March, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *56*, *941—942 (1983)* 941

Preparation of Tetraethylammonium Hexamolybdate by the Use of Extraction Method

Katsuo MURATA,* Etsuko YAMAMOTO, and Shigero IKEDA
Department of Chemistry, Faculty of Science, Osaka University 1-1 Machikaneyama-cho, Toyonaka, Osaka 560

(Received April 30, 1982)

Synopsis. It was found that cyclohexanone selectively extracts hexamolybdate from weakly acidic solutions. Tetraethylammonium hexamolybdate was prepared as precipitate in the extracted phase by the addition of alcoholic tetraethylammonium chloride solution. This compound was confirmed to be $[(C_2H_5)_4N]_2Mo_6O_{19}$ by elementary analysis and Raman measurements.

Alkylammonium salt of hexamolybdate was at first prepared from the acidified aqueous molybdate solutions by the use of precipitation and recrystallization.[1] However, it has not been claimed that $Mo_6O_{19}^{2-}$ species is present in the aqueous molybdate solutions.[2] The authors found a small amount of hexamolybdate ion in the acidified molybdate solutions,[3] which was selectively extracted into cyclohexanone. This finding revealed a new extracting procedure for preparation of hexamolybdate salt.

Experimental

Reagent and Apparatus. A molybdenum solution was prepared from sodium molybdate $Na_2MoO_4 \cdot 2H_2O$ of analytical reagent grade and was standardized by gravimetric method of oxinate.[4] Polynuclear molybdate complexes were produced by means of acidification of this molybdate solution.

Extraction procedure is as follows. Ten ml of acidified molybdate solution and equal volume of cyclohexanone were shaken for 20 min. The molybdenum content of the aqueous solutions before and after extraction was determined by atomic absorption spectrometry.[5] Tetraethylammonium hexamolybdate was obtained as precipitate by the addition of alcoholic tetraethylammonium chloride solution to the extracted phase.

Raman spectra were taken with a JASCO Model R750 Raman Spectrophotometer with a triple monochromator by using 514.5 nm line of Ar^+ laser as the excitation source.

Results and Discussion

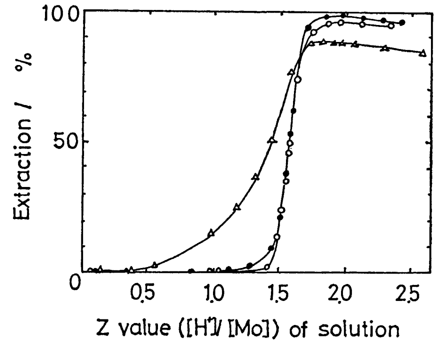

Fig. 1. Extraction curves plotted against Z value of solutions.
—○—: $[Mo]=1.0\times10^{-1}$ M, —●—: $[Mo]=1.0\times10^{-2}$ M, —△—: $[Mo]=1.0\times10^{-3}$ M.

TABLE 1. ELEMENTARY ANALYSIS OF SOME EXTRACTS AND THE CALCULATED VALUES

	Found[a] (%)			Calculated (%)	
	(A)	(B)	(C)	$[(C_2H_5)_4N]_2$-Mo_6O_{19}	$[(C_2H_5)_4N]_4$-Mo_8O_{26}
C	16.67	16.97	17.17	16.86	7.06
H	3.51	3.55	3.57	3.54	5.88
N	2.45	2.50	2.42	2.46	3.95
Mo	49.26	50.23	49.79	50.49	54.18

a) The extracts (A), (B), and (C) were prepared from acidic solutions of pH 2.24(Z=1.58), pH 1.87(Z=1.67), and pH 0.97(Z=2.34), respectively, and then the products were precipitated as tetraethylammonium salt.

$$7\,MoO_4^{2-} + 8\,H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4\,H_2O \qquad Z = 1.14 \quad (1)$$

$$8\,MoO_4^{2-} + 12\,H^+ \rightleftharpoons Mo_8O_{26}^{4-} + 6\,H_2O \qquad Z = 1.50 \quad (2)$$

$$6\,MoO_4^{2-} + 10\,H^+ \rightleftharpoons Mo_6O_{19}^{2-} + 5\,H_2O \qquad Z = 1.67 \quad (3)$$

