Synthesis and Characterization of Vanadium-Substituted Heteropoly Molybdosulfate(VI) Complexes

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Monovanadium derivatives of 12-molybdosulfate(VI) and 18-molybdodisulfate(VI), $[S(VMo_{11})O_{40}]^{3-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$, have been prepared as tetrabutylammonium (n-Bu_4N^+) salts from a Mo(VI)–V(V)–H_2SO_4–CH_3CN system. Both mixed molybdosulfate(VI) comlexes were characterized by their IR and UV spectra and their voltammetric behaviors. These mixed complexes are stable in nonaqueous solutions. In a 90% (v/v) CH_3CN–0.1 M (M=mol dm^{-3}) $HClO_4$ system, the $[S(VMo_{11})O_{40}]^{3-}$ anion transforms spontaneously into 12-molybdovanadate(V), whereas the $[S_2(VMo_{17})O_{62}]^{5-}$ anion is stable. In a 90% (v/v) CH_3CN–0.5 M $HClO_4$ system, on the other hand, both mixed complexes change into 18-molybdodisulfate(VI), $[S_2Mo_{18}O_{62}]^{4-}$.

Increasing attention has been directed towards the preparation of mixed heteropoly complexes in which Mo or W atoms are partially substituted by V atoms, because these mixed compounds are important in redox catalysis.[1] However, most of the work has been restricted to the preparation of vanadium-substituted derivatives of polyoxotungstates,[2-11] and only limited research has been conducted on mixed polyoxomolybdates with P as a central heteroatom.[12,13] Recently, we have prepared and characterized a series of vanadium-substituted mixed molybdovanadates(V), $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ (x=1—3).[14]

We have continued the preparative studies of heteropoly molybdosulfate(VI) complexes from a Mo(VI)–H_2SO_4 system containing water-soluble organic solvents such as acetonitrile and acetone.[15-17] The present study has shown that the $[S(VMo_{11})O_{40}]^{3-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$ anions, which are the monovanadium derivatives of 12-molybdosulfate(VI) and 18-molybdodisulfate(VI), are formed in the presence of V(V) in the system. Both mixed heteropoly complexes underwent successive reduction to mixed-valence heteropoly blues at a glassy carbon (GC) electrode. This study was undertaken to elucidate their formation conditions and to investigate the role of the peripheral V atom in the electrochemical properties. These mixed complexes were also characterized by IR and UV spectra. In addition, this paper reported on the spontaneous conversion of the vanadium-substituted mixed complexes into two types of non-substituted heteropoly complexes in acidified aqueous-organic solutions.

Experimental

The electrochemical measurements were made with a PARC Model 174-A polarographic analyzer equipped with a Yokogawa Model 3023 X–Y recorder. A Tokai glassy carbon (GC-30S) with a surface area of 0.071 cm^2 was used as a working electrode. A saturated calomel electrode (SCE) was used as a reference, along with a platinum counter electrode. Voltammetric measurements were made at 25±0.1 °C. Controlled potential electrolysis was carried out with a Hokuto Denko Model HA-501 potentiostat equipped with a Model HF-202D coulometer. IR spectra were obtained with a Hitachi Model 270-30 spectrophotometer as KBr pellets. A Hitachi Model 220-A spectrophotometer was used to record UV-visible spectra.

All reagents were of analytical grade and were used as received.

Preparation of Vanadium-Substituted Molybdosulfate(VI) Complexes. (n-$Bu_4N)_3S(VMo_{11})O_{40}$: A solution of 0.29 g (2.5 mmol) NH_4VO_3 in 150 ml of 2 M H_2SO_4 was added to a solution of 6.05 g (25 mmol) $Na_2MoO_4 \cdot 2H_2O$ in 50 ml of water. After the addition of 300 ml of acetonitrile, the solution was stirred for 1 h at room temperature. By the additon of 10 g of n-Bu_4NBr, the solution changed from orange to reddish-orange, and produced gradually orange precipitates (yield 1.5 g). The precipitates were purified by recrystallization from acetonitrile.

Anal. Calcd for (n-$Bu_4N)_3S(VMo_{11})O_{40}$: Mo, 42.12; V, 2.03; S, 1.28; C, 23.01; H, 4.34; N, 1.68%. Found: Mo, 42.01; V, 2.25; S, 1.12; C, 23.23; H, 4.28; N,1.97%.

