

FORMATION OF SALTS OF HETEROPOLYACIDS IN NITRATE MELTS

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The acid-base reaction between $\text{Na}_2\text{MoO}_4 + \text{Na}_4\text{As}_2\text{O}_7$ as Lux bases dissolved in an $\text{NaNO}_3 + \text{KNO}_3$ melt and an $\text{NO}_2 + \text{O}_2$ gas mixture as a Lux acid gave a novel heteropolyacid salt whose composition is approximately $(\text{Na}, \text{K})_{18}\text{As}_2\text{Mo}_{17}\text{O}_{65}$, $(\text{Na}, \text{K})_{16}\text{As}_2\text{Mo}_{18}\text{O}_{56}$, $(\text{Na}, \text{K})_{16}\text{As}_2\text{Mo}_{17}\text{O}_{64}$. This compound can also be obtained by direct fusion of the components ($\text{Na}_4\text{As}_2\text{O}_7$, Na_2MoO_4 and MoO_3) over the temperature region of 420–600°C. Based on the study of the arsenate and diarsenate ions in a nitrate melt and the molecular spectra of the compound obtained it is suggested that the basic unit of the heteropolyanion structure is the diarsenate anion. The formation of analogous compounds can generally be expected for X/Z combinations with $X = \text{P(V)}, \text{As(V)}, \text{V(V)}$ and $Z = \text{Mo(VI)}, \text{W(VI)}$.

Part of our study aimed at the preparation of new substances and investigation of the crystal growth from salt melts as solvents^{1–3}, this work is concerned with salts with heteropolyanions of a new type, the formation of which has been observed during acid-base titrations in nitrate melts using potentiometric indication¹. Acid-base reactions took place between a mixture of two Lux bases, *viz.* XO_4^{3-} (or $\text{X}_2\text{O}_7^{4-}$) and ZO_4^{2-} where $X = \text{P(V)}, \text{As(V)}, \text{V(V)}$ and $Z = \text{Mo(VI)}, \text{W(VI)}$, and iodine pentoxide as a Lux acid. The formation of a salt with the $(\text{X}_2\text{Z}_{24}\text{O}_{87})^{20-}$ anion was inferred from the shape of the potentiometric curves, colour changes and separation of a substance insoluble in the nitrate melt. Of the X/Z combinations, the As/Mo system received most attention because the compound appeared to be suitable for the separation in a quantity sufficient for the analysis and study of its properties; the substance separates from the nitrate melt as a low-soluble polycrystalline precipitate whose temperature coefficient of solubility, on the other hand, is fairly high.

In addition to iodine pentoxide, use has been also made of a gaseous mixture of $\text{NO}_2 + \text{O}_2$ acting as N_2O_5 acid conjugate to NO_3^- as a Lux base. Previous potentiometric measurements have given evidence that this gas mixture can act as an efficient Lux acid also at atmospheric pressure^{2,3}.

EXPERIMENTAL

Chemicals

Sodium and potassium nitrates of reagent grade purity (Lachema, Brno) were recrystallized from aqueous solutions. An equimolar mixture of the two salts was fused and filtered over an S1 glass filter and dried in the molten state with flowing dry oxygen. For some preparations the filtration over a glass frit was omitted and the drying with oxygen was conducted in Teflon. Anhydrous sodium molybdate was prepared by dehydration of its hydrate, anhydrous sodium diarsenate, by dehydration of sodium hydrogenarsenate heptahydrate, and iodine pentoxide, by dehydration of iodic acid. The remaining crystalline chemicals used were of reagent grade purity (Lachema, Brno, and BDH Chemicals, England).

Gases from pressure cylinders (O_2 , N_2 , NH_3 , Ar) were dried with potassium hydroxide or sulphuric acid. The nitrogen dioxide-oxygen gas mixture was prepared and dried similarly as previously^{2,3}.

