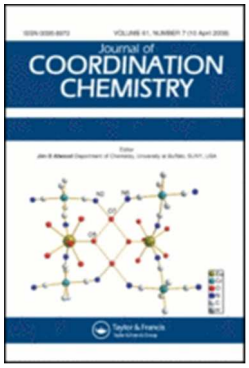

Synthesis and structure characterization of two new lithium–heptamolybdates

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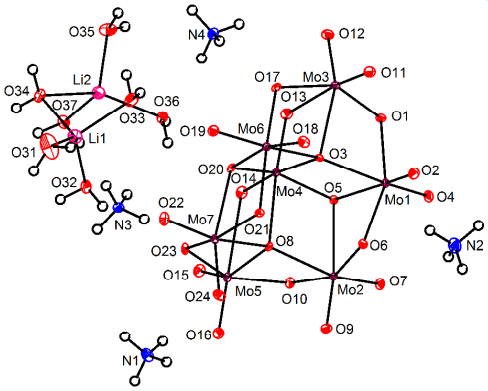
Cif data(Compound 1).CIF
Cif data(Compound 2).CIF

Synthesis and structure characterization of two new lithium–heptamolybdates

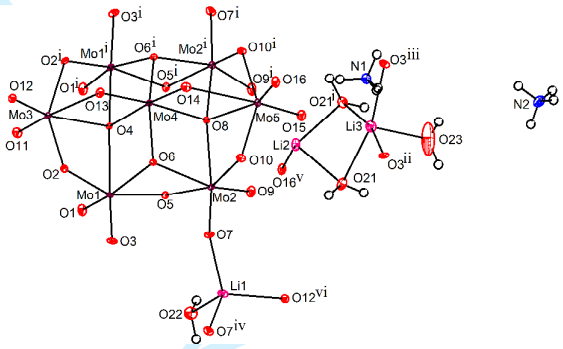
Savita S. Khandolkar[a], Christian Näther[b], Wolfgang Bensch[b], Bikshandarkoil R. Srinivasan[a],
[a]Department of Chemistry, Goa University, Goa 403206, India
Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184
[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel
Max-Eyth Straße 2, D-24098 Kiel, Germany

Graphical Abstract

Synthesis, spectroscopy and structural characterization of two new lithium-heptamolybdates are reported.



$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$



$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$

Synthesis and structure characterization of two new lithium–heptamolybdates

Savita S. Khandolkar[a], Christian Näther[b], Wolfgang Bensch[b], Bikshandarkoil R. Srinivasan[a],
[a]Department of Chemistry, Goa University, Goa 403206, India
Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184
[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel
Max-Eyth Straße 2, D-24098 Kiel, Germany

Abstract

The synthesis, crystal structures, IR, UV-Vis, ^{7}Li NMR spectra, electrochemical investigations and conductivity studies of two new lithium-heptamolybdates viz. $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** are reported. In **1**, the unique $(NH_4)^+$ cations and $[Li_2(H_2O)_7]^{2+}$ cations are charge balanced by the heptamolybdate anion. In **2** the $[Mo_7O_{24}]^{6-}$ anion is coordinated to three unique Li^+ ions via a μ_6-hexadentate binding mode resulting in the formation of a two dimensional (2-D) $[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]^{3-}$ anionic complex, charge neutralised by three $(NH_4)^+$ ions. The cations, anions and the lattice water molecules in **1** and **2** are linked by several weak H-bonding interactions.

Keywords: Lithium; Heptamolybdate; counter anion; μ_6-hexadentate ligand; H-bonding interactions

1. Introduction

The study of polyoxometalates (POMs) is a topical area of research in view of their diverse structures and interesting properties [1, 2]. Although several POM's with high metal nuclearity for example {Mo_{368}}, {Mo_{248}}, {Mo_{176}} {Mo_{154}} etc. with interesting structure types like hedgehog or wheel shape are known for molybdenum [3], the low nuclearity POM's viz. $[Mo_6O_{19}]^{2-}$, $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$ still continue to be of considerable research interest. Of the POM's containing less than 10 Mo atoms, the heptamolybdate $[Mo_7O_{24}]^{6-}$ ion is an extensively studied species by several research groups [4-34] in view of its facile formation by acidification of an aqueous molybdate $[MoO_4]^{2-}$ solution to pH = 6. These studies reveal the structural flexibility of heptamolybdate and have resulted in the discovery of a rich and diverse chemistry demonstrating the ability of $[Mo_7O_{24}]^{6-}$ to exist in a variety of environments viz. in combination with organic ammonium cations and or metal complex cations (Table S1). In all these structurally characterized compounds, the primary function of $[Mo_7O_{24}]^{6-}$ is a charge balancing anion for the organic or metal-organic cation. In addition, heptamolybdate can also function as a pure inorganic ligand, binding to metals via the terminal oxygen atoms (entry Nos. 2 to 33 in Table S1). In a recent report we have shown that the acidic nature of heptamolybdate can be exploited for the synthesis of new *s*-block metal heptamolybdates by reacting it with an appropriate base. Using this strategy we recently reported on the synthesis of a heptamolybdate bridged dimagnesium compound $[Mg(H_2O)_5(\mu_2\text{-}Mo_7O_{24})Mg(H_2O)_5]^{2-}$[10]. Since no structurally characterized lithium compound containing $[Mo_7O_{24}]^{6-}$ is reported in literature till date, we have used the same synthetic methodology namely reaction of heptamolybdate with a basic reagent (LiOH) for the synthesis of the first examples of lithium-heptamolybdates. The results of these investigations describing the synthesis, crystal structure, spectral characteristics and

electrochemistry of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** are described in this report.

2. Experimental

2.1. Materials and methods

All chemicals were used as purchased from the commercial sources without any further purification. Infrared spectra of the samples diluted in KBr were recorded in the 4000 – 400 cm^{-1} region using a Shimadzu (IR Prestige-21) FT-IR spectrometer, at a resolution of 4 cm^{-1}. Raman spectra were recorded using 785 nm radiation for excitation on an Agiltron PeakSeeker Pro Raman instrument in the range 4000–200 cm^{-1}. The UV-Visible absorption spectra were recorded using a UV-3600 Shimadzu UV-Vis spectrophotometer. X-ray powder patterns were measured on a Rigaku Miniflex II powder diffractometer using Cu-K_α radiation with Ni filter. Thermal studies of **1** and **2** were carried out in a temperature controlled electric furnace at 600 ^oC. ^7Li NMR spectra of **1** and **2** were recorded in D_2O with lithium chloride as a reference in a Bruker 500 MHz FT-NMR spectrometer. Conductivity measurements were carried out at 30^oC using Digital conductivity meter model-LT-16 LABTRONICS with a standard conductometric cell composed of two platinum black electrodes calibrated with KCl solution. Cyclic voltammetry was performed in Electrochemical Workstation-CH Instrument (Inc. CHI6107), under inert atmosphere by using platinum as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as the reference. The redox properties of the aqueous solutions of **1** and **2** were studied using 0.2 M KCl solution as supporting electrolyte at a scan rate of 0.03 Vs^{-1} in the potential region -2.0 V to 2.0 V. For comparison, $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ was investigated under identical conditions.

2.2. *Synthesis of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ 1 and $(NH_4)_3[Li_3(H_2O)_4\{\mu_6\text{-}Mo_7O_{24}\}]\cdot 2H_2O$ 2*

Ammonium heptamolybdate (1.236 g, 1 mmol) was taken and crushed with lithium hydroxide (0.083 g, 2 mmol) using a mortar and pestle for ~ 5 min, resulting in the evolution of ammonia. The reaction mixture was then transferred into a beaker containing 20 mL of distilled water and was heated on a water bath till the volume of the solution is reduced to half. At this stage the pH of the solution was ~5. The reaction mixture was then filtered and the colorless filtrate was kept aside for crystallization at room temperature. Colourless crystals separated out after a week and when kept for further crystallization, **1** was obtained in 74% yield.

The use of 3 mmol of LiOH in the above procedure with 1 mmol of ammonium heptamolybdate followed by work up afforded crystals of compound **2** in 78% yield.

Compound **1:** Anal. Found (Calcd.) % NH_4, 5.35 (5.61); % Mo, 51.87 (52.23).

Molar conductivity (λ_m) (0.02 M): 1119 S cm^2 mol^{-1}.

IR data: 3500-2500, 2878, 2814, 1641,1410, 837, 884, 653, 570, 487 cm^{-1}; Raman data: 936 (υ_1), 888, 361, 234 cm^{-1}; UV- Vis data : 208 nm.

Compound **2:** Anal. Found (Calcd.) % NH_4, 4.13 (4.36); % Mo, 53.90 (54.21).

Molar conductivity (λ_m) (0.02 M): 953 S cm^2 mol^{-1}.

IR data: 3500-2500, 2804, 1659, 1419, 893, 819, 644, 579, 477cm^{-1}; Raman data: 936 (υ_1), 888, 361, 234 cm^{-1}; UV- Vis data : 208 nm.

2.3 Crystal structure determination

The intensity data for **1** and **2** were collected with an Image Plate Diffraction System (IPDS-1) from STOE. The structures were solved with direct methods using SHELXS-97 [35] and refinement was done against F^2 using SHELXL-97 [35]. All non-hydrogen atoms were

refined anisotropically. The O-H and N-H, H atoms were located in difference map, their bond lengths were set to ideal values and afterwards they were refined using a riding model. A numerical absorption correction was performed ($T_{min/max}$: 0.5782/0.6971) (**1**) ($T_{min/max}$: 0.5742/0.6545) (**2**). One lattice water molecule (O38 in **1** and O24 in **2**) is disordered and was refined using a split model. The H atoms on O38 and O24 could not be located. Technical details of data acquisition and selected refinement results are listed in (Table 1).

3. Results and Discussion

3.1. Synthetic aspects

The synthesis of lithium-heptamolybdate compounds **1** and **2** was carried out by a base promoted cation exchange reaction between $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (acid) with $LiOH\cdot H_2O$ (base). The synthetic protocol involves a solid state reaction of grinding stoichiometric amounts of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ with $LiOH\cdot H_2O$ and then bringing it into aqueous solution followed by crystallization (equations 1 and 2). The reaction involves replacement of $(NH_4)^+$ cation by Li^+ with displacement of the weaker base ammonia by the strong base lithium hydroxide keeping intact the $\{Mo_7O_{24}\}$ core. It is interesting to note that despite the use of a strong base LiOH, due to the removal of ammonia, the final reaction medium is acidic pH ~5, which is essential for the isolation of heptamolybdate.

$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O + 2\ LiOH\cdot H_2O \rightarrow (NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** $+ 2\ NH_3\uparrow$ .. (1)

$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O + 3\ LiOH\cdot H_2O \rightarrow (NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** $+ 3\ NH_3\uparrow$ .. (2)

The slow evaporation of aqueous solutions results in the formation of crystalline products of **1** and **2**. The phase purity of **1** and **2** was confirmed by comparing their respective calculated and experimental powder patterns (Figure S1). The presence of lithium in both compounds was initially identified by flame test and the ammonium and molybdenum content were determined gravimetrically following standard procedures [36]. Pyrolysis at 600 ^oC showed

mass losses of 17.6 % and 15.8% for **1** and **2** respectively in reasonable agreement with the calculated mass loss (19.3 % and 15.0 %) yielding probable residual compositions $\{Mo_7Li_2O_{22}\}$ for **1** and $\{Mo_7Li_3O_{22.5}\}$ for **2**. Based on the gravimetric analysis of $(NH_4)^+$, Mo and the residue obtained on pyrolysis, the NH_4^+:Li ratio for **1** and **2** was inferred as 4:2 and 3:3 respectively. Thus by changing the stoichiometry of the reactants two heptamolybdates containing different amounts of Li are formed.

3.2. Description of the crystal structures of 1 and 2

The compounds $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** are the first examples of structurally characterized lithium-heptamolybdates. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with all atoms located in general positions. Its crystal structure consists of four unique ammonium cations, two crystallographically independent Li atoms and seven coordinated water molecules making up a $[Li_2(H_2O)_7]^{2+}$ unit, an unique $[Mo_7O_{24}]^{6-}$ anion, and a disordered lattice water molecule O38 (Figure 1). The geometrical parameters of the $[Mo_7O_{24}]^{6-}$ are in normal range (Table S2). The unique Li^+ cation (Li1) is coordinated to four water molecules (O31 to O34) at Li1-O distances ranging from 1.888(10) to 1.959(10) Å (Table 2). The O-Li1-O bond angles between 94.9(4)° and 121.2(5)° indicate distortion of the $\{LiO_4\}$ tetrahedron. For Li2, three Li-O bond lengths range from 1.926(10) to 2.032(10) Å for the water molecules (O35 to O37) and the fourth Li-O34 bond is at a slightly longer distance of 2.115(10) Å (Table 2) due to the μ_2-bridging bidentate coordination mode of O34 resulting in a water bridged dinuclear cationic complex of formula $[Li_2(H_2O)_7]^{2+}$ (Figure S2). Unlike Li1, the O-Li2-O angles scatter in a very wide range viz. 91.1(4)° to 147.8(5)°. A scrutiny of the structure of **1** reveals that the ammonium cations, $[Li_2(H_2O)_7]^{2+}$ complex and the $[Mo_7O_{24}]^{6-}$ anion are interlinked by three varieties of H-bonding interactions namely O−H···O, N−H···O, O−H···N (Table S3). The coordinated

water molecules are involved in intramolecular and intermolecular O−H···O interactions with surrounding heptamolybdates (Figure 2). The unique NH_4^+ cations "N1" "N3" and "N4" are H bonded to three heptamolybdates via different numbers of N−H···O interactions while "N2" is H bonded to two heptamolybdates (Figure 3). It is interesting to note that all H atoms of the NH_4^+ cations are involved in N−H···O bonding (Figure S3). The net result of the H-bonding, is the arrangement of the $(NH_4)^+$ and $[Li_2(H_2O)_7]^{2+}$ cations and $[Mo_7O_{24}]^{6-}$ anions in **1** in alternating layers (Figure 4 and Figure S4).

