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Sodium paramolybdate revisited

Bikshandarkoil R Srinivasan* & Sudesh M Morajkar
Department of Chemistry, Goa University, Goa 403206, India
Email: srini@unigoa.ac.in

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The term paramolybdate refers to the species of formula $[\text{Mo}_7\text{O}_{24}]^{6-}$. A convenient method for the rational synthesis of a sodium paramolybdate namely hexasodium heptamolybdate(VI) 14-hydrate $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ and its spectral and thermal characterization are reported. Cyclic voltammetric and conductivity studies of an aqueous solution of $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ reveal the presence of hydrated Na^+ ions and heptamolybdate anions in solution unlike a sodium coordinated heptamolybdate in the solid state.

Keywords: Paramolybdate, Sodium, Hexasodium heptamolybdate 14-hydrate, Cyclic voltammetry

The ammonium and sodium salts of molybdic acid have been the subject of several investigations in older literature¹⁻⁴ which were performed to determine the compound composition in terms of ammonium (or sodium):molybdenum:water content. In a very early study Zenker² proposed a Na:Mo ratio of 4:9 for a sodium compound of molybdic acid. Although the correct ratio of 6:7 for X:Mo (X = Na or NH_4) was identified in 1865 by Delafontaine³, Rosenheim⁴ proposed a composition of 5:6 for X:Mo (X = Na or NH_4) in 1917. Based on a measurement of the lattice constants, the correct composition as well as the formula $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (**1**) was determined by Sturdivant⁵ for ammonium paramolybdate. This formula was later unambiguously confirmed by Lindqvist^{6,7} with the aid of a chemical analysis⁶ and single crystal structure determination⁷ showing that the $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion is made up of edge sharing MoO_6 octahedra. A single crystal X-ray study of potassium paramolybdate by Gatehouse and Everett⁸ showed $\text{K}_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ to be isostructural with (**1**), demonstrating the importance of the Lindqvist structure type viz. edge sharing MoO_6 octahedra in Mo chemistry.

The term 'paramolybdate' refers to the species of formula $[\text{Mo}_7\text{O}_{24}]^{6-}$ and was more in use in older literature. The $[\text{Mo}_7\text{O}_{24}]^{6-}$ unit is known as heptamolybdate, a

terminology which is currently used instead of the traditional name, paramolybdate. Interestingly, ammonium heptamolybdate tetrahydrate (**1**) is also referred to as ammonium molybdate tetrahydrate⁹ and is marketed under this name by several chemical companies¹⁰. In contrast, the term sodium molybdate dihydrate does not refer to any heptamolybdate of sodium but to a monomeric Mo compound viz. $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ which is also commercially available. Based on a chemical analysis of sodium paramolybdate, Lindqvist⁶ proposed the formula $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 22\text{H}_2\text{O}$ showing that it is a water rich compound unlike ammonium paramolybdate which is a tetrahydrate. However, a single crystal X-ray study of sodium paramolybdate by Sjobom and Hedman¹¹ in 1973 proved its formula to be $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (**2**) with the structure containing a Lindqvist type $[\text{Mo}_7\text{O}_{24}]^{6-}$ unit and coordination to Na. In addition, a monoclinic unit cell for another crystalline phase of sodium paramolybdate $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot \text{XH}_2\text{O}$ (X=21-23) was also reported in this work. Although papers describing structures of sodium rich¹² and sodium deficient¹³ heptamolybdates, and heptamolybdates charge balanced by a combination of sodium organic cations¹⁴⁻¹⁶ (Supplementary data, Table S1) have appeared in the literature, no report is available on a sodium paramolybdate with $\sim 22\text{H}_2\text{O}$ other than the works of Delafontaine⁴ and Lindqvist⁶ and the unit cell data¹⁰ reported in 1973. A redetermination of the structure of hexasodium heptamolybdate(VI) 14-hydrate $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (**2**) by Hao *et al.*¹⁷ not only reports the location of the H atoms of the water molecules but also confirms the original findings of Sjobom and Hedman¹¹. For the structure redetermination, Hao *et al.*¹⁷ synthesized $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ by a hydrothermal method which involves heating at 160 °C for three days a mixture of 2,4'-biphenyldicarboxylic acid, 2-pyridylpyrazole, $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$, and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in water. Interestingly, the product of the hydrothermal reaction does not contain any carboxylic acid or pyrazole or copper but is a sodium paramolybdate tetradecahydrate. In view of our interest in the chemistry of alkali metal heptamolybdates¹⁸ and a very unusual methodology requiring many reagents, some of which are costly, for synthesis of a

sodium heptamolybdate, we have undertaken this study in search of a rational synthetic procedure for the facile synthesis of hexasodium heptamolybdate(VI) 14-hydrate (**2**). The details of this investigation are described in this report.