Analyses

Arsenic and molybdenum in the samples were determined by two independent methods. Arsenic was determined either iodometrically after reduction to As(III) and distillation in the chloride form⁴, or spectrophotometrically by an adapted procedure after Reed⁵ on a VSU 2 instrument (Carl Zeiss, Jena). Molybdenum was determined cerimetrically after reduction with mercury⁶, or by atomic absorption spectroscopy according to David⁷ using $AlCl_3$ in high concentrations to eliminate interferences.

Alkali metals were determined by atomic absorption spectroscopy, nitrate spectrophotometrically according to Kadič⁸. Iodate was reduced with disulphite to iodide and determined argentometrically using potentiometric indication.

Qualitative detection of the elements and ions was performed by common methods. Peroxidic substances were identified based on the oxidation of manganese(II) hydroxide in alkaline solutions under argon. Semiquantitative spectrographic analyses on a Q 24 instrument (Carl Zeiss, Jena) were carried out at the Central Geological Institute.

The powder X-ray diffraction patterns were obtained by the Debye-Scherrer method on a Mikrometa 2 instrument in Siemens chambers, similarly as the diffractograms using radiation of 154, 178 pm wavelength.

The thermal stability of the compound synthesized was studied by thermogravimetry and differential thermal analysis on a Derivatograph instrument (MOM, Budapest) at a heating rate of $10^\circ C/min$, any by quasi-steady decomposition, by heating the preparations for 24 h in a controlled electric furnace and increasing the temperature in $50^\circ C$ steps.

The infrared spectra were scanned on a UR 20 spectrophotometer (Carl Zeiss, Jena) in Nujol mulls. A Perkin-Elmer 684 instrument was used for the far infrared region. The Raman spectra were run on a JRS-S1 spectrometer (Jeol, Tokyo) equipped with an argon laser working at 488 nm.

The magnetic properties were examined on a torsion balance based on the Faraday principle with electrostatic deflection compensation. The Gouy method was used for measuring the temperature dependence of the magnetic susceptibility; the temperatures were -196 , -77 , 0 , and $23^\circ C$.

Preparation Procedure

The molybdatoarsenate was synthesized by acid-base reaction in a melt of an equimolar mixture of $NaNO_3 + KNO_3$ at $260^\circ C$. Various modifications of the procedure were used. When using

iodine pentoxide, glass vessels and stirrers were employed and the molybdoarsenate separated was decanted with the nitrate melt and allowed to sediment in glass vessels. When using the nitrogen dioxide–oxygen gas mixture, a Teflon reaction vessel was employed, two times with glass feeding tubes and once with Teflon tubes. In a modification, the precipitate was centrifuged in Teflon cells, in another it was allowed to sediment in glass or Teflon.

Nitrates were removed from the samples with liquid ammonia in an adapted Soxhlet extractor fitted with polystyrene heat insulation. The extraction flask, submerged in a cool Dewar flask, accommodated pieces of sodium for removing moisture. Gaseous ammonia was fed in the extraction flask, where it condensed. It was then allowed to boil by removing coolant, and it condensed in the cooler of the extractor flown through by ethanol whose temperature was about -60°C . The ethanol was delivered from a two-circuit thermostat filled with a mixture of ethanol and CO_2 ; to save the latter, the alcohol was pre-cooled to -30°C in an MK 70 cryostat.

The temperature cycling device consisted of a Zeparis controller (ZPA, Prague) with two relays in combination with a two-way working relay and a power diode. The heating and cooling rates were set by means of a regulating transformer. The higher the voltage, the faster was the heating and the slower was the cooling. Cycles from 45 to 230 min could be achieved for temperature differences from 20 to 85°C . The range from 260 to 310°C , hence, with a temperature difference of 50°C , was used most frequently.

