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# Synthesis of Sodium Tetramethylammonium Pentamolybdodisulfate(VI)(4-) Trihydrate, $Na[(CH_3)_4N]_3S_2Mo_5O_{23}\cdot 3H_2O$

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Colorless heteropoly molybdosulfate was isolated as sodium tetramethylammonium ($Me_4N^+$) salt $Na[(CH_3)_4N]_3S_2Mo_5O_{23}\cdot 3H_2O$ from the $Mo(VI)/H_2SO_4/C_2H_5OH$ system. The presence of $C_2H_5OH$ in the system favored the formation of the colorless complex rather than the previously reported yellow complex. The colorless complex was characterized by chemical analysis and IR spectroscopic measurements.

Heteropolymolybdates of P, As, Si, and Ge are well known in the early literature.[1] However, no heteropolymolybdosulfates were confirmed until we first reported the formation of the yellow molybdosulfate from the $Mo(VI)/H_2SO_4/CH_3CN$ system.[2] The yellow complex has a composition of Mo/S = 9/1, which suggests that the heteropoly anion is isomorphous with the Dawson structure. The 9/1 complex is reduced to mixed-valence blue species.[3]

In this paper we report the synthesis of new colorless heteropoly anions of $S^{6+}$ from the $Mo(VI)/H_2SO_4/C_2H_5OH$ system. The complex was prepared according to the following procedure. Twelve grams of $Na_2MoO_4\cdot 2H_2O$ was dissolved in 175 $cm^3$ of water. Then 25 $cm^3$ of 10 mol $dm^{-3}$ $H_2SO_4$ and 300 $cm^3$ of $C_2H_5OH$ were added. The solution was stirred by means of a magnetic stirrer for 24 h at room temperature. During this procedure, the solution turned to blue. Addition of 5 g of $Me_4NCl$

induced the formation of blue precipitates. After filtration, the supernatant colorless filtrate was stored in a refrigerator. Colorless transparent crystals appeared in several days. The crystals collected by filtration were washed with ethanol and dried at room temperature.

The DTA-TGA results on the crystal showed an endothermal transformation due to the evolution of water at 115 °C and an exothermal decomposition at 340-430 °C.

The results of elemental analysis for the anhydrous crystal obtained by heating at 120 °C are as follows. Found: Mo, 41.21; S, 5.35; C, 12.20; H, 3.16; N, 3.69; Na, 2.37%. Calcd for $Na(Me_4N)_3S_2Mo_5O_{23}$: Mo, 41.25; S, 5.54; C, 12.45; H, 3.14; N, 3.63; Na, 1.99%. The water content of the hydrated crystals was determined by TGA and by heating them at 120 °C. The observed weight loss of 4.34% is in agreement with the calculated value of 4.46% for $3H_2O$. Analytical data agree quite well with the empirical formula, $Na(Me_4N)_3S_2Mo_5O_{23}\cdot 3H_2O$.

The crystal of the colorless 5/2 molybdosulfate is insoluble in organic solvents such as ethanol, acetone, 1,4-dioxane, and acetonitrile. On the other hand, it dissolves in water to give a colorless solution.

IR spectra were recorded on a Hitachi 270-30 spectrophotometer as KBr pellets. Figure 1 shows an IR spectrum of the colorless crystal. The spectrum was characterized by strong bands at 1242, 1122, 1032, 937, 911, and 707 $cm^{-1}$. The three bands at 1242, 1122, and 1032 $cm^{-1}$ are of particular interest because no bands assigned to the Mo-O stretching and bending vibrations are observed above