(n-$Bu_4N)_5S_2(VMo_{17})O_{62}$: A 6.05 g quantity (25 mmol) of $Na_2MoO_4 \cdot 2H_2O$ in 50 ml of water and a 1.0 g quantity (8.5 mmol) of NH_4VO_3 in 50 ml of 3 M H_2SO_4 were mixed, and then 400 ml of acetonitrile was added. The resultant solution, which consisted of two liquid-layers, was heated to boiling for 1 h; the upper layer changed to reddish-brown as the temperature was raised. The solution was cooled to room temperature. After the colorless layer was discarded, 20 g of n-Bu_4NBr was added to the reddish-brown solution. The subsequent addition of 400 ml of ethanol led to precipitation of brown salts (yield 2.9 g), which were subsequently recrystallized from acetonitrile. Anal. Calcd for (n-$Bu_4N)_5S_2(VMo_{17})O_{62}$: Mo, 41.29; V, 1.29; S, 1.62; C, 24.32; H, 4.59; N, 1.77%. Found: Mo, 41.23; V, 1.43; S, 1.51; C, 23.87; H, 4.55; N, 1.78%.

Molybdenum and vanadium were determined with a Shimadzu Model ICPS-5000 inductively coupled argon plasma emission spectrometer, and sulfate was determined by high-performance liquid chromatography.[18]

Results and Discussion

Formation of the $[S(VMo_{11})O_{40}]^{3-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$ Anions in the Mo(VI)-V(V)-H_2SO_4-CH_3CN System. The presence of acetonitrile in concentrations >40% (v/v) is essential for the formation of the mixed

molybdosulfate(VI) anions.

The $[S(VMo_{11})O_{40}]^{3-}$ anion was formed in a 50 mM Mo(VI)–5 mM V(V) system of one liquid-layer (<70% (v/v) CH_3CN) containing 0.4—0.6 M (M=mol dm^{-3}) H_2SO_4. In the presence of higher concetrations of V(V), mixed complexes with higher vanadium contents were also obtained; however, they were much less stable and were not successfully purified. In the 50 mM Mo(VI)–5 mM V(V) system containing lower concentrations of H_2SO_4 (0.2—0.3 M), mixed salts of $[S(VMo_{11})O_{40}]^{3-}$, $[VMo_{12}O_{40}]^{3-}$, and $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ were formed, and a mixture of $[VMo_{12}O_{40}]^{3-}$ and $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ became predominant in the system containing 0.1 M H_2SO_4, which was identified by the elemental analysis and the IR spectroscopic measurement.[14] This result means that vanadium can act as a central heteroatom as well as peripheral atoms in these heteropoly complexes.

On the other hand, the $[S_2(VMo_{17})O_{62}]^{5-}$ anion was formed in a system of two liquid-layers (>70% (v/v) CH_3CN), and heating of the system accelerated the formation of the heteropolyanion, in agreement with our previous observation for the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ anion;[16] the $[S_2(VMo_{17})O_{62}]^{5-}$ anion was not formed at any appreciable amount in a system of one liquid-layer at room temperature. In a 50 mM Mo(VI)–0.3 M H_2SO_4–80% (v/v) CH_3CN system containing V(V) in concentrations <10 mM, the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ anion was formed simultaneously and a mixture of the $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$ anions was obtained by the addition of *n*-Bu_4NBr. Attempts to prepare derivatives of the Dawson-type heteropoly complexes with higher vanadium contents were unsuccessful.

IR Spectra. Figure 1 shows an IR spectrum of (*n*-$Bu_4N)_3S(VMo_{11})O_{40}$, along with that of (*n*-$Bu_4N)_2SMo_{12}O_{40}$. As reported previously,[15] the IR spectrum of (*n*-$Bu_4N)_2SMo_{12}O_{40}$ shows four prominent bands at 1155 cm^{-1}, ν(S–O); 982 cm^{-1}, ν(Mo=$O_{terminal}$); 877 cm^{-1}, ν(Mo–O–Mo, octahedral edge-sharing); 805 cm^{-1}, ν(Mo–O–Mo, octahedral corner-sharing), which are characteristic of the Keggin anions.[19] As shown in (b), it is characteristic of the spectrum of the $[S(VMo_{11})O_{40}]^{3-}$ anion that the band corresponding to the S–O vibration

