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Convenient synthesis and Raman spectral characterization of diammonium monomolybdate(VI)

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A convenient and cost-effective method is reported for the preparation of gram quantities of an ammonium-rich Mo compound viz. diammonium monomolybdate(VI) $(NH_4)_2MoO_4$ (**1**). The process involves a thorough grinding of a commercial sample of ammonium heptamolybdate tetrahydrate $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ with an excess of ammonium bicarbonate followed by thermal treatment. The facile formation of (**1**) is confirmed by its characteristic Raman spectrum. The use of Raman spectroscopy to distinguish between tetrahedral monomolybdate(VI) and heptamolybdate, dichromate and monochromate(VI), paratungstate and monotungstate(VI) as well as the identification of the species present in ammoniacal solutions of MO_3 (M = Cr, Mo, W) are reported.

Keywords: Diammonium monomolybdate(VI), Ammonium heptamolybdate tetrahydrate, Grinding, Ammonium bicarbonate

Berzelius[1] reported the formation of a crystalline yellow precipitate of ammonium phosphomolybdate $(NH_4)_3[PMo_{12}O_{40}]$ by the acidification of an aqueous solution containing molybdate $(MoO_4)^{2-}$ and phosphate $(PO_4)^{3-}$ anions in 1826. This reaction is used even today as a classical method for the qualitative[2] (and quantitative[3]) detection (and determination) of the phosphate content of a sample. In the past more than hundred and ninety years, a large number of anionic molybdates charge-balanced by ammonium cations (Table 1) have been structurally charcterized. These compounds which exhibit varying ammonium:Mo ratios serve to demonstrate the rich chemistry of molybdates[4-18]. Of the compounds listed in Table 1 excepting the mononuclear $(NH_4)_2MoO_4$ (**1**), which contains two ammonium cations per Mo all other compounds have one or less than one ammonium per Mo. Excepting the ammonium-rich Mo compound **1**, which is isolated from an alkaline medium[13], all other compounds listed in Table 1 are isolated from an acidic medium under appropriate reaction conditions[4-12,14-17].

Ammonium molybdate, molybdic acid and sodium molybdate dihydrate which are commercially available are routinely used as Mo source in synthetic inorganic chemistry research. Unlike the term ‘sodium molybdate' which refers to a compound of formula Na_2MoO_4, the name ammonium molybdate refers to a compound of formula $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (**2**) viz. ammonium heptamolybdate tetrahydrate. In the literature, the term paramolybdate[10,19] is also used for $[Mo_7O_{24}]^{6-}$. Several companies worldwide give the printed formula in a reagent bottle as $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ for a chemical sold under the name ammonium molybdate or ammonium molybdate tetrahydrate (Table 2). Wikipedia suggests alternate names viz. ammonium orthomolybdate[20] or diammonium molybdate for $(NH_4)_2MoO_4$ (**1**). Dittmann and Schweda[13] used the name ammonium monomolybdate for $(NH_4)_2MoO_4$. For the title compound, we have chosen the name diammonium monomolybdate(VI) to correctly indicate the presence of the two ammonium cations and a single Mo in +6 oxidation state in the molecular formula. Besides, this name is more appropriate given the extensive use of the term ammonium molybdate for commercial samples of a compound containing seven Mo atoms in its formula unit viz. ammonium heptamolybdate. Till 2015, Avra Synthesis Pvt Ltd used to offer a compound (catalog no ASA2417) formulated as $(NH_4)_2MoO_4$. However, this item was discontinued. Presently, no chemical of formula $(NH_4)_2MoO_4$ (**1**) is marketed by an Indian chemical supplier.

Although compound (**1**) is available from Sigma Aldrich (~ ₹ 58,600 for 100 g), it is almost sixty times costlier than the average cost of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (**2**) (Table 2). In addition to its use as an inorganic reagent, $(NH_4)_2MoO_4$ is also employed for some biological applications[21,22]. In this report, we describe a mechanothermal method for a cost-effective synthesis of

