P 2yn            |
| Moiety formula  | N), 2(Li)       | 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 O11 .. O38 .. 2.74 Ang.
PLAT430_ALERT_2_B Short Inter D...A Contact O11 .. O38' .. 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 H32 Li2 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 >O38 is Constrained at 0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O38' 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) ...... O38 Check
PLAT311_ALERT_2_G Isolated Disordered Oxygen Atom (No H's) ...... O38' 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 \((\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6-\text{Mo}_7\text{O}_{24})]\cdot2\text{H}_2\text{O}\)

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: \(\text{Mo- O} = 0.0026 \text{ A}\)  Wavelength=0.71073

| Cell       | Calculated | Reported |
|------------|------------|----------|
| a=14.0745(10) | b=10.8681(6) | c=17.2459(11) |
| alpha=90 | beta=90 | gamma=90 |
| Temperature: 200 K |

| 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), Mo7 O24, H4 O2, 4(H2 | 3(H4 N), 3(Li) |
| Sum formula  | H24 Li3 Mo7 N3 O30 | H24 Li3 Mo7 N3 O30 |
| Mr           | 1238.62   | 1238.62   |
| D, 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 | 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 >O24 is Constrained at 0.75 Check
PLAT300_ALERT_4_G Atom Site Occupancy of <O24' 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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2 ALERT type 5 Informative message, check
