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# Preparation and Characterization of an $\alpha$-Wells–Dawson-Type $[V_2Mo_{18}O_{62}]^{6-}$ Complex

**Sadayuki Himeno,***[1] **Keishi Kawasaki,**[1] **and Masato Hashimoto**[2]

[1]Department of Chemistry, Graduate School of Science, Kobe University, Kobe 657-8501

[2]Department of Material Science and Chemistry, Faculty of System Engineering,
Wakayama University, Sakaedani, Wakayama 640-8510

Received April 30, 2008; E-mail: himeno@kobe-u.ac.jp

An orange-yellow vanadomolybdate complex was prepared by heating a 100 mM $Mo^{VI}$–20 mM $V^{V}$–0.45 M HCl–20% (v/v) $CH_3CN$ system at 70 °C for 24 h, being isolated as the tetrapropylammonium ($Pr_4N^+$) salt. The $Pr_4N^+$ salt crystallized in the orthorhombic space group $P2_12_12$; the lattice constants were $a = 18.417(4)$, $b = 20.869(5)$, $c = 15.280(3)$ Å, $V = 5873(2)$ Å$^3$, and $Z = 2$. The crystallographic study revealed that the structure consists of an $\alpha$-Wells–Dawson-type $[V_2Mo_{18}O_{62}]^{6-}$ anion, in which vanadates serve as the central tetrahedra. The $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ complex underwent a two-step one-electron reduction in $CH_3CN$, and the presence of acid caused the one-electron waves to be converted into three two-electron waves. The formation conditions were elucidated by $^{51}$V NMR measurements.

Of the polyoxometalates with various structures, the so-called Keggin and Dawson complexes have received considerable attention due to their possible applications in various fields of chemistry including catalysis and electrocatalysis. It is well known that a variety of elements can act as the central heteroatom of Keggin complexes, $[XM_{12}O_{40}]^{n-}$ (M = Mo and W).[1–11] As for Wells–Dawson complexes, the $[P_2W_{18}O_{62}]^{6-}$,[12–17] $[As_2W_{18}O_{62}]^{6-}$,[17,18] $[P_2Mo_{18}O_{62}]^{6-}$,[19–27] and $[As_2Mo_{18}O_{62}]^{6-}$ complexes[27–29] have been prepared from aqueous solutions. Bond et al. prepared $\gamma^*$-$[S_2W_{18}O_{62}]^{4-}$ from an aqueous-$CH_3CN$ system.[30] They also found that the one-electron reduction of $\gamma^*$-$[S_2W_{18}O_{62}]^{4-}$ led to the formation of $\alpha$-$[S_2(W^{V}W_{17})O_{62}]^{5-}$ in $CH_3CN$.[31] We prepared $\alpha$-$[S_2M_{18}O_{62}]^{4-}$ (M = Mo and W) from a $Mo^{VI}$ or $W^{VI}$–$H_2SO_4$–$CH_3CN$ system.[32,33]

Our recent attention has been directed towards the preparation of heteropoly complexes incorporating $V^{V}$ as the central tetrahedrally coordinated heteroatom. Björnberg and Hedman first prepared a mixed-valence Keggin complex, $K_6[V(V_2{}^{V,IV}Mo_{10})O_{40}]$ from aqueous media.[34] We isolated a yellow Keggin complex, $[VMo_{12}O_{40}]^{3-}$, and its vanadium-substituted derivatives, $[V(V_xMo_{12-x})O_{40}]^{(3+x)-}$ ($x$ = 1–3).[35,36] The presence of water-miscible organic solvents such as $CH_3CN$ is essential for their preparation. Later, the crystallographic structure of the Keggin complex, $Na_3[VMo_{12}O_{40}]\cdot 19H_2O$ was determined.[37] Besides, we prepared $[VW_{12}O_{40}]^{3-}$ by heating a 50 mM $W^{VI}$–50 mM $V^{V}$–1.5 M HCl–80% (v/v) $CH_3CN$ system.[38] As far as Wells–Dawson-type complexes are concerned, Liang et al. reported the preparation of a blue species, denoted as $\alpha$-$(TEAH)_6[V_2Mo_{18}O_{62}]$, by refluxing a $Mo^{VI}$–$V^{V}$ solution (pH ca. 1) containing tris(2-hydroxyethyl)amine (TEA).[39] Under similar conditions, however, Miras et al. obtained a dark green salt, $(TEAH)_6[H_2V_2(V^{IV}Mo_{17})O_{62}]$, and they concluded that the synthetic procedure of Liang et al. did not produce the Dawson-type $[V_2Mo_{18}O_{62}]^{6-}$ complex but the $V^{IV}$-substituted $[H_2V_2(V^{IV}Mo_{17})O_{62}]^{6-}$ complex, in which $Mo^{VI}$ in the peripheral structure is replaced by $V^{IV}$.[40] Our synthetic experiments using the method of Liang et al. confirmed the results of Miras et al.

In the present paper, we developed a new route to the preparation of $\alpha$-$(Pr_4N)_5H[V_2Mo_{18}O_{62}]$ by the presence of 20% (v/v) $CH_3CN$ in a $Mo^{VI}$–$V^{V}$–HCl system. The present paper describes the preparation and characterization of the new Wells–Dawson-type $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ complex.

