Notes

Synthesis, structure and properties of a hexarubidium heptamolybdate with bridging aqua ligands

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The synthesis, single crystal structure, spectral, thermal and electrical properties of a hexarubidium heptamolybdate $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1** is reported. The bridging binding modes of the unique $(Mo_7O_{24})^{6-}$ ion and the four crystallographically independent coordinated water molecules results in coordination numbers ranging from 8 to 10 for the six unique Rb(I) ions in **1**. Thermal decomposition of **1** results in the formation of an anhydrous residue of composition $7MoO_3 \cdot 3Rb_2O$. The cyclic voltammogram of an aqueous solution of **1** exhibits a single redox event characteristic of $(Mo_7O_{24})^{6-}$ anion. Solution conductivity studies reveal the presence of hydrated Rb^+ cations and uncoordinated $(Mo_7O_{24})^{6-}$ anions. A comparative study of several alkali-metal heptamolybdates reveals a rich structural chemistry in terms of the binding modes of the $(Mo_7O_{24})^{6-}$ anion.

Keywords: Coordination chemistry, Rubidium, Molybdenum, Hexarubidium hepta–molybdate, Bridging ligands

In a very early study Sturdivant[1] demonstrated the usefulness of single crystal X-ray method for compound characterization by determining the formula of commercial ammonium para–molybdate correctly as a heptamolybdate, viz., $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$, based on a measurement of unit cell constants and the experimental density. A single crystal structure determination by Lindqvist[2] in 1950 not only confirmed the Sturdivant formula but also showed that the heptamolybdate ion consists of seven edge sharing $\{MoO_6\}$ octahedra. Two decades later the structures of the heptamolybdates of sodium[3], potassium[4], etc., were determined. Presently more than fifty structurally characterized heptamolybdates are reported in the literature. Interestingly, the structures of many of these compounds were determined in the last two or three decades[5-31]. The structural characterization of several heptamolybdates

demonstrates the flexibility of $(Mo_7O_{24})^{6-}$ anion to exist in a variety of environments namely in combination with metal complex cations[3-9] or organic cations[10-18], or a mixture of organic and inorganic cations[19-31]. Although the main function of the heptamolybdate anion in all these compounds is a charge balancing counter ion, for example in the organic heptamolybdates, in some cases it can act as a O-donor ligand binding to a metal ion as in the case of a recently reported heptamolybdate of lithium[9].

During a literature survey we noted that in the case of the oxophilic alkali metals, structurally characterized heptamolybdates are reported for Li[9], Na[3,7], K[4] and Cs[5,6]. In the case of Rb, a brief mention of a rubidium paramolybdate was made by Evans *et al*.[4] in their structural analysis of ammonium and potassium heptamolybdates. However, no single crystal structure of a rubidium heptamolybdate has been reported till date. In the present study we report on the synthesis, crystal structure and properties of an all-inorganic heptamolybdate viz. $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1** and describe a comparative study of several alkali-metal heptamolybdates.

Experimental

All the chemicals used in this study were of reagent grade and were used as received from commercial sources without any further purification. Infrared (IR) spectra of the solid samples diluted with KBr were recorded on a Shimadzu (IR Prestige-21) FT-IR spectrometer from 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Raman spectra of compounds in solid state and in aqueous medium were recorded by using an Agiltron PeakSeeker Pro Raman instrument with 785 nm laser radiation for excitation and laser power set to 100 mW. The samples for solution Raman spectra were taken in a quartz cuvette. UV-vis spectra were recorded in water using a Shimadzu UV-2450 double beam spectrophotometer (200-800 nm) with matched quartz cells. Isothermal weight loss studies were performed in a temperature controlled electric furnace. TG-DTA study was performed in oxygen atmosphere in Al_2O_3 crucibles at a heating rate of 10 K min^{-1} using a STA-409 PC simultaneous thermal analyser from Netzsch. X-ray powder patterns

were recorded on a Rigaku Miniflex II powder diffractometer using Cu-Kα radiation with Ni filter. Conductivity measurements were performed at room temperature using Digital conductivity meter (LT-16) from Labtronics equipped with a standard conductometric cell composed of two platinum black electrodes. 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 property of an aqueous solution of **1** was studied using 0.1 M KNO_3 solution as supporting electrolyte at a scan rate of 0.03 V s^{-1} in the potential range of –0.3 to –0.7 V.

[$Rb_6(H_2O)_4(Mo_7O_{24})$] **1** was synthesised as follows: ammonium heptamolybdate (2.47 g, 2 mmol) was heated at 650 °C in a furnace for 2 h. The residue thus obtained was cooled to room temperature and transferred into a beaker containing rubidium carbonate (1.38 g, 6 mmol) in distilled water (50 mL). The resultant reaction mixture was stirred and heated on a water bath to get a clear solution. The reaction mixture was cooled and filtered. The colorless filtrate (pH ~5.5) was kept undisturbed for a few days to obtain 2.58 g of crystals of **1**.

IR (cm^{-1}): 3697-2600 (broad), 2124, 1648, 898, 841, 653, 581, 474; Raman (cm^{-1}): 936, 883, 222; UV- vis (nm): 209; Molar conductivity (λ_m) (0.02 M): 407 S cm^2 mol^{-1}.