Compound **2** crystallizes in the centrosymmetric orthorhombic space group *Pnma* and its crystal structure consists of three unique $(NH_4)^+$ cations, an independent $[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]^{3-}$ anionic unit with Mo3, Mo4, Mo5 and Li2 atoms located on a mirror plane and a disordered lattice water molecule (O24) (Figure 5). In **2** the geometrical parameters of the heptamolybdate ion are in the normal range (Table S4) and comparable to those observed for **1**. The anion plays a dual role viz. charge balancing counter ion and pure inorganic ligand binding to Li. A μ_6-hexadentate binding mode also found in the structure of $Na_7[Mo_7O_{24}](OH)\cdot 21H_2O$ [7] is observed for $[Mo_7O_{24}]^{6-}$ (Figure 6) by considering Li-O bond distances up to 2.150 Å [37]. This binding mode results in the extension of crystal structure in two dimensions (Figure 7). The unique Li1 is bonded to three symmetry related heptamolybdate anions (O7, $O7^{iv}$, $O12^{vi}$) and to a coordinated H_2O (O22) at Li-O distances ranging from 1.885(10) to 2.001(10) Å. The O-Li1-O bond angles varying from 104.3(3)° to 119.3(5)° indicate a severe distortion of the $\{Li1O_4\}$ tetrahedron. In contrast, Li2 has bonds to two symmetry related water (O21 and $O21^{i}$) molecules and to the $O16^{v}$ atom of the heptamolybdate anions. The O21 (μ_2-bridging type) also functions as a ligand for Li3 which is additionally bonded to two symmetry related heptamolybdate anions via $O3^{iii}$ and $O3^{ii}$ and

a O23 of water resulting in tri- and penta-coordination around Li2 and Li3 respectively (Figure S5). The bridging nature of O21 leads to a $\{Li_2(H_2O)_3\}^{2+}$ unit covalently bonded to the heptamolybdate moiety. The O-Li2-O angles vary from 84.5(3)° to 103.3(4)° while those around Li3 range from 81.0(4)° to 166.0(5)°. The Li-O distances range from 1.885(10) to 2.150(8) Å (Table 2). Since all the unique Li^+ ions are coordinated to $[Mo_7O_{24}]^{6-}$, the entire unit can be considered as a heptamolybdate supported trilithium trianionic species of formula $[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]^{3-}$. In addition, Li-O (heptamolybdate) contacts are also observed at longer distances of 2.270, 2.370 and 2.397 Å which seem to be too long for significant interactions [37] and therefore are not considered.

The $[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]^{3-}$ complex is stabilised by extensive hydrogen bonding interactions. The inability to locate one $(NH_4)^+$ cation as well as the disorder of the lattice water molecules precludes a detailed description of the hydrogen-bonding situation. Relevant H-bonding interactions are given as Supplementary data (Table S5, Figure S6 & S7].

3.3. Structural aspects of heptamolybdates

Based on a comparative study of the structural features of thirty one heptamolybdates we had shown that the heptamolybdate anion is structurally flexible and all heptamolybdates isolated from acidic media contain at least one lattice water molecule [4]. In the present analysis of structural characteristics covering a total of fifty four heptamolybdates (Table S1) the same property is observed namely that all heptamolybdate compounds listed in Table S1 contain at least one lattice water molecule. A majority of these compounds crystallize in centrosymmetric space groups with only four (entry nos. 1 to 4) crystallizing in non-centrosymmetric space groups. In all the compounds listed in Table S1, the heptamolybdate functions as a charge balancing anion. In addition the heptamolybdate acts as a ligand by coordinating to a *s, d* or *f* block metal in many compounds (entry nos. 2-33). In these

heterometallic compounds, it is interesting to note that the denticity of $[Mo_7O_{24}]^{6-}$ varies from monodentate (entry No. 2 to 5) to hexadentate in the Li-heptamolybdate **2**. Of the two mixed cationic compounds described in this work, it is noted that in the ammonium rich compound **1** (four $(NH_4)^+$ ions) the heptamolybdate functions as a counter anion. In the alkali-metal rich heptamolybdates like $Na_6[Mo_7O_{24}]\cdot 14H_2O$ [5] and $Cs_6[Mo_7O_{24}]\cdot 7H_2O$ [6] higher denticities of 15 and 43 are observed for the purely inorganic $[Mo_7O_{24}]^{6-}$ ligand (Figure S8). In $NaCs_5[Mo_7O_{24}]\cdot 5H_2O$ [25] a total of 31 bonds are formed between the alkali metal cations and the heptamolybdate ligand (Figure S8). The high denticities of $[Mo_7O_{24}]^{6-}$ in these cases can be attributed to i) the oxophilic nature of the *s*-block metals and ii) high coordination number of 9 or more usually observed for Cs.

3.4. IR, UV-Vis and ^{7}Li NMR spectral studies

It is interesting to note that the IR as well as the Raman spectra of compounds **1**, **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (Figure S9) are very similar. In all three compounds a broad and strong absorption signal is observed in the region 3500-2500 cm^{-1} attributable to the –OH and –NH vibrations of the water molecules and ammonium cations respectively. The presence of H_2O and (NH_4^+) in all three compounds can also be evidenced by the bands at 1641 and 1410 cm^{-1} for **1** and 1659 and 1419 cm^{-1} for **2** and 1650 and 1406 cm^{-1} for $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$, assignable to the O-H and N-H bending vibrations [38]. The symmetric stretching vibration υ_1 of the MoO_6 unit is observed as an intense band in the Raman spectrum at 936 cm^{-1} [39] whereas the doubly degenerate asymmetric stretching mode υ_2 occurs as an intense signal at 884 and 893 cm^{-1} in **1** and **2** respectively (Figure S10). The IR spectra of the residues obtained by pyrolysis of **1** and **2** indicate the disappearance of signals due to water and ammonium cations (Figure S11).

The nearly identical UV-Vis spectra of **1**, **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ showing a signal centred around 208 nm also confirms the presence of the heptamolybdate core in **1** and **2** (Figure S12). It is interesting to note that both **1** and **2** exhibit nearly identical ^{7}Li NMR spectra in D_2O (Figure 8). Both compounds exhibit a single ^{7}Li chemical shift at 0.1376 ppm and 0.1385 ppm respectively for **1** and **2** which is in close agreement with the reported ^{7}Li chemical shift (0.006 ppm) for $Li_6[\alpha\text{-}P_2W_{18}O_{62}]$ [40]. The chemical shift data indicate that in **1** and **2** the Li^+ ions are equivalent and do not have different chemical surroundings as observed in the solid state structures for the unique Li^+ ions. Hence, the observation of a single chemical shift can be explained due to the hydration of Li^+ ions in solution (D_2O). This explanation gains more credence from the electrochemical and conductivity studies described below.

3.5. Electrochemistry, conductivity measurements and photochemical studies

The cyclic voltammogram of compounds **1** and **2** as well as $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ exhibit a single cathodic response below -1.0 V (Figure 9) with $E_{1/2}$ values -0.579 , -0.537 and -0.538 V measured versus SCE respectively for **1**, **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ accompanied by peak separations ΔE of 0.152 V**,** 0.147 V and 0.160 V respectively. The $E_{1/2}$ values for **1** and **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ can be readily explained for an electrochemical event centred on the anionic heptamolybdate which is formed due to hydrolysis of **1** and **2**, in addition to the hydrated Li^+ ions. It is interesting to note that the Li-heptamolybdates **1** and **2** described in the present study differ from the recently reported $(hmtH)_2[\{Mg(H_2O)_5\}_2\{Mo_7O_{24}\}]\cdot 3H_2O$ (hmt = hexamethylenetetramine) [10] in that the latter compound exhibits the same electrochemical event at -0.780 V. However no other electrode process is observed till -2.0 V for **1** or **2** indicating that the hydrated Li^+ cations do not undergo any electrochemical change.

The formation of hydrated Li^+ ions is also revealed by the conductivity measurements for various concentrations of **1** and **2** (Table 3). The molar conductivity values show an increase with dilution indicating the facile dissociation of **1** and **2** in dilute solution to produce hydrated Li^+, NH_4^+ and heptamolybdate ions. The high molar conductivity values (1119 and 935 S cm^2 mol^{-1} for **1** and **2**) indicate the presence of the above mentioned ionic species in the 0.02 M solution of **1** and **2**, while the differences in the molar conductivity data can be attributed to the presence of different concentrations of ammonium and lithium (4:2 in **1** and 3:3 in **2**) per mole of heptamolybdate in solution.

It is well documented that heptamolybdates charge balanced by organic cations exhibit interesting photochemistry [4, 41]. Recently we have shown that the dimagnesium-heptamolybdate $(hmtH)_2[\{Mg(H_2O)_5\}_2\{Mo_7O_{24}\}]\cdot 3H_2O$ [10] can be irradiated by exposure to sunlight and thus can be used as a photocatalyst. In order to study the photochemical properties, similar experiments were performed by irradiation of **1** or **2** in solid state (or in aqueous solution), but no photochemically induced changes were observed. This differing behaviour can be explained by presence of an organic cation $(hmtH)^+$ in the dimagnesium-heptamolybdate unlike the Li-heptamolybdates **1** or **2** .

4. Conclusion

Two new Li-heptamolybdates viz. $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** have been synthesized by a base promoted cation exchange reaction and have been characterized by spectroscopy and single crystal structures. The heptamolybdate moiety is coordinated to Li in the mixed cationic compound **2** which has more Li content compared to **1** in which Li is not bonded to $[Mo_7O_{24}]^{6-}$. It will be of interest to study the structural features of Li-rich $\{Li_6\}$ or Li-deficient $\{Li(NH_4)_5\}$ heptamolybdates

in order to understand the bonding nature of the anion in such compounds. Efforts in this direction are underway.

Supplementary material (SI)

Crystallographic data (excluding structure factors) for the structures reported in this article have been deposited with FIZ-Karlsruhe as supplementary publication no. CSD 430331 (**1**) and CSD 430332 (**2**) and can be obtained free of charge, on writing to FIZ, Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: 0049-7247-808-259), or Email: crysdata@fiz-karlsruhe.de. Additional figures related to the crystal structure and spectral data of **1** and **2** are available as supplementary data for this article and can be found in the online version.

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Table 1. Crystal data and structure refinement for $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2**

Empirical formula	$H_{32}Li_2Mo_7N_4O_{32}$ **1**	$H_{24}Li_3Mo_7N_3O_{30}$ **2**
Formula weight	1285.76	1238.62
Temperature	200(2) K	200(2) K
Wavelength	0.71073Å	0.71073Å
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, *Pnma*
Unit cell dimensions	a = 10.5894(8)Å,	a = 14.0745(10)Å,
	b = 15.8542(8)Å,	b = 10.8681(6)Å,
	c = 18.7820(11) Å	c = 17.2459(11) Å
	β = 101.473(9)°	$\alpha = \beta = \gamma$ = 90°
Volume	3090.2(4) Å^3	2638.0(3) Å^3
Z, Calculated density	4, 2.764 mg/m^3	4, 3.119 mg/m^3
Absorption coefficient	2.866 mm^{-1}	3.344 mm^{-1}
F(000)	2464	2352
Crystal size	0.13 x 0.11 x 0.07 mm^3	0.11 x 0.09 x 0.08 mm^3
θ range for data collection	2.21° to 28.00°	2.36° to 28.00°
Limiting indices	$-13\le h \le 13, -20\le k\le 20, -24\le l\le 24$	$-18\le h \le 18, -13\le k\le 13, -22\le l\le 22$
Reflections collected /unique	38500/ 7408 [R(int) = 0.0491]	20151/ 3327 [R(int) = 0.0431]
Observed reflections	6720	2944
Completeness θ = 28.00°	99.5%	99.3%
Absorption correction	Numerical	Numerical
Refinement method	Full- matrix least-squares on F^2	Full- matrix least-squares on F^2
Data / restraints / parameters	7408 / 0 / 416	3327 / 0 / 229
Goodness of fit on F^2	1.059	1.067
Final R indices [I>2σ(I)]	R1 = 0.0427, wR2 = 0.1112	R1 = 0.0309, wR2 = 0.0745
R indices (all data)	R1 = 0.0470, wR2 = 0.1143	R1 = 0.0366, wR2 = 0.0768
Largest diff. peak and hole	2.295 and -1.553 e.A^{-3}	0.895 and -1.504 e.A^{-3}