Table 1 — Molybdenum:ammonium ratio in ammonium and mixed cationic molybdates

No	Compound	Mo:(NH_4) ratio	Mass % of (NH_4)	Ref
1	$(NH_4)_3[PMo_{12}O_{40}]$	12:3	2.88	1
2	$(NH_4)_2[Mo_6O_{19}]\cdot 5H_2O$	6:2	3.58	4
3	$(NH_4)_8[Mo_{36}O_{112}(H_2O)_{16}]\cdot 32H_2O$	36:8	4.67	6,7
4	$(NH_4)_4[Mo_8O_{24}(C_3H_2O_2)_2]\cdot 4H_2O$	8:4	5.08	8
5	$(NH_4)_4[Mo_8O_{24}(O_2)_2(H_2O)_2]\cdot 4H_2O$	8:4	5.17	9
6	$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$	7:6	8.76	10
7	$(NH_4)_8[Mo_{10}O_{34}]$	10:8	8.76	11
8	$(NH_4)_2[Mo_2O_7]$	2:2	10.61	12
9	$(NH_4)_4[Mo_3O_7(O_2)_4]\cdot 2H_2O$	3:4	11.27	9
10	$(NH_4)_2MoO_4$	**1:2**	**18.40**	13
Mixed cationic molybdates				
11	$(NH_4)(trisH)MoO_4$	1:1	6.01	18
12	$Na(NH_4)[C_{13}N_2H_{16}]_2[Mo_7O_{24})]\cdot 8H_2O$	7:1	1.10	14
13	$(NH_4)[Cu(en)_2][Na(en)Cu(en)_2(H_2O)(Mo_7O_{24})]\cdot 4H_2O$	7:1	1.12	15
14	$Na(NH_4)[Mo_3O_{10}]\cdot H_2O$	3:1	3.56	5
15	$(NH_4)_3[Li_3(H_2O)_4(Mo_7O_{24})]\cdot 2H_2O$	7:3	4.36	16
16	$(NH_4)_4[Li_2(H_2O)_7][Mo_7O_{24}]\cdot H_2O$	7:4	5.61	16
17	$(NH_4)_{16}(C_4H_{12}NO)_4[NaMo_7O_{24}]_4\cdot 4H_2O$	28:16	5.73	17

Abbreviations used: $C_3H_2O_2$ = malonic acid; tris = tris(hydroxymethyl)methanamine; $[C_{13}N_2H_{16}]$ = 1,3- bis(4-pyridinium)propane; en = ethylenediamine; $(C_4H_{12}NO)_4$ = dimethyl(2-hydroxyethyl)ammonium

Table 2 — Details of molecular formula of commercial samples available under the name ammonium molybdate tetrahydrate and ammonium molybdate

No	Company	Compound	Formula	Quantity (g)	Price (in ₹)
1	SDFCL	Ammonium molybdate AR	-	100	934
2	LOBA CHEMIE	Ammonium molybdate tetrahydrate extra pure	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	1300
3	HPLC	Ammonium molybdate tetrahydrate AR	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	927
4	MOLYCHEM	Ammonium molybdate ACS	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	1100
5	AVRA SYNTHESIS	Ammonium molybdate tetrahydrate AR	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	1070
6	THOMAS BAKER	Ammonium molybdate AR	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	1290
7	KEMPHASOL	Ammonium molybdate 99+ % AR	-	100	1380
8	SPECTROCHEM	Ammonium molybdate		100	1600
9	LABORATORY CHEMICALS CO.	Ammonium molybdate tetrahydrate AR	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	1800
10	FISHER SCIENTIFIC	Ammonium molybdate tetrahydrate	-	250	3555
11	MERCK	Ammonium heptamolybdate tetrahydrate (ammonium molybdate) extra pure	-	250	17,110
12	RANKEM	Ammonium molybdate, 4-hydrate crystal	-	500	26,100
13	FLUKA	Ammonium molybdate tetrahydrate	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	5,759
14	ALFA AESAR	Ammonium molybdate (para) tetrahydrate	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	2193
		Ammonium molybdate	$H_8MoN_2O_4$	25	15,777
15	SIGMA ALDRICH	Ammonium molybdate tetrahydrate	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	100	16,516
		Ammonium molybdate	$(NH_4)_2MoO_4$	100	58,630

$(NH_4)_2MoO_4$ (**1**) starting from the commercially available ammonium heptamolybdate tetrahydrate (**2**). Application of this method for the preparation of other group VI tetrahedral tetraoxido compounds is described.

Materials and methods

All the chemicals used in this study were of reagent grade and were used as received from commercial sources without any further purification. The molybdenum trioxide (MoO_3) employed in this work, was freshly prepared from commercial samples of ammonium heptamolybdate tetrahydrate **2** or molybdic acid (H_2MoO_4) as described recently[23]. Ammonium paratungstate $(NH_4)_{10}[H_2W_{10}O_{42}]\cdot 4H_2O$ **3** was prepared by dissolution of commercial tungstic acid in aqueous ammonia followed by filtration to get a clear solution which was evaporated slowly to obtain **3**. Pyrolysis of **3** in an electric Bunsen afforded fresh samples of WO_3. 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 Peak Seeker 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. Ball mill reactions were carried out using the planetary ball milling machine (PULVERISETTE 7) marketed by FRITSCH. Isothermal weight loss studies were performed in a temperature controlled electric furnace. X-ray powder patterns were recorded on a Rigaku Miniflex II powder diffractometer using Cu-Kα radiation with Ni filter. Microwave reactions were performed in a Panasonic NN-SM255W Microwave oven.

