Synthesis and Characterization of 18-Molybdopyrophosphate Complex

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(Received February 7, 1990)

The existence of a heteropoly 18-molybdopyrophosphate was ascertained in both solid and solution states. The yellow complex was formed in solutions of 0.05 M (M=mol dm^{-3}) Mo(VI)/5×10^{-3} M pyrophosphate/0.1—0.7 M HCl/60% (v/v) CH_3CN at ambient temperatures, being isolated as tetraalkylammonium (R_4N^+) salts where R=n-C_4H_9 and C_2H_5. The presence of organic solvents was essential for the preparation of the complex. The 18-molybdopyrophosphate complex underwent a four-step reduction in 95% (v/v) CH_3CN-water containing 0.1 M $HClO_4$, yielding mixed-valence blue species by the electrochemical reduction at the respective steps of a reversible two-electron transfer. The heteropoly skeleton is retained in the blue complexes. The UV-visible and IR spectroscopic characteristics, and the formation conditions of the 18-molybdopyrophosphate complex were also elucidated.

Structurally, pyrophosphate can be regarded as a dimerized form of orthophosphate. In contrast to orthophosphate which can form a variety of heteropolymolybdate complexes, only few heteropoly complexes have been reported for pyrophosphate, although considerable effort has been devoted to the preparation.[1] In the presence of pyrophosphate, purplish-blue coloration is noticed with the Fiske-Subbarow's reagent,[2-4] and Lucena-Conde and Prat's Mo(VI)-Mo(V) reagent systems.[5,6] The color-developing rate is rather slow compared with that of the reduced species of 12-molybdophosphate. Based on these behaviors, the spectrophotometric determination of pyrophosphate was proposed, the chemical properties of the blue species being left uncertified. The difficulty in certifying such pyrophosphate complexes may be presumably due to the facts that pyrophosphate ion is very susceptible to the acid- and molybdenum-catalyzed hydrolytic degradation,[7] and that orthophosphate ion thus produced in situ gives stable orthophosphate complexes.

Rosenheim and Schapiro isolated lithium and sodium salts of molybdopyrophosphate with a compositional ratio of Mo/P_2O_7=12/1 by heating an acidic mixture of Mo(VI) and pyrophosphate.[8] Their method was based on the insolubility of the salts of 12-molybdopyrophosphate; 12-molybdophosphate complexes formed simultaneously were very soluble under the conditions. However, the chemical properties of 12-molybdopyrophosphate have not been elucidated so far, even though it is the first example of molybdopyrophosphate complexes.

In the present work we have found another example of a yellow molybdopyrophosphate complex with a composition of Mo/P_2O_7=18/1. The complex was purely isolated as tetrabutylammonium (n-Bu_4N^+) salts from acidic Mo(VI) solutions containing water-miscible organic solvents. One of the most interesting properties of the complex is that the yellow complex is electroreduced to blue species. The complexes in oxidized yellow and reduced blue states are characterized by UV-visible spectroscopic and voltammetric measurements. The IR spectroscopic characteristics of the complex are also described.

Experimental

UV-visible spectra were recorded on a Hitachi Model 220-A spectrophotometer. Voltammetric measurements were carried out with a PAR (Princeton Applied Research) Model 174-A polarographic analyzer. The voltammograms were recorded on a Yokogawa Model 3023 X-Y recorder. The working electrode was a glassy carbon (GC) rod of a 3 mm diameter (GC-30S, Tokai Carbon) which was mounted in a Teflon tube by a silicone rubber tubing. A saturated calomel electrode (SCE) was used as a reference, along with a platinum counter electrode. Controlled potential electrolysis was carried out with a Hokuto Denko Model HA-501 potentiostat. Coulometric analysis was made with a Hokuto Denko Model HF-202D coulometer. IR spectra were obtained with a Hitachi Model 270-30 spectrophotometer as KBr pellets. The TG-DTA measurements were made with a Rigaku Denki Model 8002-SD thermal analyzer.

All reagents were of reagent grade and used as received.