For X-ray crystal structure determination, the intensity data for **1** was collected with an Image Plate Diffraction System (IPDS-2) from STOE. The structure was solved with direct methods using SHELXS-97[32] and refinement was done against F^2 using SHELXL-2014[32]. A numerical absorption correction was performed. All non-hydrogen atoms were refined anisotropically. The O-H hydrogen atoms were located in difference map, their bond lengths were set to ideal values and finally they were refined isotropic with $U_{iso}(H) = 1.5\ U_{eq}(O)$ using a riding model. Technical details of data acquisition and selected refinement results are listed in Table 1.

Results and discussion

The synthesis of **1** was performed in a two step reaction starting from the commercially available ammonium heptamolybdate tetrahydrate **2**. The synthetic methodology is very similar to the one recently employed for the synthesis of sodium heptamolybdate[33] and includes the following steps.

$(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ (**2**) $\longrightarrow$ 7 MoO_3 (Step 1)
7 MoO_3 + 3 Rb_2CO_3 $\longrightarrow$ **1** (Step 2)
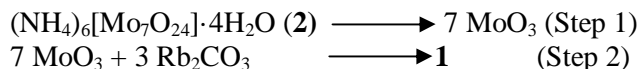
In the first step ammonium heptamolybdate tetrahydrate was pyrolysed to obtain MoO_3 free of ammonia. The freshly prepared MoO_3 was then reacted with an aqueous solution of Rb_2CO_3 maintaining a Mo:Rb ratio of 7:6 to obtain a clear solution whose pH (~5.5) is acidic (step 2). The usefulness of the above procedure can be evidenced by the preparation of $K_6(Mo_7O_{24}) \cdot 4\ H_2O$ using K_2CO_3 instead of Rb_2CO_3 in the second step.

The Raman spectrum of the acidic reaction mixture obtained at the end of step 2 exhibits an intense signal at 936 cm^{-1} characteristic of the presence of $[Mo_7O_{24}]^{6-}$ core in solution (Fig. 1). A slow evaporation of the aqueous reaction mixture results in the formation of crystalline product **1** in good yield, whose Raman spectrum with an intense signal is identical with the solution spectrum. The band at 936 cm^{-1} can be assigned for the symmetric stretching

Table 1 — Crystal data and structure refinement for [$Rb_6(H_2O)_4(Mo_7O_{24})$] **1**

|	
Empirical formula	$H_8Mo_7O_{28}Rb_6$
Formula weight	1640.46
Temperature	170(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 8.3486(17) Å
	b = 36.193(7) Å
	c = 10.133(2) Å
	β = 111.74(3)°
Volume	2844.1(11) Å^3
Z; Calculated density	4, 3.831 mg m^{-3}
Absorption coefficient	13.293 mm^{-1}
F(000)	2992
Crystal size	0.05×0.09×0.14 mm^3
θ range for data collection	1.125 to 25.186°
Limiting indices	-9$\leq$h$\leq$9, -41$\leq$k$\leq$43, -12$\leq$l$\leq$12
Reflections collected/ unique	31057 / 5102 [R(int) = 0.0531]
Observed reflections	2944
Completeness θ = 25.242°	99.3%
Absorption correction	Numerical
Refinement method	Full-matrix least-squares on F^2
Data /restraints /parameters	5102 / 0 / 371
Goodness of fit on F^2	1.109
Final R indices [I>2σ(I)]	R1 = 0.0303, wR2 = 0.0770
R indices (all data)	R1 = 0.0322, wR2 = 0.0780
Extinction coefficient	0.00124 (7)
Largest diff. peak and hole	0.783 and -0.774 e.Å^{-3}
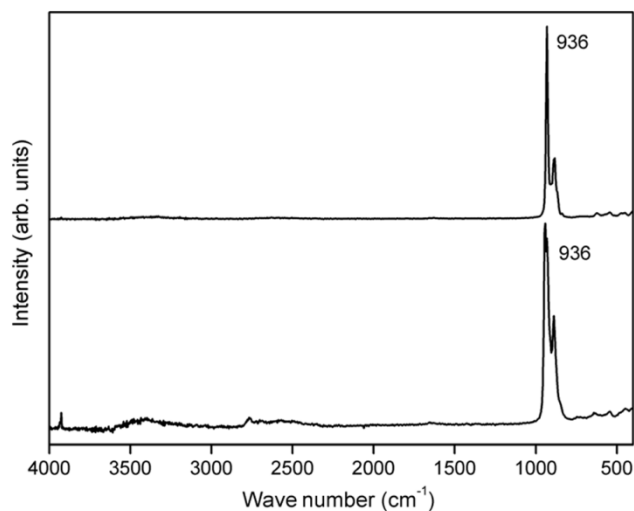
Fig. 1 — Raman spectra of crystalline [Rb$_6$(H$_2$O)$_4$(Mo$_7$O$_{24}$)] **1** (top), and, aqueous reaction mixture (bottom).