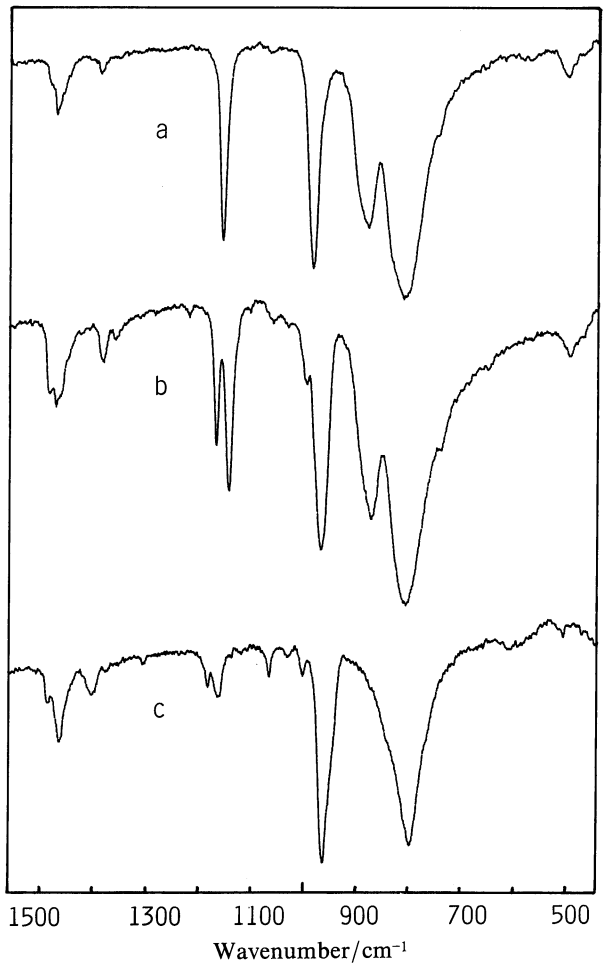

Fig. 1. IR spectra of (a) (*n*-$Bu_4N)_2SMo_{12}O_{40}$, (b) (*n*-$Bu_4N)_3S(VMo_{11})O_{40}$, and (c) the one-electron reduction species of (b).

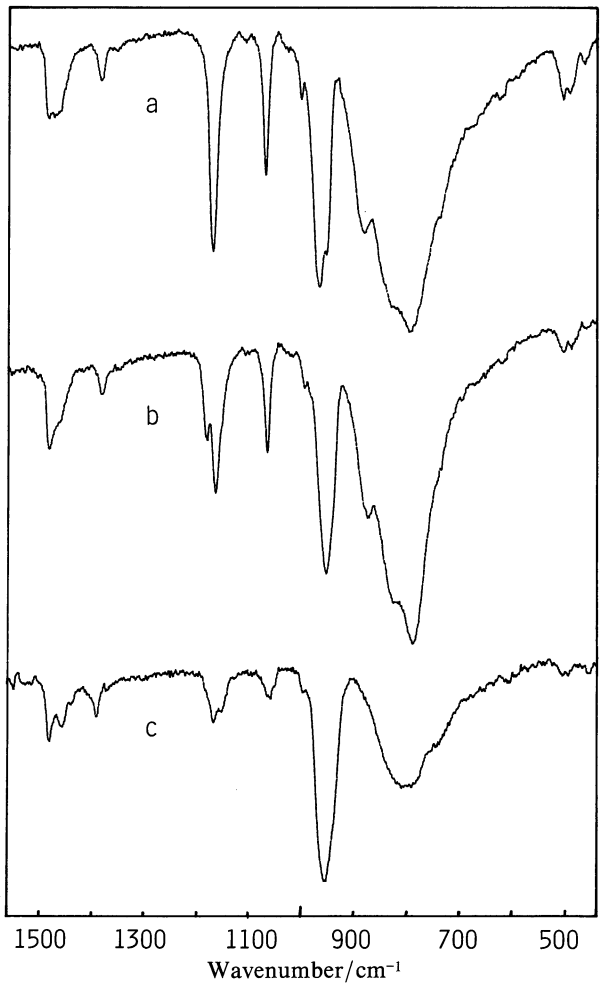

Fig. 2. IR spectra of (a) (*n*-$Bu_4N)_4S_2Mo_{18}O_{62}$, (b) (*n*-$Bu_4N)_5S_2(VMo_{17})O_{62}$, and (c) the four-electron reduction species of (b).

is split into two components at 1171 and 1148 cm^{-1}. The Mo–O stretching vibrations are observed at 971, 872, and 805 cm^{-1}; besides, a small absorption band, which can be assigned to $\nu(V{=}O_{terminal})$, appears at 998 cm^{-1}.

