

Epr Study of the 10-Tungsto-2-vanado(IV, V)phosphate Anion, $[PV(IV)W_{10}O_{40}]^{6-}$

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The polycrystalline epr spectrum of α -1,2- $[PV(IV)W_{10}O_{40}]^{6-}$ doped into host crystals and its solution spectrum are reported. The solution spectrum consists of fifteen lines, indicating that the unpaired electron is hopping fast between the two vanadium atoms. The polycrystalline spectrum, which consists of three sets of fifteen lines, was analyzed as a spectrum of an $I=7$ system and the epr parameters were determined. The spectrum cannot be interpreted by assuming that each line appears at the average magnetic field of two hyperfine lines expected for two uncoupled vanadium atoms.

Introduction

Various mixed valence complexes can be prepared by partial reduction of heteropolyanions.¹ Some of these complexes have been studied by electron paramagnetic resonance(epr) techniques. Especially fruitful studies have been carried on systems containing vanadium(IV) and vanadium(V). The solution epr spectra of $[PV(IV)W_{10}O_{40}]^{6-}$ and $[PV(IV)VMo_{10}O_{40}]^{6-}$ were reported in 1975.^{2,3} Each spectrum was interpreted as a superposition of an 8-line component and a 15-line component. The 8-line spectrum was ascribed to isomers in which two vanadium atoms are separated by at least an -O-W-O- sequence and the unpaired electron is trapped on one vanadium center. The 15-line spectrum was ascribed to the isomer in which vanadium atoms are separated by a single oxygen atom and the unpaired electron is hopping fast between the two vanadium ($I=7/2$) centers. In this case, each spectral line is expected to appear at the average magnetic field of two hyperfine lines expected when the electron is assumed to interact separately with each vanadium atom. Thus a 15-line spectrum with the intensities 1,2,3...8...1 can be understood.

As stereospecific syntheses of certain mixed-metal heteropoly anions became possible, epr spectra of α -1,2- $[SiV(IV)W_{10}O_{40}]^{7-}$, α -1,2,3- $[SiV(IV)V_2W_9O_{40}H]^{7-}$, $[P_2V(IV)W_{10}O_{40}]^{6-}$, $[P_2V(IV)V_2W_9O_{40}H]^{6-}$ and $[P_2V(IV)V_2W_9O_{40}]^{6-}$ have been measured.^{4,5} Their solution spectra at room temperature show that the unpaired electron is hopping fast among the vanadium atoms. However, at lower temperatures the electron is shown to be trapped on one vanadium center by the frozen solution spectrum.

What would a "frozen solution" spectrum look like when the unpaired electron is hopping fast among the vanadium atoms? Would each line appear at the average magnetic field of two hyperfine lines expected for two uncoupled vanadium atoms? In order to answer these questions we have measured the polycrystalline epr spectrum of α -1,2- $[PV(IV)W_{10}O_{40}]^{6-}$, an anion having the Keggin structure, doped into $K_6[PV_3W_9O_{40}]$.

Experimental

Preparation of Compounds.

α -1,2- $K_5[PV_2W_{10}O_{40}]$, α -1,2,3- $K_6[PV_3W_9O_{40}]$, and α -1,2,3- $K_6H[SiV_3W_9O_{40}]$ were prepared according to the

methods of Domaille.⁶

An aqueous solution of α -1,2- $K_5[PV_2W_{10}O_{40}]$ or α -1,2,3- $K_6[PV_3W_9O_{40}]$ was reduced to one-electron reduction state by adding hydrazine dihydrochloride or by constant-current electrolysis. The reduced form was coprecipitated at 0°C by adding $K_6[PV_3W_9O_{40}]$ or $K_6H[SiV_3W_9O_{40}]$ and potassium chloride.

Epr Measurements.

Epr spectra were recorded on a Bruker epr spectrometer (Model ER 200E) operating at 9.7 GHz. The microwave frequency was measured by a Hewlett-Packard frequency counter and DPPH was used as a g-marker. All spectra were recorded at room temperature.

Results and Discussion⁷

The Solution Spectrum.

A solution epr spectrum of the one-electron reduction product of α -1,2- $K_5[PV_2W_{10}O_{40}]$ is shown in Figure 1. The 15-line spectrum is similar to that of α -1,2- $[SiV(IV)W_{10}O_{40}]^{7-}$, but the relative intensities of the hyperfine lines in our spectrum do not agree exactly with the expected intensities 1:2:3...8...1. In fact, all the odd lines are stronger than expected, indicating that an 8-line spectrum is superimposed on a 15-line spectrum.