Preparation of $(NH_4)_2MoO_4$ (1)

Method 1

Ammonium heptamolybdate tetrahydrate **2** (4.92 g, 4 mmol) was taken in a mortar and pestle and mixed with an excess of ammonium bicarbonate. The mixture was thoroughly ground for 15 min to obtain a fine powder, which was taken in a glass beaker and kept in a laboratory oven preheated to 90 °C. After ~10 min, the reaction vessel was removed from the oven and kept in a desiccator to attain room temperature. The yield is 94%. The second step namely heating can also be performed in a microwave oven by keeping the glass vessel containing the powdered reaction mixture for ~2 min at a power setting of 320 W. The synthesis can also be performed starting from 10 g of **2**.

Method 2

Ammonium heptamolybdate tetrahydrate and ammonium hydrogen carbonate were taken in 1:8 mole ratio in a ball mill and the mixture was milled at 400 rpm for 15 min. The product obtained was heated in an oven at 90 °C for 10 min. This reaction can be performed by taking a minimum of 3 g or more of ammonium heptamolybdate.

IR (cm^{-1}): 3640-2435 (br), 1660 (w), 1411 (δ_{N-H}), 894, 841, 667, 576, 484.

Raman data (cm^{-1}): 891 (s), 833 (w), 313 (w).

Raman spectral investigations of ammoniacal solutions of MO_3 (M= Mo, Cr, W)

Freshly prepared sample of molybdenum trioxide (1.43 g, 10 mmol) was dissolved in aqueous ammonia and the reaction mixture was slowly warmed to ~50 °C. The clear solution thus obtained shows an intense Raman signal at 891 cm^{-1}. The reaction mixture was left undisturbed for crystallization. On evaporation of the solvent, colourless crystalline solid, which shows a strong Raman band at 936 cm^{-1} (Fig. 1) was obtained. The use of commercial molybdic acid (85% purity) affords the same spectral results and final product.

A commercial sample of chromium trioxide (1 g, 10 mmol) was dissolved in aqueous ammonia and the reaction mixture was stirred well to obtain a clear solution which exhibits an intense Raman signal at 838 cm^{-1}. The reaction mixture was left in a refrigerator for crystallization. This resulted in the formation of an orange crystalline solid, which shows a strong Raman band at 900 cm^{-1} (Fig. 2).

A freshly prepared sample of tungsten trioxide (1.56 g, 5 mmol) was dissolved in aqueous ammonia and heated on a water bath to dissolve the oxide. The reaction mixture was filtered to obtain a clear solution which exhibits an intense Raman signal at 928 cm^{-1}. On leaving the reaction mixture undisturbed colourless crystals were obtained after a few days. The product thus obtained exhibits an intense signal at 946 cm^{-1} in its Raman spectrum (Fig. 3). The use of commercial tungstic acid affords the same spectral results and final product in slightly less yield. Unlike the commercial sample which does not fully dissolve and some insoluble matter needs to be filtered, the freshly prepared trioxide dissolves faster in aqueous ammonia.

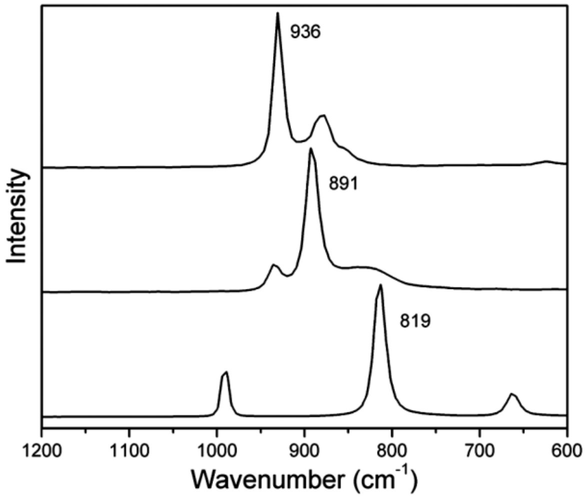


Fig. 1 — Raman spectra of solid molybdenum trioxide **(bottom)**, solution of MoO_3 dissolved in excess NH_4OH pH= ~ 12 (**middle**) and solid product $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ **(top)**

Raman spectral investigations of ammoniacal solutions of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (2) / $(NH_4)2Cr_2O_7$ / $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (3) with aqueous ammonia

A commercial sample of ammonium heptamolybdate tetrahydrate **2** (1.23 g, 1 mmol) was dissolved in hot aqueous ammonia (~10 mL) to obtain a clear solution whose pH is ~12.0. The ammoniacal solution exhibits an intense Raman signal at 891 cm^{-1} (Fig. 4). When the solution was left aside for crystallization in a refrigerator or outside in the open, this resulted in the formation of colourless product in near quantitative yield. The IR spectrum of the product is identical with that of **2** while the Raman spectrum shows an intense band at 936 cm^{-1} indicating formation of heptamlybdate.