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 were recorded using an Agiltron PeakSeeker Pro Raman instrument in the range 4000–400 cm^{-1} by employing a 785 nm laser radiation for excitation. UV-visible spectra were recorded in water using a Shimadzu UV-2450 double beam spectrophotometer 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 $\text{Cu-K}\alpha$ radiation with Ni filter. Conductivity measurements were carried out at room temperature 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 the working electrode, platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference. The redox properties of aqueous solutions of ammonium and sodium paramolybdates (**1** and **2**) were studied using 0.2 *M* KCl solution as the supporting electrolyte at a scan rate of 0.03 Vs^{-1} .

For the synthesis of (**1**), commercial molybdic acid ($\text{H}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$) was dissolved in excess ammonia and the clear ammoniacal solution was left for complete evaporation at room temperature to obtain ammonium paramolybdate tetrahydrate (**1**) in near quantitative yield. An alternate procedure based on Sturdivant's method⁵ which involves the use of cooling of a saturated solution of commercial ammonium molybdate tetrahydrate (Thomas Baker) in liquor ammonia, also afforded ammonium paramolybdate.

IR data: 3683-2500 (br), 1648, 1407 ($\delta_{\text{N-H}}$), 899 (ν_2), 841, 653, 581, 481 cm^{-1} ; Raman data: 934 (ν_1), 884, cm^{-1} ; UV- Vis data : 209 nm. Molar conductivity (λ_{m}) (0.02 *M*): 525 $\text{S cm}^2 \text{mol}^{-1}$.

Ammonium paramolybdate prepared as above (4.94 g, 4 mmol) or commercial ammonium molybdate tetrahydrate was taken in a silica crucible and heated to 650 $^\circ\text{C}$ in a furnace for 2 h. The residue thus obtained was cooled to room temperature and transferred to a beaker and sodium hydroxide (0.96 g, 24 mmol) in water (100 mL) was added. The reaction mixture was stirred well and heated on a water bath to get a clear solution. The pH of the clear solution thus obtained was 5.40. Addition of alcohol (~40 mL) afforded sodium paramolybdate (**2**) in 5.5 g (95%) yield. Alternatively a solid mixture of (**1**) and sodium carbonate was crushed well and the fine powder was heated at 500 $^\circ\text{C}$ to obtain a residue. The dissolution of this residue in water to obtain a clear solution followed by addition of alcohol also afforded (**2**). A modification of the reported procedure¹¹, viz., acidification of an aqueous sodium molybdate solution with dilute HCl to pH of ~5.5 instead of HClO_4 and allowing the reaction mixture undisturbed for many days resulted in the formation of (**2**) in moderate yields.

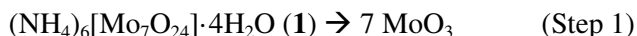
IR (cm^{-1}): 3482 (vs), 3287, 1654, 885 (ν_2), 654, 568, 483; Raman (cm^{-1}): 934 (ν_1), 884 cm^{-1} ; UV- vis: 209 nm. Molar conductivity (λ_{m}) (0.02 *M*): 560 $\text{S cm}^2 \text{mol}^{-1}$.

Results and discussion

The dissolution of commercial molybdic acid in excess ammonia followed by slow evaporation at RT afforded in excellent yields ammonium paramolybdate (**1**), which can also be obtained by Sturdivant's method. It is interesting to note that use of excess ammonia does not afford isolation of any $(\text{NH}_4)_2[\text{MoO}_4]$ viz. ammonium orthomolybdate. The IR spectra of both the above mentioned products are identical, which in turn are identical with the spectrum of the commercial ammonium molybdate tetrahydrate showing that it is $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (**1**) and is available in a state of very high purity. In contrast, the dissolution of commercial molybdic acid in excess NaOH followed by crystallization afforded the monomeric $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ but not any sodium paramolybdate.