RESULTS

The preparation procedure was modified with regard to the results of analyses so as to obtain the product in the highest possible purity. Samples labelled As/Mo-1 through As/Mo-4 were thus prepared as follows:

As/Mo-1. Iodine pentoxide (3.032 g, 8.204 mmol) was added portionwise to a solution of $\text{Na}_4\text{As}_2\text{O}_7$ (264 mg, 0.746 mmol) and Na_2MoO_4 (3 700 mg, 17.97 mmol) in 330.0 g of nitrate melt prepared and filtered in glass. Each addition was only applied after the melt cleared up perfectly. The stoichiometry corresponding to the potential jump in the titration¹, viz 11.913 mmol, was deliberately not reached because a white voluminous precipitate started to separate from the melt with additions as low as 6.064 mmol. The As : Mo ratio in the starting mixture thus was 1 : 12.05 and the concentration used was 3.745 times higher than in ref.¹. The substance separated was decanted with the pure nitrate melt (3×100 g), and the mixture was transferred to thin-walled heated glass test tubes where the precipitate was allowed to sediment. After cooling down, the solid contents on the bottom of the test tube were taken up mechanically, ground in a mortar and subjected to a 6 h extraction with liquid ammonia. After this treatment the preparation was dried for 2 h at 260°C to remove moisture and ammonia. Sample labelled As/Mo-1 was obtained in a yield of 1.1 g.

As/Mo-2. A gas mixture of $\text{NO}_2 + \text{O}_2$ was fed through glass test tubes into a Teflon vessel accommodating solution of the same composition as above. A white voluminous precipitate separated; it did not differ in appearance from that obtained using I_2O_5 . The precipitate was centrifuged in Teflon cells, decanted with 1×100 g of neat

melt and centrifuged repeatedly. The sediment was extracted with liquid ammonia for 8 h and dried at 260°C for 2 h to give 1.2 g of As/Mo-2 sample.

As/Mo-3. An $\text{NO}_2 + \text{O}_2$ gas mixture was fed through glass tubes to a solution of $\text{Na}_4\text{As}_2\text{O}_7$ (0.528 g, 1.492 mmol) and Na_2MoO_4 (7.400 g, 35.936 mmol) in 660.0 g of nitrate melt prepared and filtered in glass and accommodated in a glass vessel. The white voluminous precipitate that separated as above was decanted with 1×100 g of nitrate melt and allowed to sediment in heated thin-walled glass test tubes similarly as As/Mo-1 sample. After a 12 h extraction with liquid ammonia the preparation was dried at 260°C for 4 h to give 2.0 g of As/Mo-3 sample.

As/Mo-4. A gas mixture of $\text{NO}_2 + \text{O}_2$ was fed through Teflon tubes into a solution of $\text{Na}_4\text{As}_2\text{O}_7$ (0.264 g, 0.746 mmol) and Na_2MoO_4 (3.700 g, 17.968 mmol) in 330.0 g of nitrate melt prepared in Teflon and accommodated in a Teflon vessel (the filtration over a glass frit was omitted). The white voluminous precipitate that separated as above was allowed to sediment in the reaction vessel, the pure melt layer was decanted and the residue was subjected to a 10 h extraction with liquid ammonia.

The analyses of the samples are given in Tables I–III.

Properties of the Samples

According to the concentrations of the initial products and the yield achieved, the solubility of the molybdoarsenate in nitrate melt at 260°C is about $6 \cdot 10^{-4}$ molal, hence, 0.2%. The temperature coefficient of solubility of the substance is rather high; according to the temperature at which all the molybdoarsenate separated dissolves, the coefficient is about $3 \cdot 10^{-5} \text{ mol K}^{-1}$, or 0.1 g K^{-1} , over the region of 260–310°C. Making use of this fact, attempts were made to prepare single crystals of the substance by temperature cycling; the temperature limits of the cycles were 260 and 310°C, a cycle took 60–120 min and the whole treatment lasted several weeks. The temperature region was chosen so that a small fraction of the substance remained undissolved at the higher limit. The heat treatment only resulted in an improvement of the X-ray diffraction patterns of the polycrystalline sample: since, however, the crystals were shorter than 0.1 mm in length, they did not lend themselves to single crystal diffraction study. The polycrystalline X-ray diffraction patterns were identical for samples As/Mo-1 through As/Mo-4, and so the differences in the results of their analysis are to be ascribed to differences in their impurity contents.