Table 2. Selected bond lengths and angles (Å, °)

Bond Lengths		**Bond angles**			
$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1**					
Li1-O31	1.888(10)	O31-Li1-O32	121.2(5)	O37-Li2-O36	98.5(4)
Li1-O32	1.904(10)	O31-Li1-O33	116.2(5)	O35-Li2-O34	107.6(4)
Li1-O33	1.953(11)	O32-Li1-O33	104.5(5)	O37-Li2-O34	91.1(4)
Li1-O34	1.959(10)	O31-Li1-O34	115.6(5)	O36-Li2-O34	147.8(5)
Li2-O35	1.926(10)	O32-Li1-O34	100.2(5)		
Li2-O37	1.998(10)	O33-Li1-O34	94.9(4)		
Li2-O36	2.032(10)	O35-Li2-O37	106.6(5)		
Li2-O34	2.115(9)	O35-Li2-O36	99.0(4)		
$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2**					
Li1-O22	1.885(10)	O22-Li1-O7	104.3(3)	O23-Li3- $O3^{ii}$	97.5(4)
Li1-O7	1.905(6)	O22-Li1-$O7^{iv}$	104.3(3)	O23-Li3- $O3^{iii}$	97.5(4)
Li1-$O7^{iv}$	1.905(6)	O7-Li1-$O7^{iv}$	119.3(5)	$O3^{ii}$- Li3- $O3^{iii}$	96.7(4)
Li1-$O12^{vi}$	2.001(10)	O22-Li1-$O12^{vi}$	112.2(5)	O23-Li3- O21	93.8(4)
Li2-$O16^{vii}$	2.048(10)	O7-Li1-$O12^{vi}$	108.3(3)	$O3^{ii}$- Li3-O21	166.0(5)
Li2-O21	2.036(7)	$O7^{iv}$-Li1-$O12^{vi}$	108.3(3)	$O3^{iii}$- Li3-O21	90.00(13)
Li2-$O21^{i}$	2.036(7)	$O21^{i}$-Li2-O21	86.6(4)	O23-Li3- $O21^{i}$	93.8(4)
Li3-$O3^{ii}$	2.094(7)	$O21^{i}$-Li2-$O16^{v}$	103.3(4)	$O3^{ii}$-Li3- $O21^{i}$	90.00(13)
Li3-$O3^{ii}$	2.094(7)	O21-Li2-$O16^{v}$	103.3(4)	$O3^{iii}$-Li3- $O21^{i}$	166.0(5)
Li3-$O21^{i}$	2.150(8)	O23-Li3-$O3^{ii}$	97.5(4)	O21-Li3-$O21^{i}$	81.0(4)
Li3-O21	2.150(8)				
Li3-O23	2.067(12)				

Symmetry transformations used to generate equivalent atoms for compound **2**: i) 1+x, y, z ii) 1/2-x, 1/2+y, 3/2-z iii) 1-x, 1-y, 1-z iv) 1-x, 1-y, 1-z v) 1+x, y, z vi) -1/2+x, 3/2-y, 1/2+z.

Table 3. Specific conductivity (Ƙ) and molar conductivity (λ_m) data

Molar Concentration (M)	Specific conductivity (Ƙ) (in S cm^{-1})		Molar conductivity (λ_m) (S cm^2 mol^{-1})	
	Compound **1**	Compound **2**	Compound **1**	Compound **2**
0.1	0.040	0.037	400	371
0.08	0.038	0.038	481	444
0.06	0.036	0.032	600	542
0.04	0.031	0.027	798	685
0.02	0.022	0.019	1119	953

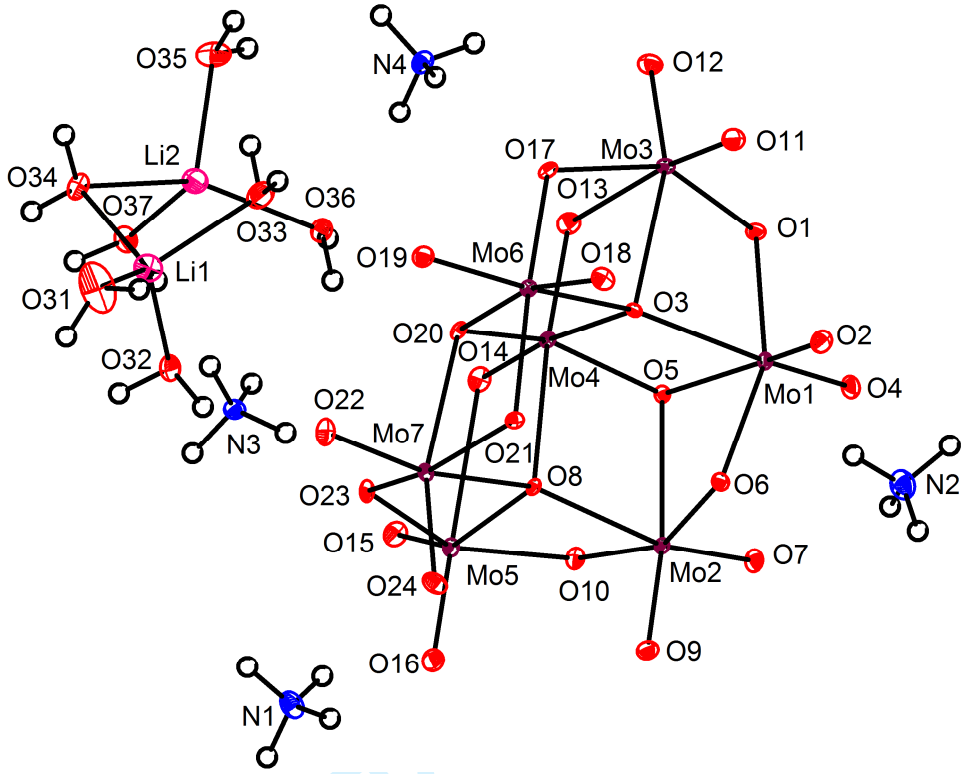


Figure 1. Crystal structure of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1** showing atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level excepting for H atoms, which are shown as circles of arbitrary radius. The disordered lattice water (O38) molecule is not shown.

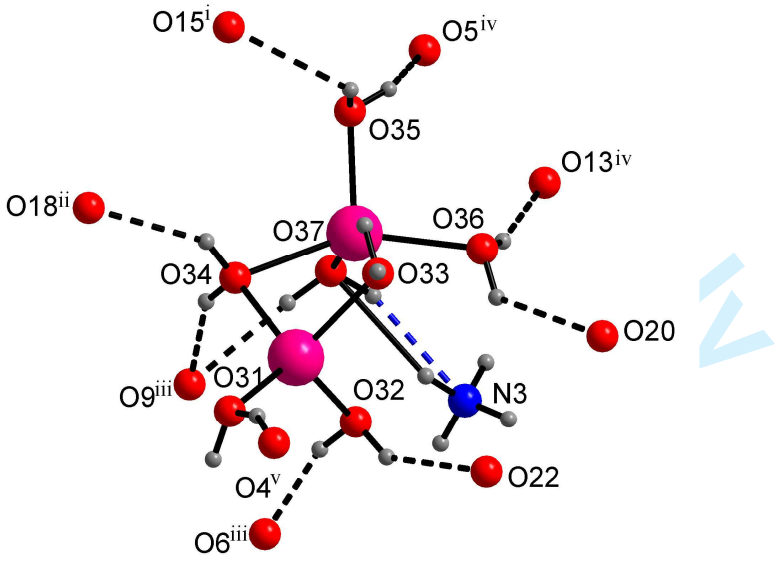


Figure 2. The hydrogen bonding situation around $[Li_2(H_2O)_7]^{2+}$ cationic unit in **1** showing intramolecular and intermolecular O–H···O interactions (black dotted lines). One intramolecular O–H···N interactions is represented by a blue dotted line. Symmetry codes: i)1+x, y, z ii) 1/2-x, 1/2+y, 3/2-z iii) 3/2-x, 1/2+y, 3/2-z iv) 1-x, 1-y, 1-z v) 1/2+x, 3/2-y,1/2+z.

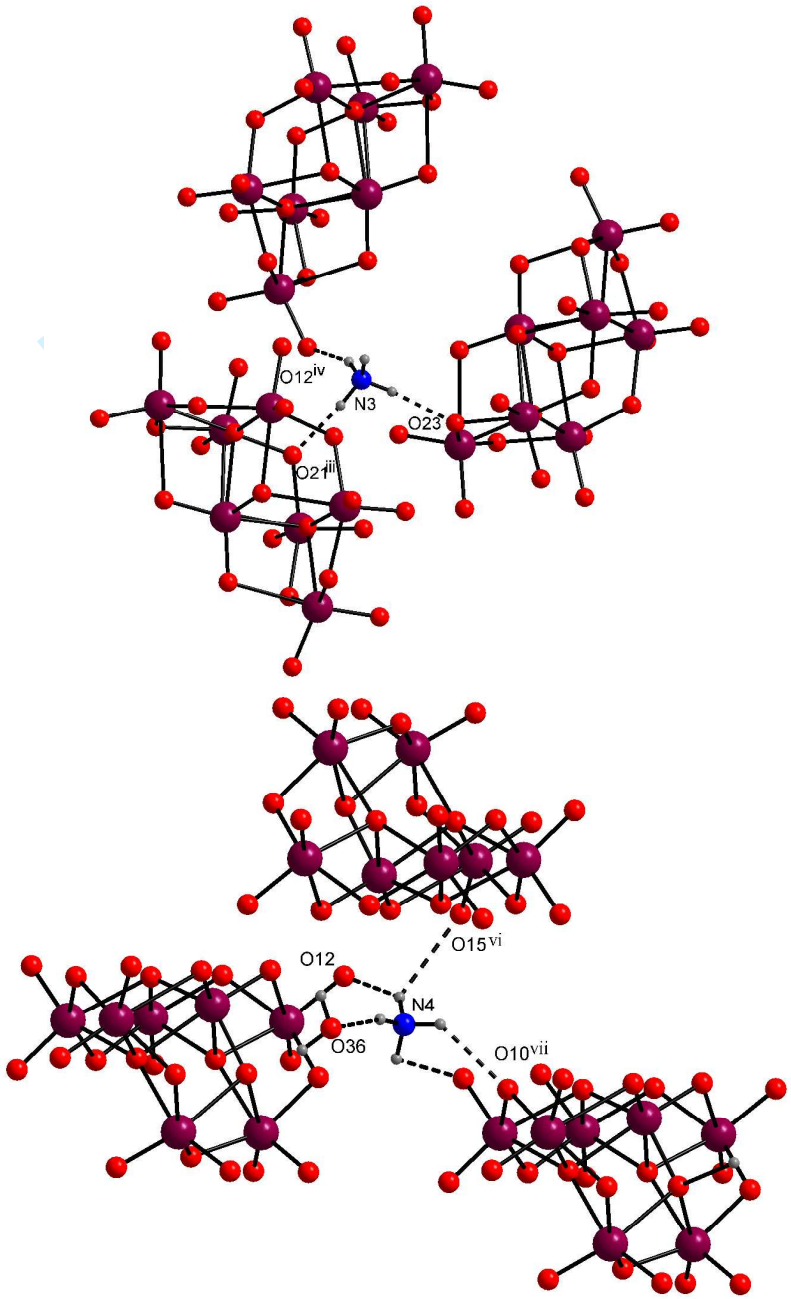


Figure 3. The hydrogen bonding situation around ammonium cations 'N3' **(top)** and 'N4' **(bottom)** showing intramolecular and intermolecular N–H···O interactions (black dotted lines). Symmetry codes: iii) 3/2-x, 1/2+y, 3/2-z vi) -1/2+x, 3/2-y, 1/2+z vii) 1+x, y, z. (For H-bonding surroundings of N1& N2 see **Figure S3**)

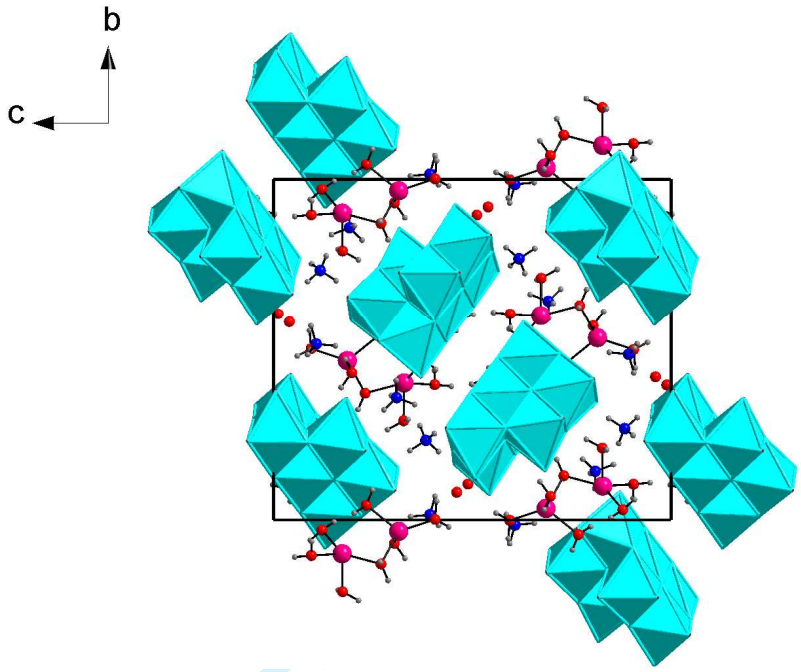


Figure 4. The unit cell packing viewed along '*a*' axis showing alternating layers of cations and anions in $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1**. Anions are shown as polyhedra. For clarity, lattice water molecules as well as H-bonding interactions are not shown. (See also **Figure S4**)