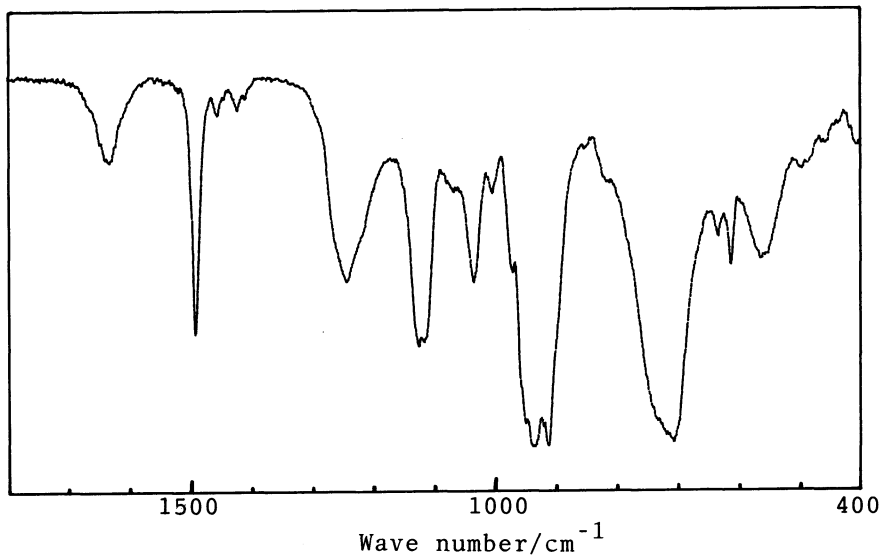


Fig. 1.
An IR spectrum of $Na(Me_4N)_3S_2Mo_5O_{23}$ $3H_2O$ in the KBr disk.

1000 $m^{-1}$. Since $\nu_1$ and $\nu_3$ bands of $SO_4^{2-}$ occur at 983 and 1105 $cm^{-1}$,[4] the 1032 and 1122 $cm^{-1}$ bands can be assigned to the symmetric and asymmetric stretches of the S-O bond. The 1242 $cm^{-1}$ band can be assigned to the $S{=}O_{terminal}$ bond. The strong bands at 937, 911, and 707 $cm^{-1}$ are very similar in appearance to those of the $P_2Mo_5O_{23}^{6-}$ anion, the structure of which was first reported by Strandberg in 1973.[5] According to Pope et al.,[6,7] the bands near 900 and 700 $cm^{-1}$ are characteristic of the pentamolybdo complexes. The bands at 1488(s), 1452(w), and 1420(w) are due to the tetramethylammonium group where s = strong and w = weak. The band at 1630 $cm^{-1}$ can be assigned to the water of hydration. In addition to these bands, the spectrum contains weak bands at 1000, 970, 816, 631, 609, 562, and 491 $cm^{-1}$ to which no assignments can be made.

On the basis of elemental analysis and IR measurements, the 5/2 heteropoly anion seems to be isostructural with the $P_2Mo_5O_{23}^{6-}$ anion. Since the structural analysis by Strandberg, the pentamolybdo anions of $P^{5+}$ and $P^{3+}$, i. e., $P_2Mo_5O_{23}^{6-}$ and $P_2Mo_5O_{21}^{4-}$, have been established.[8-11] Several salts of $[(RP)_2Mo_5O_{21}]^{4-}$ with a common structure have also been prepared so far where R = organic groups.[6,7,12] In addition, the pentamolybdo complex of $S^{4+}$, $(NH_4)_4S_2Mo_5O_{21} \cdot 3H_2O$ was prepared from a paramolybdate solution saturated with $SO_2$,[13] and the crystal structure was determined.[14] However, there have been no reports on the $S_2Mo_5O_{23}^{4-}$ anion.

Blue precipitate obtained prior to the crystals of the 5/2 molybdosulfate was identified as the $Me_4N$-salt of the reduced 9/1 molybdosulfate by IR measurement. This result indicates that the yellow 9/1 molybdosulfate formed in the $Mo(VI)/H_2SO_4/C_2H_5OH$ system was converted into the corresponding blue complex due to the reduction by $C_2H_5OH$.

As reported previously,[2] higher temperatures favored the formation of the 9/1 complex, and it was recommended to boil the $Mo(VI)/H_2SO_4/CH_3CN$ system for the preparation. Similarly, the blue precipitate increased in amount when the $Mo(VI)/H_2SO_4/C_2H_5OH$ system was heated. In contrast, heating of the reaction system had little influence on the yield of the 5/2 complex.

Ethanol is an appropriate solvent for the synthesis of the 5/2 complex. Neither the $Mo(VI)/H_2SO_4/CH_3CN$ system nor the $Mo(VI)/H_2SO_4$/acetone system yielded any appreciable amount of the 5/2 complex. Nevertheless, the 9/1 molybdosulfate was obtainable from the $Mo(VI)/H_2SO_4$ systems including acetonitrile, acetone, and

ethanol. Studies on the solvent effect on the formation of heteropoly molybdates are now in progress.

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