pentaborane(9), it was hoped that, in addition to obtaining a J_{BB} value for 1-CH(Br)(CH$_3$)B$_5$H$_8$, dehydrohalogenation of this product would be a successful route to the unknown species 1-vinylpentaborane(9). Instead, the product has been determined to be 2-bromo-1-ethylpentaborane(9) by infrared and mass spectral analysis and ^{11}B nmr spectra. This product would be expected from a free-radical bromination if halogenation of the basal position on B_5H_9 proceeds by a free-radical mechanism as proposed previously.[37]

Registry No. 1-IB$_5$H$_8$, 30624-33-0; 1-cyanopentaborane(9), 37768-70-0; 1-ethynylpentaborane(9), 37768-71-1; 1-chloropentaborane(9), 19469-13-7; 1-phenylpentaborane(9), 37768-72-2; 1-*tert*-butylpentaborane(9), 37768-68-6; pentaborane, 19624-22-7; 2-bromo-1-ethylpentaborane(9), 37768-69-7; potassium cyanide, 151-50-8; sodium acetylide, 1066-26-8; phenyllithium, 591-51-5; 1-ethylpentaborane(9), 23753-61-9; acetonitrile, 75-05-8.

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[37] D. F. Gaines, *J. Amer. Chem. Soc.*, 88, 4528 (1966).

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Optical and Electron Spin Resonance Spectra of the 11-Tungstovanado(IV)phosphate Anion. A Heteropoly Blue Analog[1]

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The anion $PV^{IV}W_{11}O_{40}{}^{5-}$ (I) may be prepared by electrolytic reduction of the corresponding vanadium(V) complex or by reaction of VO^{2+} with $PW_{11}O_{39}{}^{7-}$ at pH 4.5. The optical spectrum of the deep red-purple complex shows bands at 20 and 25 kK ascribed to V(IV) → W(VI) "intervalence" transitions, as well as ligand field bands for oxovanadium(IV) at 12.0 and 14.5 kK. The esr parameters, determined from a dilute solution of I in $K_5BW_{12}O_{40}\cdot{\sim}20H_2O$, are $g_\parallel = 1.910$, $g_\perp = 1.965$, $|A| = 167.0$, and $|B| = 59.3 \times 10^{-4}$ cm^{-1}. A single-crystal esr study confirms that the vanadium atom in I occupies one of the tungsten positions in a normal Keggin structure. The usual equations relating optical and esr parameters do not give internally consistent results for I, due principally to the low g values observed. Reasons for this are considered.

Introduction

We have recently reported the preparation and characterization of several 12-(tungstovanado)phosphates.[4] The complex $PVW_{11}O_{40}{}^{4-}$ undergoes a reversible one-electron reduction at +0.58 V *vs.* sce. This paper describes the preparation and optical and esr spectra of the reduced species $PV^{IV}W_{11}O_{40}{}^{5-}$, an intensely colored substance isoelectronic with the mixed-valence heteropoly blue $PW^{V}W_{11}O_{40}{}^{4-}$. The tungstovanado(IV)phosphate complex has apparently been made by Tourne and Tourne, who reported a partial absorption spectrum.[5]

Experimental Section

Preparation of 11-Tungstovanado(IV)phosphate Anion. Solutions containing this species could be prepared either by controlled-potential electrolysis at +0.4 V of a solution of $K_4PVW_{11}O_{40}$ in 1.0 *M* sodium sulfate, pH 2 on a platinum gauze electrode, or by adding a solution of $VOSO_4$ to one of $Na_3PW_{12}O_{40}$ buffered at pH 4.5. In the latter process the characteristic purple color of the anion formed instantaneously. Solutions prepared by both methods gave identical voltammograms and optical and esr spectra. A sample of the very soluble potassium salt was prepared as follows. Thirty grams of $Na_3PW_{12}O_{40}$, prepared as described elsewhere,[6] was dissolved in 25 ml of a 0.1 *M* acetate buffer, pH 4.5.[7] To this solution was added an equimolar amount of $VOSO_4$ as a *ca.* 1 *M* solution. The resulting solution was heated to near boiling and solid potassium acetate was added to the hot solution until no more white precipitate (probably potassium paratungstate) formed. The solution was filtered rapidly, 1 g further of potassium acetate was added and the solution placed in a refrigerator overnight. The resulting crystalline product was filtered and recrystallized from a boiling potassium acetate buffer, pH 4.5. *Anal.* Calcd for $K_5PVW_{11}O_{40}\cdot 6H_2O$: K, 6.42; V, 1.67. Found: K, 6.49; V, 1.71.