Results and Discussion

Synthesis of the 18-Molybdopyrophosphate Complex. The 18-molybdopyrophosphate complex was isolated according to the following procedure. Three grams of $Na_2MoO_4 \cdot 2H_2O$ and 0.56 g $Na_4P_2O_7 \cdot 10H_2O$ were dissolved in ca. 90 ml of water, followed by the addition of 13 ml of concd HCl. To the 100 ml quantity of the solution, 150 ml of acetonitrile was added. The final solution was stirred by means of a magnetic stirrer for 1 h at ambient temperatures. The solution changed to yellow during this procedure. Addition of 2 g of solid n-Bu_4NBr produced orange-yellow precipitates. The precipitates were collected by filtration, washed successively with water and ethanol, and dried over Drierite in a desiccator. The yield was ca. 1.4 g. The salts were further purified by recrystallization from acetonitrile, although the crystals decayed slowly in open air.

The n-Bu_4N^+ crystals were ground in an agate mortar to fine powders, which were used in the following experiments. The tetraethylammonium (Et_4N^+) salts of 18-molybdopyrophosphate were obtained in a similar manner; however, the recrystallization of the Et_4N^+ salts was unsuccessful because of the lack of proper solvents to dissolve them.

The results of elemental analysis for the purified n-Bu_4N^+ salts are summarized. Found: Mo, 45.93; P, 1.60; C, 20.46; H, 3.79; N, 1.45%. Calcd for $(n\text{-}Bu_4N)_4P_2Mo_{18}O_{61}$: Mo, 46.24; P, 1.66; C, 20.58; H, 3.89; N, 1.50%. In the TG-DTA, the evolution of water was not observed up to 290 °C.

In parallel with the elemental analysis, a known amount of the complex salts was decomposed in 1 M ammonia solution and subjected to an HPLC-flow injection analysis.[9] No orthophosphate ions were detected but the stoichiometric amount of pyrophosphate ions was found in the solution. It should be emphasized that the present heteropolyanion undoubtedly contains pyrophosphate as a heteroion.

UV-Visible Spectroscopic Measurements. The 18-molybdopyrophosphate complex dissolves in organic solvents such as acetone, acetonitrile, 1,4-dioxane, and dimethyl sulfoxide to give yellow solutions but it is insoluble in water or ethanol. Figure 1 shows a UV-visible spectrum of 1.44×10^{-5} M 18-molybdopyrophosphate in neat acetonitrile. The absorption spectrum is characterized by a round maximum at 310 nm. The spectrum is unchanged for at least a week and conforms to Beer's law in the whole spectral region studied.

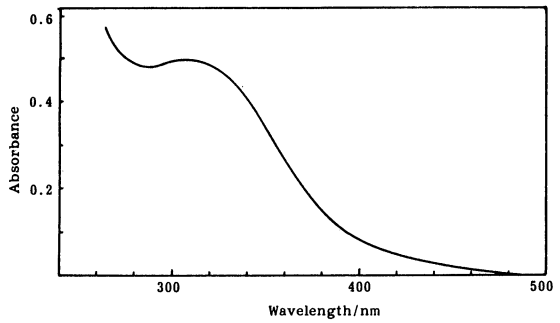

Fig. 1. A UV-visible spectrum of 1.44×10^{-5} M 18-molybdopyrophosphate in neat acetonitrile. Path length, 1 cm.

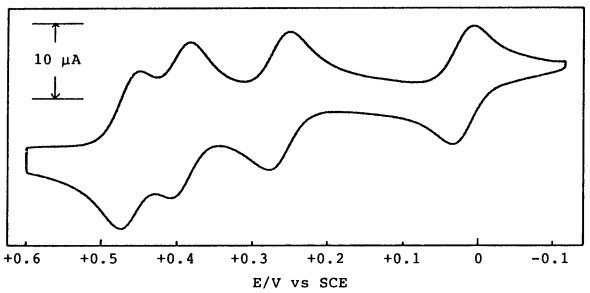

Fig. 2. A cyclic voltammogram of 1.44×10^{-4} M 18-molybdopyrophosphate in 95% (v/v) CH_3CN containing 0.1 M $HClO_4$. Scan rate, 100 mV s^{-1}.

Voltammetric Measurements. Figure 2 shows a cyclic voltammogram of 1.44×10^{-4} M 18-molybdopyrophosphate in 95% (v/v) CH_3CN-water containing 0.1 M $HClO_4$. The yellow anion is also stable under these conditions; however, it decomposes gradually in solutions of <90% (v/v) CH_3CN. Four well-defined reduction waves are well-reproduced. Each current is dependent on the square root of scan rate (20—200 mV s^{-1}), indicating that the wave is diffusion-controlled. Coulometric analysis has shown that each reduction wave corresponds to a two-electron transfer. The peak-potentials (E_p's) are independent of scan rate, and the separation of the cathodic and anodic E_p's for each couple is 27±2 mV, which shows the reversible nature of each wave.