Figure 2 compares an IR spectrum of $(n\text{-}Bu_4N)_5S_2(VMo_{17})O_{62}$ with that of $(n\text{-}Bu_4N)_4S_2Mo_{18}O_{62}$. The latter Dawson complex is characterized by two bands at 1170 and 1069 cm^{-1} due to the asymmetric and symmetric stretches of the SO_4 group.[16] Both spectra resemble very well, except that the 1170 cm^{-1} band is split into two bands at 1183 and 1166 cm^{-1} in the vanadium-substituted mixed complex.

The similarity of both spectra in Fig. 1 and of those in Fig. 2 suggests that the $[S(VMo_{11})O_{40}]^{3-}$ and $[S_2(VMo_{17})O_{62})]^{5-}$ anions are structurally related to the Keggin and Dawson anions, respectively. The splittings of bands due to the ν(S–O) vibration, which are due to the symmetry decrease of the SO_4 tetrahedron in the vanadium-substituted mixed complexes, can allow us to identify these mixed complexes.

UV-Visible Spectra. The $n\text{-}Bu_4N^+$ salts of the $[S(VMo_{11})O_{40}]^{3-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$ anions are soluble in polar aprotic solvents such as acetonitrile and acetone, where the mixed heteropolyanions are stable as judged by no change in the UV-visible spectra.

Figure 3 shows UV-visible spectra of 5×10^{-5} M solutions of the $[SMo_{12}O_{40}]^{2-}$ and $[S(VMo_{11})O_{40}]^{3-}$ anions in neat acetonitrile. In general, the Keggin anions are characterized by absorption maxima at about 310 nm. It is known that the replacement of molybdenum by vanadium makes the big change of the spectrum; for example, the spectra of the $[P(VMo_{11})O_{40}]^{4-}$ and $[V(VMo_{11})O_{40}]^{4-}$ anions appear like shoulders instead of the maxima observed for the corresponding non-substituted Keggin anions.[14,20,21] As shown in Fig. 3, however, the spectrum of the $[SMo_{12}O_{40}]^{2-}$ anion is hardly affected by the replacement of molybdenum by vanadium.

As shown in Fig. 4, both spectra of the $[S_2Mo_{18}O_{62}]^{4-}$ and $[S_2(VMo_{17})O_{62}]^{5-}$ anions are similar in appearance, in analogy with the behavior for the $[SMo_{12}O_{40}]^{2-}$ and $[S(VMo_{11})O_{40}]^{3-}$ anions.

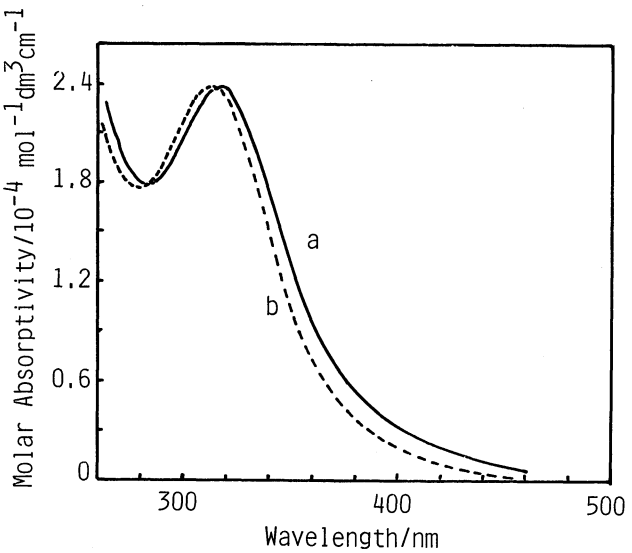

Fig. 3. UV-visible spectra of 5×10^{-5} M (a) $[S(VMo_{11})O_{40}]^{3-}$; (b) $[SMo_{12}O_{40}]^{2-}$ in neat acetonitrile.