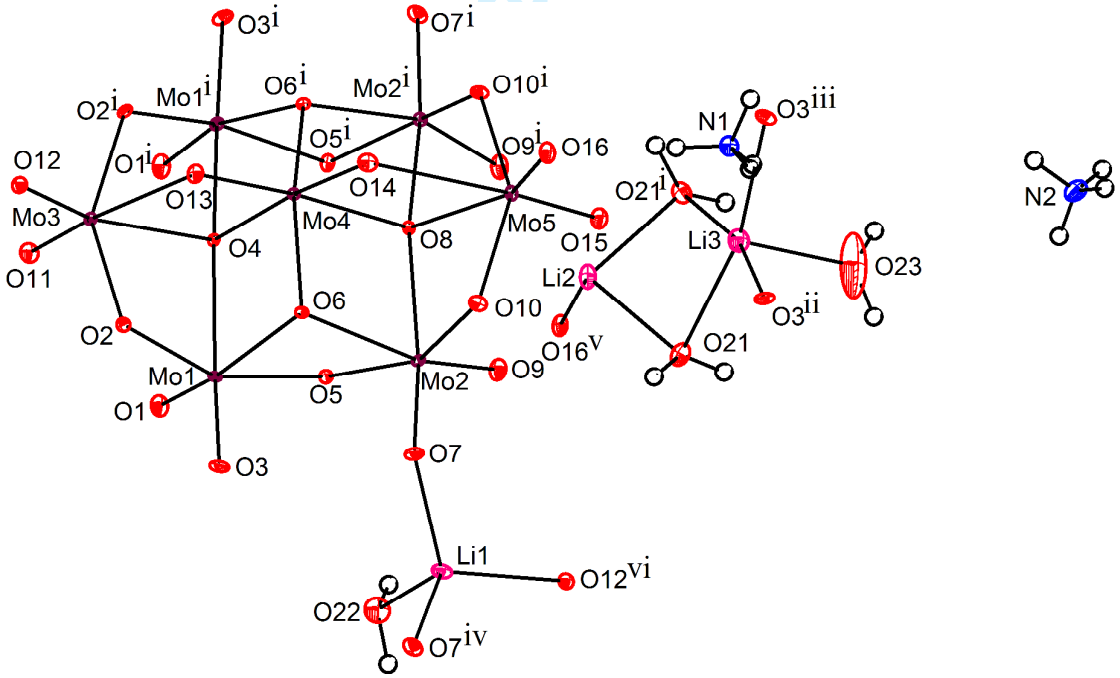


Figure 5. Crystal structure of $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2** showing atom labelling scheme. Displacement ellipsoids are drawn at the 30% probability level excepting for H atoms, which are shown as circles of arbitrary radius. The disordered lattice water (O24) molecule is not shown. Symmetry code: i) 1+x, y, z ii) 1/2-x, 1/2+y, 3/2-z iii) 1-x, 1-y, 1-z iv) 1-x, 1-y, 1-z v) 1+x, y, z vi) -1/2+x, 3/2-y, 1/2+z.

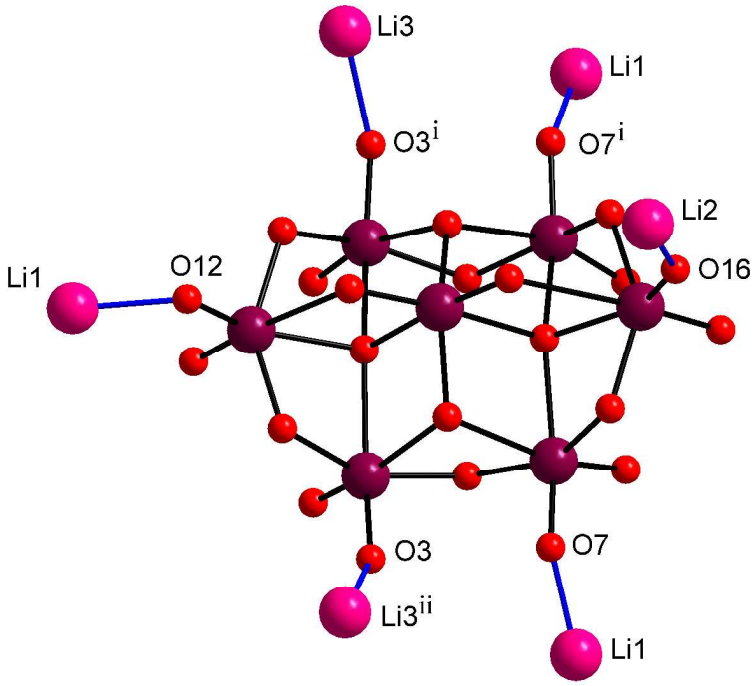


Figure 6. The μ_6-hexadentate binding mode of $\{Mo_7O_{24}\}^{6-}$ ligand in **2**. Li-O bonds are shown in blue. Symmetry code: i) x, 1/2-y, z ii) x, 3/2-y, z.

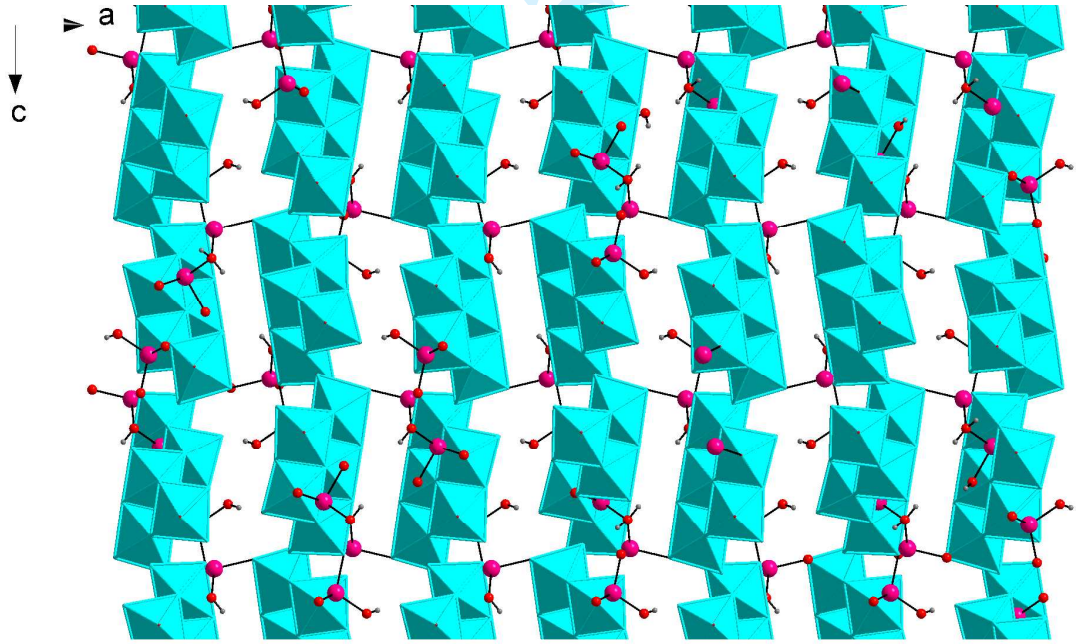


Figure 7. A view along '*b*' axis showing the two-dimensional structure formed by Li−O−Mo linkages in **2**. Colour code: Li, pink; O, red; H, medium grey; heptamolybdate anions are shown as polyhedra.

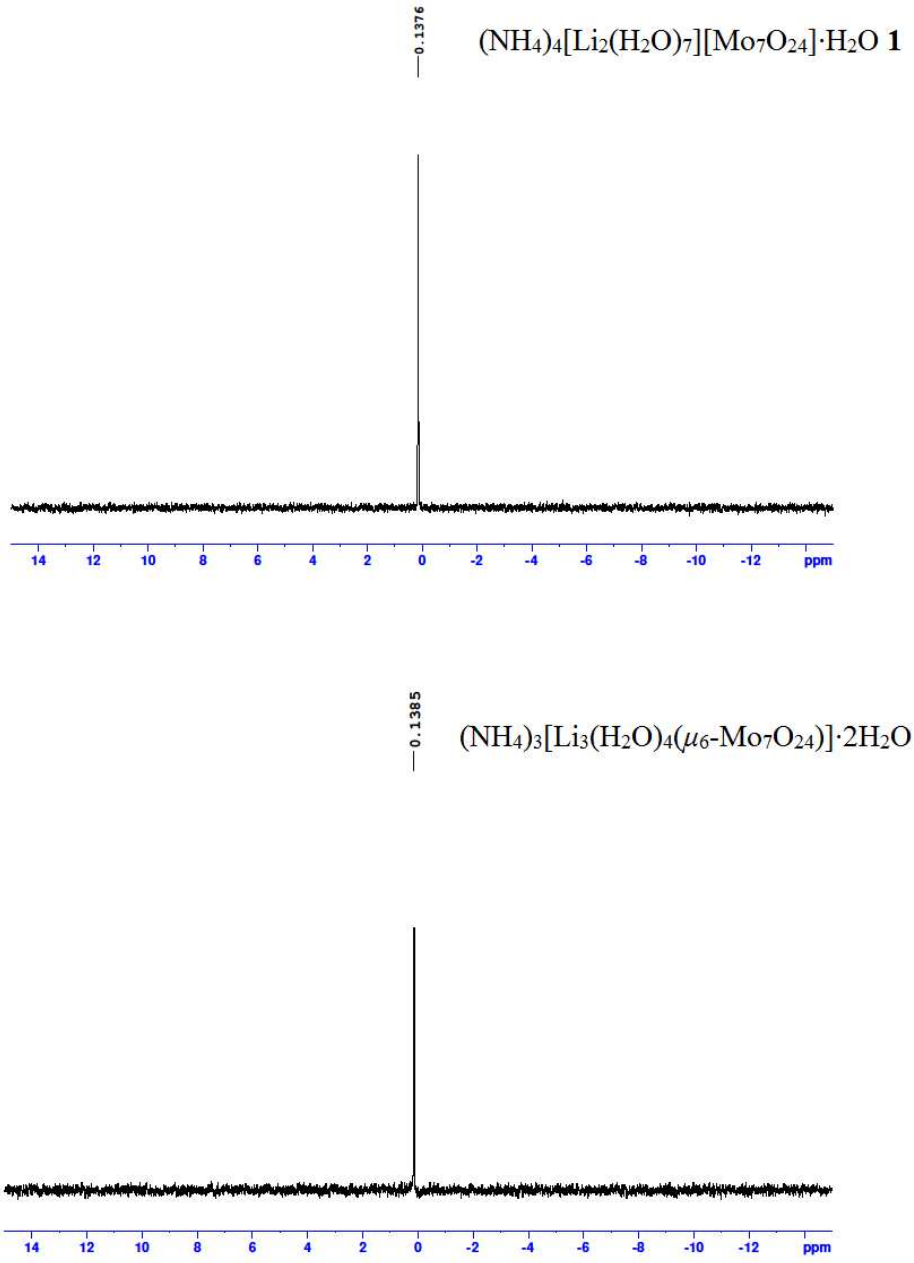


Figure 8. ^{7}Li NMR spectra of **1 (top)** and **2 (bottom)** in D_2O with lithium chloride as reference.