The samples were also examined by infrared and Raman spectroscopy over the regions of 200–4 000 and 10–2 410 cm^{-1} , respectively. No vibrations were observed in the Raman spectra in the 1 400–1 650 and 2 200–2 410 cm^{-1} ranges that could be attributed to O_2 and N_2 molecules, respectively. The spectra of the

four samples were basically identical; As/Mo-1 exhibited additional bands attributed to the ν_1 and ν_3 vibrations of iodate and to moisture (ν and δ vibrations of water),

TABLE I

Qualitative analysis of the substances prepared (+ positive, ? trace quantities, 0 negative, - not followed)

Sample	Mo	As	IO_3^-	NO_3^-	O_2^{2-} (O_2^-)
As/Mo-1	+	+	+	?	-
As/Mo-2	+	+	-	?	-
As/Mo-3	+	+	-	?	0
As/Mo-4	+	+	-	+	-

TABLE II

Semiquantitative analysis of two samples

Sample	Elements present in concentrations			
	above 1%	1-0.1%	0.1-0.01%	below 0.01%
As/Mo-3	As, Na, Mo, Si, K	B	-	-
As/Mo-4	As, Mo, Na	K, Si	Al, Ba, Fe	B

TABLE III

Quantitative analysis of the samples prepared

Sample	Concentration ^a (%) of					Balance to 100% ^b	As : Mo atomic ratio
	Mo	As	Na	K	N (NO_3^-)		
As/Mo-1	38.2	2.19	8.02	3.93	-	23.7	1 : 13.60
As/Mo-2	43.8	3.81	6.61	2.90	-	16.1	1 : 9.02
As/Mo-3	44.5	2.32	9.09	5.17	0.28	10.1	1 : 15.26
As/Mo-4	46.6	4.24	10.2	4.36	0.56	2.4	1 : 8.57

^a Averages of triplicate determinations. With As/Mo-4 sample the variance was 1.8% for Mo, 1.2% for As and 1.1% for alkali metals (relative values); ^b after conversion to oxides.

TABLE IV

Infrared and Raman spectra of As/Mo-4 sample (Nujol, Tripene, capillary). Wavenumbers in cm^{-1} ; relative intensities: s strong, m medium, w weak, vw very weak; band shape: sh shoulder, b broad; vibration: ν_s symmetric stretching, ν_{as} antisymmetric stretching, δ bending

Infrared ^a		Raman ^b		Assignment
$\tilde{\nu}$	<i>I</i>	$\tilde{\nu}$	<i>I</i>	
		35 s	46	lattice vibrations
		47 sh	22	
		75 m	30	
		120 s	67	
		200 m	17	
		227 m	22	
249 s, b	65	—		deformation of the entire skeleton and the terminal Mo = O
261 s, b	65	—		
284 sh	58	295 w	4	$\delta(\text{As—O—As})$
316 m	28	—		ν_s of the linear Mo—O—Mo bridges
334 sh	16	340 w	6	
364 s	43	365 w	7	
412 w	12	410 w	2	
478 s	66	465 vw	1	$\delta(\text{AsO}_3)$, $\nu_{\text{Mo—O}}(\text{As})$
553 s, b	81	525 w	6	
575 s, b	81	—		ν_s of the Mo—O—Mo bent bridges
722 m	55	710 vw	2	
		740 vw	2	$\nu_{as}(\text{As—O—As})^c$
772 s	89	—		$\nu_s(\text{As—O—As})$
—		815 sh	9	
827 s	95	—		ν_{as} of the bent and linear Mo—O—Mo bridges
833 s	95	832 s	45	
863 s	90	870 m	18	$\nu(\text{AsO}_3)$
880 s	90	895 w	5	ν of terminal Mo = O groups
907 s	81	905 w	9	
921 s	82	920 m	19	
942 m	63	935 s	100	
1 060 vw	10	1 058 vw	2	
1 152 vw	8			?
1 373 w, b				$\nu_3(\text{NO}_3^-)$
1 397 w, b				

^a Measured above 200 cm^{-1} . At $200\text{--}210 \text{ cm}^{-1}$ a shoulder appears of a band whose maximum lies below 200 cm^{-1} . Above 210 cm^{-1} a next broad band appears with maxima as listed in the table; ^b measured up to $1\,100 \text{ cm}^{-1}$; ^c Nujol contributes to the IR band at 722 cm^{-1} .

