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Preparation of Tetrabutylammonium Dodecamolybdosulfate(VI), $[(C_4H_9)_4N]_2SMo_{12}O_{40}$

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A yellow 12-molybdosulfate(VI) complex was isolated as the tetrabutylammonium (Bu_4N^+) salt from a 0.05 M (M = mol dm^{-3}) Mo(VI)-0.2 M H_2SO_4-50% (v/v) CH_3COCH_3 system containing traces of V(V). The IR and UV-visible spectroscopic and voltammetric characteristics were elucidated.

In spite of extensive studies on the preparation, there have been no reports on the formation of a 12-molybdosulfate(VI) complex. Recently we have succeeded in preparing two types of molybdosulfate(VI) complexes, i.e., $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_5O_{23}]^{4-}$, from Mo(VI)-H_2SO_4 systems containing water-miscible organic solvents.[1-3] Particularly, the existence of the $[S_2Mo_{18}O_{62}]^{4-}$ complex shows strong promise of the formation of 12-molybdosulfate(VI), because the 18-molybdo-complexes are derived from the 12-molybdo-complexes and vice versa.[4,5] As reported previously,[1] the $[S_2Mo_{18}O_{62}]^{4-}$ complex is formed very slowly at room temperature; heating of the reaction system is recommended for the preparation. Therefore, the occurrence of 12-molybdosulfate(VI) was sought in Mo(VI)-H_2SO_4 systems at room temperature. In the course of the preparative study, we have found that the presence of V(V) reveals marvelous effects on the formation of a molybdosulfate complex in a Mo(VI)-H_2SO_4-CH_3COCH_3 system.

Curve (a) of Fig. 1 shows a cyclic voltammogram of a 0.05 M Mo(VI)-0.2 M H_2SO_4-50% (v/v) CH_3COCH_3 system at 25 °C. A Tokai glassy carbon (GC-30S) with a surface area of 0.071 cm^2 was used as a working electrode, and all potentials were measured against a Ag/AgCl (saturated KCl) electrode. The solution showed pale-yellow due to $[Mo_6O_{19}]^{2-}$ under these conditions.[6] No reduction waves appeared until the current rise due to the reduction of $[Mo_6O_{19}]^{2-}$ around 0 V.[7] On the addition of 1 x 10^{-3} M V(V), the solution changed to orange-yellow, and three-step voltammetric waves were observed (peak-potentials (E_p's) of the reduction waves = +0.50,

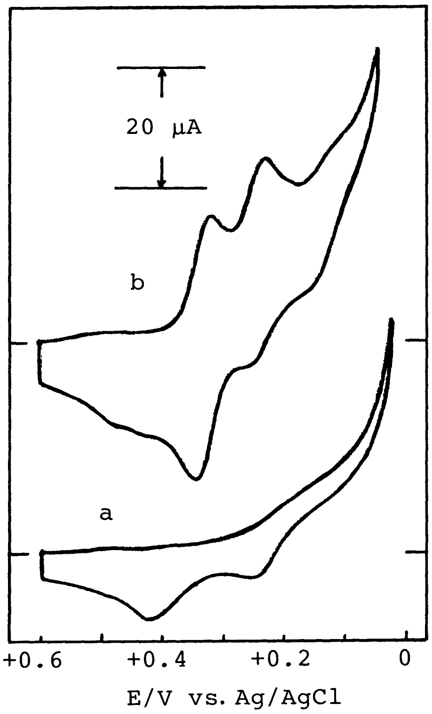

Fig. 1. Cyclic voltammograms of a 0.05 M Mo(VI)-0.2 M H_2SO_4-50% (v/v) CH_3COCH_3 system in the absence (a) and presence (b) of 1 x 10^{-3} M V(V).
Scan rate; 100 mV/s.

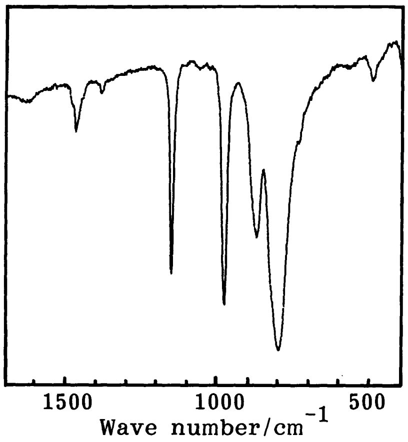

Fig. 2. An IR spectrum of the 12-molybdosulfate(VI) complex in the KBr pellet.

+0.32, and +0.23 V). As time elapsed, the 1st wave decreased in height with an increase of the 2nd and 3rd waves; simultaneously, the orange-yellow color of the solution faded gradually to yellow. Finally a steady voltammogram was obtained after 1 h and shown in curve (b). These reduction and oxidation currents were dependent on the square root of scan rate (20-200 mV/s), indicating that the electrode processes are diffusion-controlled. Since the $[S_2Mo_{18}O_{62}]^{4-}$ anion exhibited similar voltammetric reduction waves,$^{2)}$ a voltammogram for the solution of curve (a) was recorded after standing at 50 °C for 6 h. The $[S_2Mo_{18}O_{62}]^{4-}$ anion showed three-step reduction waves of equal heights with E_p's of +0.49, +0.38, and +0.19 V. These results indicate that the reduction waves shown in curve (b) cannot be ascribed to the reduction of the $[S_2Mo_{18}O_{62}]^{4-}$ anion. On the basis of these findings, attempts were made to isolate the unknown molybdosulfate complex responsible for the voltammetric waves in curve (b).