Dilute single crystals of the above salt were grown for esr purposes by slowly evaporating an acidic solution of $K_5BW_{12}O_{40}$[8] containing a small amount of an equimolar mixture of $Na_3PW_{12}O_{40}$ and $VOSO_4$ buffered at pH 4.5. A polycrystalline sample was prepared by grinding several dilute crystals.

Physical Measurements. The electrochemical equipment and techniques have been described previously.[4] Esr measurements were made as described elsewhere.[9] A homemade goniometer was used for the single-crystal measurements.

Results

Solution Properties. Visible and near-infrared absorption spectra of solutions taken during the course of controlled-potential electrolysis of 2.5 m*M* $K_4PVW_{11}O_{40}$ in 1.0 *M* sodium sulfate, pH 2.3, showed an isosbestic point at 455 nm (ϵ 520 M^{-1} cm^{-1}). Voltammograms of the fully reduced solution using rotating platinum or wax-impregnated graphite electrodes showed the expected oxidation wave or peak at +0.58 V *vs.* sce.[4]

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[1] Presented in part at the 13th International Conference on Coordination Chemistry, Krakow and Zakopane, 1970.

[2] Holder of an NSF Summer Award to Secondary School Teachers, 1965-1966; NIH Predoctoral Fellow, 1966-1968.

[3] NSF Undergraduate Research Participant, 1969.

[4] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 12, 331 (1973).

[5] C. Tourne and G. Tourne, *Bull. Soc. Chim. Fr.*, 1124 (1969).

[6] M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, 5, 1249 (1966).

[7] At this pH the 12-tungstate is converted to $PW_{11}O_{39}{}^{7-}$: see, for example, P. Souchay, "Ions Mineraux Condenses," Masson et Cie, Paris, 1969, p 93.

[8] Sample kindly supplied by D. R. Wexell.

[9] G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, 9, 662 (1970).

The optical spectrum of the reduced complex in shown in Figure 1. Besides the maximum at 20 kK (ϵ 750 M^{-1} cm^{-1}) and the shoulder at 25 kK, both noted by Tourne and Tourne,[5] two reproducible shoulders at 12.0 and 14.5 kK were also detected. No improvement in resolution of the spectrum was observed in frozen aqueous glycerol glasses at 77°K.

The esr spectrum of a 2.0 mM solution of $PVW_{11}O_{40}^{5-}$ in 1.0 M sodium sulfate, pH 2, showed the characteristic eight-line pattern expected for a vanadium(IV) complex although the lines were somewhat broader than those for vanadyl sulfate under the same conditions. The spectrum of a dilute polycrystalline sample is shown in Figure 2. This spectrum can be described by the usual axial spin Hamiltonian for a d^1 system

$$\mathcal{H} = g_{\parallel}\beta H_zS_z + g_{\perp}\beta(H_xS_x + H_yS_y) + AS_zI_z + B(S_xI_x + S_yI_y) \qquad (1)$$

Perturbation theory gives the explicit expression[10]

$$h\nu = g\beta H + Km + \frac{B^2}{4(h\nu)}\left(\frac{A^2 + K^2}{K^2}\right)\{I(I+1) - m^2\} + \frac{1}{2(h\nu)}\left(\frac{A^2 - B^2}{K}\right)\left(\frac{g_{\parallel}^2 g_{\perp}^2}{g^4}\right)\sin^2\theta\cos^2\theta m^2 \qquad (2)$$

where θ is the angle between the symmetry axis and the magnetic field and

$$g^2 = g_{\parallel}^2\cos^2\theta + g_{\perp}^2\sin^2\theta \qquad (3)$$

and

$$K^2g^2 = A^2g_{\parallel}^2\cos^2\theta + B^2g_{\perp}^2\sin^2\theta \qquad (4)$$

The above equations were used for analysis of the polycrystalline spectrum and the following expression for that of the solution spectrum at room temperature

$$h\nu = g\beta H + am + \frac{a^2}{2(h\nu)}[I(I+1) - m^2] \qquad (5)$$

The resulting parameters are listed in Table I.