As/Mo-4 displayed ν_1 and ν_3 bands of nitrate. The infrared and Raman data of As/Mo-4 are given in Table IV.

The thermal properties of the samples depended on the way of their preparation. The derivatograph curves of weight loss for a uniform temperature increase differed from the steady-state thermal decomposition curves. The weight loss observed on the derivatograph was appreciably lower than that observed during the steady-state thermal decomposition. The shape of the weight loss curves for the steady-state decomposition was qualitatively identical for the four samples. A slight decrease was observed starting from approximately 100°C, due to liberation of moisture and ammonia. The weight loss depended on how long the sample had been dried before the treatment. The loss setting in at 400–450°C depended on the weight of sample and crucible. The course of the steady-state thermal decomposition of As/Mo-4 is shown in Table V; the decomposition products were identified by means of their powder X-ray diffraction patterns. A slight endo effect was observed on the DTA curve at 420°C, and a slight exo effect was found at this temperature for the cooling process. These effects are due to a solid \rightleftharpoons liquid phase transition. Making use of the fact that the substance did not decompose above its melting point, fusion of its components (Na_2MoO_4 , MoO_3 , $\text{Na}_4\text{As}_2\text{O}_7$) in the ratio corresponding to the composition of the substance under study was attempted at 550°C. The mixture of the solid components in a platinum crucible melted in 48 h, and the powder X-ray diffraction patterns of the products were identical with those of As/Mo-1 through As/Mo-4 samples.

The magnetic susceptibility measurements revealed that the substance is slightly paramagnetic. The paramagnetic susceptibility varied with temperature over the region

TABLE V
Quasi-steady thermal decomposition of As/Mo-4 sample (left for 24 h each temperature)

Temperature °C	Weight loss %	Powder-ray diffraction patterns	Remark
250	0.29	—	
300	0.88	—	
350	0.88	—	
400	0.88	—	
450	1.75	—	sintering
500	2.34	initial	
550	3.21	initial	
600	3.80	very weak lines of the initial sample	complete clarification of melt

from 2.0 to $4.1 \cdot 10^{-10} \text{ m}^3 \text{ kg}^{-1}$ and decreased with the magnetic field intensity at any temperature. At any magnetic field intensity the temperature dependence exhibited a maximum in the 0°C range and the curves resembled those of antiferromagnetics with their Néel temperature about 0°C .

DISCUSSION

The basic orientation of this study followed from the fact that the powder X-ray diffraction patterns of the four samples were identical, hence, the differences in their analytical composition could only be due to impurities. As/Mo-1 sample contained a large amount of iodate which could not be removed by decantation because of the appreciable solubility of the molybdoarsenate in the melt. Alkali iodates are not markedly soluble in liquid ammonia, so that extraction with this agent also failed. This is why iodine pentoxide was replaced by a gas mixture of $\text{NO}_2 + \text{O}_2$, which acts as a Lux acid with respect to nitrate melt even at atmospheric pressure^{2,3}. Really, the nondetermined residue content was considerably lower for As/Mo-2 and As/Mo-3 samples. As/Mo-2 was difficult to take out of the Teflon cells and the products was contaminated by Teflon flakes. The nondetermined residue content of As/Mo-3, about 10%, was first explained by assuming that the substance under study is a peroxo or hyperoxo compound rather than an oxo compound, or that oxygen molecules are embedded in the structure. These assumptions were supported by the facts that the substance is paramagnetic and also that pure nitrate melts contain high quantities of peroxy and hyperoxy anions⁹⁻¹⁴. However, the assumption of the presence of peroxides or hyperoxides was unambiguously refuted by analytical evidence, and the occurrence of oxygen or nitrogen molecules was disproved by the Raman spectra.