The 8-line spectrum is ascribed to isomers of $PV(IV)V$, in which two vanadium atoms are separated by at least an -O-W-O- sequence and thus the unpaired electron is trapped on one vanadium center. These isomers may originate from the corresponding PV_2 species which exist as impurities in the original sample of α -1,2- $K_5[PV_2W_{10}O_{40}]$ and from the isomerization reaction of α -1,2- $PV(IV)V$. The latter origin is supported by the observation that the relative intensity of the 8-line spectrum increases with the length of time during which the reduced form is kept in solution.

The 15-line spectrum is ascribed to α -1,2- $[PV(IV)W_{10}O_{40}]^{6-}$, and analyzed by using the following equation⁸ and $I=7$.

$$h\nu = g\beta B + am + \frac{a^2}{2h\nu} [I(I+1) - m^2] \quad (1)$$

The resulting parameters are $g=1.950$ and $a=48.0 \times 10^{-4} \text{cm}^{-1}$. These values agree well with the reported values $g=1.952$ and $a=48 \times 10^{-4} \text{cm}^{-1}$, which were determined by simulating the spectrum of a non-stereospecifically prepared sample of

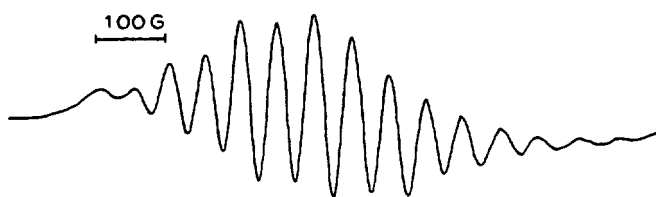


Figure 1. Epr spectrum of α -1,2-[PV(IV)VW₁₀O₄₀]⁶⁻ in aqueous acetate buffer, pH 4.7 at room temperature. An 8-line spectrum is superimposed on the 15-line spectrum.

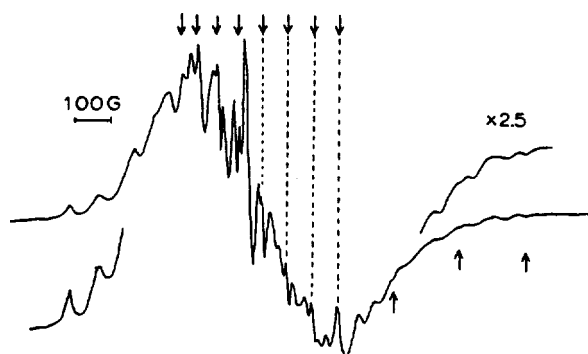


Figure 2. Polycrystalline epr spectrum of α -1,2-[PV(IV)-VW₁₀O₄₀]⁶⁻ doped into K₆[PV₃W₉O₄₀] at room temperature. Impurity peaks indicated by arrows belong to the species in which the unpaired electron is trapped on one vanadium center.

PV(IV)V.

The spectrum in Figure 1 could be simulated by combining 8- and 15-line spectra with the same g value and with $a = 96 \times 10^{-4}$ and $48 \times 10^{-4} \text{cm}^{-1}$, respectively. The relative intensities of the 8- and 15-line spectra were 1:10, indicating that the 1,2-isomer was the major species responsible for the spectrum. When two vanadium atoms are randomly positioned in the Keggin structure,³ the relative intensities of the 8- and 15-line spectra are 7:4.

It is interesting to note that the reported spectrum³ of non-stereospecifically prepared [PV(IV)V Mo₁₀O₄₀]⁶⁻ is quite similar to our spectrum in Figure 1, indicating that somehow the 1,2-isomer was prepared dominantly. This may give a clue for understanding the mechanism of formation of PV₂Mo₁₀.

The Polycrystalline Spectrum.

A polycrystalline spectrum of the reduction product of α -1,2-PV(IV)V doped into K₆[PV₃W₉O₄₀] is shown in Figure 2. It contains peaks belonging to the species in which the unpaired electron is trapped on one vanadium center. The intensities of these peaks depended on how long the reduced species was kept in solution. Since we were interested in the spectrum of pure α -1,2-PV(IV)V, we have tried to prepare a sample which does not show impurity peaks. While it was not possible to prepare a pure sample of α -1,2-PV(IV)V by reducing a sample of α -1,2-PV₃, a sample showing no impurity peaks was obtained by reducing α -1,2,3-PV₃ and coprecipitating the reduced species with K₆H[SiV₃W₉O₄₀]. Its spectrum is shown in Figure 3.