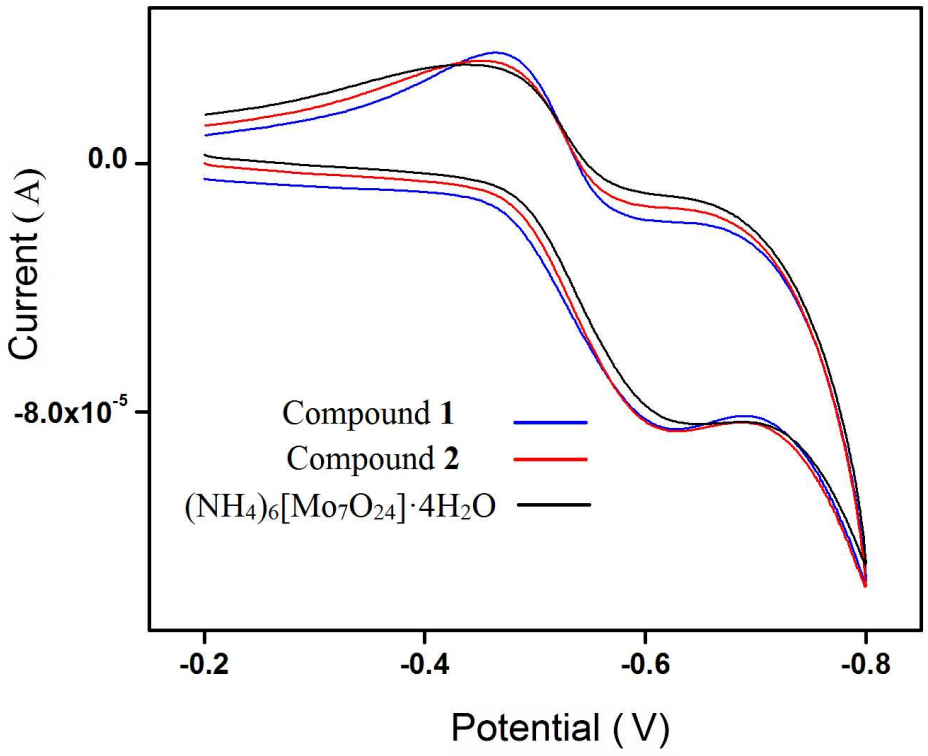


Figure 9. Cyclic voltammograms of **1**, **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ at scan rate of 0.03 Vs^{-1} .

Synthesis and structure characterization of two new lithium–heptamolybdates

Savita S. Khandolkar[a], Christian Näther[b], Wolfgang Bensch[b], Bikshandarkoil R. Srinivasan[a],
[a]Department of Chemistry, Goa University, Goa 403206, India
Email: srini@unigoa.ac.in Telephone: 0091-(0)832-6519316; Fax: 0091-(0)832-2451184
[b]Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel
Max-Eyth Straße 2, D-24098 Kiel, Germany

SUPPLEMENTARY MATERIAL FOR ONLINE VERSION

Table S1. List of structurally characterized heptamolybdate compounds.

No	Compound	Space Group	Binding mode of $\{Mo_7O_{24}\}^{-6}$	Ref
1	$(H_2DABCO)_3[Mo_7O_{24}]\cdot 4H_2O$	*Cc*	Counterion	26
2	$(2\text{-ampH})_4[Co(H_2O)_5Mo_7O_{24}]\cdot 9H_2O$	*Pna2₁*	Monodentate	9
3	$[3\text{-ampH}]_4[\{Zn(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}]\cdot 4H_2O$	*Cc*	Monodentate	15
4	$[3\text{-ampH}]_4[\{Co(3\text{-ampy})(H_2O)_4\}Mo_7O_{24}]\cdot 4H_2O$	*Cc*	Monodentate	15
5	$[2\text{-ampH}]_4[\{Zn(H_2O)_5\}Mo_7O_{24}]\cdot 9H_2O$	*Pnma*	Monodentate	15
6	$Na(NH_4)[bppH_2]_2[Mo_7O_{24}]\cdot 8H_2O$	*P2₁/m*	Tridentate	8
7	$(NH_4)_4[Ru(DMSO)_3Mo_7O_{24}]\cdot 6.5H_2O$	*C2/c*	Tridentate	14
8	$(NH_4)_4[Os(DMSO)_3Mo_7O_{24}]\cdot 4.5H_2O$	*C2/c*	Tridentate	14
9	$(ImH)_4[Ca(H_2O)_6(\mu\text{-}O)_2\{Mo_7O_{24}\}]\cdot 2\ (Im)\cdot 3H_2O$	*C2/m*	μ_2-bidentate	17
10	$(NH_4)_6H_2[Cu(C_2O_4)_2(Mo_7O_{24})]\cdot 9H_2O$	*P2₁/m*	μ_2-bidentate	18
11	$(hmtH)_2[\{Mg(H_2O)_5\}_2\{Mo_7O_{24}\}]\cdot 3H_2O$	*C2/c*	μ_2-bidentate	10
12	$(hmtH)_2[\{(Zn(H_2O)_5\}\{Zn(H_2O)_4\}\{Mo_7O_{24}\}]\cdot 2H_2O$	*C2/c*	μ_2-tridentate	11
13	$(hmtH)_2[Mn_2(H_2O)_9Mo_7O_{24}]\cdot 2H_2O$	*C2/c*	μ_2-tridentate	12
14	$(hmtH)_2[Fe_2(H_2O)_9Mo_7O_{24}]\cdot 2H_2O$	*C2/c*	μ_2-tridentate	12
15	$(NH_4)[Cu(en)_2][Na(en)Cu(en)_2(H_2O)(Mo_7O_{24})]\cdot 4H_2O$	*P*$\bar{1}$	μ_3-tridentate	19
16	$(GuaNH_2)_7Na[Co\ (H_2O)_5\{Mo_7O_{24}\}]_2\cdot 8H_2O$	*P2₁/c*	μ_2-tetradentate	13
17	$[(CH_3)_4N]_{1.33}[NH_4]_{12.67}[La_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 12H_2O$	*I*$\bar{4}$*3d*	μ_3-tetradentate	21
18	$[NH_4]_{14}[Ce_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 36H_2O$	*P*$\bar{1}$	μ_3-tetradentate	21
19	$[NH_4]_{14}[Pr_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 29H_2O$	*C2/c*	μ_3-tetradentate	21
20	$[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Sm_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 22H_2O$	*I*$\bar{4}$*3d*	μ_3-tetradentate	21
21	$[(CH_3)_4N]_{3.33}[NH_4]_{10.67}[Gd_4(MoO_4)(H_2O)_{16}(Mo_7O_{24})_4]\cdot 16H_2O$	*I*$\bar{4}$*3d*	μ_3-tetradentate	21
22	$Na_2(hmtH_2)_2[Mo_7O_{24}]\cdot 9H_2O$	*Pnma*	μ_2-pentadentate	16
23	$[(hmtH)_2\}_{1.5}\{(ahmtH)_2\}_{0.5}][Na_2(H_2O)_5Mo_7O_{24}]\cdot 4H_2O$	*Pnma*	μ_2-pentadentate	12
24	$(NH_4)_{28}[Ce_8(MoO_4)_2(H_2O)_{31}(Mo_7O_{24})_8]\cdot 74H_2O$	*P*$\bar{1}$	μ_3-tetradentate, μ_4-pentadentate	20
25	$(NH_4)_{26}[CoPr_8(MoO_4)_2(H_2O)_{33}(Mo_7O_{24})_8]\cdot 54H_2O$	*P*$\bar{1}$	μ_3-tetradentate, μ_4-pentadentate, μ_4-hexadentate	20
26	$(NH_4)_{11.9}[Nd_{4.7}(MoO_4)(H_2O)_{23}(Mo_7O_{24})_4]\cdot 19H_2O$	*P*$\bar{1}$	μ_3-tetradentate, μ_4-hexadentate	20
27	$(NH_4)_{11.9}[Pr_{4.7}(MoO_4)(H_2O)_{23}(Mo_7O_{24})_4]\cdot 34H_2O$	*P*$\bar{1}$	μ_3-tetradentate, μ_4-hexadentate	20
28	$Na_7[Mo_7O_{24}](OH)\cdot 21H_2O$	*P2/n*	μ_6-hexadentate	7
29	$Na_6[Mo_7O_{24}]\cdot 14H_2O$	*Pca2₁*	μ_{11}-pentadecadentate	5
30	$NaCs_5[Mo_7O_{24}]\cdot 5H_2O$	*P*$\bar{1}$	μ_{16}-hentriacontadentate	25
31	$Cs_6[Mo_7O_{24}]\cdot 7H_2O$	*P*$\bar{1}$	μ_{18}-tritetracontadentate	6
32	$K_6[Mo_7O_{24}]\cdot 4H_2O^{\#}$	*P2₁/c*	---	23

33	$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24}\}]\cdot 2H_2O$ **2**	*Pnma*	μ_6-hexadentate	This work
34	$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1**	$P2_1/n$	Counterion	This work
35	$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$	$P2_1/c$	Counterion	22
36	$(2\text{-ampH})_6[Mo_7O_{24}]\cdot 3H_2O$	$P2_1/n$	Counterion	24
37	$(BuNH_3)_8[(Mo_7O_{24})(MoO_4)]\cdot 3H_2O$	$P\bar{1}$	Counterion	4
38	$(BuNH_3)_6[Mo_7O_{24}]\cdot 4H_2O$	$P2_1/c$	Counterion	Unpublished work
39	$(BuNH_3)_6[Mo_7O_{24}]\cdot 3H_2O$	$P2_1/n$	Counterion	27
40	$(PyrNH_3)_6[(Mo_7O_{24}]\cdot 2H_2O$	$P\bar{1}$	Counterion	4
41	$(PrNH_3)_6[Mo_7O_{24}]\cdot 3H_2O$	$P\bar{1}$	Counterion	4, 27
42	$(PentNH_3)_6[Mo_7O_{24}]\cdot 3H_2O$	$P2_1/n$	Counterion	4, 27
43	$(HexNH_3)_6[Mo_7O_{24}]\cdot 3H_2O$	$P2_1/n$	Counterion	27
44	$(t\text{-}BuNH_3)_6[Mo_7O_{24}]\cdot 7H_2O$	$P2_1/n$	Counterion	28
45	$(TemedH_2)_3[Mo_7O_{24}]\cdot 4H_2O$	$C2/c$	Counterion	29
46	$(GuaNH_2)_6[Mo_7O_{24}]\cdot H_2O$	$C2/c$	Counterion	30
47	$(GuaNH_2)_6[Mo_7O_{24}]\cdot H_2O$	$P2_1/c$	Counterion	31
48	$(4\text{-apH})_6[Mo_7O_{24}]\cdot 6H_2O$	$P2_1/c$	Counterion	32
49	$[UreaH]_3(NH_4)_9[Mo_7O_{24}]_2\cdot 5[Urea]\cdot 4H_2O$	*Fddd*	Counterion	17
50	$(dienH_3)_2[Mo_7O_{24}]\cdot 4H_2O$	$C2/c$	Counterion	33
51	$(dienH_3)_2[Mo_7O_{24}]\cdot 4H_2O$	$P2_1/a$	Counterion	33
52	$(NMe_4)_2(NH_4)_8[(Mo_7O_{22})(\mu_2\text{-}O)_2(Mo_7O_{22})]\cdot 4H_2O$	$P\bar{1}$	Counterion	34
53	$(BuNH_3)_{10}[(Mo_7O_{22})(\mu_2\text{-}O)_2(Mo_7O_{22})]\cdot 5.5H_2O$	$P2_1/n$	Counterion	4
54	$[2,3\text{-diampH}]_4[Co(H_2O)_6][Mo_7O_{24}]\cdot 6H_2O$	$C2/c$	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 = ethylenediammine; $GuaNH_2$ = guanidinium; ahmt =*N*-(aminomethylene)-hexamethylenetetramine; $BuNH_2$=butan-1-amine; $PyrNH_2$ = pyrrolidinium; $PrNH_2$= propan-1-amine; $PentNH_2$ = pentan-1-amine; $HexNH_2$ = hexan-1-amine; *t*-$BuNH_2$ = *tert*-butylamine; Temed = *N*,*N*,*N*,*N*,-tetramethylethylenediamine; 4-ap = 4-aminopyridine; dien = diethylentriamine.; 2,3-diamp = 2,3 diaminopyridine. # Potassium coordinates unavailable.

