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Synthesis of Colorless (6/5)-Molybdophosphonate, $Na_2H_5[(C_2H_5)_4N]_3(HP)_5Mo_6O_{33}$

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The title compound was isolated from a 0.15 M(= mol/dm^3) Mo(VI)/0.3 M H_3PO_3/0.1 M HCl/60% (v/v) CH_3COCH_3 system. The existence of a new type of heteropoly complex with a composition of Mo/P = 6/5 was elucidated. The formation conditions and the IR spectroscopic characteristics were compared with those of well-established pentamolybdodiphosphonate.

In the old literature,[1,2] Rosenheim et al. described the preparation for colorless molybdophosphonates formulated as $R_2O\cdot P_2O_3\cdot 5MoO_3$ (R = NH_4^+, K^+, Na^+, and Li^+) from aqueous solutions. In addition, they obtained pale-yellow salts with a composition of $R_2O\cdot P_2O_3\cdot 12MoO_3$ which were sparingly soluble in acidic solutions. For brevity, the molybdophosphonates are referred to by their Mo/P ratios. The structure and chemical properties of the pale-yellow 12/2 complex have been left ambiguous. On the other hand, the 5/2 complex is well characterized by NMR, IR, and UV spectroscopic measurements.[3,4] Recently,[5] the X-ray crystallographic analysis has shown that the 5/2 complex contains $[(HP)_2Mo_5O_{21}]^{4-}$ heteropoly ion which is structurally related to the Strandberg type $[P_2Mo_5O_{23}]^{6-}$ anion.[6]

The present work presents the synthesis of a new type of (6/5)-molybdophosphonate from the Mo(VI)/H_3PO_3/HCl/CH_3COCH_3 system. The following procedure is recommended for the preparation. A 2.46 g quantity of H_3PO_3 was added to a solution of a 3.63 g quantity of $Na_2MoO_4 \cdot 2H_2O$ in ca. 40 ml of water, followed by the addition of 1 ml of 10 M HCl. Then 60 ml of CH_3COCH_3 was added. To the 100 ml quantity of the solution, 5 g of tetraethylammonium bromide (Et_4NBr) was added. The solution was stored overnight in a refrigerator to give colorless precipitates. The precipitates were filtered on a Fluoropore membrane filter, washed with ethanol, and dried at room temperature (yield 3.9 g). It should be noted that when acetone is added to the Mo(VI)/HCl solution prior to the addition of H_3PO_3, a pale-yellow precipitate occurs by the addition of Et_4NBr. The precipitate is identified as $(Et_4N)_2Mo_6O_{19}$ by chemical analysis and IR spectroscopy.7) All chemicals were of guaranteed-reagent grade and were used as received.

The salts were slightly hygroscopic, but could be converted to the anhydrous form by heating at 100 °C for 5 h. Elemental analysis data for the anhydrous salt were: Mo, 33.87; P, 9.00; C, 16.94; H, 4.14; N, 2.42; Na, 2.91%. Calcd for $Na_2H_5(Et_4N)_3(HP)_5Mo_6O_{33}$: Mo, 33.76; P, 9.08; C, 16.90; H, 4.14; N, 2.46; Na, 2.70%. The thermobalance analysis showed that the salts dried in open-air contained $1\text{-}2H_2O$ per formula unit.

In general, heteropolyanions are classified according to the M/X ratio where M = Mo or W and X = central heteroatoms. Recently heteropolyanions with a low M/X ratio (M/X < 4) are in increasing interest, i. e., $[P_4W_{14}O_{58}]^{12-}$ (M/X = 3.5),8) $[As_2Mo_6O_{26}]^{6-}$, $[H_4As_4Mo_{12}O_{50}]^{4-}$ (M/X = 3),9,10) $[S_2Mo_5O_{23}]^{4-}$, $[S_2Mo_5O_{21}]^{4-}$, $[Se_2Mo_5O_{21}]^{4-}$ (M/X = 2.5),11-13) $[P_4W_8O_{40}]^{12-}$ (M/X = 2),14) $[H_4As_4Mo_4O_{26}]^{4-}$, $[I_2Mo_2O_{16}]^{6-}$ (M/X = 1),15,16) etc. To our knowledge, however, no heteropolyanions with the 6 : 5 stoichiometry (M/X = 1.2) have been prepared so far.