Although it is not clear whether the species responsible for this spectrum is α -1,2-PV(IV)V or an isomer of PV(IV)V₂ in which the electron is interacting only with two vanadium nuclei,¹² the spectrum matches closely with the spectrum in Figure 2 minus the impurity peaks. Thus this spectrum may

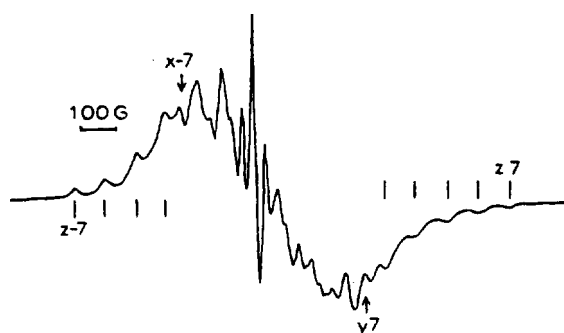


Figure 3. Polycrystalline epr spectrum of α -1,2-[PV(IV)-VW₁₀O₄₀]⁶⁻ as obtained from the reduced product of α -1,2-[PV₃W₉O₄₀]⁶⁻ coprecipitated with K₆H[SiV₃W₉O₄₀].

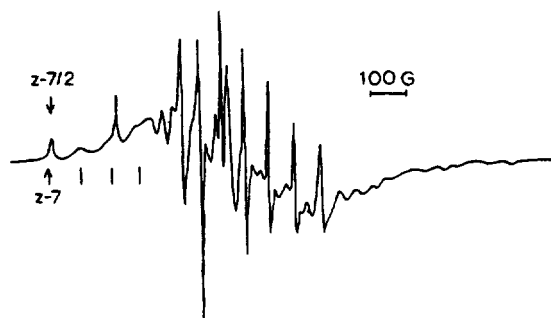


Figure 4. Polycrystalline epr spectrum of a mixture of isomers of [PV(IV)VW₁₀O₄₀]⁶⁻ doped into K₆[PV₃W₉O₄₀].

be considered to be the spectrum of α -1,2-PV(IV)V.

In order to analyze this spectrum, we assume α -1,2-PV(IV)V to be an $I = 7$ system. Then the polycrystalline spectrum is expected to consist of x -, y -, and z -components, each component showing fifteen lines. The outer nine lines of the z -component (the component with the maximum hyperfine splitting) are clearly seen in the spectrum. The x - and y -components are more difficult to assign, but the peak at 3811G (the y_7 peak in Figure 3) may be assigned as the highest-field peak of the y -component and the peak at 3289G (the $x-7$ peak in Figure 3) as the lowest-field peak of the x -component. Then the parameters could be calculated by using the following equations.^{9,10}

For x -components

$$h\nu = g_x \beta B + A_x m + \frac{1}{4h\nu} (A_y^2 + A_z^2) \{I(I+1) - m^2\} \quad (2)$$

For y -components

$$h\nu = g_y \beta B + A_y m + \frac{1}{4h\nu} (A_x^2 + A_z^2) \{I(I+1) - m^2\} \quad (3)$$

For z -components

$$h\nu = g_z \beta B + A_z m + \frac{1}{4h\nu} (A_x^2 + A_y^2) \{I(I+1) - m^2\} \quad (4)$$

$$g = \frac{1}{3} (g_x + g_y + g_z) \quad (5)$$

$$a = \frac{1}{3} (A_x + A_y + A_z) \quad (6)$$

The resulting parameters are listed below:

$$\begin{aligned}g_x &= 1.948, & |A_x| &= 30.4 \times 10^{-4} \text{ cm}^{-1} \\g_y &= 1.966, & |A_y| &= 33.5 \times 10^{-4} \text{ cm}^{-1} \\g_z &= 1.937, & |A_z| &= 80.1 \times 10^{-4} \text{ cm}^{-1}\end{aligned}$$