Heteropolyanions with the Keggin and Dawson structures undergo multi-step reversible two-electron reductions to mixed-valence blue species.[10] Similarly, the electrochemical reduction of 18-molybdopyrophosphate produces mixed-valence blue species, each of which can be distinguished by the inherent coloration characteristics. In order to obtain visible spectra of the 4-, 6-, and 8-electron reduction species, 18-molybdopyrophosphate was dissolved to a concentration of 8.9×10^{-5} M in 95% (v/v) CH_3CN-water containing 0.1 M $HClO_4$ and electrolyzed by controlled potential electrolysis at +0.35, +0.15, and −0.05 V, respectively. During controlled potential electrolysis, the solution was bubbled with nitrogen gas to avoid possible oxidation by dissolved oxygen. The absorption spectra of the respective blue species are shown in Fig. 3. The peak separation between the 1st and 2nd waves was so small that the 2-electron reduction species was not distinguished.

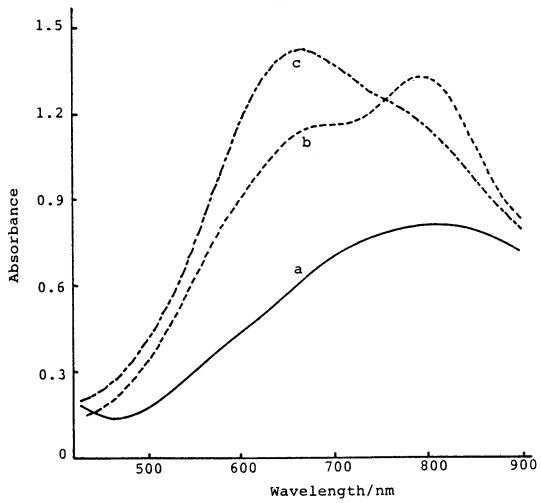

Fig. 3. Visible spectra of the reduced forms of 8.9×10^{-5} M 18-molybdopyrophosphate in 95% (v/v) CH_3CN containing 0.1 M $HClO_4$. (a), (b), (c); 4-, 6-, and 8-electron reduction species respectively. Path length, 5 mm.

The heteropoly skeleton was found to be retained in each of the reduced blue species, since the original yellow heteropolyanion was restored by the reoxidation at +0.70 V.

IR Spectroscopic Measurements. Curve (a) of Fig. 4 shows an IR spectrum of 18-molybdopyrophosphate. The spectrum is characterized by absorption bands at 1118 and 1090 cm^{-1} which can be assigned to the P_2O_7 group.[11] In the Mo-O stretching and bending region (<1000 cm^{-1}), the bands at 966 and 942 cm^{-1} can be assigned to $Mo{=}O_{terminal}$ bonds. In addition, the spectrum contains bands at 877, 810, and 780 cm^{-1} corresponding to the Mo-O-Mo bridge vibrations. The bands at 1500—1300 cm^{-1} are due to the n-Bu_4N^+ group.

In order to obtain the salts of blue species, ca. 0.06 g of the n-Bu_4N^+ salts was dissolved in 25 ml of 95% (v/v) CH_3CN-water containing 0.1 M $HClO_4$ and electrolyzed by controlled potential electrolysis at each reduction potential. An aliquot of solid Et_4NBr was added at the end of each electrolysis. The Et_4N^+ salts of blue species were precipitated by the addition of ethanol. As the typical example, an IR spectrum of the 4-electron reduction species obtained by controlled potential electrolysis at +0.35 V is shown in curve (b) of Fig. 4. The bands due to the Mo-O-Mo bridges decreased in intensities while the band due to the $Mo{=}O_{terminal}$ bond remained unchanged. Simultaneously the intensities of the bands due to the P_2O_7 group decreased and the 1118 cm^{-1} band in curve (a) shifted to shorter wave numbers. These behaviors are similar to those observed for the $[S_2Mo_{18}O_{62}]^{4-}$ and $[PMo_{12}O_{40}]^{3-}$ anions.[12-14]