## Experimental

**Instrumentation.** $^{51}$V NMR spectra were recorded on a Bruker Model AVANCE 500 spectrometer. All the $^{51}$V NMR spectra were recorded in a 5 mm diameter NMR tube with a concentric capillary containing $D_2O$ for instrumental lock. Chemical shifts were referenced to $VOCl_3$. Voltammetric measurements were made with a Hokuto Denko Model HA-101 potentiostat interfaced to a microcomputer-controlled system. The working electrode was a Tokai glassy carbon rod (GC-30S) with a surface area of 0.20 cm$^2$. The GC electrode was polished manually with 0.25 µm diamond slurry before each measurement. The potentials are referred to the redox potential of ferrocene (Fc)/ferrocenium ion ($Fc^+$) as an internal reference. The voltammetric measurements were made at 25 ± 0.1 °C. Unless otherwise noted, the voltage scan rate was set at 100 mV s$^{-1}$. A Thermo Nicolet Model Avatar 360 spectrophotometer was used to record IR spectra in KBr pellets.

**Syntheses and Materials.** **$(Pr_4N)_5H[V_2Mo_{18}O_{62}]$:** To a 12.1 g solution of $Na_2MoO_4\cdot 2H_2O$ in 365 mL of water was added 20 mL of the 500 mM $V^{V}$ stock solution, followed by the addition of 15 mL of concd HCl. After the addition of 100 mL of $CH_3CN$, the resultant orange solution was heated without stirring at 65 °C for 24 h. During this time, yellow salts precipitated and stirring of the solution caused a slight increase of the precipitate. After cool-

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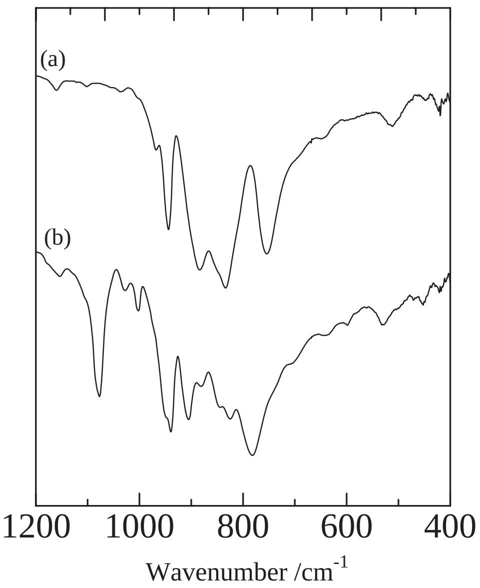

**Figure 1.** IR spectra of (a) $(Pr_4N)_5H[V_2Mo_{18}O_{62}]$ and (b) $(Bu_4N)_5H[P_2Mo_{18}O_{62}]$ in KBr pellets. Numerical data are given in the text.

ing to room temperature, the yellow precipitate was filtered off. To the filtrate was added 2.7 g of $Pr_4NCl$ to precipitate an orange-yellow salt. The salt was collected by filtration, washed with water, and air-dried (yield; 7.2 g). In order to purify the salt, a 7.0 g quantity was dissolved in 200 mL of $CH_3CN$. After undissolved solids were removed by filtration, the resultant clear solution was left to stand at room temperature. This procedure produced orange-yellow crystals suitable for X-ray structural analysis. It should be noted that the crystal, $(Pr_4N)_5H[V_2Mo_{18}O_{62}]\cdot 2CH_3CN$ becomes opaque when dried at 50 °C, owing to the liberation of $CH_3CN$. Anal. Calcd for $(Pr_4N)_5H[V_2Mo_{18}O_{62}]$: C, 19.2; H, 3.79; N, 1.87, Mo, 46.0; V, 2.71%. Found: C, 19.2; H, 3.80; N, 1.92; Mo, 46.1; V, 2.88%. IR (KBr, cm$^{-1}$): 944, 884, 834, 754, 511 (Figure 1a). The $(Pr_4N)_5H[V_2Mo_{18}O_{62}]$ salt is soluble in $CH_3CN$ to give an orange-yellow solution, which shows a single $^{51}V$ NMR line at −527 ppm.

**$(TEAH)_6[H_2V_2(V^{IV}Mo_{17})O_{62}]$:** Dark green salts were obtained following the synthetic procedure of Liang et al.[39] The elemental analysis data are in good agreement with those of Miras et al., indicating the empirical formula as $(TEAH)_6[H_2V_2(V^{IV}Mo_{17})O_{62}]\cdot 8H_2O$.[40] Attempts to prepare $[V_2Mo_{18}O_{62}]^{6-}$ from such an $Mo^{VI}$–$V^{V}$–TEA system always produced the $V^{IV}$-substituted derivative of $[V_2Mo_{18}O_{62}]^{6-}$, although Miras et al. detected small amounts of $[V_2Mo_{18}O_{62}]^{6-}$ using mass spectroscopy. Anal. Calcd for $(TEAH)_6[H_2V_2(V^{IV}Mo_{17})O_{62}]\cdot 6H_2O$: C, 11.42; H, 2.93; N, 2.22; Mo, 43.1; V, 4.04; $H_2O$, 2.9%. Found: C, 11.52; H, 2.86; N, 2.35; Mo, 43.1; V, 3.99; $H_2O$, 3.1%.

**$(Bu_4N)_5H[P_2Mo_{18}O_{62}]$:** For comparative studies, the tetrabutylammonium ($Bu_4N^+$) salt of an α-Wells–Dawson-type $(Bu_4N)_5H[P_2Mo_{18}O_{62}]$ complex with the same charge of −6 was prepared by a slight modification of our previous procedures.[27] Anal. Calcd for $(Bu_4N)_5H[P_2Mo_{18}O_{62}]$: C, 24.1; H, 4.57; N, 1.75%. Found: C, 23.8; H, 4.74; N, 1.82%.