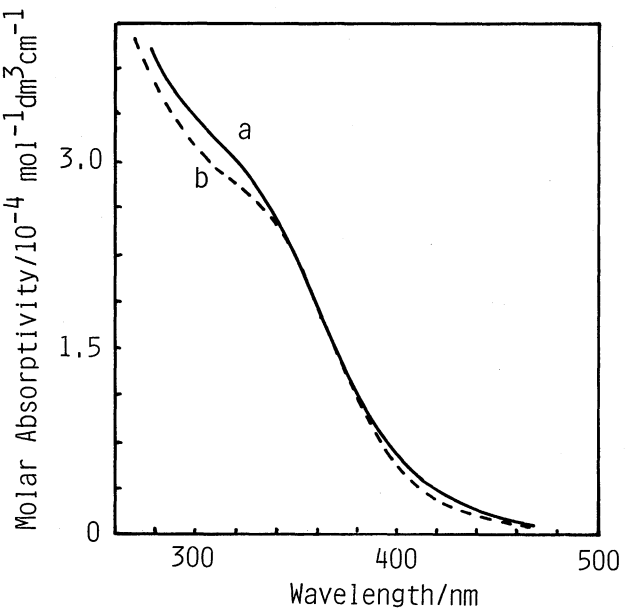

Fig. 4. UV-visible spectra of 4×10^{-5} M (a) $[S_2(VMo_{17})O_{62}]^{5-}$; (b) $[S_2Mo_{18}O_{62}]^{4-}$ in neat acetonitrile.

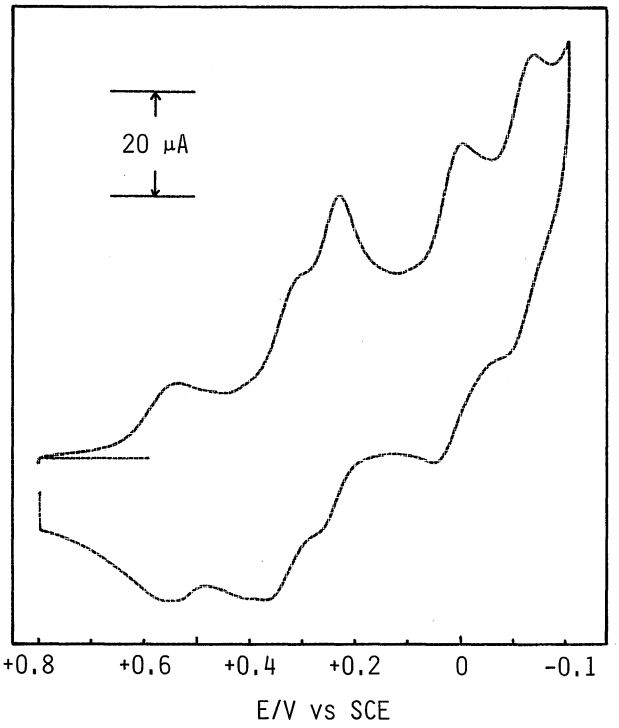

Fig. 5. A cyclic voltammogram of 4×10^{-4} M $[S(VMo_{11})O_{40}]^{3-}$ in 95% (v/v) CH_3CN–water containing 0.1 M $HClO_4$ at the GC electrode. Scan rate, 100 mV s^{-1}.

Cyclic Voltammograms. A cyclic voltammogram of 4×10^{-4} M $[S(VMo_{11})O_{40}]^{3-}$ in 95% (v/v) CH_3CN–water containing 0.1 M $HClO_4$ is shown in Fig. 5. The currents are diffusion-controlled; the 3rd wave appears to have somewhat adsorptive character. The peak-potentials (E_p's) are independent of the voltage scan rate (20—200 mV s^{-1}), indicating the reversible nature of the electrode processes. Coulometric analysis showed that the 1st three waves corresponded to the addition of one, two, and two electrons, respectively. The 1st wave, which is due to the one-electron reduction of V(V) to V(IV) in the peripheral structure,[12-14] is situated at ca. 0.2 V more positive than the 1st reduction wave due to molybdenum atoms, which is in marked contrast to the electrochemical behavior of the $[S_2(VMo_{17})O_{62}]^{5-}$ anion, as discussed below.