Table S2. Metric parameters of $(Mo_7O_{24})^{6-}$ in (Å) and angles (°) for $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **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. Geometrical parameters of the O−H···O, O−H···N and N−H···O hydrogen bonds length (Å) and (°) in the crystal structure of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **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 of $(Mo_7O_{24})^{6-}$ in (Å) and angles (°) for $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **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. Geometrical parameters of the N–H···O and O–H···O, hydrogen bonds length (Å) and (°) in the crystal structure of $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **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]

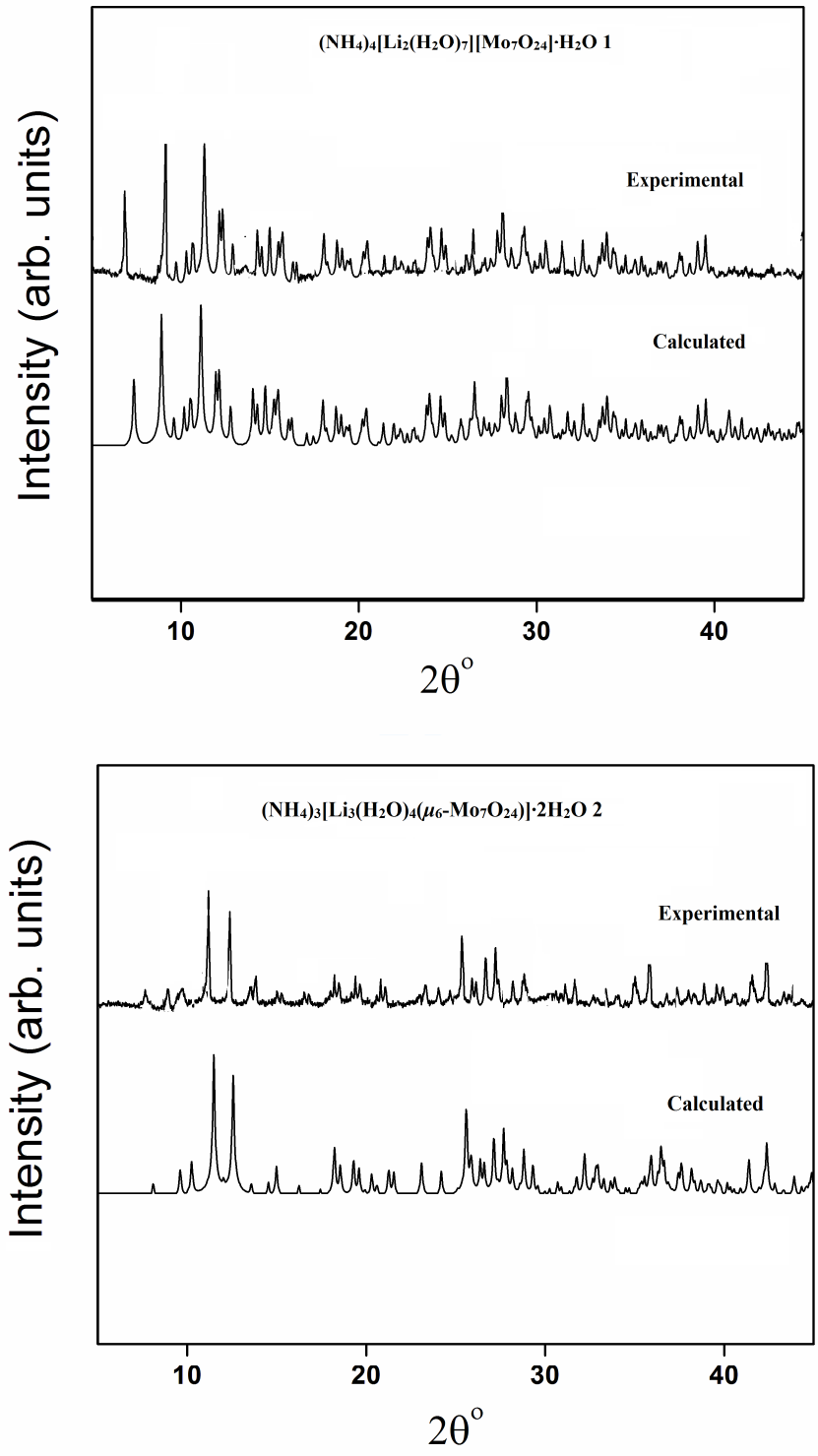


Figure S1. Calculated and experimental powder patterns of **1(top)** & **2 (bottom)**.

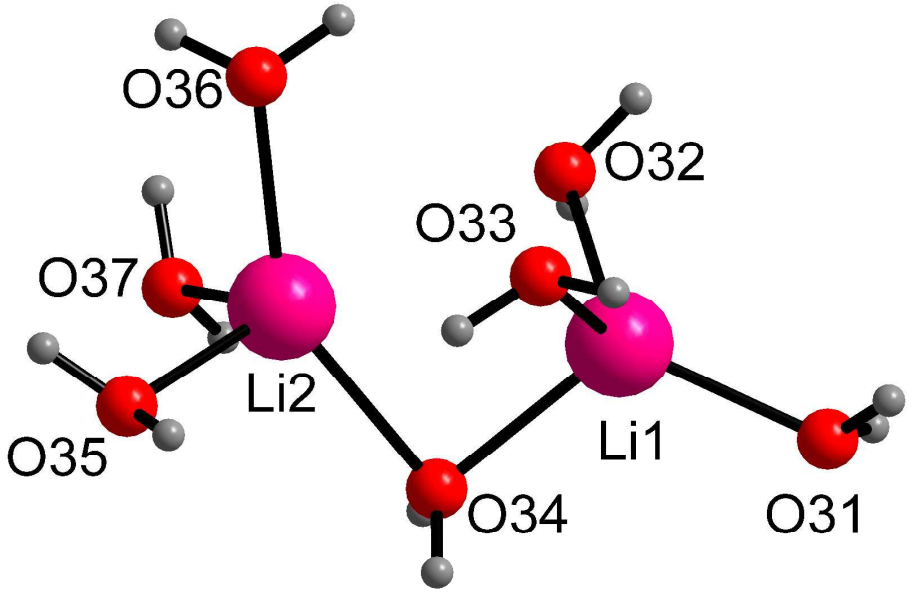


Figure S2. Coordination sphere of $\{LiO_4\}$ tetrahedra around Li1 and Li2 showing μ_2-bridging bidentate coordination of O34 resulting in a water bridged dinuclear cationic unit $[Li_2(H_2O)_7]^{2+}$ in **1**.

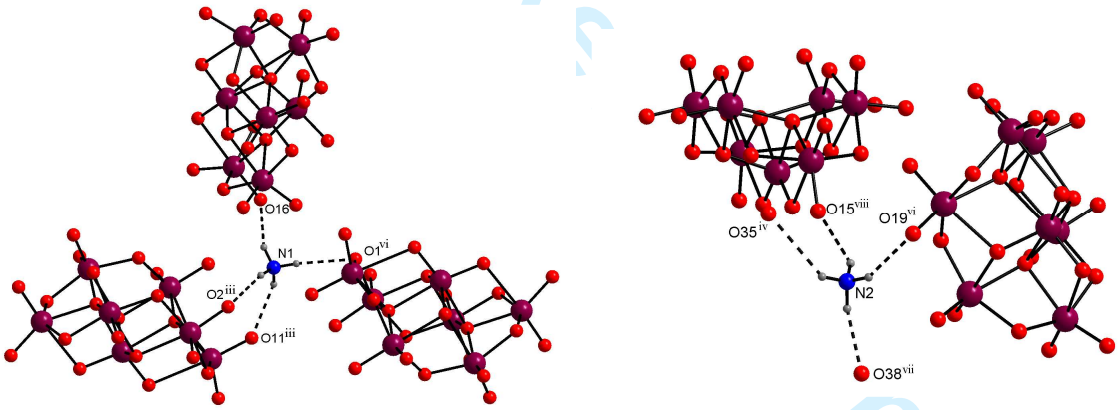


Figure S3. The hydrogen bonding situation around ammonium cations 'N1' **(left)** and 'N2' **(right)** showing intramolecular and intermolecular N−H···O interactions (black dotted lines). Symmetry codes: iii) 3/2-x, 1/2+y, 3/2- iv) 1-x, 1-y, 1-z vi) -1/2+x, 3/2-y, 1/2+z vii) 1+x, y, z viii) 1-x, 1-y,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

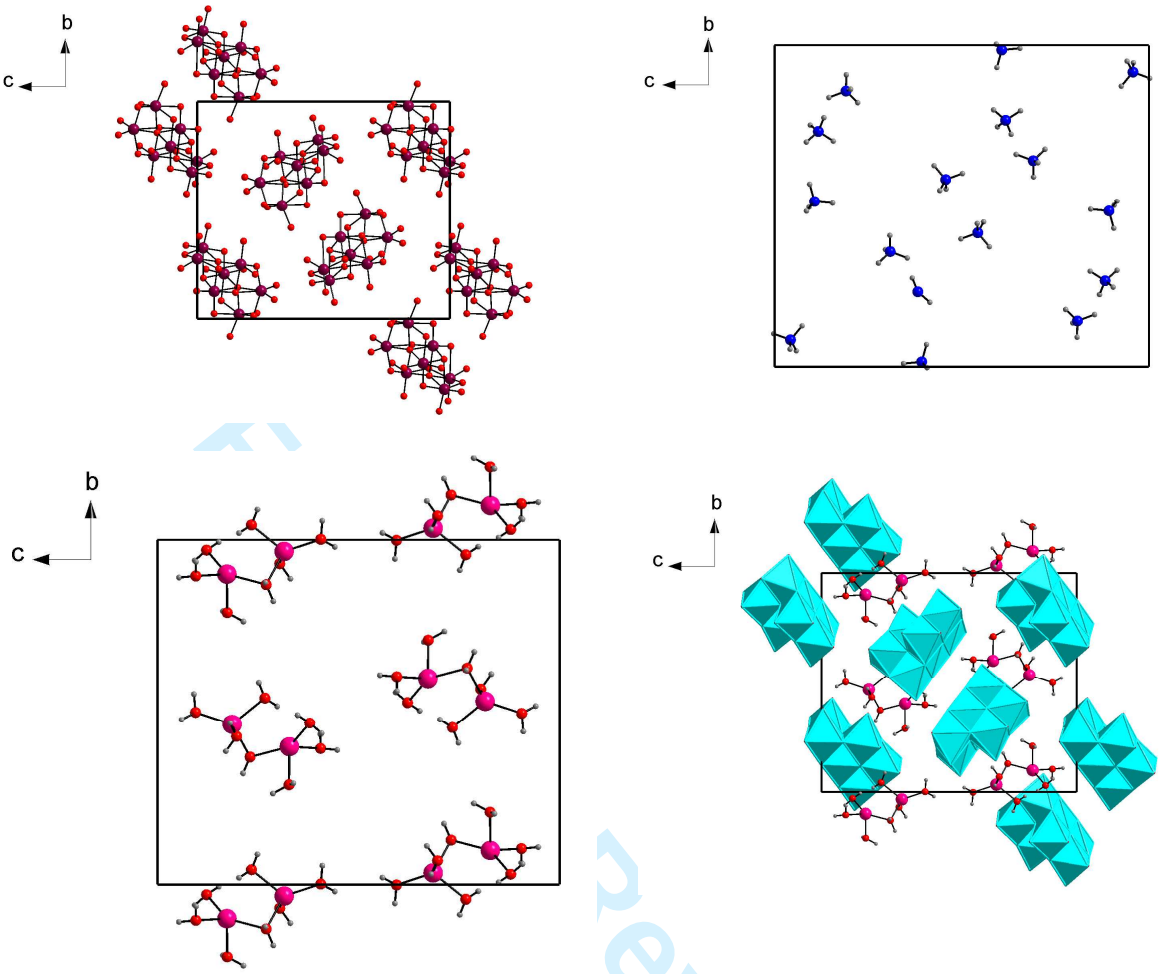


Figure S4. A view along '*a*' axis of the unit cell packing showing only heptamolybdate anions **(top left)**, ammonium cations **(top right)**, $[Li_2(H_2O)_7]^{2+}$ cationic unit (bottom left) and $[Li_2(H_2O)_7][Mo_7O_{24}]^{4-}$ unit **(bottom right)** in compound **1**.Colour codes: Mo, maroon; Li, pink; O, red; N, blue; H, medium grey; heptamolybdate anions are shown as polyhedra.

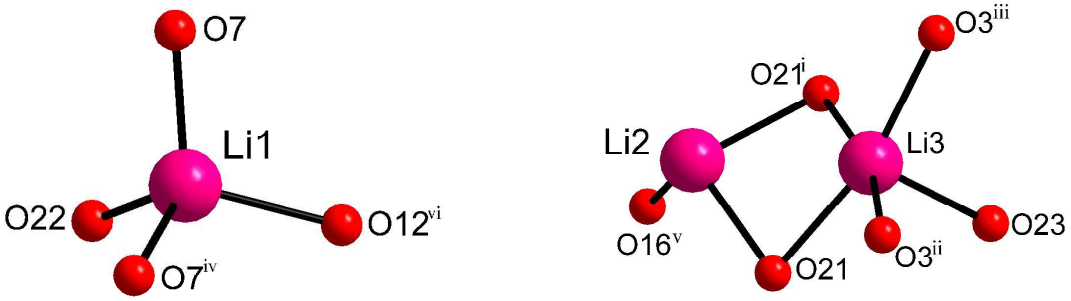


Figure S5. The coordination sphere of Li1 **(left)** and Li2, Li3 **(right)** in compound **2**. Symmetry codes: i) x, 1/2-y, z ii) x, 3/2-y, z iii) -1/2+x, 1/2-y, 3/2- z iv) 1/2-x, 1-y, -1/2+ z v) 1/2-x, -1/2+y, -1/2+z vi) -1/2+x, 3/2-y, 1/2+z.

.

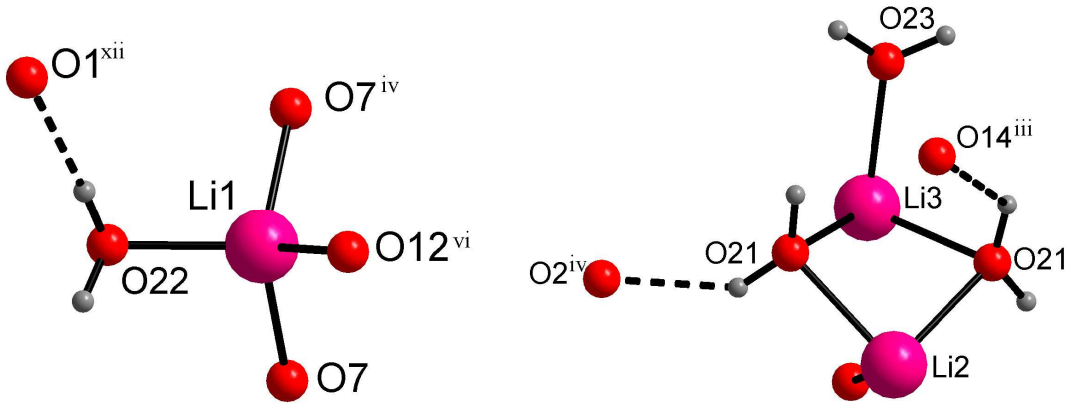


Figure S6. The hydrogen bonding situation around Li1 **(left)** and Li2, Li3 **(right)** showing O–H···O interactions (black dotted lines). Symmetry codes: iii) -1/2+x, 1/2-y, 3/2- z iv) 1/2-x, 1-y, -1/2+ z vi) 1/2-x, 1/2+y, 1/2+z xii) 1-x, -1/2+y, 2-z.

