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Formation and Conversion of Yellow Molybdophosphonate Complexes in Aqueous-Organic Media

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The reaction of Mo(VI) with $PHO_3{}^{2-}$ in acidic solution containing CH_3COCH_3 or CH_3CN led to the formation of the previously unknown 15-molybdobis(phosphonate) complex. The addition of an excess of $PHO_3{}^{2-}$ caused 15-molybdobis(phosphonate) to transform into 16-molybdotetrakis(phosphonate) in the CH_3COCH_3–water system. In the CH_3CN–water system, on the other hand, the spontaneous transformation of 15-molybdobis(phosphonate) into 12-molybdobis(phosphonate) occurred in the presence of an excess of $PHO_3{}^{2-}$ or at greater acidities; the latter complex was also formed in aqueous media. The yellow heteropolyanions underwent electrochemical reductions, yielding mixed-valence blue species.

The electrochemical properties of heteropolymolybdates have been a topic of continuing interest for many years due to their potential use in electrocatalysis and electroanalysis.[1)] In an attempt to tune the structure and redox properties, considerable effort has been devoted to the preparation of electrochemically active heteropoly complexes with new structural types. In view of the considerations that the configuration of a central hetero-anion can determine the overall structure of heteropolyanions, novel heteropoly complexes incorporating X_2O_7- and XO_3-type oxoanions instead of a usual XO_4-type oxoanion are being synthesized in our laboratory. As for heteropoly complexes based on an X_2O_7-type oxoanion, we prepared a yellow 18-molybdodiphosphate anion, $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ from an Mo(VI)–$P_2O_7^{4-}$–HCl–CH_3CN system.[2)] Recently, Kortz and Pope determined the structure as a fused dimer of B-type PMo_9 units;[3)] the usual Dawson complex is based on A-type PMo_9 units. The $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ anion transformed spontaneously into the 15-molybdodiphosphate anion, $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$,[4)] which underwent subsequent transformation into the 12-molybdodiphosphate anion, $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$ in the CH_3CN–water system.[5)]

In the Mo(VI)–$PHO_3{}^{2-}$ system, new heteropoly complexes are expected to form since the heteroatom utilizes only three oxygens to bind the heteropoly structure. Although there have been extensive studies on the preparation of heteropoly complexes, relatively little is known about molybdophosphonate complexes. In an old paper,[6)] Rosenheim and Schapiro synthesized 12-molybdobis(phosphonate) formulated as $2R_2O\cdot P_2O_3\cdot 12MoO_3\cdot nH_2O$ by heating an aqueous solution of MoO_3 and H_2PHO_3, where R = Li, Na, K, and NH_4, although its chemical properties remained to be elucidated. Kwak et al. prepared and characterized a series of salts of $[(PRO_3)_2Mo_5O_{15}]^{4-}$ where R = H, CH_3, C_2H_5, C_6H_5, $C_2H_4NH_3{}^+$ and p-$CH_2C_6H_4NH_3{}^+$.[7)] According to Stalick and Quicksall,[8)] $[(PRO_3)_2Mo_5O_{15}]^{4-}$ (R = CH_3 and $C_2H_4NH_3{}^+$) possessed the same framework as that of $[(PO_4)_2Mo_5O_{15}]^{6-}$ originally determined by Strandberg.[9)] Later, Ozeki et al. determined the crystal structure of $K_4[(PHO_3)_2Mo_5O_{15}]\cdot 2H_2O$.[10)] However, these colorless 5-molybdobis(phosphonate) complexes, which are prepared from aqueous solution, are not electrochemically reducible.

As already reported, the use of water-miscible organic solvents such as CH_3COCH_3 and CH_3CN as auxiliary solvents has offered a promising possibility to synthesize novel heteropoly complexes. In the present study, the existence of the molybdophosphonate complex with a compositional ratio of Mo/P = 15/2 was ascertained in a Mo(VI)–$PHO_3{}^{2-}$–HCl–CH_3COCH_3 or CH_3CN system. The parent 15-molybdobis(phosphonate) complex transformed spontaneously into either the 16-molybdotetrakis(phosphonate) complex or the 12-molybdobis(phosphonate) complex, depending on the nature of the organic solvent, on the Mo(VI)/$PHO_3{}^{2-}$ mole ratio, and on the acidity of the solution. The formation and conversion processes of the molybdophosphonate complexes were elucidated by the combined Raman spectroscopic and cyclic voltammetric studies.

Experimental

Apparatus and Materials. Raman spectra were obtained with a Jobin Yvon Ramanor U-1000 using an Argon laser (488 nm excitation). For quantitative measurements, the Raman intensities were normalized with the intensities of the 1069 and 920 cm^{-1} lines due to the absorption of CH_3COCH_3 and CH_3CN in the aqueous-organic media. In aqueous solution, 0.1 M (M = mol dm^{-3}) $LiNO_3$ was added to each solution and used as an internal standard; the $NO_3{}^-$ line was obtained at 1048 cm^{-1}. The Raman measurements were made at 20 °C. Voltammetric measurements were made with a microcomputer-controlled system. A Tokai GC-30S glassy carbon rod with a surface area of 0.071 cm^2 was used as a working electrode. Prior to each measurement, the electrode was polished manually with 0.25 μm diamond slurry. All potentials were referred to an Ag/AgCl (saturated KCl) electrode and a platinum wire was used as a counter electrode. Coulometric analysis was made with a Hokuto Denko HA-501 potentiostat equipped with a HF-202D coulometer. All electrochemical measurements were made at 25 °C. Infrared (IR) spectra of the solids were measured in the range of 1700—400 cm^{-1} using KBr pellets on a Hitachi 2730 spectrometer. The TG-DTA measurements were made with a Rigaku Denki Model TAS-100 thermal analyzer.