**$(Bu_4N)_3[VMo_{12}O_{40}]$ and $(Bu_4N)_4[V(VMo_{11})O_{40}]$:** In order to analyze $^{51}V$ NMR spectra in acidified $Mo^{VI}$–$V^{V}$–$CH_3CN$ systems, the $Bu_4N^+$ salts of Keggin-type complexes, $[VMo_{12}O_{40}]^{3-}$ (−554) and $[V(VMo_{11})O_{40}]^{4-}$ (−508 (peripheral V), −551 (central V)) were prepared according to our previous procedures.[34,35] The numerals in parentheses are $^{51}V$ NMR chemical shift values (ppm) in $CH_3CN$. As described in a later part of this paper, the $[V(VMo_{11})O_{40}]^{4-}$ lines were obtained at −514 and −552 ppm in aqueous-$CH_3CN$ media.

**Table 1.** Crystallographic Data and Results of Refinement of $[Pr_4N]_5H[V_2Mo_{18}O_{62}]\cdot 2CH_3CN$[a)]

| | |
|---|---|
| Formula | $C_{62}H_{147}Mo_{18}N_7O_{62}V_2$ |
| FW | 3811.66 |
| Crystal system | Orthorhombic |
| Space group | $P2_12_12$ |
| $a$/Å | 18.417(4) |
| $b$/Å | 20.869(5) |
| $c$/Å | 15.280(3) |
| $V$/Å$^3$ | 5873(2) |
| $Z$ | 2 |
| $D_x$/Mg m$^{-3}$ | 2.16 |
| Temperature/K | 100(2) |
| $\theta$ range/° | 1.73–27.10 |
| $R_{int}$ | 0.0300 |
| No. unique reflns. | 12858 |
| No. param. | 761 |
| $R1$ ($F_o{}^2 > 2.0\sigma(F_o{}^2)$) | 0.0245 |
| $wR2$ (all data) | 0.0713 |
| Goodness of fit (all data) | 1.148 |
| $\Delta/\sigma_{max}$ | 0.004 |
| Max/min residue (e Å$^{-3}$) | 1.20/−0.85 |

a) $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma(w(F_o{}^2 - F_c{}^2)^2)/\Sigma(w(F_o)^2)\}^{1/2}$ where $w = 1/\{\sigma^2(F_o)^2 + (0.0456P)^2 + 6.7375P\}$ and $P = 0.33333\{(0, F_o^2)\max\} + 0.66667F_c^2$.

A 500 mM $V^V$ stock solution was prepared by dissolving 29.3 g of $NH_4VO_3$ in 500 mL of 0.85 M NaOH solution. All the chemicals were of analytical grade and were used without further purification.

**Crystal Structure Determination.** A single crystal with dimensions 0.20 × 0.20 × 0.20 mm$^3$ was subjected to X-ray intensity collection at −150(2) °C on a RIGAKU Mercury CCD diffractometer at the Department of Chemistry, Faculty of Science, Kanazawa University. Numerical absorption correction based on the shape of the crystal and the formula was applied. Molybdenum and vanadium atoms were located by a direct method. Oxygen, nitrogen, and carbon atoms were located by successive differential Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full matrix calculations. All calculations were carried out with the SHELX97 program.[41] Crystallographic data and the results of refinements are summarized in Table 1. The CIF file has been deposited at the Cambridge Crystallographic Data Centre with CCDC-686262. Copies of the data can be obtained on request free of charge by quoting the publication citation and the deposition number via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

## Results and Discussion

**Crystallographic Studies.** An ORTEP[42] view of the present heteropolyanion along with atomic numberings is shown in Figure 2. The heteropolyanion possesses an α-Wells–Dawson type structure formed by dimerization of trilacunary A-α-

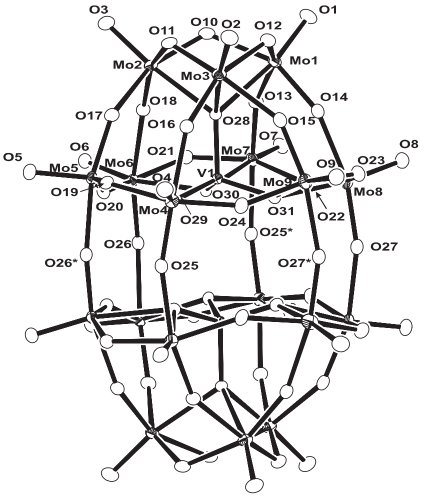

**Figure 2.** An ORTEP diagram of the anion along with atomic notations. Ellipsoiids are drawn in 30% probability. Symmetric operation: * $-x + 1$, $-y + 1$, $z$.

