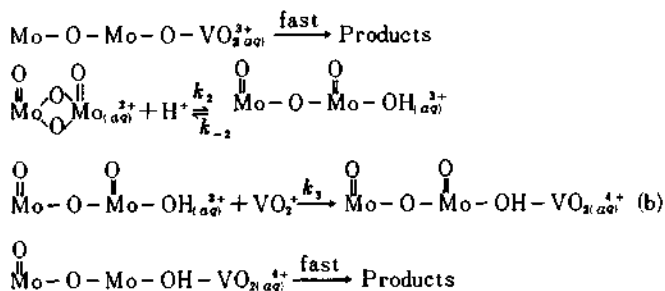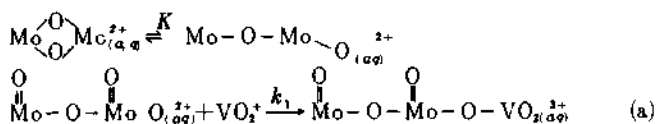intercept and slope of Figure 2 were 8.34×10^{-4} sec^{-1} and 4.92×10^{-2}M^{-1} sec^{-1}, respectively. Rate equation (2) shows two terms involving [H⁺]-dependent and –independent rates. The [H⁺]-independent term indicates the presence of a dimeric Mo(V) species in which one of the oxo bridges was broken.[6,8] The [H⁺] dependence is due to catalytic ring-opening of Mo(O)(O)Mo, forming Mo-O-Mo-OH³⁺ which is much more reactive than Mo(O)(O)Mo. In the oxidation of the [Mo₂O₄(edta)]²⁻ and [Mo₂O₄(hedta) (H₂O)]⁻ (H₃ hedta = N-(2-hydroxyethyl) ethylenediamine-N,N′,N′-triacetic acid) by oxidants, molybdenum(V,VI) atoms were held together by edta⁴⁻ and hedta³⁻, and thus formed Moⱽ-Moⱽᴵᐨᐟedtaᐧ or MoⱽᐧMoⱽᴵᐨhedta as an intermediate.[6] However, in the oxidation of [Mo₂O₄(H₂O)₆]²⁺ it is considered that there is fast dissociation of MoⱽᐧMoⱽᴵ. We assume that rate determining step of the reaction(1) is the process which the coordination number of vanadium in aqueous solution is increased from four or five in V(V) to six in V(IV) since redox step accompanying structural change seem energetically prohibitive.[10]

The mechanism for the oxidation of the aquaoxomolybdenum(V) dimer by VO₂⁺ may be described by the steps

$$\text{Mo}\underset{O}{\overset{O}{\diamondsuit}}\text{Mo}^{2+}_{(aq)} \overset{K}{\rightleftharpoons} \text{Mo-O-Mo}\underset{O}{\diagdown}{}^{2+}_{(aq)}$$

$$\text{Mo-O-Mo O}^{2+}_{(aq)} + \text{VO}_2^+ \overset{k_1}{\longrightarrow} \text{Mo-O-Mo-O-VO}^{3+}_{2(aq)} \quad (a)$$

$$\text{Mo-O-Mo-O-VO}^{3+}_{2(aq)} \overset{fast}{\longrightarrow} \text{Products}$$

$$\text{Mo}\underset{O}{\overset{O}{\diamondsuit}}\text{Mo}^{2+}_{(aq)} + \text{H}^+ \overset{k_2}{\underset{k_{-2}}{\rightleftharpoons}} \text{Mo-O-Mo-OH}^{3+}_{(aq)}$$

$$\text{Mo-O-Mo-OH}^{3+}_{(aq)} + \text{VO}_2^+ \overset{k_3}{\longrightarrow} \text{Mo-O-Mo-OH-VO}^{4+}_{2(aq)} \quad (b)$$

$$\text{Mo-O-Mo-OH-VO}^{4+}_{2(aq)} \overset{fast}{\longrightarrow} \text{Products}$$

Assuming steady state for the concentration of Mo-O-Mo-H$^{3+}_{(aq)}$ in mechanism (b) we obtain

$$-\frac{d[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]}{dt} = \{k_1K + \frac{k_2k_3[\text{H}^+]}{k_{-2}+k_3[\text{VO}_2^+]}\}$$
$$[\text{VO}_2^+][\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \quad (3)$$