In view of the above, an alternate synthetic route involving a base promoted cation exchange reaction¹⁸

of ammonium heptamolybdate tetrahydrate (**1**) with aqueous NaOH in 1:6 mole ratio was attempted for synthesis of (**2**). However this reaction did not yield the expected hexasodium product as evidenced by the presence of ammonium ions in the product¹⁹ and also characteristic infrared signals for N-H vibrations (Supplementary data, Fig. S1). In view of the difficulty to obtain sodium heptamolybdate devoid of ammonium by the base-promoted cation exchange process, a two step reaction as shown below was envisaged to get rid of the ammonium interference.



In the first step, commercial ammonium heptamolybdate tetrahydrate (**1**) was thermally decomposed to obtain the trioxide MoO₃. The formation of a trioxide residue free of ammonia was revealed by a mass loss of 18.79 (expected 18.46). The freshly prepared trioxide thus obtained was then reacted with an aqueous solution of NaOH maintaining a Mo:Na ratio of 7:6 to obtain a clear solution whose pH (~5.4) is acidic (step 2). Addition of alcohol into this precipitated the desired sodium paramolybdate (**2**) free of ammonium impurities, in good yields. In this synthetic methodology, the second step is amenable to changes viz. the residue obtained by the thermal decomposition of (**1**) can also be reacted with other basic sodium reagents like sodium carbonate (or sodium bicarbonate) in 1:3 (or 1:6) mole ratio instead of aqueous NaOH to obtain the same product in good yields. The formation of the same product irrespective of the sodium reagent used was revealed by the identical infrared and Raman spectra and X-ray powder patterns (Supplementary data, Fig. S2-S4) exhibited by the products in all the cases. Further, the powder pattern was in good agreement with the theoretically calculated pattern for Na₆[Mo₇O₂₄]·14H₂O. Pyrolysis of a mixture of (**1**) and Na₂CO₃ in 1:3 ratio at 500°C followed by dissolution of the residue in water also afforded the same product. The same product was also isolated by acidification of an aqueous solution of commercial Na₂[MoO₄]·2H₂O with dilute HCl.

The presence of the heptamolybdate chromophore in (**2**) was evidenced from the optical spectrum of its aqueous solution which is identical to that of the UV-vis spectrum of (**1**) with an absorption maximum at 209 nm (Supplementary data, Fig. S5). Thermal analysis of (**2**) performed on a water bath at 100 °C

showed a mass loss of 17.26%, (expected 17.45%), indicating that the degree of hydration is 14. The TG-DTA study of (**2**) was in accordance with this mass loss, as evidenced by an endothermic event at 97°C in its DTA curve (Fig. 1) accompanied by a weight loss (16.32%) assignable for the loss of fourteen water molecules. The endothermic signals at ~285 and 538°C can be attributed to phase transitions yielding a mixed oxide residue. This result gains credence from a pyrolysis experiment of **2** performed at 600°C in a furnace with an observed mass loss of 17.6 % in excellent agreement with the calculated mass loss (17.42) for a probable residual composition 7MoO₃·3Na₂O. The IR spectrum reveals that the residue is devoid of all water (Supplementary data, Fig. S6).

All our efforts to prepare a differently hydrated sodium paramolybdate containing 22 moles of water were not fruitful. The different synthetic routes described earlier as well as use of different bases viz. NaOH, Na₂CO₃ or NaHCO₃ for dissolution of the freshly prepared MoO₃ afforded only the tetradecahydrate (14H₂O) product and no other sodium paramolybdate with a higher degree of hydration. In all the cases, the formation of the 14-hydrate was confirmed by the results of a thermal analysis of the different products at 100 °C all of which showed a mass loss assignable for the loss of fourteen moles of water.