Keggin moieties through six oxygen atoms to have a point group $D_{3h}$ ideally. In the present compound, the anion has one crystallographic two-fold axis running through the center of the equatorial plane, passing the middle points between O25 and O25*, O26 and O26*, and O27 and O27*. The anion has two $V^V$ atoms as the central hetero atoms. Other examples of Wells–Dawson type heteropolymolybdates have been obtained so far with $P^V$, $As^V$, and $S^{VI}$ as the heteroatom.[19–23,28,29,32]

Selected interatomic distances and bond angles are in the normal range and are listed in Table 2. The interatomic distances in the six-membered linkage, Mo1–O10–Mo2–O11–Mo3–O12–Mo1, show an alternate long (Mo1–O10, Mo2–O11, and Mo3–O12)–short (Mo1–O12, Mo3–O11, and Mo2–O10) pattern. Similar patterns are also observed in meridian linkages (Mo1–O14–Mo8–O27–Mo9*–O15*–Mo3*, Mo2–O18–Mo6–O26–Mo5*–O17*–Mo2*, and Mo3–O16–Mo4–O25–Mo7*–O13*–Mo1*, where * indicates an atom transferred by a symmetry operation $-x + 1$, $-y + 1$, $z$). The distances of the shorter bonds in these linkages (1.770(3)–1.842(3) Å) are obviously shorter than those of the longer ones (2.025(3)–2.116(3) Å), but somehow longer than those of Mo–O (terminal) bonds (1.685(3)–1.703(3) Å). However, this tendency is less pronounced in the latitudinal twelve-membered linkage (Mo4–O19–Mo5–O20–Mo6–O21–Mo7–O22–Mo8–O23–Mo9–O24–Mo4) where shorter and longer distances are in the range of 1.874(3)–1.963(3) and 1.926(3)–2.007(3) Å, respectively. Similar tendency has been observed for the Wells–Dawson type heteropolymolybdates of $P^V$ and $As^V$.[19–23,28,29] Besides, the bond angles are in good agreement with those for the $P^V$ and $As^V$ analogues. In the present Wells–Dawson complex, V–O distances are similar to As–O distances in the As(V) complexes, reflecting similar ionic radius of ca. 0.5 Å, but much longer than P–O distances in the $P^V$ analogues. The V–O($\mu^4$) distance (1.752(3) Å) is slightly longer than those of V–O($\mu^3$) (1.692(3)–1.698(3) Å) due to difference in coordination, in agreement with the corresponding bonds in the $As^V$ analogues.[28,29] Angles around V1 ranges 106.3(1)–112.7(1)°, smaller angles being concerned in the V1–O28($\mu^4$) bond. These indicate that the tetrahedral geometry of the vanadium atom is slightly distorted.

The position of the proton was not able to be located. However, the rather low bond valence sum[43] of 1.62 may indicate that O22 is a candidate for a protonated site. Although the value is not distinctive, this is quite possible because one proton

**Table 2.** Selected Interatomic Distances/Å and Bond Angles/° in $[Pr_4N]_5H[V_2Mo_{18}O_{62}]\cdot 2CH_3CN$[a)]

| | | | | | |
|---|---|---|---|---|---|
| Mo1–O10 | 2.025(3) | Mo2–O17 | 2.054(3) | Mo4–O24 | 1.895(3) |
| Mo2–O10 | 1.842(3) | Mo5–O17 | 1.805(3) | Mo9–O24 | 1.926(3) |
| Mo2–O11 | 2.060(3) | Mo2–O18 | 1.792(3) | Mo4–O25 | 1.789(3) |
| Mo3–O11 | 1.827(3) | Mo6–O18 | 2.116(3) | Mo7[a)]–O25 | 2.077(3) |
| Mo1–O12 | 1.820(3) | Mo4–O19 | 1.954(3) | Mo5[a)]–O26 | 2.096(3) |
| Mo3–O12 | 2.044(3) | Mo5–O19 | 1.880(3) | Mo6–O26 | 1.770(3) |
| Mo1–O13 | 2.083(3) | Mo5–O20 | 1.952(3) | Mo8–O27 | 1.793(3) |
| Mo7–O13 | 1.799(3) | Mo6–O20 | 1.880(3) | Mo9[a)]–O27 | 2.082(3) |
| Mo1–O14 | 1.806(3) | Mo6–O21 | 1.973(3) | V1–O28 | 1.752(3) |
| Mo8–O14 | 2.069(3) | Mo7–O21 | 1.874(3) | V1–O29 | 1.694(3) |
| Mo3–O15 | 2.073(3) | Mo7–O22 | 2.007(3) | V1–O30 | 1.698(3) |
| Mo9–O15 | 1.810(3) | Mo8–O22 | 1.963(3) | V1–O31 | 1.692(3) |
| Mo3–O16 | 1.796(3) | Mo8–O23 | 1.940(3) | | |
| Mo4–O16 | 2.104(3) | Mo9–O23 | 1.910(3) | | |

| | | | |
|---|---|---|---|
| Mo1–O10–Mo2 | 120.8(1) | Mo4–O19–Mo5 | 122.1(1) |
| Mo2–O11–Mo3 | 119.1(1) | Mo5–O20–Mo6 | 154.0(2) |
| Mo1–O12–Mo3 | 120.0(1) | Mo6–O21–Mo7 | 120.8(1) |
| Mo1–O13–Mo7 | 151.0(2) | Mo7–O22–Mo8 | 150.6(2) |
| Mo1–O14–Mo8 | 159.1(2) | Mo8–O23–Mo9 | 120.6(2) |
| Mo3–O15–Mo9 | 149.4(2) | Mo4–O24–Mo9 | 153.6(2) |
| Mo3–O16–Mo4 | 157.1(2) | Mo4–O25–Mo7[a)] | 161.3(2) |
| Mo2–O17–Mo5 | 148.4(2) | Mo5[a)]–O26–Mo6 | 161.2(2) |
| Mo2–O18–Mo6 | 156.5(2) | Mo8–O27–Mo9[a)] | 161.9(2) |

a) Symmetry operation; $-x + 1$, $-y + 1$, $z$.