The IR spectrum of the 6/5 complex is shown in Fig. 1, together with that of the 5/2 complex, $Na_2(Et_4N)_2(HP)_2Mo_5O_{21}$ prepared according to ref. 4. A Hitachi 270-30 spectrophotometer was used to record IR spectra in KBr pellets. The spectrum of the 6/5 complex showed bands at 1210, 1168, 1137, 1102, 1028, 995, 935, 910, 775, 616, 589, 548, and 417 cm^{-1}. According to Tsuboi,17) the asymmetric and symmetric vibrations of the HPO_3^{2-} anion occur at 1100 and 980 cm^{-1} respectively. On this basis bands at 1210, 1168, 1137, 1102, and 1028 cm^{-1} can be assigned to the P-O bond. In the Mo-O stretching and bending region

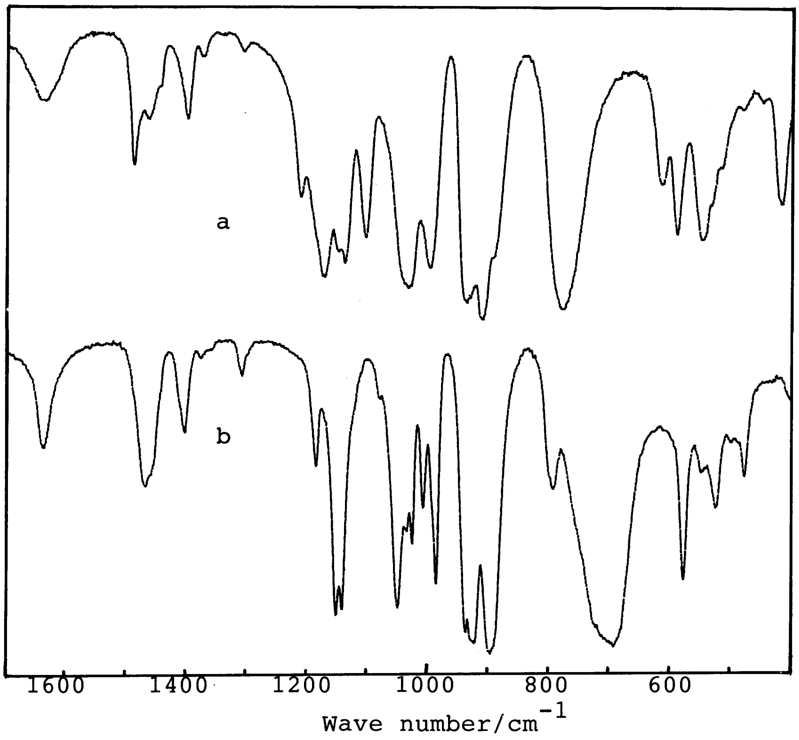

Fig. 1.
IR spectra of the 6/5 (a) and 5/2 (b) complexes in the KBr disk.

(below 1000 cm^{-1}), the spectrum was characterized by strong bands near 900 cm^{-1} (at 935 and 910 cm^{-1}) and at 775 cm^{-1}. As shown in curve (b), on the other hand, the spectrum of the 5/2 complex showed strong bands near 900 cm^{-1} (at 936, 921, and 895 cm^{-1}) and at 693 cm^{-1} which were characteristic of the 5/2 complex.3) The bands at 1350-1500 cm^{-1} are assigned to the tetraethylammonium group. The band at 1640 cm^{-1} is due to the water of hydration.

It seems that the presence of organic solvents plays essential role in the formation of the 6/5 complex. The 6/5 complex was isolated when acetone concentrations > 40% (v/v). The 6/5 complex was also obtained at concentrations > 60% (v/v) of ethanol and 1, 4-dioxane. In contrast, the 5/2 complex was not isolated in the presence of organic solvents such as acetone, acetonitrile, ethanol, and 1, 4-dioxane at concentrations of 40% (v/v) or more.

The 6/5 complex is insoluble in common organic solvents (acetone, acetonitrile, ethanol, and benzene). The 6/5 complex dissolves in water to give a clear solution. However, the complex is not electrochemically reduced to mixed-valence heteropoly blue species, which is in common with the behavior of other heteropolyanions with a low M/X ratio.

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