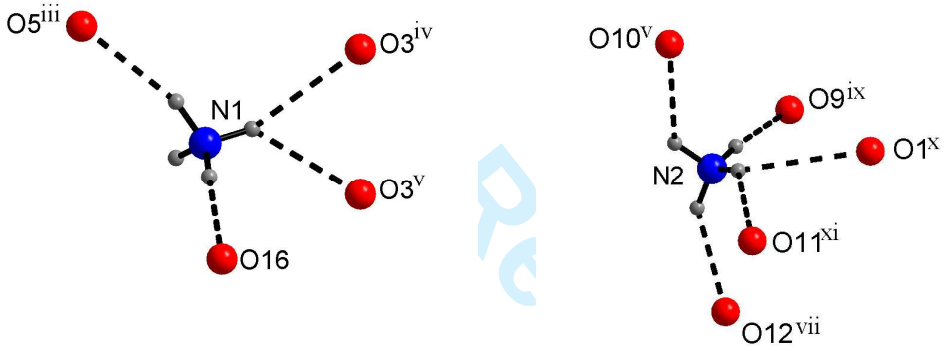
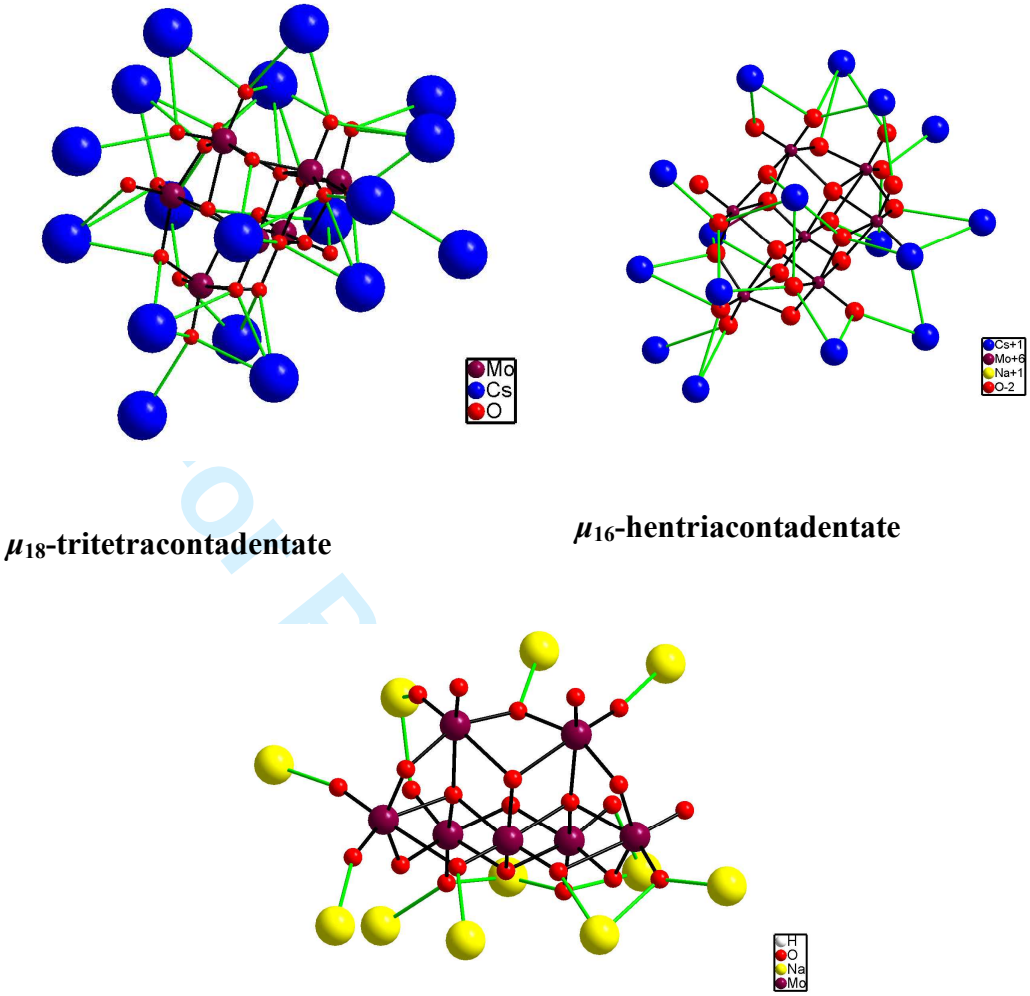


Figure S7. The hydrogen bonding situation around ammonium cations 'N1' **(left)** and 'N2' **(right)** shown by black dotted lines. Symmetry codes: iii) -1/2+x, 1/2-y, 3/2- z iv) 1/2-x, 1-y, -1/2+ z v) 1/2-x, -1/2+y, -1/2+z vii) 1/2+x, y, 3/2-z ix) 1-x, 1/2+y, 1-z x) x, 1/2-y, -1+z xi) x, y, 1+z.



μ_{18}-tritetracontadentate

μ_{16}-hentriacontadentate

μ_{11}-pentadecadentate

Figure S8. The binding modes of heptamolybdate in $Cs_6[Mo_7O_{24}]\cdot 7H_2O$ **(top left)**, $NaCs_5[Mo_7O_{24}]\cdot 5H_2O$ **(top right)** and $Na_6[Mo_7O_{24}]\cdot 14H_2O$ **(bottom)**.

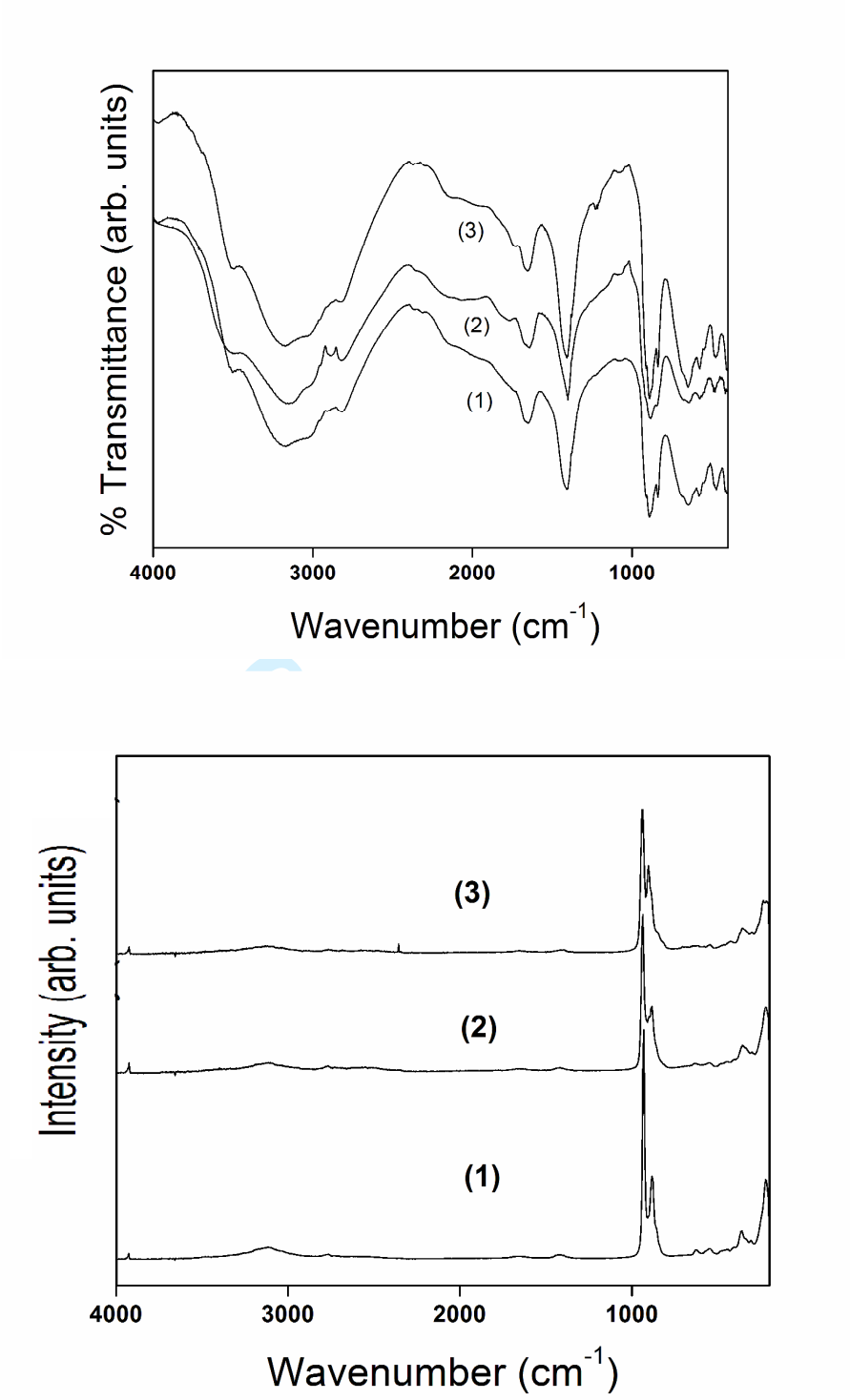


Figure S9. IR **(top)** and Raman spectra **(bottom)** of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ (1), $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ (2) and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (3).

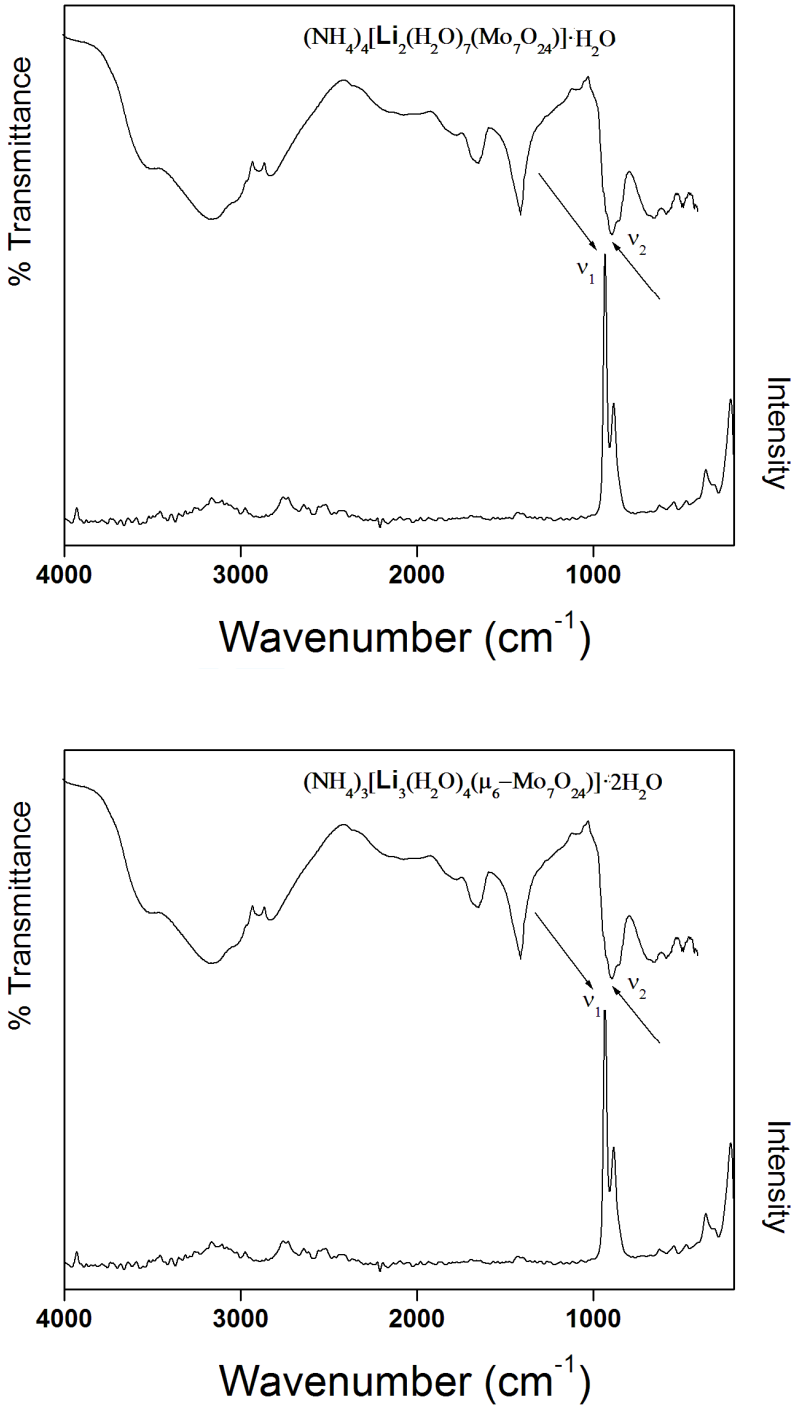


Figure S10. IR and Raman spectra of $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ **1 (top)** and $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **2 (bottom)**.