In order to understand the photochemical properties of **2**, the pristine solid (or its aqueous solution) was irradiated by sunlight or by focusing the visible light emitted from a tungsten filament bulb (60 W) of a table lamp. However, no photochemically induced changes were observed, indicating that

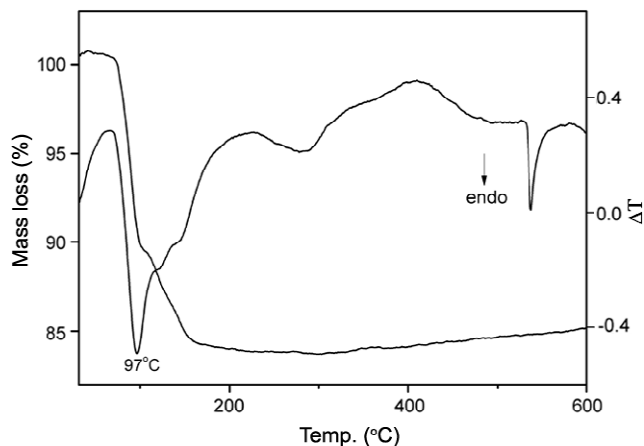


Fig. 1—TG-DTA curves of Na₆[Mo₇O₂₄]·14H₂O (**2**).

the all-sodium compound (**2**) exhibits very similar photochemical behavior to the recently reported lithium-heptamolybdates¹⁸, unlike the heptamolybdates charge balanced by organic cations which can be reduced photochemically²⁰⁻²².

It is interesting to note that the vibrational spectra of the paramolybdates **1** and **2** exhibit similarities and differences. The profiles of the IR spectra in the high energy region (3500-2500 cm^{-1}) are very different (Fig. 2). Compound **1** exhibits a broad and strong absorption signal centered at 3170 cm^{-1} , attributable to the stretching vibrations of -OH and -NH moieties of the water molecules and ammonium cations respectively. Due to the absence of -NH vibrations in the all sodium heptamolybdate **2**, the strong band centered at $\sim 3482 \text{ cm}^{-1}$ can be assigned for the stretching vibration (ν_{OH}) of the water molecule. A noticeable difference is the appearance of a strong signal at 1407 cm^{-1} , assignable for the bending vibration ($\delta_{\text{N-H}}$) of the ammonium ion of **1**, which is conspicuous by its absence in **2**. In the lower energy region below 1000 cm^{-1} , both compounds exhibit nearly similar features. The doubly degenerate asymmetric stretching mode ν_2 of the MoO_6 unit occurs as an intense signal at 899 and 885 cm^{-1} respectively in **1** and **2** in the IR spectrum and as a weak band in Raman spectrum (Supplementary data, Fig. S7). Both compounds exhibit nearly identical Raman spectra with strong bands observed below 1000 cm^{-1} (Supplementary data, Fig. S8). The symmetric stretching vibration ν_1 of the MoO_6 unit is observed as an intense band at 934 cm^{-1} in both **1** and **2**.

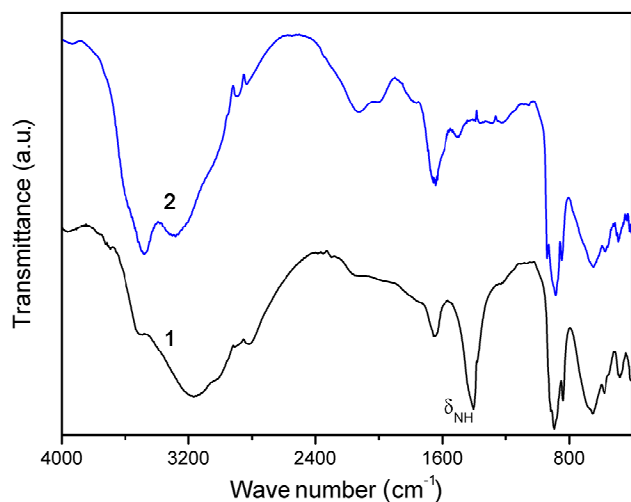


Fig. 2—Infrared spectra of $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (**1**) and $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (**2**).

