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Preparation of a Yellow Heteropoly Molybdosulfate

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By heating the $Na_2MoO_4 \cdot 2H_2O/H_2SO_4$ system in the presence of acetonitrile (AN) as an auxiliary solvent, a yellow molybdosulfate complex was formed. The complex was isolated as tetraalkylammonium salts, and the Mo/S ratio was found to be close to 9. The IR and UV spectroscopic characteristics and some chemical properties were elucidated.

In the course of treating a mixture of molybdenum oxide and sulfuric acid at an elevated temperature, Berzelius observed the formation of a yellow solid which was fairly soluble in water and slightly soluble in ethanol.$^{1)}$ Indeed, when the powder of sodium molybdate is dispersed in concentrated sulfuric acid, the surface of the molybdate salt changes to bright yellow. However, it is quite difficult to isolate the pure yellow solid. In spite of the observation by Berzelius, therefore, the formation of heteropolymolybdates from sulfuric acid solutions has long been left ambiguous. In this letter we describe a method to prepare a yellow molybdosulfate complex from AN—water mixed solvents.

The following procedure is recommended to prepare the molybdosulfate. 20 ml of concentrated sulfuric acid (0.36 mol) was added to a solution of 24.2 g of $Na_2MoO_4 \cdot 2H_2O$ (0.1 mol) in ca. 80 ml of water, and was followed by the addition of 400 ml of AN. The mixture which consisted of two liquid-layers was heated to boiling with a continuous stirring for 1 h; the upper AN layer changed to orange-yellow as the temperature was raised. The mixture was cooled to room temperature, and the colorless lower layer was discarded. The orange-yellow layer was heated again at 40 °C, then 10 g of $(CH_3)_4NBr$, 12 g of $(C_2H_5)_4NBr$, or 15 g of $(n\text{-}C_4H_9)_4NBr$ was added to the solution to precipitate the respective tetraalkylammonium salts. The precipitate was filtered on a Fluoropore membrane filter, washed successively with ethanol and distilled water, and dried at 40 °C. The yield of each salt was ca. 15 g.

Figure 1 shows an IR spectrum of the tetramethylammonium salt of the molybdosulfate (Me_4N-salt). The spectrum shows sharp bands at 1300—1500 cm^{-1} assigned to bending vibrations of the methyl group. In the Mo—O stretching and bending region (below 1000 cm^{-1}), a sharp band at 950 cm^{-1} and a broad band at 770 cm^{-1} are observed, although the band at 950 cm^{-1} overlaps the C—N stretching of the $(CH_3)_4N$ unit. In addition, the spectrum contains bands at 1060 and 1160 cm^{-1}. It is known that the ν_1 and ν_3 bands of SO_4^{2-} occur at 983 and 1105 cm^{-1}, respectively.2) On this basis the 1060 and 1160 cm^{-1} bands can be assigned to the symmetric and asymmetric stretches of the S—O bond.

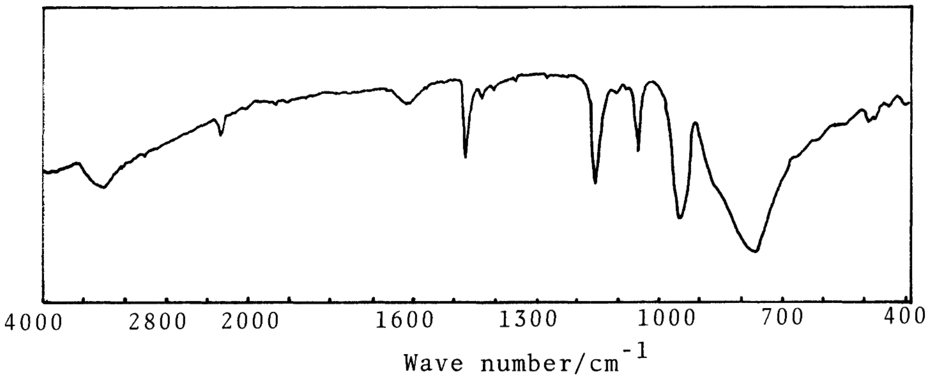

Fig. 1. An IR spectrum of the Me_4N-salt in the KBr disk.

The tetraethylammonium and tetrabutylammonium salts (Et_4N- and Bu_4N-salts, resp.) also gave 1060 and 1160 cm^{-1} bands, which suggests that both bands are characteristic of the molybdosulfate complex.

The DTA-TGA measurements were made up to 600 °C. Exothermal decompostions of the Me_4N-, Et_4N-, and Bu_4N-salts commenced at 410, 335, and 330 °C, respectively. From the curves it follows that the salts contain no water of crystallization, which is a unique property of the compounds because almost all the salts of heteropolymolybdates are known to be highly hydrated. A white solid was obtained by heating each salt in air at 500 °C. The IR spectrum of the solid shows strong bands at 990 cm^{-1} (sharp), 850 cm^{-1} (broad), 810 cm^{-1} (shoulder), and 550 cm^{-1} (broad), being identical with that of sublimed MoO_3 in orthorhombic form;3) the spectrum shows no bands due to the tetraalkylammonium and sulfate groups.