A commercial sample of ammonium dichromate **4** (1.52 g, 10 mmol) was dissolved in aqueous ammonia (~8 mL) to obtain an yellow coloured solution. The pH of the solution was alkaline (~12.0). The yellow solution exhibits an intense Raman signal at 838 cm^{-1} indicating the presence of tetrahedral monochromate(VI) species in solution. When the solution was left undisturbed in a refrigerator, orange crystals were obtained. The orange solid shows a Raman spectrum with a band at 900 cm^{-1} which is identical with the spectrum of ammonium dichromate **4**.

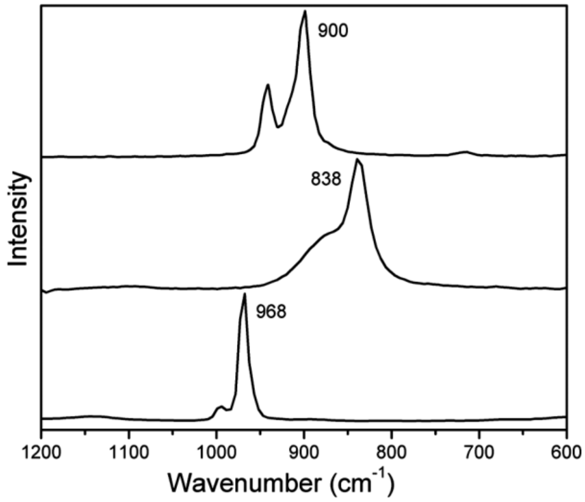


Fig. 2 — Raman spectra of solid CrO_3 (**bottom**), solution of CrO_3 dissolved in excess NH_4OH pH= ~ 12 (**middle**) and solid product $(NH_4)_2Cr_2O_7$ (**top**)

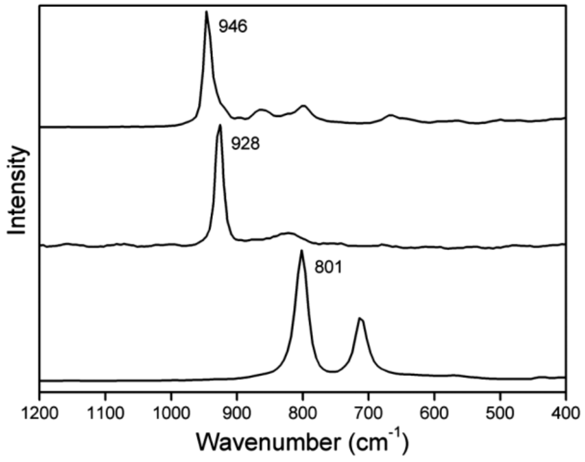


Fig. 3 — Raman spectra of solid tungsten trioxide **(bottom)**, solution of WO_3 dissolved in excess NH_4OH pH= ~ 12 (**middle**) and solid product $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ **(top)**

Freshly prepared ammonium paratungstate tetrahydrate **3** (1 g, 0.3 mmol) was dissolved in aqueous ammonia (~10 mL) to obtain an alkaline solution (~12.0). The clear solution exhibits an intense Raman signal at 928 cm^{-1}. The solution was left aside for crystallization in a refrigerator, to obtain a colourless product in 0.98 g yield which shows an intense Raman band at 946 cm^{-1}.

Studies of aqueous solutions of 1

A sample of diammonium monomolybdate viz. $(NH_4)_2MoO_4$ **1** (1.04 g) was dissolved in 10 mL of distilled water. The clear solution thus obtained (pH= 7.1) was kept aside undisturbed and was studied by Raman spectra periodically (Fig. 5). After three days, transparent crystals of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (0.94 g) were obtained. Solution Raman studies confirmed the transformation of the tertrahedral $(MoO_4)^{2-}$ to heptamolybdate anion in the solution.