Lithium molybdate Li_2MoO_4 was recrystallized twice from water, then used for Raman measurements in aqueous solution. All other chemicals were of reagent grade and were used as received.

Synthesis of the Molybdophosphonates. Three types of molybdophosphonates were synthesized according to the following procedures, and characterized by elemental analysis, cyclic voltammetry, and IR and Raman spectroscopies.

15-Molybdobis(phosphonate): To a solution of 6.05 g of $Na_2MoO_4\cdot 2H_2O$ in ca. 200 ml of water were added 17.4 ml of concd HCl and 150 ml of acetone. A 0.54 g quantity of $Na_2PHO_3\cdot 5H_2O$ in 130 ml of water was added to the solution. After the solution was stirred for 2 h at room temperature, 3 g of $(n\text{-}C_4H_9)_4NBr$ ($n\text{-}Bu_4NBr$) was added to precipitate a pale-yellow salt. The salt was isolated by filtration, washed with water, ethanol, and acetone, and air-dried. In order to purify further the salt, a 5.0 g quantity was dissolved in 500 ml of acetone; any undissolved solid was removed by filtration, and was reprecipitated by the addition of 80 ml of *n*-hexane. Anal. Calcd for $(n\text{-}Bu_4N)_4[H_6(PHO_3)_2Mo_{15}O_{48}]$: Mo, 43.05; P, 1.85; C, 22.99; H, 4.58; N, 1.68%. Found: Mo, 43.13; P, 1.97; C, 22.95; H, 4.59; N, 1.54%. IR (1300—400 cm^{-1}) 1085, 950, 880, 815, 537 cm^{-1} (Fig. 1a). The TG-DTA measurements showed the weight loss corresponding to the liberation of three water molecules per one empirical formula.

16-Molybdotetrakis(phosphonate): To a solution of 6.05 g of $Na_2MoO_4\cdot 2H_2O$ in 100 ml of water were added 17.4 ml of concd HCl and 350 ml of acetone. To the solution was added 2.7 g of $Na_2PHO_3\cdot 5H_2O$ in 30 ml of water. The resultant yellow solution was stirred for 2 h at room temperature, and the addition of 10 g of $n\text{-}Bu_4NBr$ yielded a colloidal precipitate; a precipitate which could be filtered easily was obtained by the addition of 100 ml of water. The yellow precipitate was filtered off, washed with water and ethanol, and air-dried. Anal. Calcd for $(n\text{-}Bu_4N)_5H_3[H_6(PHO_3)_4Mo_{16}O_{51}]$: Mo, 39.44; P, 3.18; C, 24.69; H, 5.00; N, 1.80%. Found: Mo, 39.67; P, 3.30; C, 25.02; H, 4.75; N, 1.77%. IR (1300—400 cm^{-1}) 1091, 953, 931, 850, 769, 613, 546, 518 cm^{-1} (Fig. 1b). The TG-DTA results showed the weight loss corresponding to the liberation of three water molecules per one empirical formula. The tetrameric nature of the empirical formula is discussed in a later part of this paper.

12-Molybdobis(phosphonate): Twelve grams of $Na_2MoO_4\cdot 2H_2O$ were dissolved in 155 ml of water, and 45 ml of concd HCl and 300 ml of CH_3CN were added. After the addition of 1.0 g of $Na_2PHO_3\cdot 5H_2O$, the solution was stirred for 1 h at ambient temperature. By the addition of 15 g of $n\text{-}Bu_4NBr$, a yellow salt was precipitated; it was collected by filtration, washed with water and ethanol, and air-dried. The $n\text{-}Bu_4N^+$ salt was soluble in CH_3CN to give yellow solutions, and further purified by recrystallization from a 1 : 2 (v/v) $CH_3CN\text{–}C_2H_5OH$ solution. Anal. Calcd for $(n\text{-}Bu_4N)_3H[H_{12}(PHO_3)_2Mo_{12}O_{42}]$: Mo, 42.27; P, 2.27; C, 21.17; H, 4.55; N, 1.54%. Found: Mo, 42.74; P, 2.19; C, 21.76; H, 4.27; N, 1.66%. IR (1300—400 cm^{-1}) 1084, 939, 805, 525 cm^{-1} (Fig. 1c). In the TG-DTA measurements, the observed weight loss corresponded to six water molecules per one empirical formula.