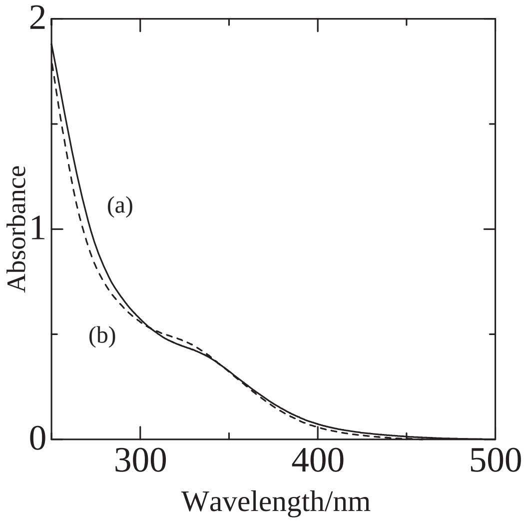

**Figure 3.** UV–vis spectra for $4.0 \times 10^{-5}$ M solutions of (a) $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ and (b) $\alpha$-$[P_2Mo_{18}O_{62}]^{6-}$ in $CH_3CN$. Pathlength: 5.0 mm.

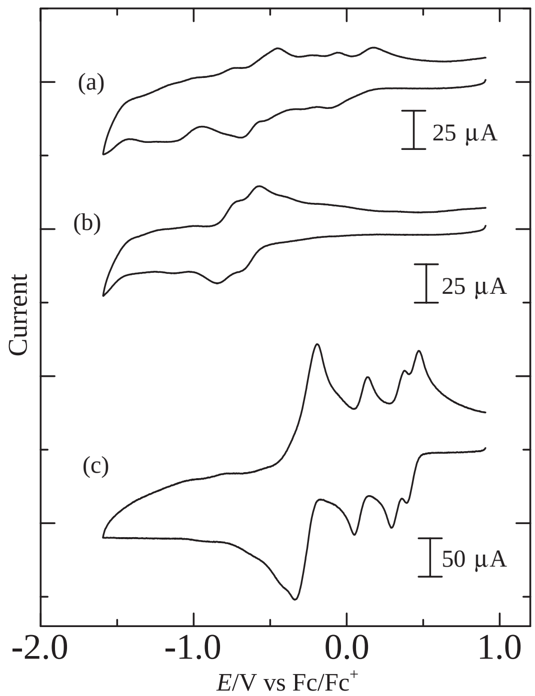

**Figure 4.** Cyclic voltammograms of 0.50 mM $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ in $CH_3CN$ containing 0.1 M $Bu_4NClO_4$. $[Bu_4NOH]$/mM: (a) none; (b) 0.55. $[HClO_4]$/mM: (c) 5.0.

should occupy two sites related by a twofold axis in an anion with an occupancy factor of 0.5, which may cause weakened effect of the protonation to the bond valence sum.

**UV–Vis Spectra.** Figure 3a shows a UV–vis spectrum of $4.0 \times 10^{-5}$ M $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ in $CH_3CN$. The Wells–Dawson anion shows a broad absorption band at wavelengths <430 nm. The spectrum was unchanged with time, indicating that the $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ complex is kinetically stable in $CH_3CN$. For comparison, Figure 3b shows a UV–vis spectrum of $\alpha$-$[P_2Mo_{18}O_{62}]^{6-}$. Both spectra are very similar, and conformed to Beer's Law in the whole spectral region studied (molar extinction coefficients at 320 nm are found to be $2.28 \times 10^4$ and $2.42 \times 10^4$ $cm^{-1}$ $M^{-1}$ for $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ and $\alpha$-$[P_2Mo_{18}O_{62}]^{6-}$, respectively).

**Voltammetric Characterization.** The voltammetric properties of Keggin and Wells–Dawson complexes have received increasing attention in view of their potential use in electrocatalysis.[44] The voltammetric properties of the Keggin complexes ($\alpha$-$[XMo_{12}O_{40}]^{n-}$ (X = S, V, P, As, Si, and Ge; $n = 2$–4) and $\alpha$-$[XW_{12}O_{40}]^{n-}$ (X = S, V, P, As, Si, Ge, and Al; $n = 2$–5)) have been well characterized. All the Keggin anions exhibit successive one-electron redox waves in neutral solution, and with the exception of $[SW_{12}O_{40}]^{2-}$,[9] they undergo two-electron reductions in acidified solutions. In 1967, Pope and Papaconstantinou found that the Wells–Dawson-type $[P_2W_{18}O_{62}]^{6-}$ complex underwent one-electron reductions in neutral media.[45] However, no one-electron waves had been reported for the Mo-analogues, $[X_2Mo_{18}O_{62}]^{6-}$ (X = P and As)[46,47] until 1993.[48,49] Recently, we found that both $\alpha$-$[S_2Mo_{18}O_{62}]^{4-}$ and $\alpha$-$[S_2W_{18}O_{62}]^{4-}$ exhibited successive one-electron reductions in $CH_3CN$.[33,50] Although it is known that the Wells–Dawson complexes undergo two-electron reductions in acidified media, their voltammetric behaviors have not been entirely characterized so far.