Fig. 2 — IR spectra of [Rb$_6$(H$_2$O)$_4$(Mo$_7$O$_{24}$)] **1** (top) and (NH$_4$)$_6$[Mo$_7$O$_{24}$]·4H$_2$O (**2**) bottom.

vibration of the {MoO$_6$} unit. It is interesting to note that the Raman spectrum of **1** is nearly identical with the Raman spectra of the ammonium and K$^+$ analogs (Supplementary data, Fig. S1).

The optical spectrum of **1** with an intense absorption centered at around 209 nm (Supplementary data, Fig. S2) is identical with the spectra of the ammonium, sodium and potassium analogs and is thus indicative of the presence of a heptamolybdate core. A comparison of the IR spectra of **1** with that of the ammonium salt **2** reveals a noticeable difference especially the absence of a strong signal at ~1407 cm^{-1} assignable for the bending vibration (δ_{N-H}) of the ammonium ion of **2** (Fig. 2). In addition, the profiles of the IR spectra in the high energy region (3500-2500 cm^{-1}) are very different. Due to the absence of –NH vibrations in **1** the strong band centered at ~3375 cm^{-1} can be assigned for the stretching vibration (υ_{OH}) of the water molecule. Interestingly, in the lower energy region below 1000 cm^{-1} both compounds **1** or **2** exhibit nearly similar features. The doubly degenerate asymmetric stretching mode the MoO$_6$ unit occurs as an intense signal at 898 and 899 cm^{-1} respectively in **1** and **2** in the IR spectrum and as a weak band in Raman spectrum (Supplementary data, Fig. S3). A photochemical study of **1** was performed by exposing the pure solid or its aqueous solution to visible light emitted from a tungsten filament bulb (60 W) of a table lamp or solar radiation. Unlike organic heptamolybdates, which are transformed to bis (μ_2-oxo) diheptamolybdates on irradiation[17,18] no photochemically induced changes were observed.

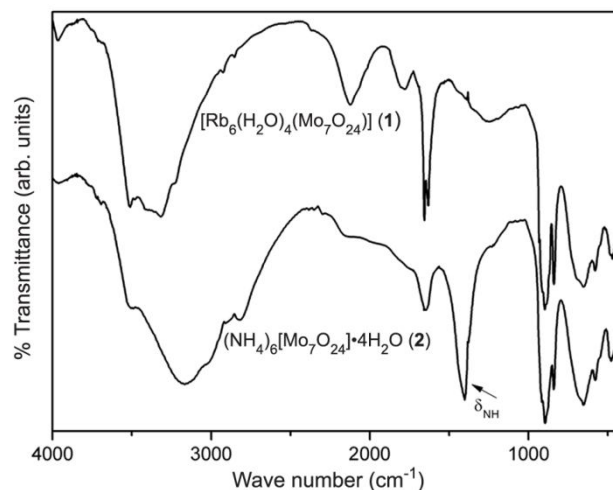Thermal analysis of **1** does not show any mass loss till ~100 °C. In the TG curve a decrease in mass of 4.60% accompanied by an endothermic event at 160 °C in DTA curve is observed (Supplementary data, Fig. S4). This can be attributed to the loss of four water molecules which is in close agreement with calculated mass loss of 4.39%. This is further supported by IR spectroscopic investigations of the residue formed in the first TG step, which does not show any signals for the O-H vibration. The endothermic signal at 486 °C can be attributed to the decomposition of the anhydrate formed as intermediate yielding a mixed oxide residue. The results obtained are in accordance with the pyrolysis experiment of **1** carried out at 600 °C in a furnace with an observed mass loss of 4.25%, which is in very good agreement with the calculated mass loss of 4.39% for a probable residual composition 7MoO$_3$·3Rb$_2$O.

The all-inorganic hexarubidium heptamolybdate compound **1** crystallizes in the centrosymmetric monoclinic space group *P2$_1$/n* and is isostructural with the previously reported K$^+$ and the NH$_4^+$ analogues[4]. The phase purity of **1** was confirmed by a comparison of the calculated powder pattern from the single crystal data with the experimental pattern (Supplementary data, Fig. S5). An increase in cell volume of **1** (2844.1 Å^3) in comparison with the cell of K$^+$ (2710.02 Å^3) is in accordance with the larger size of Rb$^+$ ion. The structure of **1** consists of six unique Rb$^+$ cations (Supplementary data, Fig. S6), four independent water molecules and a crystallographically unique (Mo$_7$O$_{24}$)$^{6-}$ anion (Fig. 3)

with all atoms situated in general positions. The unique $(Mo_7O_{24})^{6-}$ anion is built up of seven edge sharing $\{MoO_6\}$ octahedra, and is very similar to the heptamolybdate anion first reported for the ammonium salt by Lindqvist[2]. The Mo-O bond lengths and the O-Mo-O bond angles of the unique $[Mo_7O_{24}]^{6-}$ anion (Supplementary data, Table S1) agree well with reported data.
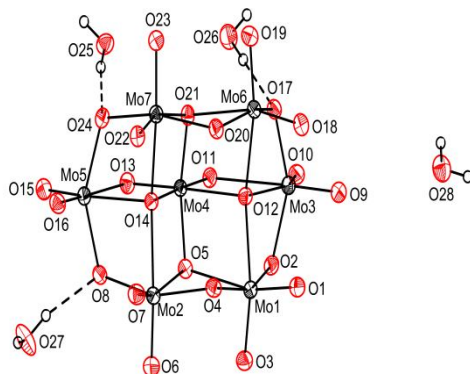