Formation of 18-Molybdopyrophosphate in the Mo(VI)/HCl/CH_3CN System. It is known that acidification of aqueous Mo(VI) solutions causes condensation in definite steps to produce a family of isopolymolybdates, i.e., $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$, and $[Mo_{36}O_{112}]^{8-}$ etc. In the presence of water-miscible organic solvents such as acetonitrile, acetone, ethanol, and 1,4-dioxane,[15] Mo(VI) solutions turned pale-yellow due to $[Mo_6O_{19}]^{2-}$ which shows absorption maxima at 222, 257, and 325 nm.[16] This behavior makes it difficult to certify the formation of yellow heteropolyanions in aqueous organic solutions. We have recently demonstrated that α- and β-$[PMo_{12}O_{40}]^{3-}$, and $[Mo_6O_{19}]^{2-}$ formed in aqueous organic solutions can easily be distinguished from each other by voltammetric measurements.[17] Similarly voltammetric measurements were carried out to obtain the formation conditions of 18-molybdopyrophosphate.

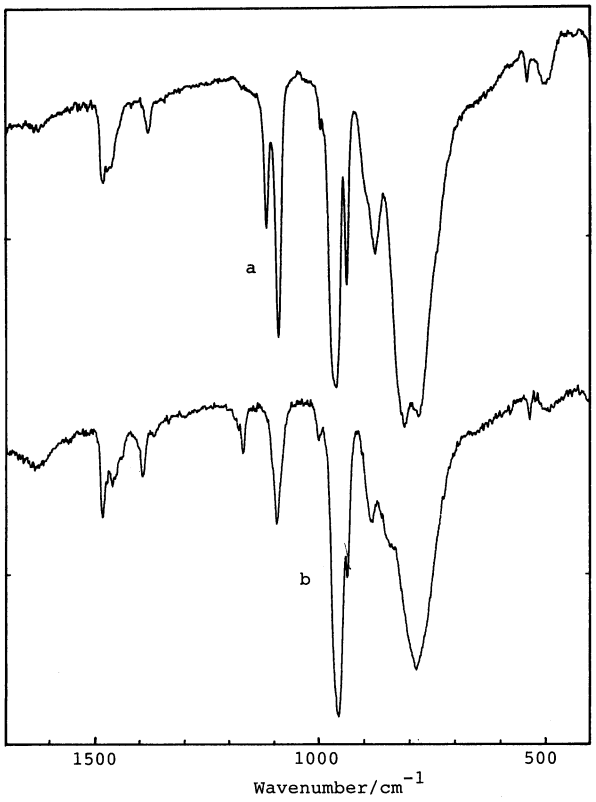

Fig. 4. IR spectra of $(n\text{-}Bu_4N)_4P_2Mo_{18}O_{61}$ in the KBr pellets. (a) The yellow species; (b) the 4-electron reduction species.

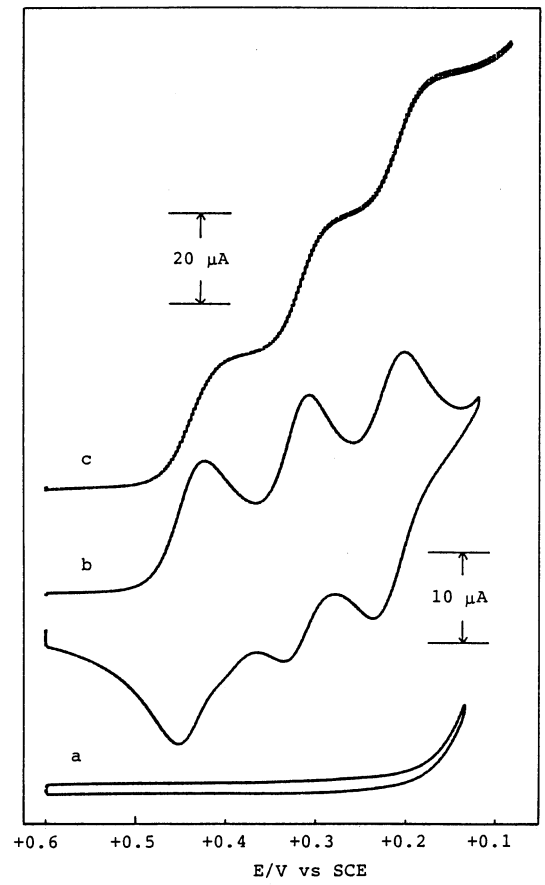

Fig. 5. Cyclic (a, b) and normal pulse (c) voltammograms of the 0.05 M Mo(VI)-50% (v/v) CH_3CN-0.5 M HCl system. (a) Without pyrophosphate; (b), (c) with 4×10^{-4} M pyrophosphate. Scan rate, (a), (b) 100 mV s^{-1}; (c) 5 mV s^{-1}.