The voltammetric characterization of $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ seems essential to understand the whole electrochemical properties of Wells–Dawson complexes. A cyclic voltammogram was recorded for $(Pr_4N)_5H[V_2Mo_{18}O_{62}]$ dissolved in $CH_3CN$ containing 0.1 M $Bu_4NClO_4$. As shown in Figure 4a, the present Wells–Dawson anion exhibited only ill-defined waves. In order to avoid the effect of the acidic proton in the $(Pr_4N)_5H[V_2Mo_{18}O_{62}]$ salt on the voltammetric behavior, we neutralized it by the addition of $Bu_4NOH$. As expected, the irreversible redox waves decreased gradually as the $Bu_4NOH$ concentration was increased. In the presence of an equivalent amount of $Bu_4NOH$, $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ exhibited two well-defined one-electron redox waves with mid-point potentials ($E_{mid}$) of −0.62 and −0.78 V (Figure 4b), where $E_{mid} = (E_{pa} + E_{pc})/2$; $E_{pc}$ and $E_{pa}$ are cathodic and anodic peak-potentials, respectively. The $E_{pc}$ and $E_{pa}$ values for each redox couple were independent of the voltage scan rate, indicating the reversible nature of each wave.

With the addition of 5.0 mM $HClO_4$, as shown in Figure 4c, the one-electron redox waves were converted into a three-step wave with $E_{mid}$ values of 0.43, 0.33, and 0.09 V. The normal pulse voltammetric measurement confirmed that each wave corresponded to a two-electron transfer. This conversion behavior can be accounted for in terms of protonation of the reduced species at the electrode surface.[51–54]

In order to study the role of the central V atoms in the voltammetric properties of $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$, we recorded cyclic voltammograms for $(Bu_4N)_5H[P_2Mo_{18}O_{62}]$ dissolved in $CH_3CN$ containing 0.1 M $Bu_4NClO_4$ (Figure 5). In the presence of an equivalent amount of $Bu_4NOH$ (Figure 5b), $\alpha$-$[P_2Mo_{18}O_{62}]^{6-}$ underwent a two-step one-electron reduction with $E_{mid}$ values of −0.68 and −0.83 V. With the addition of 5 mM $HClO_4$ (Figure 5c), a three-step two-electron wave was obtained with $E_{mid}$ values of 0.39, 0.29, and 0.01 V.

For both one- and two-electron redox processes, the voltammetric behaviors of $\alpha$-$[V_2Mo_{18}O_{62}]^{6-}$ paralleled those of $\alpha$-

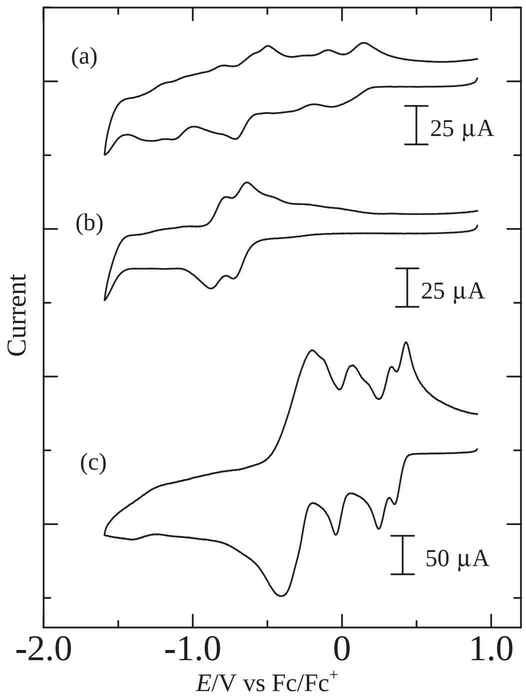

**Figure 5.** Cyclic voltammograms of 0.50 mM $\alpha$-[$P_2Mo_{18}O_{62}$]$^{6-}$ in $CH_3CN$ containing 0.1 M $Bu_4NClO_4$. [$Bu_4NOH$]/mM: (a) none; (b) 0.55. [$HClO_4$]/mM: (c) 5.0.

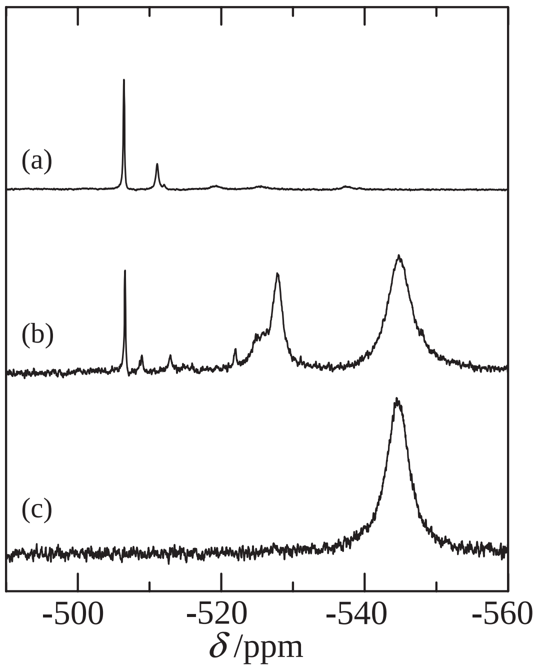

**Figure 6.** $^{51}V$ NMR spectra for an aqueous 100 mM $Mo^{VI}$–20 mM $V^{V}$ system. [HCl]/M: (a) 0.20 (pH 2.8); (b) 0.30 (pH 1.3); (c) 0.35. Recorded after heating at 70 °C for 24 h.