Fig. 3 — The atom-labelling scheme for the unique $[Mo_7O_{24}]^{6-}$ ion and the crystallographically independent water molecules (O25–O28) in $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1**. [Displacement ellipsoids are drawn at 30% probability level excepting for H atoms which are shown as spheres of arbitrary radii. Intramolecular H-bonding is shown by dotted lines. For clarity, the unique Rb^+ ions in the crystal structure of **1** are not shown].

A recent study of bond-length distributions of alkali and alkaline-earth metal ions bonded to oxygen reveals that these ions can adopt a range of coordination numbers[34]. Coordination numbers from 4 to 18 with maximum Rb-O distances up to 3.945 Å (coordination number 15) have been reported for Rb^+ by Gagne and Hawthorne[34] based on a statistical analysis of 4675 Rb-O bonds. The title Rb compound is a good example demonstrating the structural flexibility of Rb(I) cations. A total number of fifty four Rb-O bond distances ranging from 2.764(4) to 3.546(4) Å (Table 2) are observed in the crystal structure of **1** resulting in coordination numbers ranging from 8 to 10 for the six unique Rb(I) ions (Fig. 4). In addition, the O-Rb-O bond angles in **1** scatter in a very wide range (Supplementary data, Table S2) indicating that the coordination polyhedra around Rb are irregular. For example in the case of Rb1 which exhibits a coordination number of 10, the bond lengths vary from 2.787(5) to 3.522(4) Å accompanied by O-Rb-O angles between 46.69(10) and 177.80(10). The Rb1 is bonded to nine O atoms from three symmetry related heptamolybdates and one O (O27) of water. The mean Rb-O distance for Rb1 is 3.0804 which is in agreement with Gagne and Hawthorne's study reporting a mean Rb-O distance of

Table 2 — Selected bond lengths (Å) for $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1**

Rb1-O27[ii]	2.787(5)	Rb2-O26[i]	3.452(5)	Rb4-O2[iv]	3.212(4)
Rb1-O1[ix]	2.796(4)	Rb3-O20[ix]	2.764(4)	Rb5-O19	2.860(4)
Rb1-O11	2.824(4)	Rb3-O4[ix]	2.776(4)	Rb5-O25	2.944(4)
Rb1-O22[xii]	2.870(4)	Rb3-O25	2.824(5)	Rb5-O23	2.963(4)
Rb1-O16[xii]	3.023(4)	Rb3-O26	2.857(5)	Rb5-O26	2.996(5)
Rb1-O10	3.043(4)	Rb3-O11	3.008(4)	Rb5-O28[iii]	3.036(5)
Rb1-O24[xii]	3.150(4)	Rb3-O13	3.066(4)	Rb5-O28[xi]	3.145(5)
Rb1-O2	3.315(4)	Rb3-O7[ix]	3.196(4)	Rb5-O9[iii]	3.152(4)
Rb1-O4[ix]	3.474(4)	Rb3-O22[ix]	3.228(4)	Rb5-O9[xi]	3.203(4)
Rb1-O3[ix]	3.522(4)	Rb3-O14[ix]	3.546(4)	Rb5-O21	3.212(4)
Rb2-O1	2.804(4)	Rb4-O6	2.886(4)	Rb6-O7[ix]	2.901(4)
Rb2-O10[i]	2.901(4)	Rb4-O7[ii]	2.961(5)	Rb6-O15	2.905(4)
Rb2-O18	2.922(4)	Rb4-O15[vii]	2.993(4)	Rb6-O15[ii]	2.960(4)
Rb2-O19[vi]	2.931(4)	Rb4-O3[iv]	3.005(4)	Rb6-O16[ii]	2.992(4)
Rb2-O23[viii]	2.989(4)	Rb4-O27	3.054(6)	Rb6-O3[x]	3.099(4)
Rb2-O28	3.072(5)	Rb4-O22[ii]	3.058(4)	Rb6-O13	3.130(4)
Rb2-O9	3.214(4)	Rb4-O16[ii]	3.065(4)	Rb6-O6[x]	3.193(5)
Rb2-O18[vi]	3.394(4)	Rb4-O25[vii]	3.112(4)	Rb6-O8	3.430(4)
Rb1-O (Mean)	3.0804	Rb3-O (Mean)	3.029	Rb5-O (Mean)	3.057
Rb2-O (Mean)	3.075	Rb4-O (Mean)	3.038	Rb2-O (Mean)	3.076