Results and Discussion

Synthetic aspects and solution Raman spectral studies

Of the several molybdates listed in Table 1, excepting the ammonium-rich $(NH_4)_2MoO_4$ compound, all other compounds are isolated from an acidic

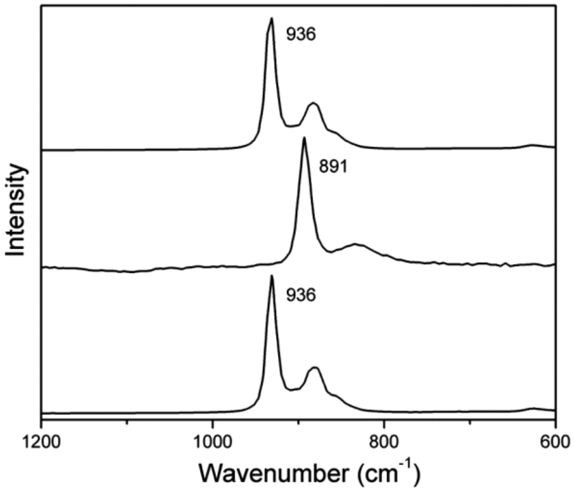


Fig. 4 — Raman spectra of solid $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ **(bottom)**, solution of $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ dissolved in excess NH_4OH pH= ~ 12 (**middle**) and solid product $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ **(top)**

medium. In terms of ease of synthesis $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ **2** can be readily prepared by dissolution of commercial MoO_3 in excess of aqueous ammonia followed by evaporation of the clear solution at room temperature to obtain **2**[24] in a high state of purity in near quantitative yield. A pure sample of **2** exhibits an intense Raman signal at ~ 935 cm^{-1} characteristic of the $(Mo_7O_{24})^{6-}$ moiety (Supplementary Data, Fig. S1) and a saturated solution of **2** is acidic (pH= 5.6). In contrast, the tetrahedral $(MoO_4)^{2-}$ can be readily identified by its symmetric stretching vibration, which occurs as an intense band at ~890 cm^{-1} in the Raman spectrum[25] (Fig. S1). The symmetric stretching vibrations of $(CrO_4)^{2-}$ and $(WO_4)^{2-}$ occur at ~830 and 930 cm^{-1}, respectively. All the four normal modes of vibrations of a MO_4 tetrahedron are Raman active[25]. The Raman active (but IR inactive) symmetric stretching υ_1 (A_1) vibration is the most intense and is used for compound characterization in this work. The IR active asymmetric stretching υ_3 (F_1) vibration occurs as a weak band at around ~835 cm^{-1}, while the bending υ_4 vibration is hidden by υ_2 in $(MoO_4)^{2-}$. Unlike compound **2**, the synthesis of $(NH_4)_2MoO_4$ **1** (pH of saturated solution = 7.9) requires special conditions as can be evidenced from the work of Dittmann and Schweda[13]. These authors reported that crystals of two polymorphic modifications of $(NH_4)_2MoO_4$ can be prepared by dissolution of MoO_3 or $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ respectively in a saturated ammoniacal solution at 323 K followed by crystallization at 298 K or alternatively in a gas-solid reaction by passage of ammonia gas over $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$.

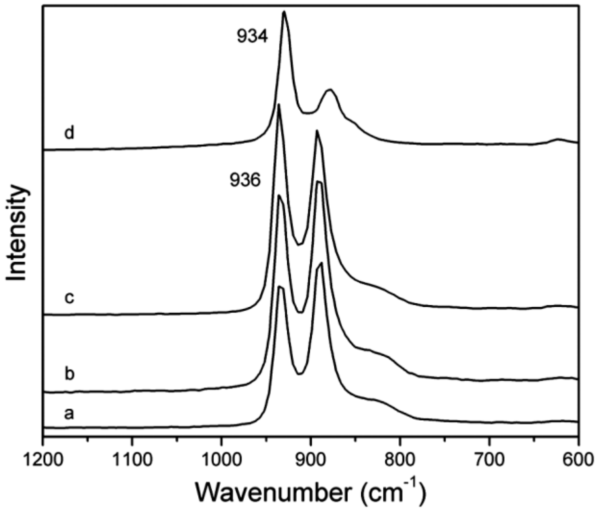


Fig. 5 — Solution Raman spectra of $(NH_4)_2MoO_4$ dissolved in distilled water on day 1 (**a**), day 2 (**b**), day 3 (**c**) and solid product $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ (**d**) obtained from the solution on day 4.