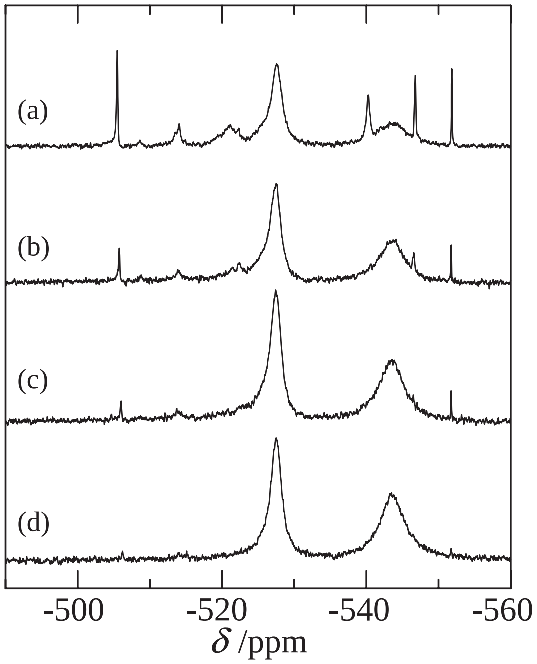

**Figure 7.** $^{51}V$ NMR spectra for a 100 mM $Mo^{VI}$–20 mM $V^{V}$–20% (v/v) $CH_3CN$ system. [HCl]/M: (a) 0.30; (b) 0.35; (c) 0.40; (d) 0.45. Recorded after heating at 70 °C for 24 h.

[$P_2Mo_{18}O_{62}$]$^{6-}$, although the redox waves for the former anion were situated at slightly more positive potentials than those for the latter. Thus, the voltammetric waves in Figure 4 can be ascribed to the reduction of $Mo^{VI}$ in the peripheral position. In conclusion, no voltammetric waves for $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$ can be assigned to the reduction of the central $V^{V}$ atom.

**Formation of $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$ in Acidified Aqueous-$CH_3CN$ Media.** With the aim of clarifying the formation conditions of $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$, $^{51}V$ NMR spectra were recorded after heating a 100 mM $Mo^{VI}$–20 mM $V^{V}$ system of various acidities at 70 °C for 24 h. Turbidity is apt to occur at greater acidities, and $^{51}V$ NMR measurements were made for clear filtrates. In the pH range of 4.0–1.0, the $^{51}V$ NMR spectrum was characterized by a sharp line at −506 ppm, due to [$VMo_5O_{19}$]$^{3-}$ (Figure 6a).[55,56] Around pH 1.3, new lines grew at −527 and −544 ppm (Figure 6b). By comparison with chemical shift values of $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$ in $CH_3CN$, the former line is assigned to $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$, and the latter to $VO_2^{+}$.[57] Simultaneously, the aqueous system gave additional minor lines, to which no assignments can be made. As the HCl concentration was further increased, the additional lines disappeared completely, but the −527 ppm line also disappeared, leaving the −544 ppm line due to $VO_2^{+}$ (Figure 6c). Despite various attempts, $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$ was not successfully prepared from the acidified aqueous system.

Remarkable progress in the preparation of polyoxometalates has been made with the use of $CH_3CN$ as an auxiliary solvent. Therefore, we recorded again $^{51}V$ NMR spectra after heating a 100 mM $Mo^{VI}$–20 mM $V^{V}$–20% (v/v) $CH_3CN$ system of various acidities at 70 °C for 24 h, and the results are shown in Figure 7. Besides the [$VMo_5O_{19}$]$^{3-}$ line at −506 ppm, a pair of $^{51}V$ NMR lines with equal intensities appeared at −514 and −552 ppm, indicating the formation of the Keggin-type [$V(VMo_{11})O_{40}$]$^{4-}$ complex. Like the aqueous 100 mM $Mo^{VI}$–20 mM $V^{V}$–0.3 M HCl system, the 20% (v/v) $CH_3CN$-containing system also showed the $\alpha$-[$V_2Mo_{18}O_{62}$]$^{6-}$ line. As shown in Figure 7, the additional lines decreased with an increase of

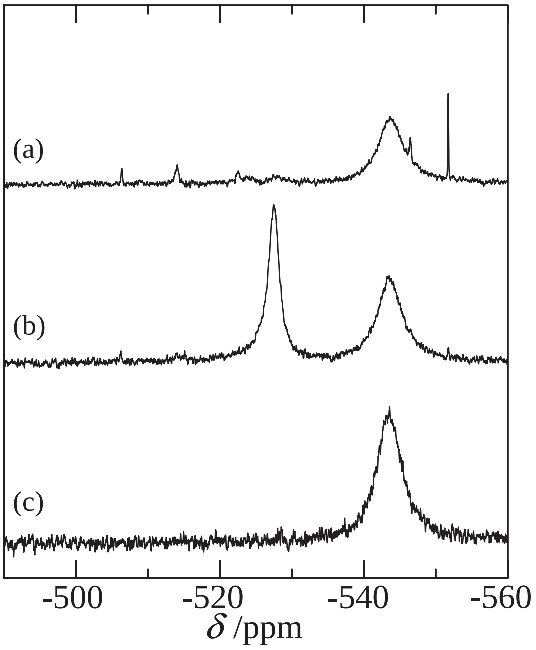

**Figure 8.** $^{51}$V NMR spectra for a 100 mM $Mo^{VI}$–20 mM $V^{V}$–0.45 M HCl–20% (v/v) $CH_3CN$ system. Recorded: (a) without heating; after heating at 70 °C for (b) 24 h and (c) 8 days.

the HCl concentration, and the α-$[V_2Mo_{18}O_{62}]^{6-}$ complex became predominant at the HCl concentration of 0.45 M HCl (Figure 7d). The $V^V$ concentration of 20 mM was chosen as optimum under these conditions, because the intensity of the α-$[V_2Mo_{18}O_{62}]^{6-}$ line became lower at lower $V^V$ concentrations, and the presence of $V^V$ at concentration ≧30 mM only caused the $VO_2^+$ line to grow in relation to the α-$[V_2Mo_{18}O_{62}]^{6-}$ line.