Single-Crystal Esr. According to X-ray powder patterns the host crystal $K_5BW_{12}O_{40}\cdot{\sim}20H_2O$ is isomorphous with $K_5CoW_{12}O_{40}\cdot 20H_2O$ and $K_4SiW_{12}O_{40}\cdot 17H_2O$, the structures of which have been described.[11-13] These salts crystallize in the hexagonal space group $P6_222$ with three molecules per cell. The single-crystal spectra of $PVW_{11}O_{40}^{5-}$ doped into the tungstoborate salt were quite complicated since the vanadium atom is disordered over the 12 tungsten sites in the Keggin structure (see below). Sufficient structural information could however be obtained by examining the position of the hyperfine line at highest field (m = $^7/_2$) when the magnetic field was in the ac plane. As illustrated in Figure 3, maxima were found at γ = 45 and 80°, where γ is the angle between the c axis and the magnetic field.

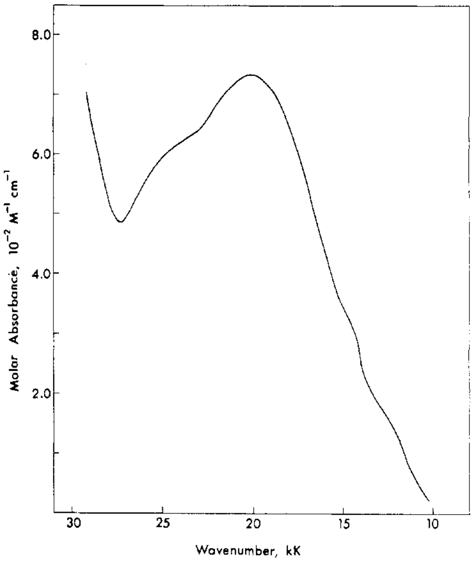

Figure 1. Absorption spectrum of $PVW_{11}O_{40}^{5-}$, 2.5 mM in 1.0 M sodium sulfate, pH 2.0.

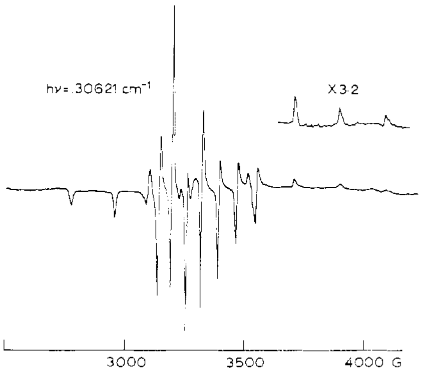

Figure 2. Esr spectrum of a polycrystalline sample of $PVW_{11}O_{40}^{5-}$ in $K_5BW_{12}O_{40}\cdot{\sim}20H_2O$.

Table I. Esr Parameters[a] for 11-Tungstovanado(IV)phosphate Anion

	298°K	298°K	77°K
g	1.9474		
$g_{\parallel}$		1.9104	1.9232
$g_{\perp}$		1.9655	1.968
a	(–)95.9		
A		(–)167.0	(–)169.3
B		(–)59.3	(–)59.6

[a] Hyperfine parameters are in units of 10^{-4} cm^{-1}. Their signs are assumed to be negative. Estimated errors are ±0.001 for g values and ±0.5 × 10^{-4} cm^{-1} for hyperfine parameters.

Discussion

Molecular Structure. Most heteropoly 12-tungstate anions have the "Keggin" structure illustrated in Figure 4. The tungsten atoms in this structure occupy the corners of a cuboctahedron, each tungsten being in sixfold coordination by oxygen. The approximate point symmetry for each of the tungsten atoms is C_{4v}, the terminal ("exterior") W-O bond length being close to that for a double bond.[14,15] It can be presumed that V(IV) in $PVW_{11}O_{40}^{5-}$ occupies a site of similar symmetry.[16]

In order to interpret the single-crystal esr data we assume that the $g_{\parallel}$ direction for vanadium in this complex coincides with the V=O vector and, through the random replacement of each tungsten atom by vanadium, that the $g_{\parallel}$ directions will roughly coincide with the W=O vectors in the Keggin anion. Figure 5 shows a projection of the 12 W=O vectors, each protruding from the corners of the cuboctahedron men-

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(10) B. Bleaney, *Phil. Mag.*, 42, 441 (1951).

(11) N. F. Yannoni, Ph.D. Thesis, Boston University, 1961; K. Eriks, N. F. Yannoni, U. C. Agarwala, V. E. Simmons, and L. C. W. Baker, *Acta Crystallogr.*, 13, 1139 (1960).

(12) P. M. Smith, Ph.D. Thesis, Georgetown University, 1971 [X-ray and neutron diffraction of α-$K_4SiW_{12}O_{40}\cdot 17H_2O$].

(13) That salts of two different charge types should be isomorphous is explained by the fact that much of the water and some of the cations are disordered in zeolytic-like channels.

(14) M. T. Pope, *Inorg. Chem.*, 11, 1973 (1972).