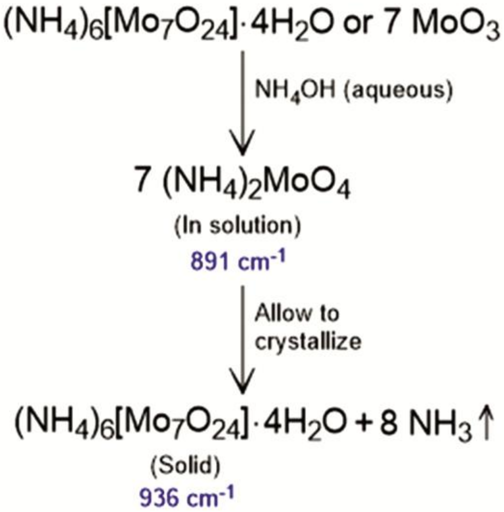
However, our many efforts to prepare **1** by the solution method have not been fruitful and all our investigations reveal that the favored product from the above reactions is invariably the heptamolybdate viz. $(NH_4)_6[Mo_7O_{24}]\cdot4H_2O$ **2** as evidenced by an intense Raman signal at 936 cm^{-1} (Figs 1 and 4). It is well documented that acidification of an alkaline solution of $(MoO_4)^{2-}$ results in condensation of tetrahedral $(MoO_4)^{2-}$ units to give rise to polyoxometalate products which are made up of edge-sharing (MoO_6) octahedra[26,27]. A similar chemistry is well documented[26,27] for the analogous $(WO_4)^{2-}$ while in the case of $(CrO_4)^{2-}$ the major product formed in acidic medium is $(Cr_2O_7)^{2-}$. The first product of acidification of $(MoO_4)^{2-}$ is heptamolybdate, which starts crystallizing at a pH of 6.5[26]. In the present case, the acidic medium is attained by the release of ammonia. The loss of ammonia can also account for the formation of paratungstate and dichromate for the other group VI metals. Hence the difficulties in isolating a tetrahedral $(MO_4)^{2-}$ containing product are in accordance with reported work[18,26].

Interestingly a Raman spectral study provides proof for the presence of tetrahedral $(MO_4)^{2-}$ (M = Cr, Mo, W) species in ammoniacal solution as can be evidenced by the observation of an intense signal at 891 cm^{-1} assignable for the υ_1 symmetric stretching vibration of the $\{MoO_4\}$ tetrahedron. The presence of $(MoO_4)^{2-}$ moiety is further confirmed by a comparison of the spectra with the Raman spectra of pure solid and aqueous solution of Na_2MoO_4 (Supplementary Data, Fig. S2). Since the medium is ammoniacal in both cases namely reaction of MoO_3 or compound **2** with aqueous ammonia, it implies that the species in solution is the ammonium-rich compound $(NH_4)_2MoO_4$ (Scheme 1). The difficulty in isolation of **1** can also be evidenced by a study of the solution Raman spectra of **1** (Fig. 5). A freshly prepared solution of **1** exhibits two signals of nearly equal intensity at 891 and 936 cm^{-1} and the intensity of the 936 cm^{-1} signal increases with time accompanied by a reduction of the intensity of the other signal and an increase in acidity. The final product of this experiment afforded colourless crystals which exhibit a Raman signal at 936 cm^{-1} indicating the formation of the ammonium deficient compound ammonium heptamolybdate tetrahydrate **2**. The Raman spectral investigations of ammoniacal solutions of MO_3 (M=Cr or W) show that in these cases the final product formed is not the tetrahedral monometalate $(MO_4)^{2-}$ but the dichromate or the paratungstate **3** (see Fig. 2 and 3). Based on the above investigations, the species present in ammoniacal solutions of MO_3 or heptamolybdate or dichromate or paratungstate as well as the final solid product obtained on dissolution of **1** in water can be represented as shown in Scheme 1 and 2.

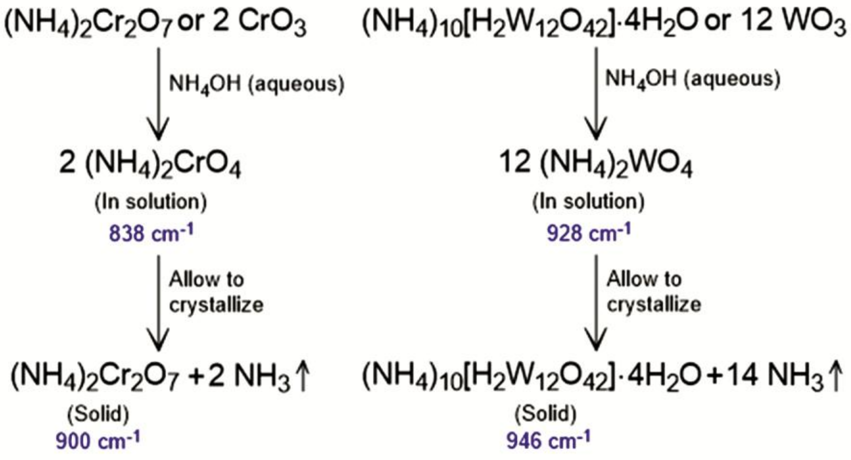
The above mentioned results indicate that the driving force for the formation of the ammonium deficient $\{Mo_7\}$ product is the transformation of the tetrahedral $(MoO_4)^{2-}$ units in solution to $(Mo_7O_{24})^{6-}$ with concomitant loss of eight moles of ammonia in the process. In this context, it is to be noted that depending on the base employed for dissolution of MoO_3, the product of the reaction differs. For example use of an excess of a strong base like NaOH affords Na_2MoO_4 while the use of an excess of organic amine like n-butylamine results in the formation of a compound containing both heptamolybdate and monomolybdate[28,29].