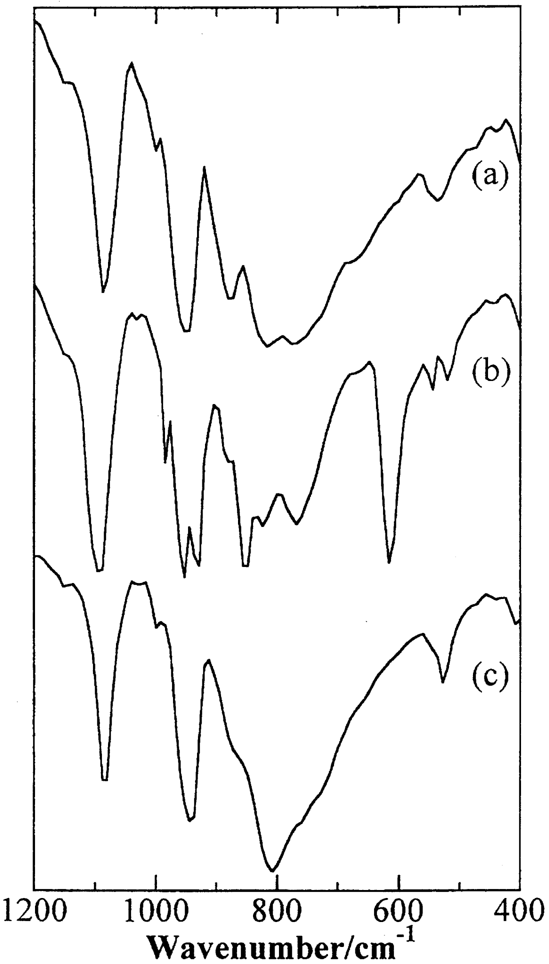

Fig. 1. IR spectra of (a) $(n\text{-}Bu_4N)_4[H_6(PHO_3)_2Mo_{15}O_{48}]$, (b) $(n\text{-}Bu_4N)_5H_3[H_6(PHO_3)_4Mo_{16}O_{51}]$, and (c) $(n\text{-}Bu_4N)_3H\text{-}[H_{12}(PHO_3)_2Mo_{12}O_{42}]$ in the KBr pellets. Numerical data are given in the text.

The 12-molybdobis(phosphonate) complex was also isolated as the Na^+ salt from aqueous solution of high concentrations of Mo(VI) and PHO_3^{2-}. A 60.5 g quantity of $Na_2MoO_4\cdot 2H_2O$ was dissolved in 435 ml of water, followed by the addition of 65 ml of concd HCl. Then, 5.4 g of $Na_2PHO_3\cdot 5H_2O$ was added with stirring to the solution. The addition of an aliquot of NaCl led to immediate precipitation of a yellow salt, which was subsequently washed with water and ethanol. The Na^+ salt was insoluble in water, ethanol, CH_3CN, and CH_3COCH_3, and in other organic solvents. Anal. Calcd for $Na_4[H_{12}(PHO_3)_2Mo_{12}O_{42}]\cdot 12H_2O$: Mo, 49.98; P, 2.69; Na, 3.99%. Found: Mo, 49.74; P, 2.75; Na, 3.81%. The TG-DTA results showed endothermic transformation due to the evolution of water corresponding to 18 water molecules per one empirical formula. Since there was no distinction between the loss of water of hydration and constitutional water, the empirical formula of the Na^+ salt was derived from the corresponding $n\text{-}Bu_4N^+$ salt.

12-Molybdodiphosphate: For comparison studies, the Cs^+ salt of the 12-molybdodiphosphate complex, $Cs_4[H_{12}(P_2O_7)Mo_{12}O_{42}]\cdot 2H_2O$, was prepared according to our previous method.[5)]

Molybdenum was determined spectrophotometrically at 390 nm as the complex with 1,2-dihydroxybenzene-3,5-disulfonic acid (Tiron).[11)] Phosphonate was determined with a Hitachi high-performance liquid chromatograph; this determination procedure confirmed that each heteropoly complex contained PHO_3^{2-} as a heteroion.

For the sake of brevity, the 15-molybdobis(phosphonate), 16-molybdotetrakis(phosphonate), and 12-molybdobis(phosphonate) complexes are sometimes referred to by their Mo/P ratios as the 15/2, 16/4, and 12/2 complexes, respectively.

Results and Discussion

IR and Raman Spectra in the Solid State. The IR spectra for the n-Bu_4N^+ salts of the 15/2, 16/4, and 12/2 complexes are shown in Fig. 1. The three molybdophosphonate complexes were characterized by a band around 1090 cm^{-1}, assigned to the asymmetric stretch of the PO_3 group.[12)]

In order to characterize further the molybdophosphonate complexes, their Raman spectra were compared in Fig. 2, along with that for the Cs^+ salt of 12-molybdodiphosphate, $Cs_4[H_{12}(P_2O_7)Mo_{12}O_{42}]\cdot 2H_2O$ (Fig. 2d). The 15/2 and 16/4 complexes were characterized by sharp Raman lines at 978 and 969 cm^{-1} respectively, while the 12/2 complex showed a pair of Raman lines at 968 and 803 cm^{-1}. The 16/4 and 12/2 complexes exhibited a strong Raman line at nearly the same wavenumber. However, the 968 cm^{-1} line of the latter complex was accompanied by a strong Raman line at 803 cm^{-1}, which makes it possible to distinguish between the two complexes. In the following, the Raman intensities at 978, 969, and 803 cm^{-1} were used as reference to study the formation and conversion of the 15/2, 16/4, and 12/2 complexes in solution. No discussion was made to Raman lines below 800 cm^{-1}, because they were too weak to allow us to study the solution chemistry of the molybdophosphonates.