The voltammogram of $[S(VMo_{11})O_{40}]^{3-}$ anion was found to change gradually with time in the acidified aqueous-organic solution; the rate of change became faster as the CH_3CN concentration was decreased, and the change was followed in 90% (v/v) CH_3CN–water. The $[S(VMo_{11})O_{40}]^{3-}$ anion transformed spontaneously into two types of heteropolyanions, mainly depending on the concentration of $HClO_4$. First, in 90% (v/v) CH_3CN–water containing 0.1 M $HClO_4$, the 1st wave due to the reduction of the pheripheral V atom decreased in height with time, and the ultimate voltammogram was obtained after standing for one day and shown in curve (b) of Fig. 6. Yellow salts were obtained by the addition of tetraethylammonium bromide (Et_4NBr) to the solution, being identified as the $[VMo_{12}O_{40}]^{3-}$ complex by the elemental analysis and the IR spectroscopic measurement.[14] Thus, the peripheral VO_6 octahedron changed into the central VO_4 tetrahedron. Secondly, in 90% (v/v) CH_3CN–water containing 0.5 M $HClO_4$, the voltammogram of $[S(VMo_{11})O_{40}]^{3-}$ changed gradually into curve (b) of Fig. 7 in five days, which was entirely different from curve (b) of Fig. 6 obtained in the system of 0.1 M $HClO_4$. It was found that curve (b) of Fig. 7 corresponded to the voltammogram of the $[S_2Mo_{18}O_{62}]^{4-}$ anion.[16] This result was further confirmed by the fact that the IR spectrum for the Et_4N^+ salts obtained from the solution of curve (b) was identical with Fig. 2 (a). Cartié has reported similar transformation of the Keggin-type $[SMo_{12}O_{40}]^{2-}$ anion into the Dawson-type $[S_2Mo_{18}O_{62}]^{4-}$ anion in acetic acid containing perchloric acid.[22]

Figure 8 compares cyclic voltammograms of $[S_2(VMo_{17})O_{62}]^{5-}$ and $[S_2Mo_{18}O_{62}]^{4-}$ in 95% (v/v) CH_3CN–water containing 0.1 M $HClO_4$. As shown in curve (a), the voltammogram of the $[S_2Mo_{18}O_{62}]^{4-}$ anion showed a four-step redox process; each wave corresponded to a

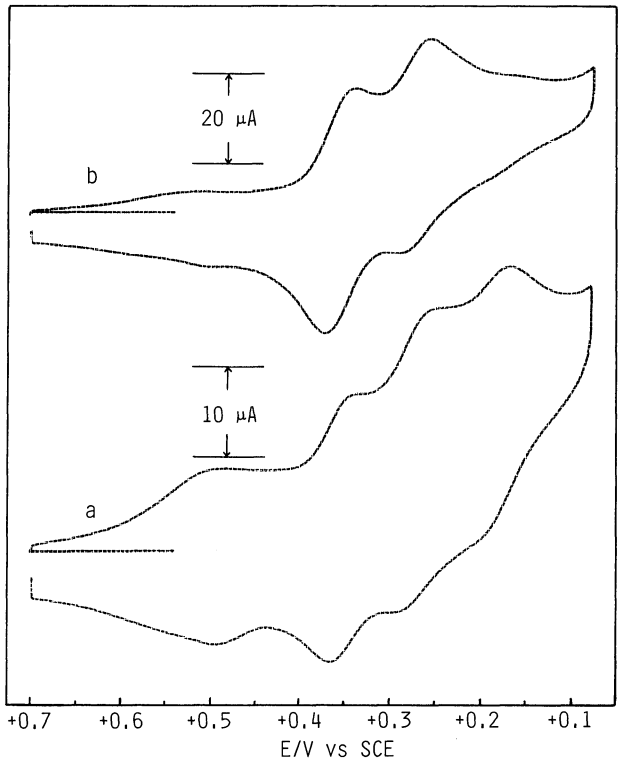

Fig. 6. Cyclic voltammograms of 4×10^{-4} M $[S(VMo_{11})O_{40}]^{3-}$ in 90% (v/v) CH_3CN–water containing 0.1 M $HClO_4$ at the GC electrode. Recorded (a) immediately after the addition of $[S(VMo_{11})O_{40}]^{3-}$; (b) after one day. Scan rate, 100 mV s^{-1}.