Conductivity measurements for various concentrations of **1** and **2** (Table 1) show an increased molar conductivity with dilution which can be attributed to the facile dissociation of **1** (or **2**) in solution to produce hydrated NH_4^+ (or Na^+) and heptamolybdate ions. The solid state structure of **1** consists of isolated Lindqvist type $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion, ammonium ions and lattice water while in **2** the Lindqvist type $[\text{Mo}_7\text{O}_{24}]^{6-}$ ion is coordinated to the unique sodium ions¹⁷ (Supplementary data, Fig. S9). In spite of this structural difference, the observed molar conductivity values of 525 and 560 $\text{S cm}^2 \text{ mol}^{-1}$ for **1** and **2** in 0.02 M solution are very close indicating that in solution similar species are present. The conductivity data can be explained due to the hydration of Na^+ ions in dilute solution, because of which the Na^+ ions are no longer coordinated to heptamolybdate. Thus the solution behavior of **2** resulting in the formation of hydrated alkali metal ions and free heptamolybdate ions is very similar to that observed for the recently reported lithium-heptamolybdates¹⁸.

The cyclic voltammograms of **1** and **2** exhibit a single cathodic response below -1.0 V (Fig. 3)

Table 1 – Specific conductivity (K) and molar conductivity (λ_m) data of $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (**1**) and $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (**2**)

Conc. (M)	K (S cm^{-1})		λ_m ($\text{S cm}^2 \text{ mol}^{-1}$)	
	1	2	1	2
0.1	0.0265	0.0256	265	256
0.08	0.0233	0.0212	291	265
0.06	0.0191	0.0191	318	318
0.04	0.0165	0.0159	412	398
0.02	0.0105	0.0112	525	560
0.01	0.0068	0.0070	680	700

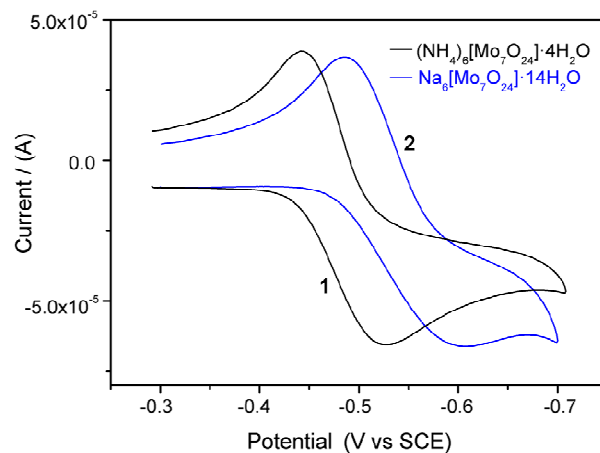


Fig. 3—Cyclic voltammograms of $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (**1**) and $\text{Na}_6[\text{Mo}_7\text{O}_{24}] \cdot 14\text{H}_2\text{O}$ (**2**).

with $E_{1/2}$ values -0.538 and -0.605 V measured versus SCE respectively. The $E_{1/2}$ of (**2**) is at a slightly more negative potential compared to the $E_{1/2}$ values of -0.579 and -0.537 V respectively for the lithium heptamolybdates¹⁸ $(\text{NH}_4)_4[\text{Li}_2(\text{H}_2\text{O})_7][\text{Mo}_7\text{O}_{24}]\cdot\text{H}_2\text{O}$ and $(\text{NH}_4)_3[\text{Li}_3(\text{H}_2\text{O})_4(\mu_6\text{-Mo}_7\text{O}_{24})]\cdot 2\text{H}_2\text{O}$. The electrochemical event in **2** can be attributed to a reduction of the anionic heptamolybdate, which is formed due to hydrolysis of **2**, in addition to the hydrated Na^+ ions. It is interesting to note that the all-sodium heptamolybdate **2** differs from the mixed cationic $(\text{hmtH})_2[\{\text{Mg}(\text{H}_2\text{O})_5\}_2\{\text{Mo}_7\text{O}_{24}\}]\cdot 3\text{H}_2\text{O}$ (hmt = hexa-methylenetetramine)²² in that the latter compound exhibits the same electrochemical event at -0.780 V. However no other electrode process is observed at higher negative potentials for **2**, indicating that the hydrated Na^+ cations do not undergo any electrochemical change.

In summary, we have described a convenient and rapid synthesis of sodium paramolybdate 14-hydrate (**2**) using the commercially available ammonium molybdate heptahydrate **1** as an useful precursor, and studied its spectral, thermal and electrochemical properties.

Supplementary data

Supplementary data associated with this article, viz., Figs S1-S9 and Table S1, are available in electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_55A\(06\)676-680_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_55A(06)676-680_SupplData.pdf).

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