Symmetry transformations used to generate equivalent atoms:

i) $x+1$, y, z; ii) $x-1/2$, $-y+1/2$, $z-1/2$; iii) $-x+1$, $-y+1$, $-z+1$; iv) $x+1/2$, $-y+1/2$, $z+1/2$; v) $x+1$, y, $z+1$; vi) $-x+2$, $-y+1$, $-z+1$; vii) $x+1/2$, $-y+1/2$, $z-1/2$; viii) x, y, $z-1$; ix) $x-1$, y, z; x) $x-1/2$, $-y+1/2$, $z+1/2$; xi) x, y, $z+1$; xii) $x-1$, y, $z-1$; xiii) $-x+1$, $-y+1$, $-z+2$
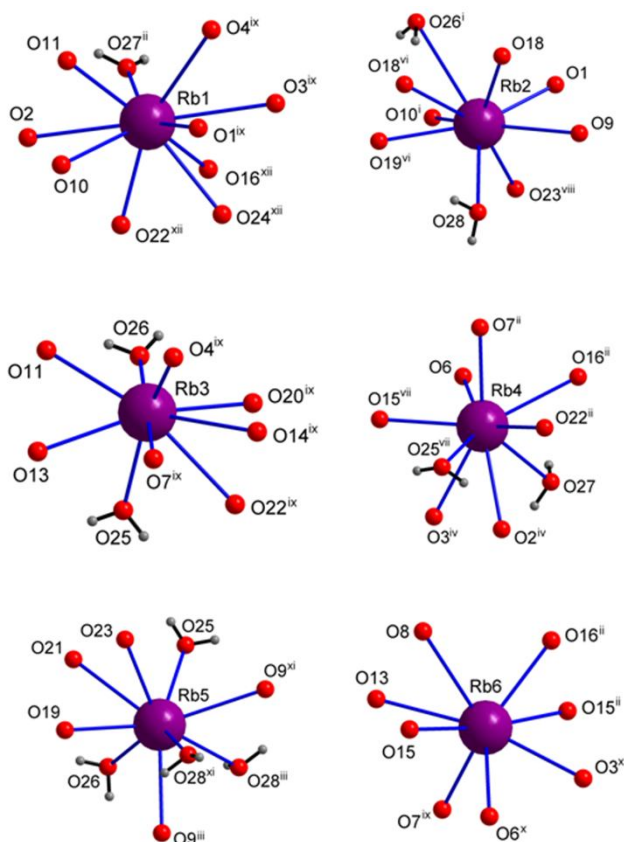
Fig. 4 — The coordination environment around the unique Rb^+ ions in $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1**. [For clarity only the O atom of the heptamolybdate and not the entire heptamolybdate is shown. For symmetry relations see Table 2].

Fig. 5 — The $(Mo_7O_{24})^{6-}$ ligand in $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1** is bonded to 20 symmetry related Rb(I) ions with the aid of forty three Rb-O bonds (in blue). [For symmetry relations see Table 2].

3.146 Å for a deca coordinated Rb. Similarly the mean Rb-O distances of the other unique Rb^+ ions viz. 3.075, 3.029, 3.038 and 3.057 Å respectively for Rb2, Rb3, Rb4 and Rb5 all of which exhibit a coordination number of nine are in agreement with literature report[34]. It is interesting to note that the eight coordinated Rb6 is not bonded to any of the coordinated water molecules but only to eight O atoms from four symmetry related heptamolybdate anions.

Of the fifty four Rb-O bond distances in **1**, eleven bonds ranging from 2.787(5) to 3.452(5) Å are contributed by the coordinated water molecules (O25 to O28) three of which namely O25, O26 and O28 function as μ_3-bridging tridentate ligands (Supplementary data, Fig. S7). O27 links Rb1 and Rb4 via a μ_2-bridging bidentate mode. The unique $(Mo_7O_{24})^{6-}$ anion makes a total of forty three Rb-O bonds and is bonded to twenty symmetry related Rb^+ ions (Fig. 5). In the isostructural K^+ compound the situation is identical as in **1** with coordination numbers ranging from 8 to 10 for the unique K^+ ions
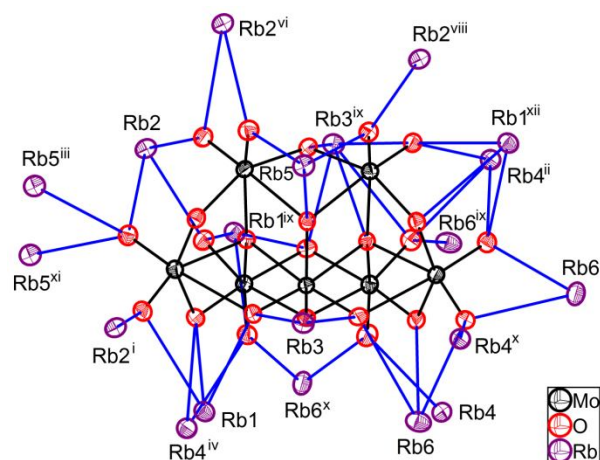
resulting in a total of fifty four K-O bonds of which forty three are due to the μ_{20}-bridging binding mode of the unique $(Mo_7O_{24})^{6-}$ anion. An analysis of the crystal structures of both compounds reveals that the forty three M-O (M= K or Rb) bonds are contributed by a combination of all the twelve terminal O atoms, seven μ_2-bridging bidentate O atoms and one each of a μ_3-bridging tridentate and a μ_4-bridging O atom of the unique heptamolybdate ligand (Supplementary data, Table S3). The interaction between the different types of oxide (O^{2-}) anions of the heptamolybdate ligand with the surrounding Rb^+ cations is highlighted in Fig. 5. As can be seen from this drawing, of the twenty four oxido (O^{2-}) anions of the heptamolybdate only twenty one have links to Rb^+ and also several have bonds to more than one Rb^+. In addition, the shape and size of the heptamolybdate ligand is reflected by the binding modes of the different O^{2-} ions. For example, the unique Rb2 sits on top of a triangle formed by three O^{2-} anions while $Rb6^x$ fits into a niche formed by two O^{2-} ions.