Only a semiquantitative spectrographic analysis gave evidence of the presence of $10^0\%$ Si and $10^{-1}\%$ B which, converted to oxides, account for the nature of the impurities and indicate an interaction of the nitrate melt with glass: acting as Lux acids with respect to nitrate melt, silicon dioxide or polysilicate anions decompose the melt and pass into the solution in a minute concentration in the form of silicate anions. These anions then concentrate in the substance under study as the nitrates are being washed out with liquid ammonia with which silicates and borates are not removed. Moreover, silicon and boron probably can replace arsenic in the heteropoly compound without altering appreciably the character of its X-ray diffraction lines. This substitution can also account for the differences in the As : Mo ratio in the samples. Those prepared in glass vessels (As/Mo-1 and As/Mo-3) exhibit a lower As : Mo ratio probably because part of the arsenic is substituted by silicon. Prepared from nitrate melt filtered over a glass frit, As/Mo-2 displays a lower As : Mo ratio than As/Mo-4, which, on the other hand, contains some other elements in trace quantities.

When deriving the empirical formulae of the compound under study, the analytical data for As/Mo-4 sample, which was obtained in a satisfactory purity, were used in combination with the shape of the titration curves of the acid-base reactions¹. The trace quantities of silicate and borate are assumed to be roughly compensated by electropositive metal cations (Ba, Al, Fe). The small amount of nitrate anions seems to be compensated by potassium rather than sodium cations because sodium nitrate is washed out with liquid ammonia more readily than potassium nitrate. After subtracting potassium nitrate and nondetermined impurities, the following data were derived from Table III for the composition of the pure substance (%):

As	Mo	Na	K
4.53	49.75	10.90	3.00

Several alternative formulae are consistent with this composition. The formulae, however, should also be consistent with the consumption of the Lux acid in the titration of the $\text{As}_2\text{O}_7^{4-}$ and MoO_4^{2-} Lux bases yielding the substance studied. According to the results of analysis, however, the As: Mo ratio is 2 : 17 whereas the potentiometric titration¹ indicate the formation of an anion with the As : Mo ratio 2 : 24. This can be explained so that although the heteropoly anion is formed preferentially, it shares the potential jump with the reaction of the remaining molybdate to dimolybdate; the latter reaction, though, concerns only the molybdate that has remained unused after the formation of the heteropoly anion. The combined results of the analyses and of the potentiometric titrations lead to three empirical formulae with the lowest deviation of the calculated values from the observed ones, *viz.*

TABLE VI

Calculated and observed elemental composition of As/Mo-4 sample and takeup of I_2O_5

Sample	Elemental composition, %				I_2O_5 takeup, mol per mol MoO_4^{2-} , for the As: Mo molar ratio of		
	As	Mo	Na	K	1 : 8	1 : 12	1 : 24
Found	4.53	49.75	10.90	3.00	0.670	0.668	0.576
Calculated for:							
$(\text{Na},\text{K})_{18}\text{As}_2\text{Mo}_{18}\text{O}_{68}$	4.35	50.11	10.96	3.01	0.612	0.582	0.543
$(\text{Na},\text{K})_{16}\text{As}_2\text{Mo}_{17}\text{O}_{64}$	4.64	50.52	10.29	2.83	0.648	0.604	0.551
$(\text{Na},\text{K})_{16}\text{As}_2\text{Mo}_{18}\text{O}_{67}$	4.44	51.22	9.84	2.71	0.668	0.626	0.562

$(\text{Na,K})_{18}\text{As}_2\text{Mo}_{18}\text{O}_{68}$, $(\text{Na,K})_{16}\text{As}_2\text{Mo}_{17}\text{O}_{64}$, and $(\text{Na,K})_{16}\text{As}_2\text{Mo}_{18}\text{O}_{67}$ (Table VI).