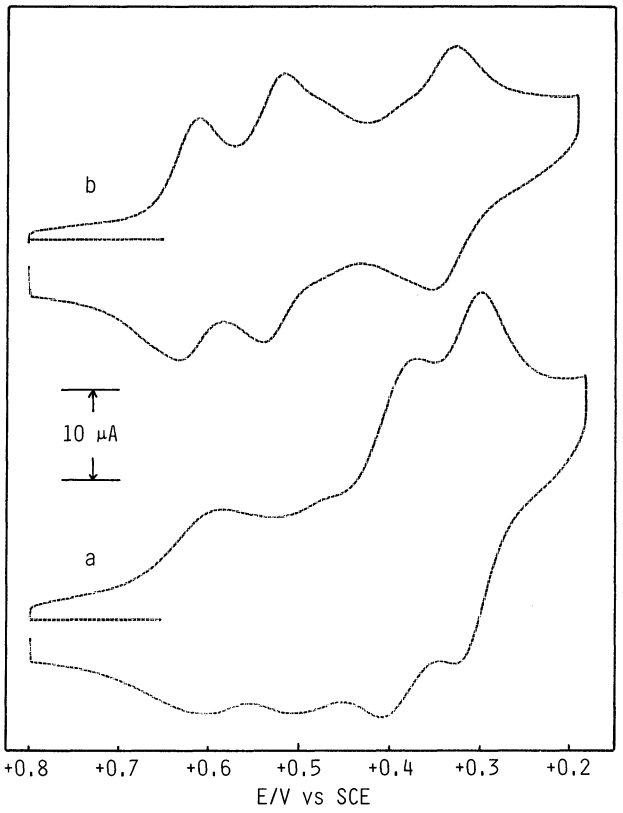

Fig. 7. Cyclic voltammograms of 4×10^{-4} M $[S(VMo_{11})O_{40}]^{3-}$ in 90% (v/v) CH_3CN–water containing 0.5 M $HClO_4$ at the GC electrode. Recorded (a) immediately after the addition of $[S(VMo_{11})O_{40}]^{3-}$; (b) after five days. Scan rate, 100 mV s^{-1}.

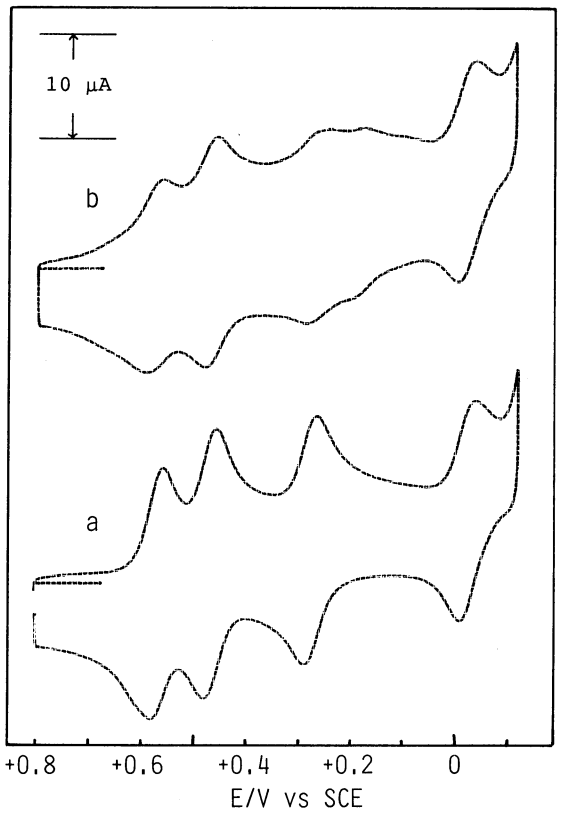

Fig. 8. Cyclic voltammograms of 2×10^{-4} M (a) $[S_2Mo_{18}O_{62}]^{4-}$; (b) $[S_2(VMo_{17})O_{62}]^{5-}$ in 95% (v/v) CH_3CN–water containing 0.1 M $HClO_4$ at the GC electrode. Scan rate, 100 mV s^{-1}.