As shown in Figure 8, heating of the 20% (v/v) $CH_3CN$-containing system is essential for the formation of α-$[V_2Mo_{18}O_{62}]^{6-}$, while $[V(VMo_{11})O_{40}]^{4-}$ is formed without heating of the system. However, both α-$[V_2Mo_{18}O_{62}]^{6-}$ and $[V(VMo_{11})O_{40}]^{4-}$ complexes are kinetically unstable under these conditions, as judged by the decrease of the $^{51}$V NMR line intensities with time. Ultimately, the $^{51}$V NMR lines disappeared completely with prolonged heating at 70 °C for eight days (Figure 8c).

**Effect of the $CH_3CN$ Concentration on the Formation of α-$[V_2Mo_{18}O_{62}]^{6-}$.** Figure 9 shows $^{51}$V NMR spectra after heating a 100 mM $Mo^{VI}$–20 mM $V^V$–0.45 M HCl system containing various concentrations of $CH_3CN$. In addition to the α-$[V_2Mo_{18}O_{62}]^{6-}$ and $VO_2^+$ lines, the $[V(VMo_{11})O_{40}]^{4-}$ lines appeared at the $CH_3CN$ concentration of 30% (v/v) (Figure 9b), and were increased in intensity at the expense of the α-$[V_2Mo_{18}O_{62}]^{6-}$ and $VO_2^+$ lines as the $CH_3CN$ concentration was further increased. In the presence of 50% (v/v) $CH_3CN$, as shown in Figure 9d, the α-$[V_2Mo_{18}O_{62}]^{6-}$ and $VO_2^+$ lines were replaced by the $[V(VMo_{11})O_{40}]^{4-}$ lines. It should be added that the Keggin complex, $[VMo_{12}O_{40}]^{3-}$ becomes predominant at $CH_3CN$ concentrations ≧60% (v/v). Thus, the interconversion between the Keggin and Dawson complexes can occur as a function of the $CH_3CN$ concentration.

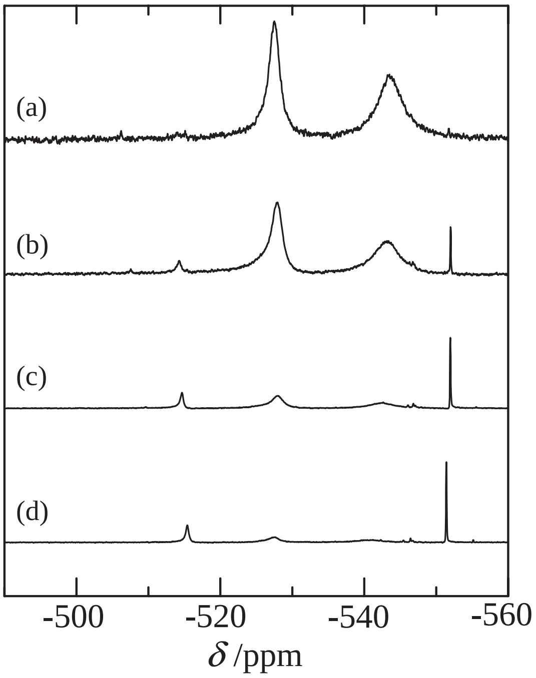

**Figure 9.** $^{51}$V NMR spectra for a 100 mM $Mo^{VI}$–20 mM $V^V$–0.45 M HCl system. $[CH_3CN]$/% (v/v): (a) 20; (b) 30; (c) 40; (d) 50. Recorded after heating at 70 °C for 24 h.

Similar behavior has been observed for the Wells–Dawson-type $[P(As)_2Mo_{18}O_{62}]^{6-}$ and Keggin-type $[P(As)Mo_{12}O_{40}]^{3-}$ complexes. Unlike the Wells–Dawson complex that is kinetically stable in aqueous media, the corresponding Keggin complex is stable only in the presence of $CH_3CN$. In general, the presence of $CH_3CN$ is essential for the formation of Keggin and Dawson complexes with lower ionic charges such as $[SMo_{12}O_{40}]^{2-}$ and $[S_2Mo_{18}O_{62}]^{4-}$. The lower relative permittivity of $CH_3CN$ ($\varepsilon_r = 36.0$) would be a factor.

## Conclusion

The formation of an α-Wells–Dawson-type $[V_2Mo_{18}O_{62}]^{6-}$ complex was ascertained in an aqueous 100 mM $Mo^{VI}$–20 mM $V^V$ system of very narrow acidity range (around 0.3 M HCl). However, several vanadomolybdate complexes inevitably coexisted with α-$[V_2Mo_{18}O_{62}]^{6-}$ at HCl concentrations <0.35 M (Figure 6). We found that the presence of 20% (v/v) $CH_3CN$ in the system caused the acidity range to expand to greater concentrations of HCl (Figure 7), which makes it possible to prepare α-$[V_2Mo_{18}O_{62}]^{6-}$ in pure form.

Like the usual α-Wells–Dawson-type $[P_2Mo_{18}O_{62}]^{6-}$ complex with the same ionic charge of −6, α-$[V_2Mo_{18}O_{62}]^{6-}$ underwent a two-step one-electron reduction in neutral media, and the one-electron wave was converted into a three-step two-electron waves under conditions where protonation accompanied the electrochemical reduction.

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