An analysis of the crystal structure of **1** reveals that all four coordinated water molecules (O25, O26, O27 and O28) act as H-donors and are involved in a total of eight O-H···O hydrogen bonding interactions, three of which are intramolecular (Table 3, Supplementary data, Fig. S8). The O atoms of the heptamolybdate act as H-bonding acceptors. The net result of O-H···O bonding interactions is that the water molecules (O25, O26, O27 and O28) serve as links between the Rb(I) ions and the heptamolybdate anions.

A comparative study of the structural features of ammonium (Table 4, entry 1) and several

Table 3 — Hydrogen bonding geometry of $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1**

D-H	d(D-H) (Å)	d(H⋯A) (Å)	<DHA (°)	d(D⋯A) (Å)	A	Symmetry code
O25-H1O	0.84	1.92	169.1	2.749(6)	O24	x, y, z
O25-H2O	0.84	2.03	164.8	2.851(6)	O2	$x, y, z+1$
O26-H3O	0.84	2.06	172.9	2.897(6)	O18	$-x+1, -y+1, -z+1$
O26-H4O	0.84	1.95	174.2	2.786(6)	O17	x, y, z
O27-H5O	0.84	2.04	149.7	2.793(6)	O5	$x+1/2, -y+1/2, z+1/2$
O27-H6O	0.84	1.95	165.2	2.769(6)	O8	x, y, z
O28-H7O	0.84	2.13	172.0	2.965(6)	O20	$-x+2, -y+1, -z+1$
O28-H8O	0.84	2.27	178.4	3.106(7)	O10	$-x+1, -y+1, -z$

Table 4 — Structural characteristics of alkali metal heptamolybdates

No.	Compound[a]	Space group	Coordinated: lattice water	Alkali metal coord no.[b]	$(Mo_7O_{24})^{6-}$ binding mode[c]	Ref.
1	$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$	$P2_1/c$	0:4	---------	Counterion	4
2	$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$	$P2_1/n$	7:1	4, 4	Counterion	9
3	$Na(NH_4)[C_{13}N_2H_{16}]_2[Mo_7O_{24}]\cdot 8H_2O$	$P2_1/m$	3:5	6	(η^3) (3)	27
4	$(CH_6N_3)_7Na[CoMo_7O_{24}(H_2O)_5]_2\cdot 8H_2O$	$P2_1/c$	10:8	6	$\mu_2 (4)^d$	26
5	$(C_6H_{14}N_4)_{1.5}(C_7H_{17}N_5)_{0.5}[Na_2(H_2O)_5Mo_7O_{24}]\cdot 4H_2O$	$Pnma$	5:4	6, 6	$\mu_2 (5)$	24
6	$[Na_2(OH_2)_5][C_6H_{12}N_4H_2]_2[Mo_7O_{24}]\cdot 4H_2O$	$Pnma$	5:4	6, 6	$\mu_2 (5)$	21
7	$(NH_4)_{16}(C_4H_{12}NO)_4[NaMo_7O_{24}]_4\cdot 4H_2O^e$	$Pmmn$	0:4	6,	$\mu_2 (6)$	20
8	$(NH_4)[Cu(en)_2][Na(en)Cu(en)_2(H_2O)(Mo_7O_{24})]\cdot 4H_2O$	$P\bar{1}$	1:4	4	$\mu_3 (3)^f$	22
9	$Na_7[Mo_7O_{24}]OH\cdot 21H_2O^g$	$P2/n$	18:3	6, 6, 6, 6,	$\mu_4 (4)$	7
10	$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})]\cdot 2H_2O$	$Pnma$	4:2	3, 4, 5	$\mu_6 (6)$	9
11	$Na_6(Mo_7O_{24})\cdot 14H_2O$	$Pca2_1$	13:1	6, 6, 6, 6, 6, 6	$\mu_{11} (15)$	3
12	$Cs_6[Mo_7O_{24}]\cdot 7H_2O$	$P\bar{1}$	7:0	9, 10, 11, 11, 11, 11	$\mu_{18} (43)$	5
13	$K_6[Mo_7O_{24}]\cdot 4H_2O$	$P2_1/c$	4:0	8, 9, 9, 9, 9, 10	$\mu_{20} (43)$	4
14	$[Rb_6(H_2O)_4(Mo_7O_{24})]$	$P2_1/n$	4:0	8, 9, 9, 9, 9, 10	$\mu_{20} (43)$	This work