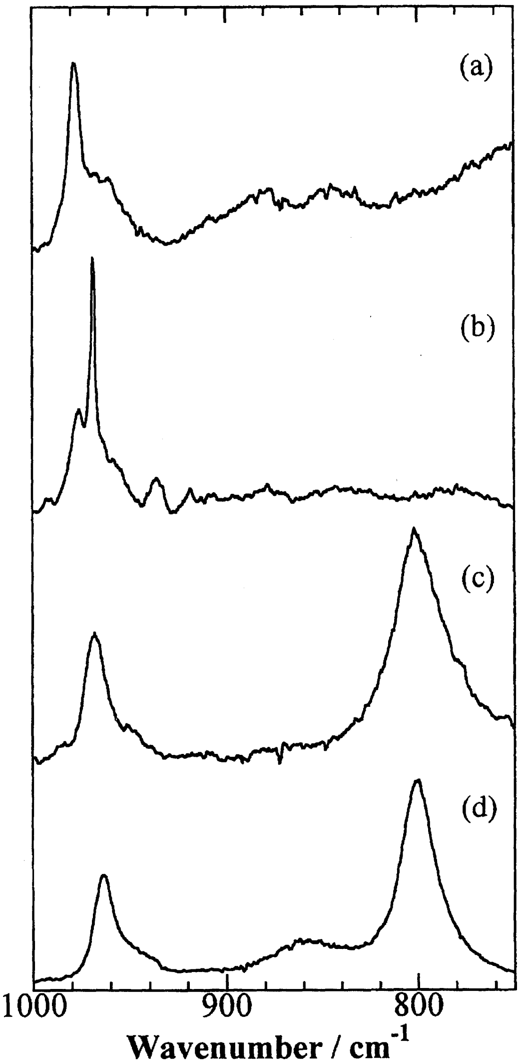

Fig. 2. Raman spectra of (a) $(n\text{-}Bu_4N)_4[H_6(PHO_3)_2Mo_{15}O_{48}]$, (b) $(n\text{-}Bu_4N)_5H_3[H_6(PHO_3)_4Mo_{16}O_{51}]$, (c) $(n\text{-}Bu_4N)_3H[H_{12}(PHO_3)_2Mo_{12}O_{42}]$, and (d) $Cs_4[H_{12}(P_2O_7)Mo_{12}O_{42}]\cdot 2H_2O$.

Voltammetric Behaviors. Figure 3a shows a cyclic voltammogram of 0.5 mM of the 15/2 complex in 98% (v/v) CH_3COCH_3–water containing 0.15 M $HClO_4$, where the heteropolyanion is kinetically stable. An apparent three-step reduction wave was obtained with a current ratio of 2 : 1 : 1. Each wave was diffusion-controlled. Coulometric study showed that the first wave corresponded to a four-electron transfer, and each of the remaining two waves to a two-electron transfer per the empirical formula. Logarithmic

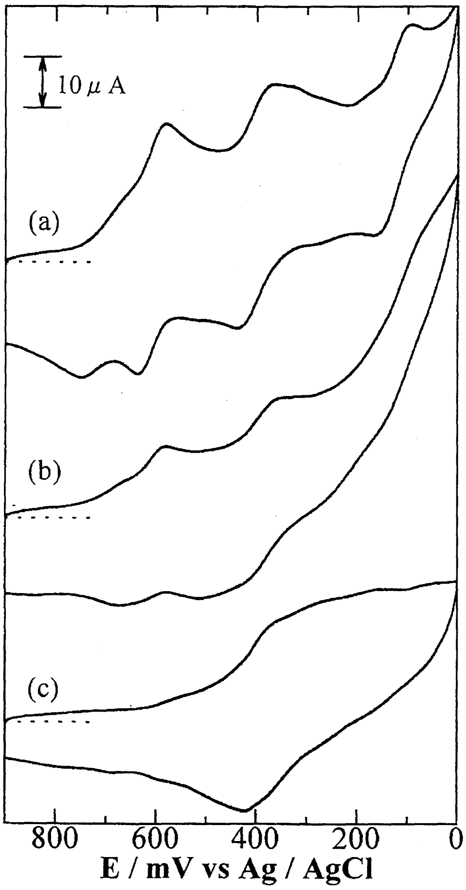

Fig. 3. Cyclic voltammograms for 0.5 mM solutions of (a) the 15/2 and (b) 16/4 complexes in 98% (v/v) CH_3COCH_3–water containing 0.15 M $HClO_4$, and (c) the 12/2 complex in 95% (v/v) CH_3CN–water containing 0.15 M $HClO_4$. Scan rate, 100 mV s^{-1}.

analysis for the first wave in the corresponding normal pulse voltammogram showed that two two-electron waves were united as the apparent four-electron wave at virtually the same potential.

As shown in Fig. 3b, the 16/4 complex showed a two-step reduction wave with a current ratio of 1 : 1, followed by an ill-defined wave. Coulometric analysis indicated that each reduction step involved two electrons per one empirical formula. In general, heteropolymolybdate complexes undergo successive two-electron reductions per a discrete polyanion in the presence of acid.[1,13)] This voltammetric behavior is the basis for the tetrameric nature of the empirical formula, although the first two-electron wave appears to split into two waves. As discussed later, the two one-electron reduction behavior was more clearly seen in the 50 mM Mo(VI)–25 mM PHO_3^{2-}–0.4 M HCl–70% (v/v) CH_3COCH_3 system (Fig. 6e).

On the other hand, the 12/2 complex exhibits only an ill-defined reduction wave in 95% (v/v) CH_3CN–water containing 0.15 M $HClO_4$ (Fig. 3c). Coulometric experiments cannot be made due to the decomposition of the reduced species.