The composition, especially regarding to the Mo/S ratio of each salt, was determined as follows. Approximately 200 mg of the salt was weighed and heated in 15 ml of 0.1 mol dm^{-3} NaOH in a Teflon beaker, followed by diluting to 100 ml with water. The molybdenum content was determined gravimetrically[4)] and spectrophotometrically.[5)] For analysis of sulfate ions, an aliquot of the solution was pretreated with a cation-exchange resin (Dowex 50W-X8 in H^+ form, 100—200 mesh) to remove tetraalkylammonium cations. The sulfate ion was then determined by ion-chromatography.

The results of the elemental analyses on 10 samples of each salt are summarized in Table 1. The total average of the Mo/S ratio in the molybdosulfate is calculated as 8.72 ± 0.20. The ratio is scarcely dependent on the kind of the tetraalkylammonium cations used, which suggests that the compounds are the salts of a distinct heteropoly anion rather than double salts. In general, heteropoly anions are classified according to the ratio of molybdenum atoms to central heteroatoms (X).

Table 1. Elemental analysis data on the tetraalkylammonium salts of the heteropoly molybdosulfate

Compounds	Composition(%): $\frac{\text{Calcd}}{\text{Found}}$ [a)]				
	H	C	N	Mo	S
Me_4N-salt	1.57	6.24	1.82	56.08	2.08
	1.67 ± 0.03	6.51 ± 0.02	1.95 ± 0.09	54.35 ± 0.74	2.11 ± 0.07
Et_4N-salt	2.44	11.63	1.70	52.27	1.94
	2.41 ± 0.05	12.02 ± 0.02	1.73 ± 0.09	52.38 ± 0.40	2.02 ± 0.02
Bu_4N-salt	3.87	20.48	1.49	46.02	1.71
	3.85 ± 0.08	20.40 ± 0.04	1.49 ± 0.07	46.50 ± 0.69	1.78 ± 0.02

a) Calculated based on such salts as $[R_4N]_2(SO_4)(MoO_3)_9$, where R = CH_3, C_2H_5, or C_4H_9.

Heteropoly anions have been prepared so far with Mo/X of 18/2 for X = As^{5+} and P^{5+} and 9/1 for X = Ni^{4+} and Mn^{4+}. On the basis of the elemental analyses in Table 1, it seems likely that the molybdosulfate anion is isomorphous with either the 18/2 series or the 9/1 series. An X-ray diffraction study is being undertaken to elucidate the structure of the molybdosulfate.

The heteropoly salts are not soluble in water, but soluble in dilute acid and alkaline solutions; however, the heteropoly skeleton may undergo an irreversible decomposition because colorless solutions are resulted. In contrast to this, the salts are soluble in certain organic solvents such as nitrobenzene, AN, acetone, and dimethyl sulfoxide.

Figure 2 shows a UV spectrum of the molybdosulfate complex in AN. The complex was characterized by a broad absorption band in 270–450 nm, and the yellow solution obeyed Beer's law in the spectral region studied. No change in the spectrum was observed for at least one month under these conditions. However, the addition of water by more than 10 v/v % to the AN solution caused the gradual change of the spectrum, which suggests the decomposition of the heteropoly ion. The rate of decomposition increased with an increase in the water content.

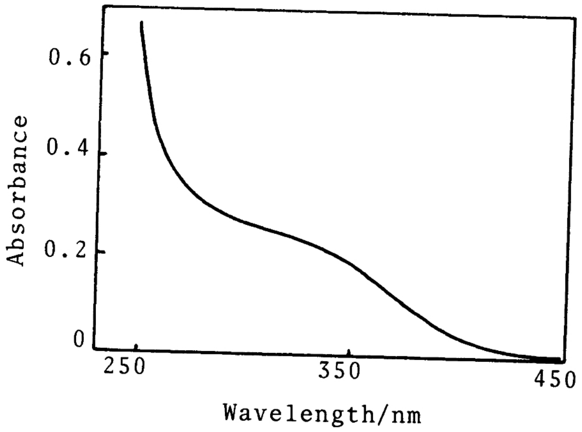

Fig. 2. A UV spectrum of the molybdosulfate complex in AN: 28.8 mg Et_4N-salt/1000 ml AN.

The molybdosulfate complex can be electrochemically reduced by using carbon wool as a working electrode and applying zero V vs. SCE. During electrolysis, the solution changed from yellow to blue. The resultant blue solution is fairly stable even in the presence of dissolved oxygen. Inherent properties of the blue species will be described elsewhere.

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