Solid state synthesis of 1

Despite the difficulties associated with solution synthesis of **1**, Scheme 1 does provide a clue that the formation of the ammonium-rich compound **1** can be achieved by ammoniating **2**. Hence we chose a solid state synthetic route by using an ammonia source viz. ammonium bicarbonate also known as ammonium hydrogen carbonate. Since ammonium salts are known sources of ammonia vapour, we performed a mechanochemical reaction by grinding ammonium heptamolybdate tetrahydrate with a stoichiometric amount of ammonium bicarbonate equivalent to 8 moles of ammonia. Although this reaction did afford the desired compound **1**, the product was contaminated with heptamolybdate **2**, as evidenced by the Raman spectrum. The use of a slight excess of the ammoniating reagent equivalent to 10 moles of ammonia still did not result in the formation of pure product as evidenced by a Raman signal 936 cm^{-1} in addition to the intense Raman signal at 891 cm^{-1} of **1** (Fig. 6). In order to avoid the contamination of **2**, the ammoniating agent was taken in large excess and the reagents were thoroughly crushed to a fine powder by grinding the mixture for ~15 minutes. Although the product of this mechanochemical reaction afforded the desired product **1** devoid of any starting material **2**, the Raman spectrum revealed the presence of an intense band at 740 cm^{-1} and a weak signal at 1052 cm^{-1} (Fig. 6), indicating presence of some impurities. The Raman spectra of pure ammonium bicarbonate



Scheme 1 — The tetrahedral $(MoO_4)^{2-}$ species which exists in solution transforms to heptamolybdate when left undisturbed for crystallization



Scheme 2 — The tetrahedral $(MO_4)^{2-}$ species (M = Cr, W) in ammoniacal solution transforms to ammonium dichromate or ammonium paratungstate when left undisturbed for crystallization

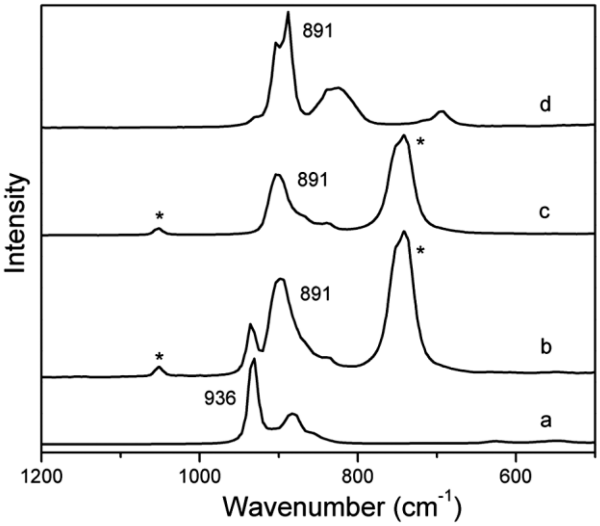
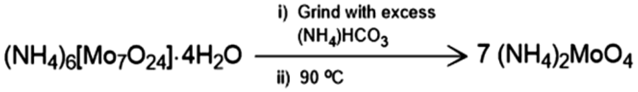


Fig. 6 — Raman spectra of solid $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ (**a**), $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ ground with slight excess of $(NH_4)HCO_3$ (**b**), $(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ ground with large excess of $(NH_4)HCO_3$ (**c**) and solid product $(NH_4)_2MoO_4$ **1** after thermal treatment (**d**)



$$(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O \xrightarrow[\text{ii) 90 °C}]{\text{i) Grind with excess } (NH_4)HCO_3} 7\ (NH_4)_2MoO_4$$

Scheme 3 — Mechanothermal synthesis of **1**

and its aqueous solution were recorded (Supplementary Data, Fig. S3) to understand if the additional bands originate from the ammoniating reagent which was used in excess.

The spectra of solid and aqueous solution of ammonium bicarbonate exhibit an intense Raman band at 1045 cm^{-1} for pure solid (1018 cm^{-1} for solution) in addition to signals at 1265, 704 cm^{-1} (1362, 670 cm^{-1} for solution). The solution Raman spectrum is in agreement with reported data[30]. However, samples of heptamolybdate thoroughly ground with ammonium bicarbonate exhibit a weak signal at 1052 cm^{-1} and an intense signal at 740 cm^{-1} (Fig. 6), both of which disappear when the fine powder obtained from the mechanochemical reaction was heated in an oven at 90 °C for 10 min or in a microwave oven for ~2 min. The strong band at 740 cm^{-1} can be ruled out as originating from unreacted heptamolybdate. Although the reason for getting a weak signal at 1052 cm^{-1} for the mechanochemically treated sample (instead of the intense 1045 cm^{-1} band) is not clear, the additional bands disappear only after a thermal treatment (Scheme 3). The yield of the product obtained after the thermal treatment was as expected for the monomolybdate(VI) compound **1**. The formation of a pure tetrahedral compound without impurities was confirmed by an identical Raman spectrum with that of a commercial sample of **1** from Sigma Aldrich.