Heteropolymolybdic acid has been easily extracted by oxygen-containing solvents such as ethers, alcohols, esters, and ketones,[6] but isopolymolybdic acid is not extracted so well by these solvents.[7] The present authors found a good solvent for the extraction of isopolymolybdic acid. Cyclohexanone can efficiently extract yellow polynuclear molybdate from the weakly acidic solutions. The extraction curves for the acidified molybdate solutions of 100, 10, and 1 mM were shown in Fig. 1. The abscissa indicates Z value (the molar ratio of reacted H^+ ion to initially present MoO_4^{2-} ions in the polymerization reaction of molybdate) of molybdate solutions, which exhibits approximately polymerization degree of polynuclear molybdate.[2] It can be seen that each extraction curve shows a similar range of Z value for the optimum extraction as shown in Fig. 1. It is expected from the steep rise of the extractability about Z=1.5 that octamolybdate or hexamolybdate might be concerned with this extraction. The authors could obtain a solid yellow extract as precipitate from the organic phase by the addition of 1% methanol solution of tetraethylammonium chloride. In order to clarify the extracted species, three kinds of extracts were obtained by means of the extraction from different acidic solutions followed by the precipitation as tetraethylammonium salt. Table 1 gives the results of elementary analysis. Three kinds of extracts show similar results. Moreover, these results are close to the calculated value

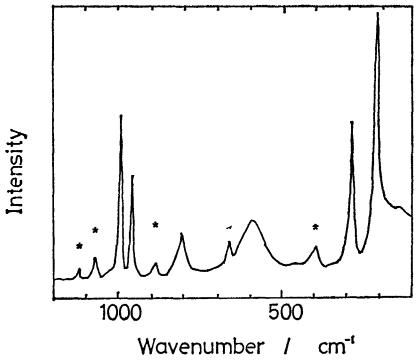

Fig. 2. Raman spectrum of the extract (B), which was obtained by extracting from pH 1.87 (Z=1.67) and then precipitating as tetraethylammonium salt in cyclohexanone.
*Raman lines are attributed to tetraethylammonium group.

of hexamolybdate, not octamolybdate. Therefore, these results indicate that the extracted species would be hexamolybdate. Figure 2 shows Raman spectrum of the extract (B). It exhibits four intense Raman lines at 990, 963, 286, and 210 cm^{-1}. Raman lines marked with an asterisk are attributed to tetraethylammonium group. This Raman spectrum resemble closely to that of tetrabutylammonium hexamolybdate $[(C_4H_9)_4N]_2Mo_6O_{19}$, which was previously prepared by means of precipitation from acidified aqueous solution and then recrystallization with acetone.[8] Thus the Raman spectrum also indicates that the extract (B) is hexamolybdate. Raman spectra of acidified molybdate solutions, however, are different from those of solid hexamolybdate. The authors found only small amounts of hexamolybdate ion in the weakly acidic solution (Z=1.56—2.05).[3] Consequently, the precipitate obtained from these solutions always contains small amounts of hexamolybdate and large amounts of other molybdate, and recrystallization is necessary to obtain pure hexamolybdate. The yield of hexamolybdate is small. In contrast to this, the extraction method by the use of cyclohexanone results in the production of hexamolybdate with a high yield. The extraction of hexamolybdate is so selective that recrystallization is not required. Since the formation of $Mo_6O_{19}^{2-}$ species is limited to a small extent in the weakly acidic solutions, a longer time of 20 minutes is needed to attain the extraction equilibrium. But this extraction method is better to obtain pure solid hexamolybdate than the previous preparative method by the use of precipitation procedure alone from the weakly acidic solution.

The authors wish to express their thanks to Professor Yukiyoshi Sasaki, the University of Tokyo, for his helpful discussions.

References

1) J. Fuchs and K. F. Jahr, *Z. Naturforsch., Teil B*, **23**, 1380 (1968).
2) K. Tytko and O. Glemser, *Adv. Inorg. Chem. Radiochem.*, **19**, 239 (1976).
3) K. Murata and S. Ikeda, *Spectrochim. Acta*, in press.
4) M. Borrel and R. Paris, *Anal. Chim. Acta*, **4**, 267 (1950).
5) H. Oguro, *Bunseki Kagaku*, **23**, 1362 (1974).
6) C. Wadelin and M. G. Mellon, *Anal. Chem.*, **25**, 1668 (1953).
7) T. Fujinaga, T. Hori, and Y. Kaneda, *Bunseki Kagaku*, **27**, 395 (1978).
8) R. Mattes, H. Bierbusse, and J. Fuchs, *Z. Anorg. All. Chem.*, **385**, 230 (1971).