Compared to the parameters ($g_{\parallel} = 1.910$, $g_{\perp} = 1.966$, $|A_{\parallel}| = 167.0 \times 10^{-4} \text{ cm}^{-1}$, $|A_{\perp}| = 59.3 \times 10^{-4} \text{ cm}^{-1}$) of $[PV(IV)W_{11}O_{40}]^{5-}$ in which the unpaired electron is trapped on one vanadium center, the g anisotropy of our mixed valence system is considerably smaller and the hyperfine values are about half as large.⁹

Now we will consider the most interesting question, namely whether each line in the polycrystalline spectrum appears at the average magnetic field of two hyperfine lines expected for two uncoupled vanadium atoms. The positions of these average lines may be estimated from the epr parameters of $[PV(IV)W_{11}O_{40}]^{5-}$ or isomers of $PV(IV)V$ in which the electron is trapped on one vanadium center. The polycrystalline spectrum of the latter was obtained by keeping a sample of α -1,2- $PV(IV)V$ in solution for two weeks and coprecipitating it with $K_4[PV_3W_9O_{40}]$. The spectrum is shown in Figure 4. The lines belonging to the species in which the electron is trapped on one vanadium center are easily identified and the spectrum has been analyzed by using equations similar to eqs. (2)–(4). The system is found to be axial and the resulting parameters are as follows:

$$\begin{aligned}g_{\parallel} &= 1.915, & |A_{\parallel}| &= 167.1 \times 10^{-4} \text{ cm}^{-1} \\g_{\perp} &= 1.968, & |A_{\perp}| &= 58.5 \times 10^{-4} \text{ cm}^{-1}\end{aligned}$$

The angle between the two $V=O$ vectors in the Keggin structure is estimated to be 62° from a single crystal epr study of $PV(IV)$ doped into $K_3[BW_{12}O_{40}]$.¹¹ We have calculated average line positions for all combinations of hyperfine lines of two uncoupled vanadium atoms at various orientations of the magnetic field. According to this calculation, the lowest-field line is expected to appear at a position 70G higher than the observed lowest-field line (the $z-7$ line in Figure 4) of α -1,2- $PV(IV)V$. In fact, the $z-7$ line appears at a lower field than the lowest-field line (the $z-7/2$ line in Figure 4) of the species in which the electron is trapped on one vanadium center, while the lowest-field average line cannot appear at a lower field than the $z-7/2$ line. Therefore, we believe that the polycrystalline epr spectrum cannot be interpreted by assuming that each line appears at the average magnetic field of two hyperfine lines expected for two uncoupled vanadium atoms. However, a computer simulation based on this model will be needed in order to arrive at a definitive conclusion.

Another interesting problem is apparently selective coprecipitation of a reduced species obtained from α -1,2,3- PV_3 . The solution epr spectrum of its one-electron reduction product is completely different from that of α -1,2- $PV(IV)V$. But

when the reduced species is coprecipitated with $K_8H[SiV_3W_9O_{40}]$, both the solution and polycrystalline spectra of the precipitate are similar to those of α -1,2- $PV(IV)V$. Of course, some isomers of $PV(IV)V_2$ may show the same spectra.¹² This problem is currently under investigation.

Concluding Remarks

To our knowledge the spectrum of α -1,2- $PV(IV)V$ reported in this work is the first polycrystalline epr spectrum of a mixed valence complex doped into a host crystal. We showed that the spectrum could be analyzed by assuming that it belonged to a system with $I=7$ and that it could not be interpreted by assuming that each line appeared at the average magnetic field of two hyperfine lines expected for two uncoupled vanadium atoms. Further work is needed to clarify the reason why the second model works for the solution spectrum but fails for the polycrystalline spectrum.

References and Notes

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- When there is no confusion, tungsten and oxygen have been omitted from the chemical formula of the complexes.
- See, for example, R. Wilson and D. Kivelson, *J. Chem. Phys.*, **44**, 154 (1966). In this equation g is the g value, a is the hyperfine splitting constant, I is the nuclear spin, and m is the nuclear spin quantum number $I, I-1, \dots, -I$.
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- Note added in proof. On the basis of pH-dependent epr spectra of $[PV(IV)V_2W_{10}O_{40}]^{7-}$, now we believe that the species responsible for the 15-line spectrum is the diprotonated species $[H_2PV(IV)V_2W_{10}O_{40}]^{5-}$, in which the unpaired electron is hopping between the two vanadium atoms in the $OH-V-O-V-OH$ group.