The magnetic behaviour of the substance can hardly be explained in terms of unpaired electrons in an antiferromagnetic interaction. A number of hexavalent molybdenum compounds exhibit temperature-independent paramagnetism^{15,16}, some substances prepared from nitrate melts are capable of retaining a very low amount of molecular oxygen¹⁷, and the presence of reducing impurities results in the occurrence of a small amount of molybdenum in a lower oxidation state. Very probably, all of these effects contribute, to various degrees, to the resultant magnetic behaviour. It should be noted that the magnetic moment is very low.

As to the thermal treatment, the substance remains virtually unchanged up to 400°C. The endo effect at 420°C is reversible and is due to melting. The weight loss up to 600°C is due to evaporation of the melt, as indicated by the dependence on the weight of the batch and of the crucible; no decomposition takes place at these temperatures. At higher temperatures, changes are observed in the X-ray diffraction patterns, hence, irreversible decomposition can be assumed to take place above 600°C. The successful preparation of the substance by direct fusion of the components gives evidence that the substance can be considered a sodium salt where the sodium ions can be replaced to an extent by potassium ions without appreciably changing the X-ray diffraction patterns. Moreover, the direct synthesis of the sodium molybdatarsenate by fusion of the components above its melting point seems to be a convenient route to some other analogous heteropoly compounds the solubility of which is less favourable for their preparation from nitrate melts, or to single crystals which are necessary for the complete structure elucidation.

The interpretation of the molecular spectra is based on the published data for $[\text{X}^n+(\text{Mo,W})_{12}\text{O}_{48}^{(8-n)-}]$ anions¹⁸. The absorption bands could thus be assigned to the vibrations of four Mo—O bond types differing in the bond order, their number in the molecule, and, for bridge bonds, in the Mo—O—Mo angle. Considering some other heteropoly anion with a known structure (*e.g.*, $\text{As}_2\text{Mo}_{18}\text{O}_{62}^{6-}$) we found the four bond types basically preserved; only a deeper differentiation occurs between them, which — owing to the lower symmetry of the anion — gives rise to a greater number of bands and a shift in their positions with respect to the former ion. The nature of the bonds in the unknown heteropoly anion under study can be evaluated qualitatively by comparing the corresponding vibrational bands with those in the spectrum of some heteropoly anion of a known structure.

The following conclusions can be drawn from the spectra of the samples studied. The positions of the highest-wavenumber infrared and Raman bands indicate a bond order lowering for the terminal Mo=O groups, which points to a lower degree of crosslinking of the MoO₆ octahedra, a result of which is the occurrence of a greater fraction of such terminal groups in the compound in comparison not only with the $\text{AsMo}_{12}\text{O}_{40}^{3-}$ ion, but also with the $\text{As}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ ion. This is consistent

with the data from analyses, where owing to the higher oxygen content the heteropoly-anion possess a higher negative charge and bonds more alkali metal. A lower degree of crosslinking also implies a smaller number of octahedra connected by their edges which is manifested in a higher intensity of the antisymmetric stretching vibrations of linear Mo–O–Mo bonds with respect to the bent ones. A strengthening of the Mo–O bonds bonded to arsenic can be expected. Although the spectrum is too complex to give unambiguous evidence, the position of some attributable bands is consistent with the above effects. In the arsenate skeletal vibration region, the bands at 710 cm^{-1} and 740 cm^{-1} can be attributed to bridge As–O–As bonds¹⁹, suggesting that the basic hetero unit is the diarsenate ion. This again is in agreement with the experiment, the preparation of the substance studied failing if tetraoxoarsenate is used in place of diarsenate¹. That no heteropoly anion with diarsenate as the hetero unit has been described in the literature seems to be due to the fact that the substances are usually prepared from aqueous systems where diarsenate hydrolyzes instantaneously. No heteropoly anion whose structure is based on the As–O–As bond and which emerged from nonaqueous system and thus is unhydrated has been so far reported^{20,21}, and so the substance studied by us can be considered a heteropoly compound of a novel type. The composition and structure of the substance, however, could only be elucidated based on X-ray diffraction data for which single crystals would be requisite.

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