It must be noted that all the yellow molybdophosphonate anions produce mixed-valence blue species by the controlled potential electrolysis at the respective reduction waves.

Formation and Conversion of the 15/2 and 16/4 Complexes in the CH_3COCH_3–Water System. Raman Spectroscopic Investigation: In order to study the formation of the molybdophosphonate complexes, Raman spectra were recorded by keeping [Mo(VI)] = 50 mM, $[PHO_3^{2-}] = 5$ mM, and $[CH_3COCH_3] = 70\%$ (v/v) while varying the HCl concentration (0.1—1.0 M); these spectra are shown in Fig. 4. At HCl concentrations < 0.1 M, only a Raman line due to $[Mo_6O_{19}]^{2-}$ appeared at 986 cm^{-1}.[14,15)] With an increase of the HCl concentration, there appeared a new Raman line at 976 cm^{-1} which, by comparison with the Raman frequency of the reference compounds (Fig. 2a), was assigned to the 15/2 complex. The 976 cm^{-1} line grew with time and attained to the constant value 2 h after the addition of PHO_3^{2-}. It was found that the 15/2 complex was formed in the HCl concentration range of 0.1—0.7 M. At HCl concentrations > 0.6 M, the 976 cm^{-1} line decreased in height with an appearance of a new Raman line at 956 cm^{-1}, indicating the decomposition of the 15/2 complex into $Mo_2O_5^{2+}$.[16)]

After the intensity-increase period, the Raman intensities at 976 cm^{-1} were unchanged with respect to time under the above conditions. With the addition of an excess of PHO_3^{2-}, however, the gradual Raman spectral change was observed. In order to explain this behavior, Raman spectra were also recorded for a 50 mM Mo(VI)–0.4 M HCl–70% (v/v) CH_3COCH_3 system containing various concentrations of PHO_3^{2-}; the results are shown in Fig. 5. The equilibrium was established within 2 h at room temperature, and measurements were made on fully equilibrated solutions. With an increase of the PHO_3^{2-} concentration, the 976 cm^{-1} line arising from the 15/2 complex increased in intensity at the expense of the 986 cm^{-1} line due to $Mo_6O_{19}^{2-}$, and the Raman intensity attained to the maximum value around $[PHO_3^{2-}] = 7$ mM. The 976 cm^{-1} line decreased with further increase of the PHO_3^{2-} concentration. Simultaneously, there appeared a new Raman line at 967 cm^{-1}, indicating the formation of the 16/4 complex and/or the 12/2 complex. The species formed cannot be deduced from the Raman measurements due to the strong absorption of acetone at 792 cm^{-1}. As already described in the Experimental section, however, the 16/4 complex is isolated from these acetone-contain-

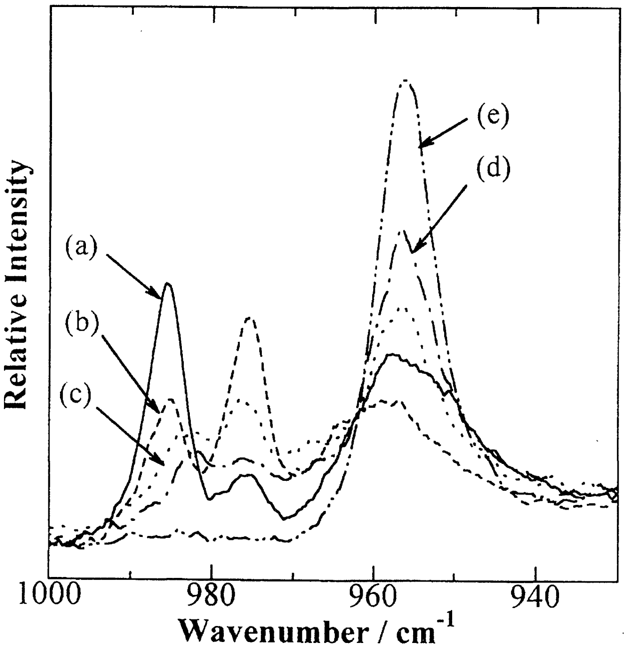

Fig. 4. Raman spectra for 50 mM Mo(VI)–5 mM PHO_3^{2-}–70% (v/v) CH_3COCH_3 systems. [HCl]/M: (a) 0.1; (b) 0.2; (c) 0.6; (d) 0.7; (e) 1.0.

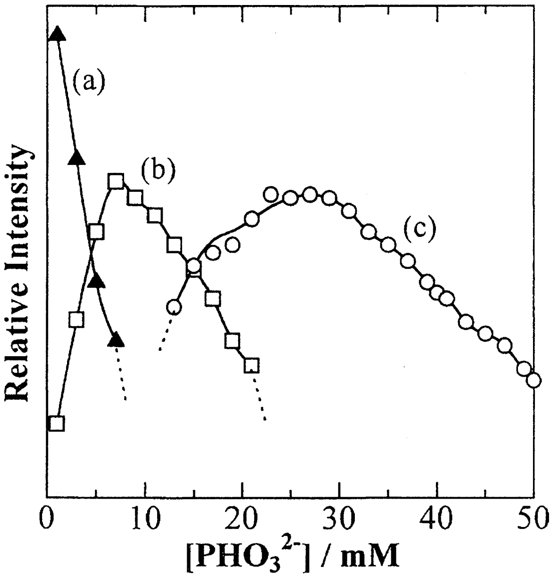

Fig. 5. Effect of the PHO_3^{2-} concentration on Raman intensities at (a) 986, (b) 976, and (c) 967 cm^{-1} for 50 mM Mo(VI)–0.4 M HCl–70% (v/v) CH_3COCH_3 systems.

ing solutions, without the formation of the 12/2 complex at any appreciable concentrations. This fact demonstrates the transformation of the 15/2 complex into the 16/4 complex, depending on the PHO_3^{2-} concentration. For 50 mM Mo(VI)–25 mM PHO_3^{2-}–70% (v/v) CH_3COCH_3 systems, the 967 cm^{-1} line due to the 16/4 complex was obtained at the HCl concentration range of 0.2—0.8 M.