Curve (a) in Fig. 5 shows a cyclic voltammogram of 0.05 M Mo(VI) in 50% (v/v) CH_3CN-water containing 0.5 M HCl. No reduction waves were observed until the sharp current rise around +0.1 V, which is due to the reduction of $[Mo_6O_{19}]^{2-}$.[18] As described above, the solution shows pale-yellow due to $[Mo_6O_{19}]^{2-}$. On the addition of 4×10^{-4} M pyrophosphate, the solution turned yellow, and three reduction waves appeared with peak-potentials (E_p's) of +0.425, +0.308, and +0.202 V, as shown in curve (b). Oxidation peaks occurred at +0.452, +0.335, and +0.235 V in the reverse anodic scan. Each wave was diffusion-controlled. The reduction currents increased gradually with time, attaining the constant value around 20 min after the addition of pyrophosphate. In normal pulse voltammetry, it is shown that the three reduction waves are of equal height (curve c). This behavior can be accounted for in terms of the formation of the yellow 18-molybdopyrophosphate complex. After the 20-min current increase period, the yellow complex is stable in the solution as judged by no current change.

Since pyrophosphate ions were very susceptible to hydrolytic degradation in acid solutions, a cyclic voltammogram was taken for the 0.05 M Mo(VI)-50% (v/v) CH_3CN-0.5 M HCl solution containing 4×10^{-4} M orthophosphate instead of pyrophosphate. As shown in curve (b) of Fig. 6, three reduction waves of different height were obtained with E_p's of +0.375, +0.275, and +0.17 V. When the solution was allowed to stand, the 1st reduction wave decreased with a simultaneous increase of the 3rd wave while the 2nd wave remained unchanged, which is due to the transformation of $[\beta\text{-}PMo_{12}O_{40}]^{3-}$ to the α-form.[17] Thus, voltammetric behaviors for orthophosphate are entirely different from those for pyrophosphate shown in Fig. 5. It can be concluded that the voltammetric waves in Fig. 5 are ascribed to the reduction of 18-molybdopyrophosphate.

In order to elucidate the formation conditions of the yellow 18-molybdopyrophosphate complex, normal pulse voltammetric measurements were made for a series of 0.05 M Mo(VI)-70%(v/v) CH_3CN solutions containing 2×10^{-4} M pyrophosphate. Curve (a) of Fig. 7 shows the 1st reduction current as a function of the HCl concentration. The 18-molybdopyro-

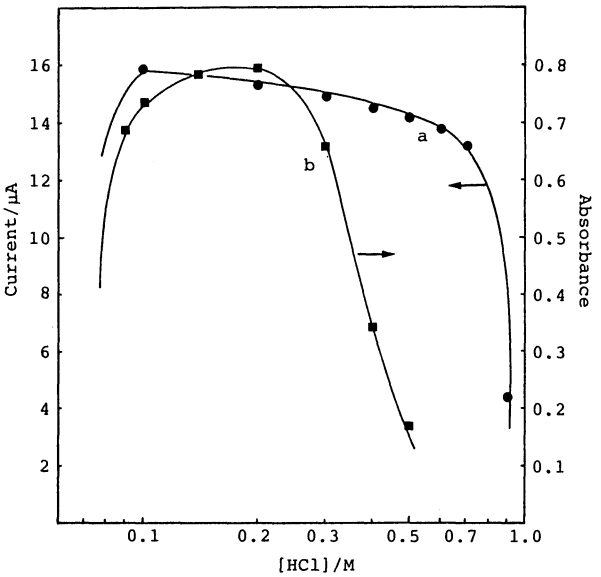

Fig. 7. The formation range of 18-molybdopyrophosphate and $[Mo_6O_{19}]^{2-}$ for the 0.05 M Mo(VI)-70% (v/v) CH_3CN system as a function of the HCl concentration.
(a) Normal pulse voltammetric 1st reduction currents in the presence of 2×10^{-4} M pyrophosphate; (b) absorbances at 400 nm in the absence of pyrophosphate. Path length, 1 cm.