Under the condition $k_{-2} \gg k_3$ [VO₂⁺], rate equation (3) reduces to equation (4).

$$-\frac{d[\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}]}{dt} = \{k_1K + (k_2k_3/k_{-2})[\text{H}^+]\}$$
$$[\text{VO}_2^+][\text{Mo}_2\text{O}_4(\text{H}_2\text{O})_6^{2+}] \quad (4)$$

From this equation $k_{obsd} = \{k_1K \ (k_2k_3/k_{-2})\ [\text{H}^+]\}$ [VO₂⁺] [Mo₂O₄(H₂O)₆²⁺], $k_1K = k_0$, and $k_2k_3/k_{-2} = k_H$.

Detailed mechanisms of the reaction should be the subject of further investigations.

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Temperature Variation of the Polycrystalline EPR Spectrum of α-1,2,3-[H₂PV(IV)V₂W₉O₄₀]⁵⁻ Doped into K₅[H₂SiV₃W₉O₄₀]

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Recently we have reported the polycrystalline electron paramagnetic resonance (EPR) spectrum of α-1,2,3-[H₂PV(IV)V₂W₉O₄₀]⁵⁻ doped into K₅[H₂SiV₃W₉O₄₀] and its solution spectrum at room temperature.[1,2] The solution spectrum consists of fifteen lines, indicating that the unpaired electron is hopping fast between the two vanadium ($I = 7/2$) atoms of the OH-V-O-V-OH group. The V-OH-V bridge prevents effectively the electron transfer between the vanadium atoms. The polycrystalline spectrum consists of three sets of fifteen lines and it was analyzed as a spectrum of an $I = 7$ system.

Now we have measured EPR spectra of the polycrystalline sample at low temperatures and found that the behavior of this complex, in which the VO₆ octahedra are corner-shared,[3] is quite different from that of [P₂V(IV)VW₁₆O₆₂]⁹⁻ and related complexes in which the VO₆ octahedra are edge-shared.[4]

Three EPR spectra measured at 300, 200, and 100K are shown in Figure 1. The 300K spectrum may be interpreted as consisting of x-, y-, an z-components, each component showing fifteen lines. In fact, only nine outer lines of the z component can be clearly seen; inner lines are overlapped with x-
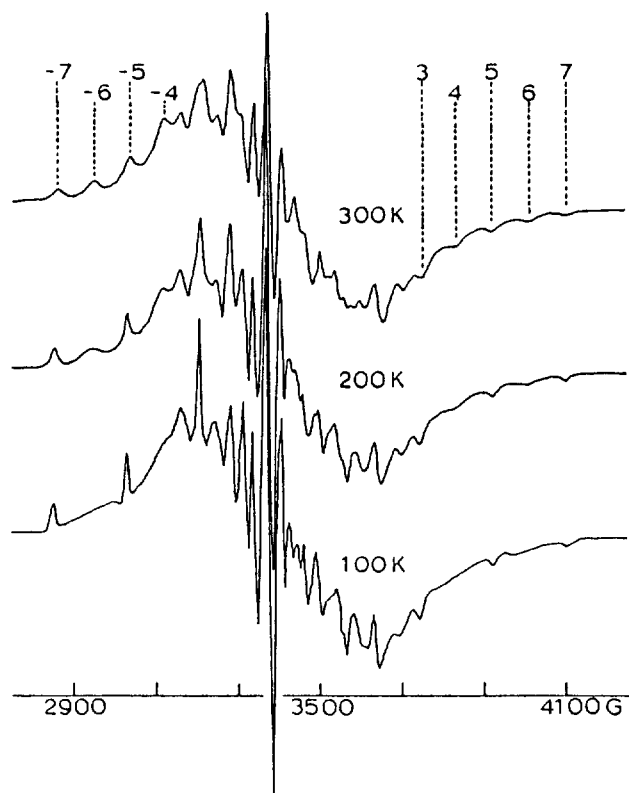
Figure 1. Temperature variation of the polycrystalline EPR spectrum of α-1,2,3-[H$_2$PV(IV)V$_2$W$_9$O$_{40}$]$^{5-}$ doped into K$_5$[H$_2$SiV$_3$W$_9$O$_{40}$]. Parallel lines are designated by the m_i values of an I = 7 system. Microwave frequency: 9.4394 GHz.