Voltammetric Investigation: Figure 6a shows a cyclic voltammogram for a 50 mM Mo(VI)–5 mM PHO_3^{2-}–0.4 M HCl–70% (v/v) CH_3COCH_3 system. Well-defined reduction waves whose current ratios were 2 : 1 were observed until the current rise due to the reduction of $[Mo_6O_{19}]^{2-}$ around +50 mV.[17] From the Raman results in Fig. 4, it follows that the voltammetric wave can be ascribed to the reduction of the 15/2 complex. The reduction currents increased with time and attained to a constant value 2 h after the addition of PHO_3^{2-}. After the 2-h current increase period, the 15/2 complex was stable, as judged by the absence of changes of the cyclic voltammogram. This behavior is in line with the Raman spectroscopic observations. Coulometric analysis showed that the first wave consumed two electrons per PHO_3^{2-} anion added, which means that the reduction consumed four electrons per the 15/2 complex, in agreement with that shown in Fig. 3a.

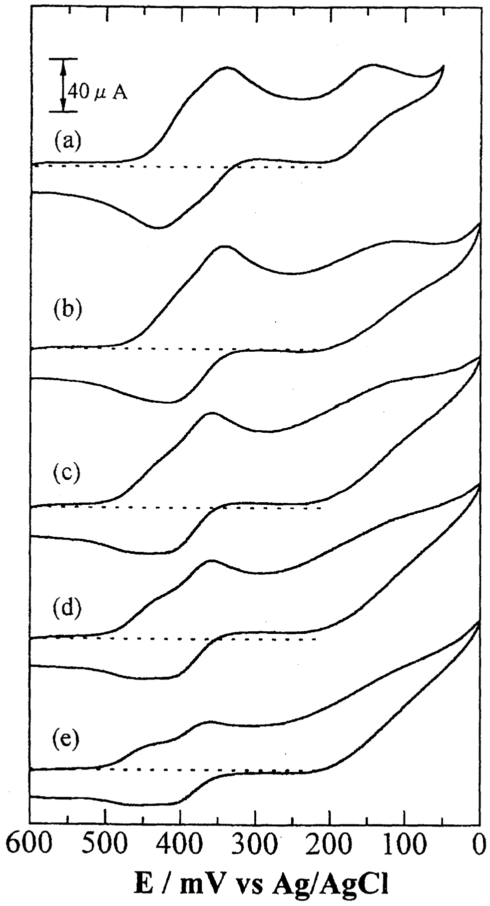

Fig. 6. Cyclic voltammograms for 50 mM Mo(VI)–0.4 M HCl–70% (v/v) CH_3COCH_3 systems. $[PHO_3^{2-}]$/mM: (a) 5; (b) 10; (c) 15; (d) 20; (e) 25. Scan rate, 100 mV s^{-1}.

When $[PHO_3^{2-}] < 10$ mM, the reduction current grew with an increase of the PHO_3^{2-} concentration added. When $[PHO_3^{2-}] > 15$ mM, on the other hand, the voltammetric wave arising from the 15/2 complex showed a gradual decrease in current, and the first wave split into a two-step wave with equal heights (Fig. 6e). On the basis of the Raman results, this behavior cannot be ascribed to the change of the electrode processes of the 15/2 complex, but to the transformation of the 15/2 complex into the 16/4 complex. The voltammetric wave in Fig. 6e is due to the two-step one-electron reduction of the 16/4 complex. The Raman lines at 967 cm^{-1} and the reduction currents were obtained at the same acidities.

Formation and Conversion of the 15/2 and 12/2 Complexes in the CH_3CN–Water System. Raman Spectroscopic Investigation: In the CH_3CN–water system, entirely different behaviors were observed. When Raman spectra were recorded for a 50 mM Mo(VI)–5 mM PHO_3^{2-}–0.3 M HCl–60% (v/v) CH_3CN system, the 976 cm^{-1} line due to the 15/2 complex appeared and increased in intensity with time. After the intensity-increase period, the Raman line remained unchanged on standing, indicating that the 15/2 complex is kinetically stable. As the PHO_3^{2-} concentration was increased, however, the 976 cm^{-1} line decreased and a new Raman line appeared at 805 cm^{-1}. This result clearly shows the transformation of the 15/2 complex into the 12/2 complex, the behavior being in marked contrast to that observed in the acetone-containing solution.

When the HCl concentration was made greater than 0.5 M, the 976 cm^{-1} line decreased with an increase of a Raman line at 805 cm^{-1} even in the presence of 5 mM PHO_3^{2-}. The 976 cm^{-1} line disappeared completely after 1 h equilibration. To obtain the formation conditions for the 15/2 and 12/2 complexes, the Raman intensities at 976 and 805 cm^{-1} were measured after the equilibration for 50 mM Mo(VI)–5 mM PHO_3^{2-}–60% (v/v) CH_3CN systems containing various concentrations of HCl. The results are shown in Fig. 7. The 15/2 complex is the dominant species at HCl concentrations < 0.5 M (Fig. 7a), while the 12/2 complex predominates at the HCl concentration of 0.7 M (Fig. 7b).