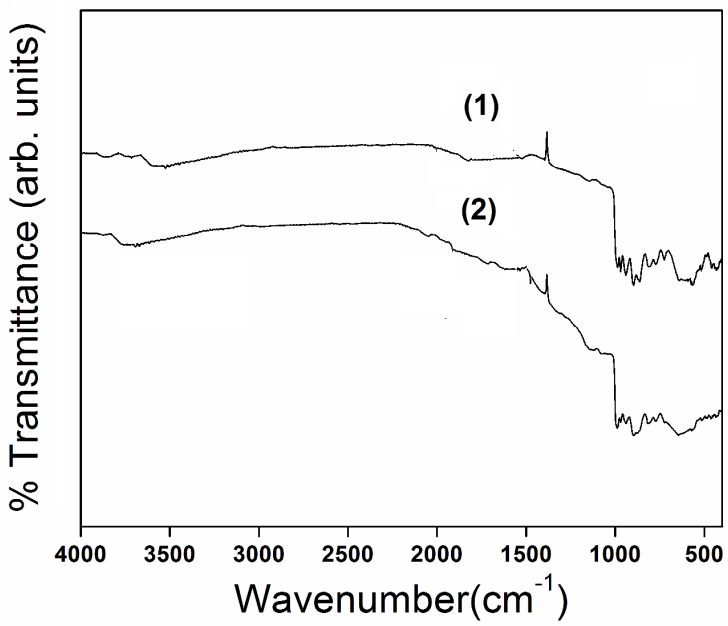


Figure S11. IR spectra of the residue obtained after heating $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ (1), $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ (2) at 600 °C.

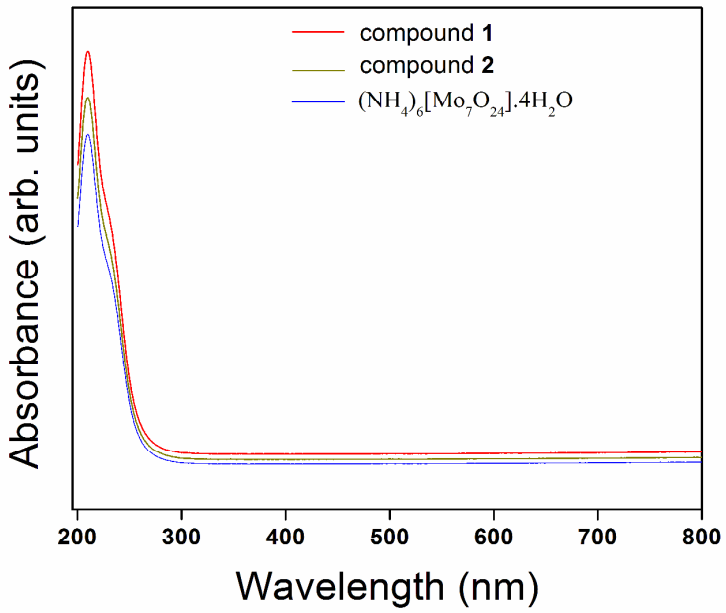


Figure S12. UV-Vis spectra of compound **1**, **2** and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$.

checkCIF/PLATON report $(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$ 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

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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

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PLAT430_ALERT_2_B Short Inter D...A Contact  O11     .. O38'     ..       2.80 Ang.
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Alert level C

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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
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Alert level G

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           _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

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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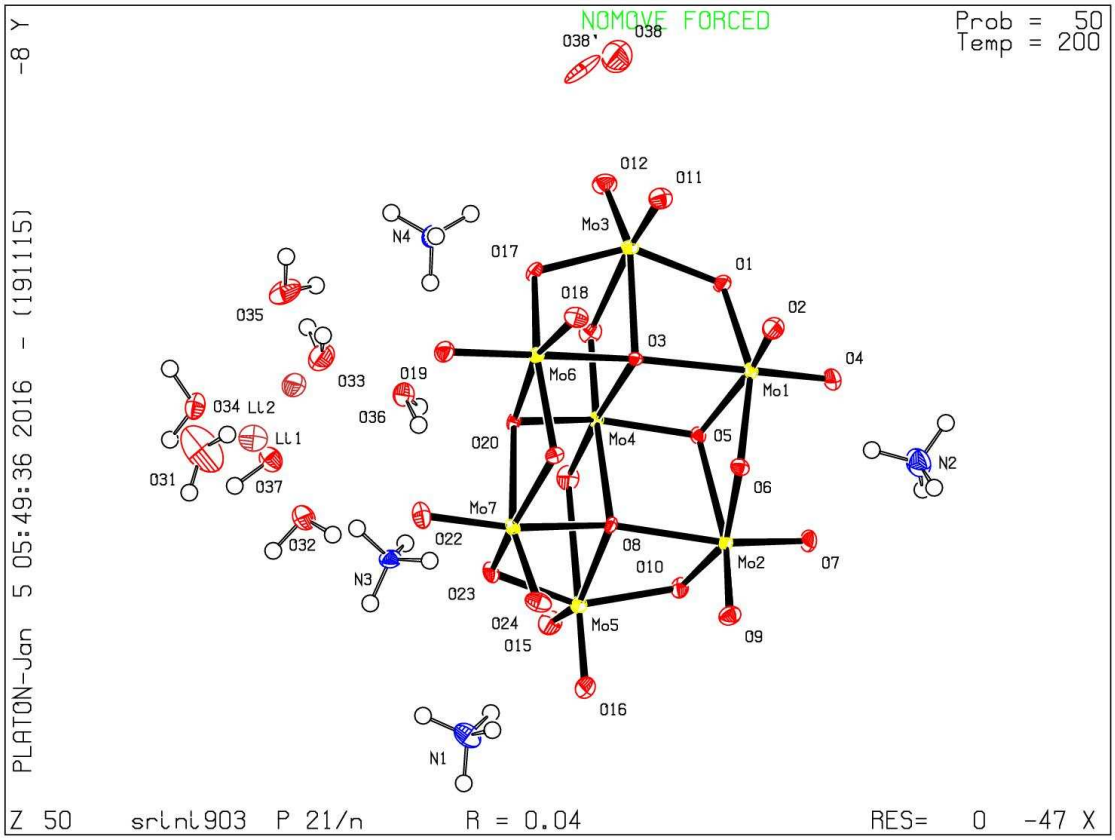
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock srini903 - ellipsoid plot



checkCIF/PLATON report of $(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$ **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

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                 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	
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Data completeness= 0.993 Theta(max)= 28.000

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S = 1.067 Npar= 229

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Click on the hyperlinks for more details of the test.

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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

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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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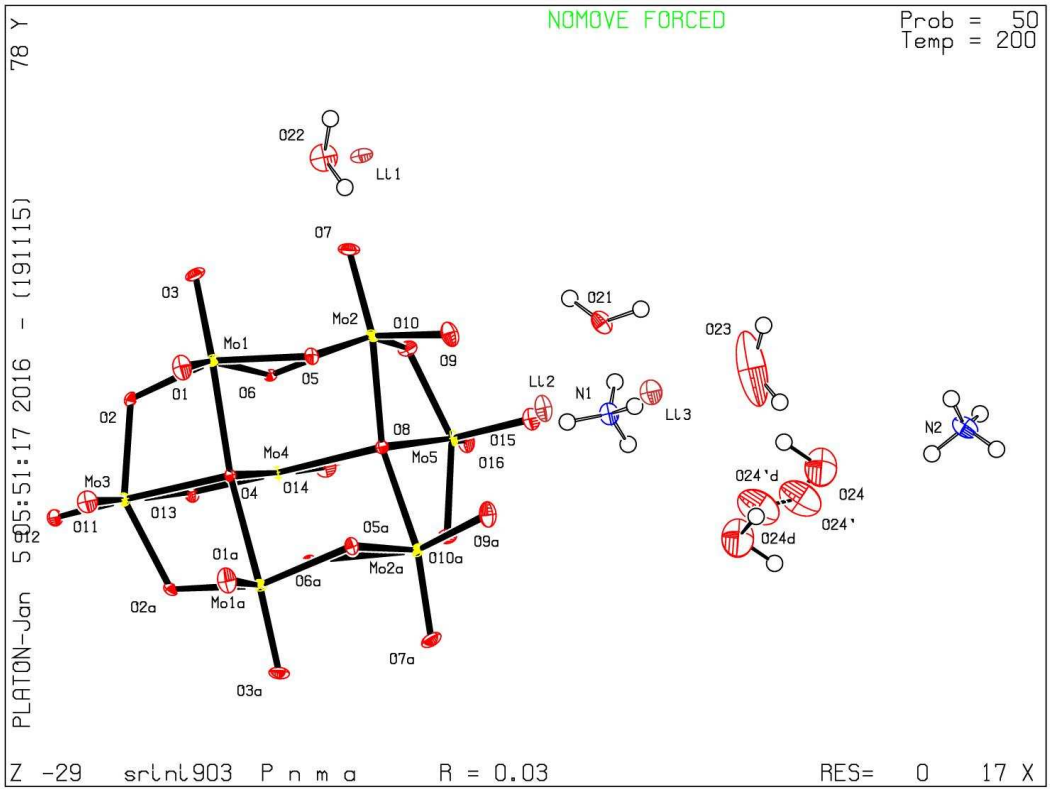
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock srini903 - ellipsoid plot



checkCIF/PLATON report

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

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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
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   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
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```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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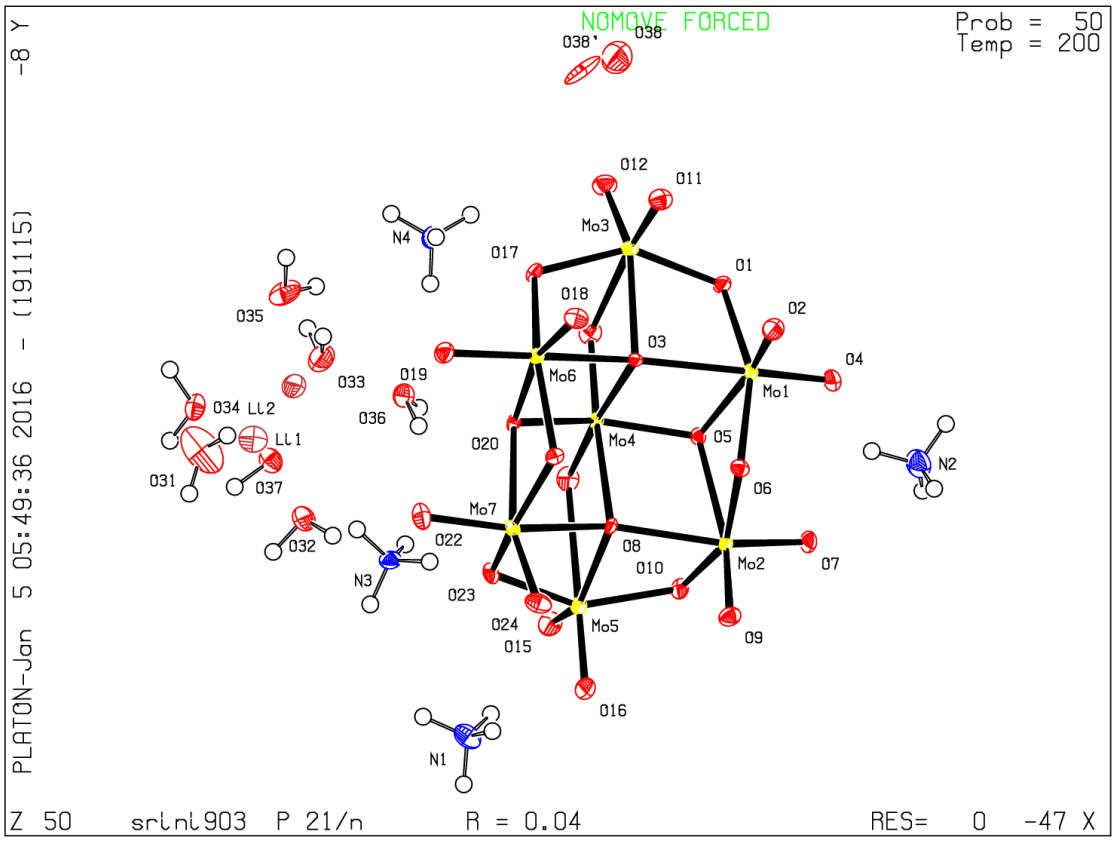
PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock srini903 - ellipsoid plot



checkCIF/PLATON report

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

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

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 >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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Datablock srini903 - ellipsoid plot