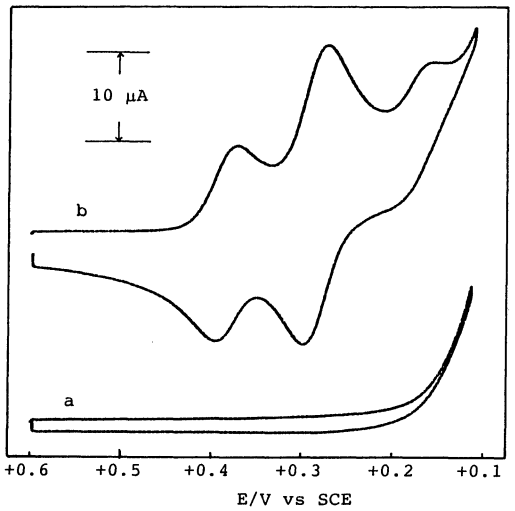

Fig. 6. Cyclic voltammograms of the 0.05 M Mo(VI)-50% (v/v) CH_3CN-0.5 M HCl system.
(a) Without orthophosphate; (b) with 4×10^{-4} M orthophosphate. Scan rate, 100 mV s^{-1}.

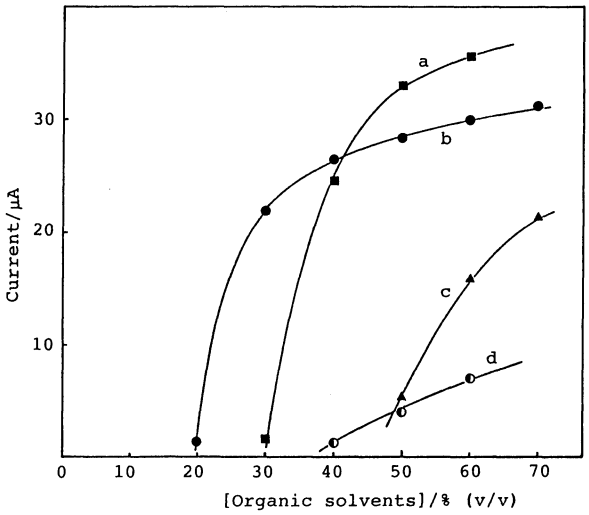

Fig. 8. Effect of concentrations of organic solvents on normal pulse voltammetric 1st reduction currents for the 0.05 mM Mo(VI)-0.4 M HCl-5×10^{-4} M pyrophosphate system containing (a) acetonitrile; (b) acetone; (c) ethanol; (d) 1,4-dioxane.

phosphate anion occurs in the HCl concentration range 0.1—0.7 M. It should be noted that the α- and β-isomers of $[PMo_{12}O_{40}]^{3-}$ form in approximately the same HCl concentration range as 18-molybdopyrophosphate. This formation range shifted to stronger acidities with an increase in the Mo(VI) concentration while other conditions were kept unchanged. For comparison, curve (b) of Fig. 7 shows absorbances at 400 nm for 0.05 M Mo(VI)-70% (v/v) CH_3CN-water solutions to illustrate the formation range of $[Mo_6O_{19}]^{2-}$.

The effects of the nature and concentrations of organic solvents were investigated in solutions containing acetonitrile, acetone, ethanol, and 1,4-dioxane. Figure 8 shows the normal pulse voltammetric 1st reduction currents for 0.05 M Mo(VI)-0.4 M HCl solutions containing 5×10^{-4} M pyrophosphate. In the absence of organic solvents, no voltammetric waves due to the reduction of 18-molybdopyrophosphate were observed. It was found that the formation of 18-molybdopyrophosphate was favored at greater concentrations of organic solvents. Among the organic solvents studied, acetonitrile and acetone were suitable for the preparation of the molybdopyrophosphate. However, our preliminary experiments have shown that the formation of $[Mo_6O_{19}]^{2-}$ is more favorable in acetone-containing solutions than in acetonitrile-containing solutions. Therefore, acetonitrile was chosen as the best for the preparation of 18-molybdopyrophosphate.

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