[a]$[C_{13}N_2H_{16}]$ = 1,3-bis(4-pyridinium)propane, $(C_4H_{12}NO)_4$ = dimethyl(2-hydroxyethyl)ammonium, en = ethylenediammine, CH_6N_3 = guanidinium, $(C_6H_{12}N_4)$ = hexamethylenetetramine, $(C_7H_{16}N_5)$ = N-(aminomethylene) hexamethylenetetramine.
[b]Coordination number of all unique alkali-metals; [c]Values in bracket are the number of alkali metal-O bonds; [d]coord no. of Co is 6; [e]Unique Na and independent $(Mo_7O_{24})^{6-}$; [f]coord no. of Cu is 5,6,6; [g]four unique Na.

alkali-metal heptamolybdates, which includes pure-inorganic heptamolybdates (entry 2, 9-14) and mixed cationic heptamolybdates containing organic counter cations (entry 3-8) is described below. All compounds excepting $Na_6(Mo_7O_{24})\cdot 14H_2O^3$ crystallize in centrosymmetric space groups. In the hetero-bimetallic heptamolybdate $(NH_4)[Cu(en)_2]$ $[Na(en)Cu(en)_2(H_2O)(Mo_7O_{24})]\cdot 4H_2O$ (Supplementary data, Fig. S9), where the unique Na is bonded to two N atoms of ethylenediamine in addition to two O atoms one of which is from a $(Mo_7O_{24})^{6-}$. In all other compounds, the alkali metal is bonded to O atoms of water and heptamolybdate. The structural flexibility of the alkali-metals to exhibit variable coordination number as well as their oxophilic nature to bind to O-donor ligands viz. H_2O or heptamolybdate can

be evidenced in Table 4. The coordination number of Li varies from 3 to 5, while that of Na in many compounds is 6. A coordination number of 4 is reported for Na in the mixed bimetallic heptamolybdate (entry 8). The heavier congeners K and Rb exhibit higher coordination numbers viz. 8-10, while a very high coordination number of 11 is observed for Cs.

In all compounds listed in Table 4, the heptamolybdate ion functions as a charge balancing anion. In addition, it acts as an O-donor ligand in all compounds excepting $(NH_4)_4[Li_2(H_2O)_7]$ $[Mo_7O_{24}]\cdot H_2O$ and $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$. In the mixed cationic heptamolybdate $Na(NH_4)$ $[C_{13}N_2H_{16}]_2[Mo_7O_{24})]\cdot 8H_2O$ the unique $(Mo_7O_{24})^{6-}$ ion acts as a tridentate (η^3) ligand and forms three Na-O

bonds via three terminal O atoms of heptamolybdate and three terminal water molecules complete the octahedron around Na. In all other compounds (entry 4-14) the unique heptamolybdate ion is linked to more than one metal and thus functions as a bridging (μ-) ligand. This bridging can be to two different metals, for example Na(I) and Co(II) in $(CH_6N_3)_7Na[CoMo_7O_{24}(H_2O)_5]_2 \cdot 8H_2O$ (Supplementary data, Fig. S9) or three different metals, one Na and two Cu(II), in $(NH_4)[Cu(en)_2][Na(en)-(en)_2(H_2O)(Mo_7O_{24})] \cdot 4H_2O$ (Supplementary data, Fig. S9) or many metals for example the six unique Rb(I) ions in the title compound. Thus, a variety of bridging binding modes, viz., μ_2- (entry 4-7), μ_3- (entry 8), μ_4- (entry 9) μ_6- (entry 10), μ_{11}- (entry 11), μ_{18}- (entry 12) μ_{20}- (entry 13, 14) are observed in these compounds.

The number of alkali-metal (M') to oxygen bonds contributed by the $(Mo_7O_{24})^{6-}$ ligand varies from three to forty three (entry 3-14). In addition to the (M'-O) bonds provided by the heptamolybdate ligand, the water molecules also are bonded to the alkali-metal making M'-O contacts. Although the heptamolybdates of K^+ and Cs^+ are referred to by the formulae $K_6[Mo_7O_{24}] \cdot 4H_2O$, $Cs_6[Mo_7O_{24}] \cdot 7H_2O$, etc., in the literature, it is to be noted that not all the water molecules in these compounds are lattice water molecules. An analysis of the nature of water molecules reveals that excepting the last three entries (entry 12-14), all the other heptamolybdates contain at least one lattice water. The presence as well as the number of coordinated water molecules and their mode of binding, can also influence the number of (M'-O) bonds of the $(Mo_7O_{24})^{6-}$ ligand. The very high number of 43 connectivities to Cs, Rb, or K (entry12-14) from

the $(Mo_7O_{24})^{6-}$ ligand can be explained due to the presence of fewer number of coordinated water molecules in these all-inorganic heptamolybdates (entry 12-14) having six oxophilic alkali-metals which exhibit higher coordination number. It is interesting to note that in $Cs_6[Mo_7O_{24}] \cdot 7H_2O$, the seven aqua ligands contribute a total of twenty Cs-O bonds in addition to the 43 Cs-O bonds made by $(Mo_7O_{24})^{6-}$ ligand. Like in the title compound all the water molecules exhibit only bridging binding modes in $Cs_6[Mo_7O_{24}] \cdot 7H_2O$.