As the results, the following procedure is recommended for the preparation. A 12.1 g quantity of $Na_2MoO_4 \cdot 2H_2O$ was dissolved in 400 ml of water and a 0.12 g quantity of NH_4VO_3 dissolved in 100 ml of 2 M H_2SO_4 was added. To the 500 ml quantity of the solution, 500 ml of CH_3COCH_3 was added. The resultant yellow solution was stirred by means of a magnetic stirrer for 1 h at room temperature, and the addition of 20 g n-Bu_4NBr

caused yellow precipitates. The precipitates were filtered, washed with water and C_2H_5OH, and dried in open air. When the precipitates were dispersed in 300 ml of CH_3CN, bright-yellow salts remained in solution. This procedure is based on the preliminary results that the bright-yellow salts are much less soluble in CH_3CN than any other salts of heteropoly- and isopoly-molybdates formed simultaneously. The salts were collected by filtration, washed with CH_3CN, and dried in open air (yield ca. 170 mg). The bright-yellow salts were further purified by recrystallization from 100 ml of acetone. The elemental analysis data for the purified salts were as follows. Calcd for $(Bu_4N)_2SMo_{12}O_{40}$: Mo, 49.88; S, 1.39; C, 16.65; H, 3.14; N, 1.21%. Found: Mo, 49.91; S, 1.28; C, 17.06; H, 3.18; N, 1.28%. It should be stressed that vanadium is not detected in the compound.

Figure 2 shows an IR spectrum of the 12-molybdosulfate(VI) complex. The spectrum, which is characterized by four strong bands at 1155, 982, 877, and 805 cm^{-1}, resembles very well to those of a series of 12-molybdo-complexes with Si, Ge, P, and As as the central hetero-atoms. Therefore the three bands in the Mo-O stretching and bending region (< 1000 cm^{-1}) can be assigned by comparison with those of the 12-molybdo-complexes.[8)] On this basis we can tentatively assign the 982 cm^{-1} band to the $Mo=O_{terminal}$ bond, and the 877 and 805 cm^{-1} bands to the Mo-O-Mo bridges between corner-sharing octahedra and between edge-sharing octahedra, respectively. The 1155 cm^{-1} band can be assigned to the SO_4 group because ν_3 band of SO_4^{2-} occurs at 1105 cm^{-1}.[9)] The corresponding bands for the $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2Mo_5O_{23}]^{4-}$ complexes were observed at 1170 and 1122 cm^{-1},[2,3)] respectively. The bands in the 1500-1300 cm^{-1} region are due to the Bu_4N^+ group.

Figure 3 shows a UV-visible spectrum of 5.2×10^{-5} M 12-molybdo-

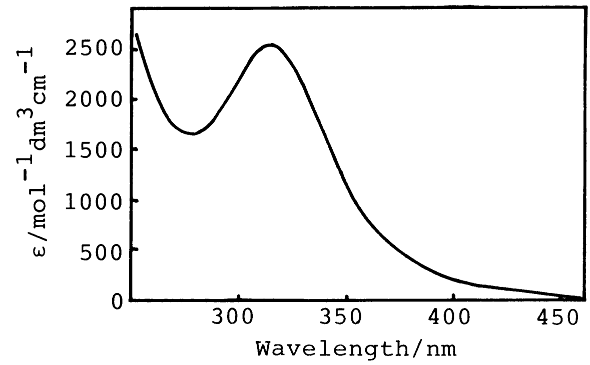

Fig. 3. A UV-visible spectrum of 5.2×10^{-5} M 12-molybdosulfate(VI) in CH_3CN. Path length, 1 cm.

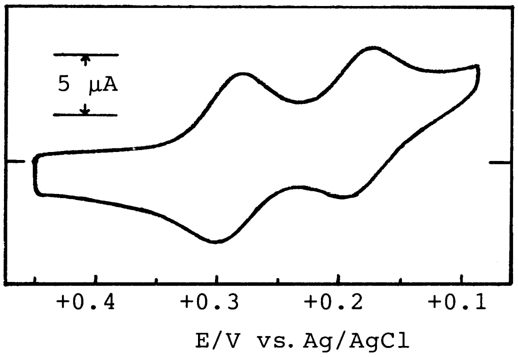

Fig. 4. A cyclic voltammogram of 3.5×10^{-4} M 12-molybdosulfate(VI) in 95% (v/v) CH_3CN containing 0.1 M $NaClO_4$. Scan rate, 200 mV/s.

sulfate(VI) in CH_3CN. An absorption maximum appeared at 315 nm, being situated at slightly longer wavelengths than that for 12-molybdophosphate(V) in CH_3CN (at 308 nm).[10] The yellow solution obeyed Beer's law in the spectral region studied (molar absorption coefficient, $\varepsilon = 25400$ mol^{-1} dm^3 cm^{-1} at 315 nm).

Figure 4 shows a cyclic voltammogram of 3.5×10^{-4} M 12-molybdosulfate(VI) in 95% (v/v) CH_3CN-water containing 0.1 M $NaClO_4$. Two well-defined voltammetric waves were obtained (E_p's of the reduction waves = +0.280 and +0.175 V). These waves were diffusion-controlled. The E_p's were independent of scan rate (20-200 mV/s), and the separation of the anodic and cathodic E_p's was found to be 25-28 mV. These results show that the two waves are due to reversible 2-electron reduction. The solution turned from yellow to blue by the electroreduction at each step. The complex anion is stable as judged by no change in the reduction currents under these conditions. However, the presence of acid in concentrations of $>$ 0.1 M caused the voltammetric waves to distort, which indicates the decomposition of the complex.

It should be emphasized that the presence of vanadium is essential for the formation of 12-molybdosulfate(VI), although the role of vanadium in the formation processes cannot be explained at present. The mechanism for the formation of the complex is now being investigated.

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