Voltammetric Investigation: When a cyclic voltammogram was recorded for a 50 mM Mo(VI)–5 mM PHO_3^{2-}–0.3 M HCl–60% (v/v) CH_3CN system, there appeared a two-step reduction wave with a 2 : 1 current ratio which indicated the formation of the 15/2 complex. Actually the reduction current showed essentially the same dependence on the HCl concentration as the Raman intensities at 976 cm^{-1} (Fig. 7c). As described above, the 15/2 complex was stable under these conditions. In agreement with the Raman results, however, the spontaneous current decrease, which was due to the transformation of the 15/2 complex into the 12/2 complex, was observed with further increase of the PHO_3^{2-} concentration.

Similar behavior was also observed when the HCl concentration was > 0.6 M. As an example, Fig. 8 shows a series of cyclic voltammograms for 50 mM Mo(VI)–0.7 M HCl–60% (v/v) CH_3CN systems. The voltammetric wave due to the 15/2 complex once appeared on the addition of

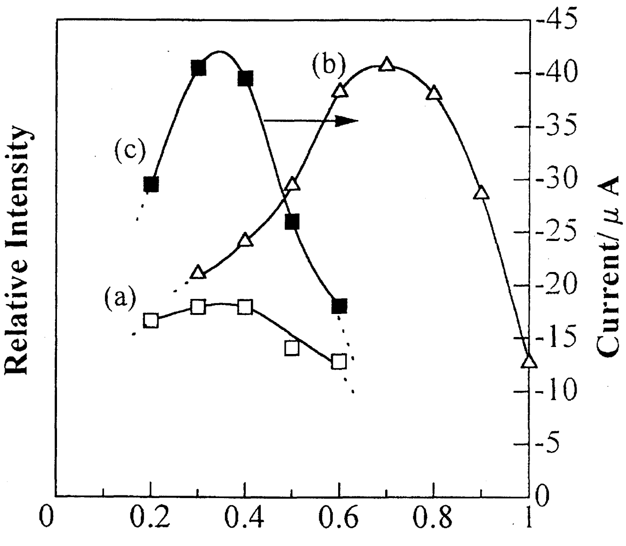

Fig. 7. Effect of acidities on Raman intensities at (a) 976 and (b) 805 cm^{-1} and on (c) reduction currents for 50 mM Mo(VI)-5 mM PHO_3^{2-}–60% (v/v) CH_3CN systems. Measurements were made after equilibration for 2 h.

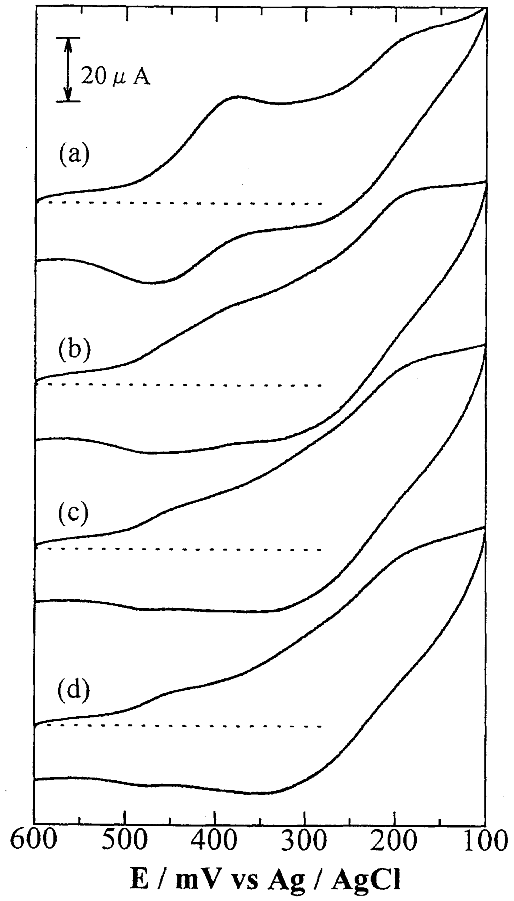

Fig. 8. Cyclic voltammograms for 50 mM Mo(VI)–5 mM PHO_3^{2-}–0.7 M HCl–60% (v/v) CH_3CN systems. Recorded (a) immediately; (b) 5 min; (c) 10min; (d) 20 min after the addition of PHO_3^{2-}.

5 mM PHO_3^{2-}, and the first wave showed a gradual current decrease with time. The ultimate voltammogram was obtained after 20 min equilibration (Fig. 8d).

In conclusion, the conversion processes of the parent $[H_6(PHO_3)_2Mo_{15}O_{48}]^{4-}$ anion into the $[H_6(PHO_3)_4Mo_{16}O_{51}]^{8-}$ and $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ anions were elucidated in aqueous-organic media. It must be added that there is no conversion process between the $[H_6(PHO_3)_4Mo_{16}O_{51}]^{8-}$ and $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ anions.