The cyclic voltammograms of the title compound **1** is nearly identical with that of the ammonium salt **2**, both of which exhibit a single cathodic response below -1.0 V (Fig. 6) with $E_{1/2}$ values -0.531 and -0.538 V measured versus SCE respectively. The electrochemical event in **1** can be attributed to a reduction of the anionic heptamolybdate, which is formed due to hydrolysis of **1**, in addition to the hydrated Rb^+ ions. In recent works[9,33] we have shown that hydrolysis is a favored process occuring in alkali metal heptamolybdates. No other electrode process is observed at higher negative potentials for **1**, indicating that the hydrated Rb^+ cations do not undergo any further electrochemical change.

The presence of uncoordinated heptamolybdate ions in solution accompanied by hydrated Rb^+ ions can also be evidenced from the conductivity measurements. A comparison of the molar conductivity of 0.02 *M* solution of **1** with other alkali-metal heptamolybdates shows a steady decrease (Table 5) of conductivity value starting from lithium to rubidium. This behavior can be attributed to the increased size of the Rb^+ cation. It is interesting to note that replacement of two or three ammonium ions of $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ by smaller Li^+ ions leads to a pronounced increase in conductivity (Entry nos 1 & 2 in Table 5) while substitution of all ammonium by Na^+, K^+ or Rb^+ results in conductivity values which fall in a smaller range and the values exhibit a trend. The least conductivity of 407 S cm^2 mol^{-1} is observed for the larger cationic Rb^+ containing compound **1**.
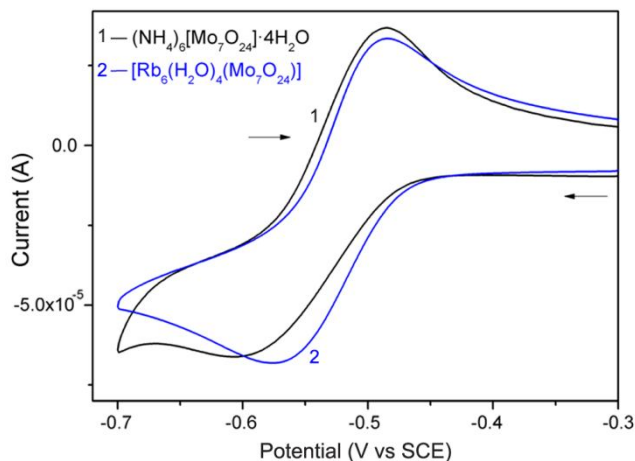

Fig. 6 — Cyclic voltammograms of $[Rb_6(H_2O)_4(Mo_7O_{24})]$ **1** and $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ **2**.

Table 5 — Molar conductivity (λ_m) data of some alkali metal heptamolybdates (0.02 *M*)

No.	Compound	λ_m (S cm^2 mol^{-1})
1	$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}] \cdot H_2O$	1119
2	$(NH_4)_3[Li_3(H_2O)_4(\mu_6\text{-}Mo_7O_{24})] \cdot 2H_2O$	953
3	$[Na_6(H_2O)_{13}(Mo_7O_{24})] \cdot H_2O$	560
4	$(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$	525
5	$[K_6(Mo_7O_{24})(H_2O)_4]$	458
6	$[Rb_6(Mo_7O_{24})(H_2O)_4]$	407

The title compound can function as a precursor for mixed metal oxide. MoO_3 is a widely used heterogeneous catalyst and only one of the two polymorphs exhibits catalytic activity[35,36]. In most cases MoO_3 is deposited on an inert substrate. Hence, impregnation of a substrate with a solution of the title compound followed by thermal decomposition may lead to formation of nanosized Rb-containing MoO_3 particles which can be then investigated in catalytic partial oxidation reactions. The promoting effect of alkali metal cations on the catalytic performance of heterogeneous catalysts is well documented in the literature, with the Haber-Bosch catalyst being the most prominent example.

In the present study, we have described a convenient synthesis of a hexarubidium hepta–molybdate (**1**) with bridging aqua ligands using the commercially available $(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O$ (**2**). This work demonstrates the usefulness of solution Raman spectra for the characterization of heptamolybdate product in the reaction medium. The thermal study reveals that **1** is an useful precursor for the preparation of Rb-containing MoO_3 particles. From the crystal structure determination it can be inferred that the title heptamolybdate is a unique example showing the structural flexibility of Rb(I) to exist in variable coordination numbers ranging from 8–10 as well as the ability of heptamolybdate to function as a multidentate O-donor ligand. The comparative study of several alkali-metal heptamolybdates reveals the rich coordination chemistry of the $(Mo_7O_{24})^{6-}$ ligand.

Supplementary data

Crystallographic data for the structure reported in this article have been deposited with FIZ-Karlsruhe as supplementary publication no. CSD 432485 (**1**) 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. Other supplementary data associated with this article, viz., Figs S1-S9 and Table S1-S3 as well as the Check CIF report for **1**, are available in electronic form in the online version at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(06)601-609_SupplData.pdf.

Acknowledgment

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