and y-components. The hyperfine lines of the z component are designated by their m_i values. As the temperature is lowered, the odd lines ($m_i = -7, -5, ..., 3, 5, 7$) get narrower while the even lines ($m_i = -6, -4, ..., 4, 6$) broaden. At 100K, the even lines become very broad and the odd lines alone look similar to the z component typical of a mononuclear vanadyl complex. However, the whole spectrum is still much more complicated than that of a typical mononuclear vanadyl complex.[5]

In order to understand temperature variation of the EPR spectrum, we will consider a simple model system where an electron is hopping between two equivalent vanadyl groups, each of which is assumed to be an axial system.

When the unpaired electron is trapped on one vanadium atom at a very low temperature, the polycrystalline spectrum is expected to show parallel and perpendicular components, each set consisting of eight lines. The hyperfine lines may be designated by their m_i values, $-7/2, -5/2, ..., 7/2$.

When the unpaired electron is hopping between two vanadium atoms, the line shapes will vary according to the electron hopping rate. As the hopping rate increases, the two hyperfine lines broaden and move towards each other until they collapse into a single broad line, and finally become a sharp exchange-narrowed line centered at the average magnetic field of the two lines.[6]

How will this phenomenon affect the polycrystalline spectrum? Let us first consider the behavior of the lowest-field line. When the electron is trapped on one vanadium atom, this line corresponds to the $m_i = -7/2$ line with the magnetic field

directed along the V = O vector. On the other hand, when the hopping rate is so fast that a sharp line appears at the average magnetic field of two lines, the lowest-field line will be the exchange-narrowed line for two vanadyl groups both having $m_i = -7/2$ with the magnetic field directed exactly halfway between the two V = O vectors in the plane containing them. This line corresponds to the $m_i = -7$ line in Figure 1. Other odd lines are related in the same manner with two vanadium atoms having the same m_i values. Since the $m_i = -7/2$ line should occur at a lower field than the $m_i = -7$ line, the lowest-field line would gradually shift up-field at the intermediate hopping rates.

Now the question arises whether the odd lines in the 100K spectrum represents the parallel lines of a mononuclear vanadyl system or exchange-narrowed lines of a mixed-valence system. When these lines are assumed to be the z-component of a mononuclear vanadyl system and fitted to the following equation,[1]

$$h\nu = g_{11}\beta B + Am + \frac{B^2}{2h\nu}(I(I+1) - m^2)$$

the resulting hyperfine parameters, $|A| = 161.8 \times 10^{-4}$cm^{-1} and $|B| = 40 \times 10^{-4}$cm^{-1} are considerably smaller than those of a typical mononuclear vandyl complex; compare with the EPR parameters[5] $g = 1.9232$, $g_{\perp} = 1.968$, $|A| = 169.3 \times 10^{-4}$cm^{-1}, and $|B| = 59.6 \times 10^{-4}$cm^{-1} of [PV(IV)W$_{11}O_{40}$]$^{5-}$. In addition, when the temperature goes up to 300K, the lowest-field line is shifted upfield by only 8G, while a 30G shift is expected from $\alpha = 44°$. Here α is the angle between the two V = O vectors, which has been determined from an X-ray crystal structure of a Keggin anion.[8] Thus we believe that the odd lines in the 100K spectrum are exchange-narrowed lines. In fact, the observed positions of all odd lines could be calculated by using the above-given EPR parameters of [PV(IV)W$_{11}$O$_{40}$]$^{5-}$ with a slight modification g to 1.933 and by varying the α value. The resulting angle $\alpha = 36.5°$ is somewhat smaller than $\alpha = 44°$, indicating perhaps that the hyperfine parameters used here are smaller than the true values.

When the m_i values of the two vanadium atoms are m_1 and m_2 ($m_1 \neq m_2$), the resulting average lines will contribute to the line corresponding to $m_i = m_1 + m_2$, either odd or even. For example, if the m_i values of the two vanadium atoms are $-7/2$ and $-5/2$, the average magnetic field lines contribute to the $m_i = -6$ line. But this line will be broader than the $m_i = -7$ line at 100K, since the separation between the two hyperfine lines is larger when the m_i values are different for any given direction of the magnetic field. Other even lines can be interpreted in a similar manner. In this way we can explain that the odd lines are sharp while even lines are broad at 100K and that the even lines get narrower as the temperature goes up. But we cannot yet explain the observation that the odd lines broaden slightly as the temperature goes up.