Formation of the 12/2 Complex in Aqueous Media. According to Rosenheim and Schapiro,[6] the 12/2 complex was precipitated by heating an acidic solution of MoO_3 and H_2PHO_3 at high concentrations. In order to obtain direct information on the formation of the 12/2 complex in aqueous solution, the Raman spectra were also recorded as a function of the HCl concentration (0.7—1.7 M) and of the Mo(VI) concentration (50—500 mM) while maintaining the molar ratio of $[Mo(VI)]/[H_2PHO_3] = 10/1$; in this experiment, Li_2MoO_4 was used instead of $Na_2MoO_4{\cdot}2H_2O$, because of the low solubility of the Na^+ salt of the 12/2 complex. It should be noted that the 807 cm^{-1} line characteristic of the 12/2 complex appeared only at Mo(VI) concentrations > 300 mM. In order to study the formation process of the 12/2 complex, Raman spectra were obtained for a 500 mM Mo(VI)–1 M HCl system containing various concentrations of H_2PHO_3 (Fig. 9). In the absence of PHO_3^{2-}, three Raman lines at 982, 954, and 901 cm^{-1}, assigned to $Mo_{36}O_{112}^{8-}$, were observed.[18—22] The Raman intensities at 982 and 901 cm^{-1} decreased with the addition of PHO_3^{2-}. Simultaneously, the 954 cm^{-1} line shifted to longer wavenumbers, to the limit of 965 cm^{-1} with a simultaneous appearance of the 807 cm^{-1} line, indicating the formation of the 12/2 com-

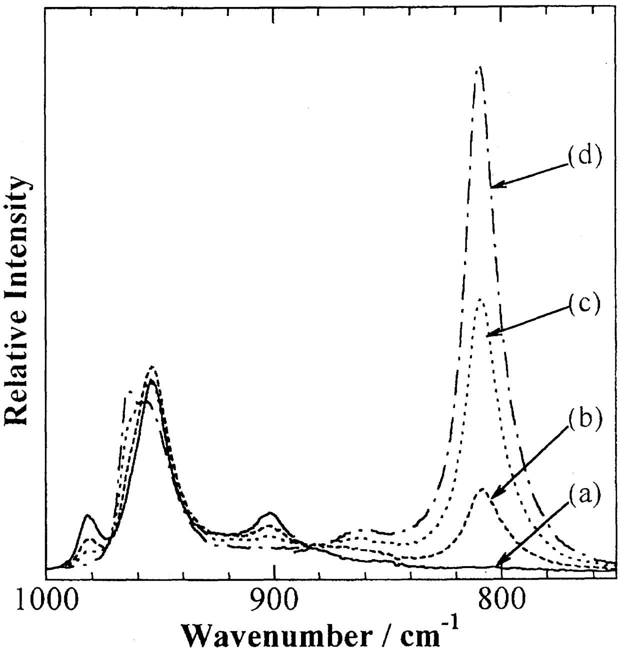

Fig. 9. Raman spectra for 500 mM Mo(VI)–1.0 M HCl systems. $[H_2PHO_3]$/mM: (a) 10; (b) 40; (c) 60; (d) 80. Measurements were made after equilibration for 2 h.

plex. From these solutions, the 12/2 complex was in fact isolated as the Na^+ salt. The Raman intensity at 807 cm^{-1} became maximal at the PHO_3^{2-} concentration of 80 mM. In conclusion, the 12/2 complex was formed in both aqueous and aqueous–CH_3CN media. However the formation processes in the two solutions were entirely different. In the aqueous–CH_3CN media, the 12/2 complex was formed as the result of the transformation of the 15/2 complex, whereas the direct formation of the 12/2 complex occurred in aqueous solution where neither of the 15/2 and 16/4 complexes was detected.

Comparison with the Mo(VI)–$P_2O_7^{4-}$–HCl–CH_3CN System. In the Mo(VI)–$P_2O_7^{4-}$–HCl–CH_3CN system, the 15-molybdodiphosphate $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$ anion transformed spontaneously into the 12-molybdodiphosphate $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$ anion.[4,5] The $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$ anion was also formed in aqueous media containing high concentrations of Mo(VI) and $P_2O_7^{4-}$. The structure of the parent $[(P_2O_7)Mo_{18}O_{54}]^{4-}$ anion is based on a fused dimer of B-type PMo_9 units.[3]

The present study has demonstrated that similar reactions also occur in the Mo(VI)–PHO_3^{2-}–HCl system; viz. the spontaneous transformation reaction of the $[H_6(PHO_3)_2Mo_{15}O_{48}]^{4-}$ anion into the $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ anion in the aqueous CH_3CN solution and the direct formation reaction of the $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ anion in aqueous solution at high concentrations of Mo(VI) and PHO_3^{2-}. On the basis of these findings and the results of elemental analysis, we can assume that the $[H_6(PHO_3)_2Mo_{15}O_{48}]^{4-}$ and $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ anions have structures related to the $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$ and $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$ anions, respectively. The resemblance of the corresponding Raman spectra further supports the above assumption: the $[H_6(PHO_3)_2Mo_{15}O_{48}]^{4-}$ and $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$ ions show the most intense Raman line at nearly the same wavenumber of 978 cm^{-1}, and the $[H_{12}(PHO_3)_2Mo_{12}O_{42}]^{4-}$ ion shows a Raman spectrum similar to that of the $[H_{12}(P_2O_7)Mo_{12}O_{42}]^{4-}$ ion, as shown in Figs. 2c and 2d. On the other hand, no discussion was possible on the structure of the 16/4 complex at present.

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