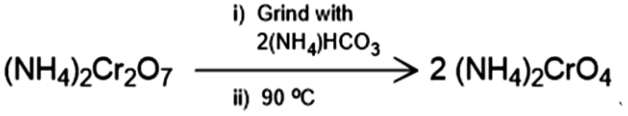
Use of ammonium carbonate instead of the bicarbonate also afforded identical results[31]. The Mo reagent used should be ammonium heptamolybdate tetrahydrate and not molybdic acid or molybdenum trioxide to obtain monomolybdate product under mechanothermal condition. Thorough grinding of both the reagents (Mo source and ammoniating reagent) is essential for successful synthesis of **1**. It is observed that mere heating of a mixture of compound **2** with a large excess of ammonium reagent (in the absence of any grinding) results in the formation of a mixture of products of **1** containing substantial amounts of heptamolybdate. The powder pattern (Supplementary Data, Fig. S4) and IR spectrum (Supplementary Data, Fig. S5) of the final product were compared with those of a commercial sample of **1** from Sigma Aldrich, to conclusively prove that the product obtained is $(NH_4)_2MoO_4$ **1**.

Thermal analysis of the product adds further credence to the formation of **1**. Unlike **2**, which shows a mass loss of 5.23% at 100 °C, compound **1** exhibits a mass loss of 9.21%. Pyrolysis of **1** at 600 °C resulted in the formation of 73.58% residue (mass loss = 26.42%) which is in very good agreement with the theoretical value for the formation of molybdenum trioxide (MoO_3) as shown below.

$$(NH_4)MoO_4 \xrightarrow{600\ °C} H_2O + 2NH_3 + MoO_3$$

The formation of MoO_3 was confirmed by its characteristic Raman band (Supplementary Data, Fig. S6) at 819 cm^{-1}. Instead of mechanical grinding in a mortar and pestle, the synthesis of **1** can also be performed in a ball mill by milling a mixture of a commercial sample of ammonium heptamolybdate tetrahydrate **2** with a stoichiometric amount of ammonium bicarbonate. The advantage of this method is that the reaction can be performed on a larger scale. The fine powder obtained after ball milling for 10 min was subjected to thermal treatment as before to obtain pure **1**. Thus the above methodology which uses ammonium bicarbonate as ammoniating reagent, provides a convenient and cost-effective method for the synthesis of **1**.

In order to check the suitability of the grinding method for the synthesis of the other two group VI tetraoxidometalates the mechanothermal reaction was performed by using the commercially available



Scheme 4 — Mechanothermal synthesis of diammonium chromate(VI)

ammonium dichromate (or freshly prepared ammonium paratungstate) with ammonium bicarbonate (Supplementary Data, Fig. S7). In the case of Cr, the diammonium monochromate(VI) can be obtained using stoichiometric amount of ammonium bicarbonate (Scheme 4), while no diammonium monotungstate(VI) could be obtained in the case of W.

Conclusions

In this work we have demonstrated the use of Raman spectroscopy to (i) distinguish between the tetrahedral $(MoO_4)^{2-}$ and $[Mo_7O_{24}]^{6-}$, (ii) $(CrO_4)^{2-}$ and dichromate (iii) $(WO_4)^{2-}$ and paratungstate and iv) identify the species present in ammoniacal solutions of MO_3 (M = Cr, Mo, W). The facile transformation of the ammonium rich monomolybdate to an ammonium deficient heptamolybdate compound precludes the solution synthesis of $(NH_4)_2MoO_4$. Hence we have developed a solid-state methodology, which involves a mechanical grinding of a commercial sample of ammonium heptamolybdate tetrahydrate with an excess of ammonium bicarbonate followed by a thermal treatment. This reaction can also be successfully applied for the facile synthesis of $(NH_4)_2CrO_4$. Efforts are underway to apply this methodology for the preparation of the elusive $(NH_4)_2WO_4$ which is not known so far. In summary, the mechanothermal method developed in this work constitutes a convenient as well as cost-effective synthesis of diammonium monomolybdate(VI) **1**.

Supplementary Data

Supplementary Data (Figs S1-S7) associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(12)1760-1767_SupplData.pdf.

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