The most interesting property of this complex is that the unpaired electron is not trapped on a vanadium atom at a temperature as low as 100K. This property must be related with the structure of this complex, in which the VO$_6$ octahedra are corner-shared.[3] Electron trapping was found to occur at a temperature as high as 211K for [P$_2$V(IV)VW$_{16}$O$_{62}$]$^{9-}$ in which the VO$_6$ octahedra are edge-shared.[4] It was argued that electron hopping in the latter complex occurs via the bridging oxygen atom, electron transfer is facilitated as the π bond order of the V–O–V bonds increases since the unpaired elec-

tron on V^{4+} occupies the d_{xy} orbital that has π symmetry with respect to the bridging V–O bonds, and electron trapping occurs at high temperatures since the extent of V–O–V π bonding is low as a result of the 125° bridge bond angle.[4,7] The same argument may be applied to our system. However, since the V–O–V bridge bond is 158° for this complex[8] and the extent of V–O–V bonding is relatively large, electron transfer will be facilitated.

We have shown that temperature variation of the polycrystalline EPR spectrum of α-1,2,3-$[H_2PV(IV)V_2W_9O_{40}]^{5-}$ can be explained qualitatively and that the large V–O–V bridge bond angle is responsible for facile electron transfer in this complex. More information may be obtained from EPR spectra of this complex at temperatures below 100K and from simulation of the spectra at various temperatures. Also needed is a better analysis of the dependence of electron transfer rate on the V–O–V bridge bond angle.

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A Thermodynamic Consideration on the DBC–Bivalent Cation Complexes in Some Nonaqueous Solvents

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In the previous paper the stability constants of the complexes formed between dibenzo-18-crown-6(DBC) and alkaline earth metal cations in dimethyl sulfoxide(DMSO), dimethyl formamide(DMF), and acetonitrile(AN) at 25°C were reported[1]. The results were interpreted in terms of ion–cavity radius ratio concept, solvent donocity, and solvation of the cations with little obviosity.

However, little attention has been paid to the thermodynamic consideration on the complexation of the crown ether type ligands in the nonaqueous solvents. In this work the stability constants of the DBC–bivalent cation complexes at two more different temperatures, 35°C and 40°C, were measured by the same methods described in the previous paper and are shown in Table 1. The enthalpy and entropy contribution to the free energy of binding for DBC were calculated from Van't Hoff equation are given in Table 2. The results showed that complex formation of DBC is enthalpic in orgin[2,3]. For all the bivalent cations complexation in the basic solvents is favorable from enthalpic point of view with either unfavorable for Ca^{2+} and Sr^{2+} or favorable but low entropic contribution for Ba^{2+}. In spite of the facts that the charge density of Ca^{2+} is the largest among the cations, and that complex formation involves replacement of the solvent molecules by a single DBC molecule, the overall entropy of the complexation processes is negative. Apparently Ca^{2+} and Sr^{2+} ions act as structure breakers in the basic solvents and formation of the DBC–bivalent cation complexes results in an overall increase of organization in the solution[4].

X-ray crystallographic studies also showed the cavity of the 18-crown-6 type ligands to be celliptical in the uncomplexed state, but nearly circular in the complex[5,6]. The significant conformational change followed by the change of ligand solvation might play an important role for the decrease in the entropy. Higher charge density of Ca^{2+} ($Z^2/r = 10.3$)[7] than that of Ba^{2+} (7.6) may be attributed to it. It is also probable that the difference in solvation of the ligand in the different sol-

Table 1. Stability constants (log K) of the DBC complexes in AN, DMF, and DMSO at various temperatures

Solvents	AN			DMF			DMSO		
Salts	CaI_2	SrI_2	BaI_2	CaI_2	SrI_2	BaI_2	CaI_2	SrI_2	BaI_2
25°C*	2.30	3.36	3.50	2.17	3.18	3.38	1.76	2.83	3.20
35°C	1.93	3.18	3.40	1.52	3.15	3.28	1.13	2.52	3.16
40°C	1.67	3.03	3.37	1.08	2.92	3.23	0.83	2.34	3.14

*Values from reference 1.