reversible two-electron transfer.[16] On the other hand, the $[S_2(VMo_{17})O_{62}]^{5-}$ anion underwent a five-step reduction (curve (b)). These waves were diffusion-controlled, being distorted similar to irreversible ones. However, the E_p's were independent of the voltage scan rate (20—200 mV s^{-1}), indicating that the electrode processes are reversible. It should be noted that the E_p's for the 1st, 2nd, and 5th waves are in agreement with those for the 1st, 2nd, and 4th waves of the $[S_2Mo_{18}O_{62}]^{4-}$ anion, which suggests that the 3rd wave for the $[S_2Mo_{18}O_{62}]^{4-}$ anion splits into two waves (the 3rd and 4th waves) for the $[S_2(VMo_{17})O_{62}]^{5-}$ anion. Since the 1st and 2nd waves for the $[S_2(VMo_{17})O_{62}]^{5-}$ anion correspond to two-electron reduction, respectively, this splitting may be accounted for by assuming the existence of isomers in the 4-electron reduction species. As also shown in curve (b), the reduction current shows gradual rise at the foot of the 1st wave, suggesting that the 1st wave may be ascribed to the reduction of a V(V)–Mo(VI) pair. As for vanadium-substituted polyoxotungstates, on the other hand, vanadium atoms are electroreduced at more positive potentials than tungsten atoms in both $[P(VW_{11})O_{40}]^{4-}$ and $[P_2(VW_{17})O_{62}]^{7-}$ anions,[3,4,10] because the reduction potentials of tungsten atoms are more negative than those of molybdenum atoms.

In contrast to the $[S(VMo_{11})O_{40}]^{3-}$ anion, the $[S_2(VMo_{17})O_{62}]^{5-}$ anion showed no change of the voltammogram for at least three days in 90% (v/v) CH_3CN–water containing 0.1 M $HClO_4$. In 90% (v/v) CH_3CN–water containing 0.5 M $HClO_4$, on the other hand, the voltammogram of the $[S_2(VMo_{17})O_{62}]^{5-}$ anion changed into that of the $[S_2Mo_{18}O_{62}]^{4-}$ anion in five days, in the same manner as the $[S(VMo_{11})O_{40}]^{3-}$ anion. This observation was further confirmed by the elemental and the IR spectroscopic measurement for the Et_4N^+ salts, as described above.

In conclusion, the transformation reactions in 90% (v/v) CH_3CN–water can be given stoichiometrically as follows:

1) at lower acidities

$$2[S(VMo_{11})O_{40}]^{3-} + 6H^+ = [VMo_{12}O_{40}]^{3-} + 5Mo_2O_5^{2+} + VO_4^{3-} + 2SO_4^{2-} + 3H_2O$$

2) at higher acidities

$$2[S(VMo_{11})O_{40}]^{3-} + 12H^+ = [S_2Mo_{18}O_{62}]^{4-} + 4MoO_2^{2+} + 2VO_2^+ + 6H_2O$$

$$3[S_2(VMo_{17})O_{62}]^{5-} + 36H^+ = 2[S_2Mo_{18}O_{62}]^{4-} + 15MoO_2^{2+} + 3VO_2^+ + 2SO_4^{2-} + 18H_2O$$

Mixed-Valence Blue Species. In contrast to the behavior of the $[H_{x-1}V(V_xMo_{12-x})O_{40}]^{4-}$ anions (x=1—3),[14] the electrochemical reduction of the $[S(VMo_{11})O_{40}]^{3-}$ anion yielded mixed-valence blue species. In order to obtain the salts of the blue species, an aliquot of the n-Bu_4N^+ salts was dissolved in 95% (v/v) CH_3CN–water containing 0.1 M $HClO_4$ and electrolyzed by controlled potential electrolysis at each reduction potential. The salts of the blue species were obtained by the addition of Et_4NBr dissolved in ethanol at the end of the electrolysis. As the typical example, Fig. 1 (c) shows an IR spectrum of the one-electron reduction species obtained by controlled potential electrolysis at +0.05 V. Similarly, mixed-valence blue species of the $[S_2(VMo_{17})O_{62}]^{5-}$ anion were obtained by controlled potential electrolysis at the respective steps of curve (b) of Fig. 8, being isolated as the Et_4N^+ salts. Fig. 2 (c) shows an IR spectrum of the four-electron reduction species obtained by controlled potential electrolysis at +0.04 V.

For the $[S_2Mo_{18}O_{62}]^{4-}$,[16] $[P_2Mo_{18}O_{61}]^{4-}$,[23] and $[PMo_{12}O_{40}]^{3-}$ anions,[24,25] it has been known that the reduction of peripheral Mo atoms causes the bands due to the XO_4 group (X=P or S) to decrease in intesity. It is interesting to note that similar behavior has been observed as a result of the reduction of the peripheral V atom in the vanadium-substituted mixed heteropolyanions, as shown in Fig.1 (c) and Fig. 2 (c).

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