(15) H. So and M. T. Pope, *Inorg. Chem.*, 11, 1441 (1972).

(16) It may perhaps be helpful to regard the polyanion as $[(PW_{11}O_{39})VO]^{5-}$, a complex containing the pentadentate ligand $PW_{11}O_{39}^{7-}$.

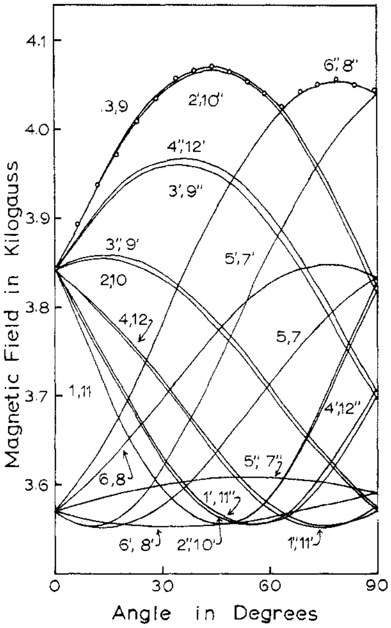

Figure 3. The angular dependence of experimental and calculated positions of the hyperfine lines corresponding to $m = {}^7/_2$; magnetic field in *ac* plane. Numbers identify the positions of vanadyl groups in the anion (see Figure 5). Primes and double primes designate the corresponding groups in anions rotated by 60 and 120° around the *c* axis.

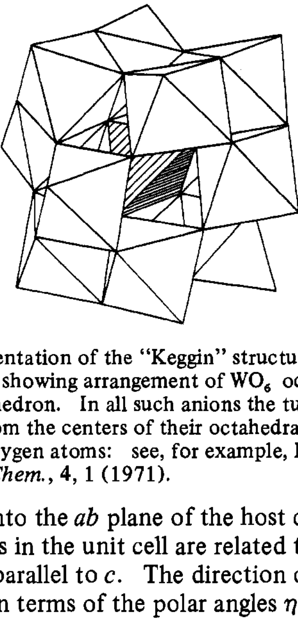

Figure 4. Representation of the "Keggin" structure for $XW_{12}O_{40}{}^{n-}$ heteropoly anions showing arrangement of WO_6 octahedra around a central XO_4 tetrahedron. In all such anions the tungstens are found to be displaced from the centers of their octahedra toward the terminal unshared oxygen atoms: see, for example, H. T. Evans, Jr., *Perspect. Struct. Chem.*, 4, 1 (1971).

tioned above, onto the *ab* plane of the host crystal. The other two anions in the unit cell are related to this by a threefold screw axis parallel to *c*. The direction of these vectors can be defined in terms of the polar angles η and ϕ shown in Figure 5. If the anion has complete tetrahedral symmetry, only four such angles need be specified, namely, ϕ_3, η_3, ϕ_6, and η_6. Moreover, since $\phi_6 = 45°$ and $\tan\phi_3 \tan\eta_6 = \sqrt{2}$, there are only two independent angles. The two maxima in Figure 3 show these to be 45° (η_3) and 80° (η_6). When these angles and the parameters listed in Table I are substituted in eq 2, the angular variation of the $m = {}^7/_2$ line can be calculated. The results of this calculation are also shown in Figure 3 and the agreement is seen to be good.

Values for η_3 and η_6 found by diffraction methods for some other 12-tungstates are listed in Table II. The figures for $K_4SiW_{12}O_{40}\cdot 17H_2O$ are most pertinent since this salt is isomorphous with the crystal used here and since the oxygen positions can be more precisely located with neutron diffraction.

Electronic Structure. The esr spectrum of $PVW_{11}O_{40}{}^{5-}$ is

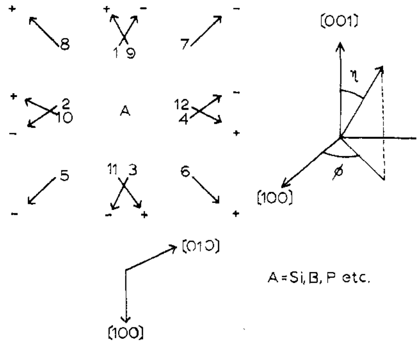

Figure 5. Projection of W=O vectors in $SiW_{12}O_{40}{}^{4-}$ onto the *ab* plane and definition of polar angles η and ϕ. W=O vectors and their orientations with respect to the *ab* plane are indicated by arrows and + and − signs.

that of an axial vanadyl(IV) complex and the two shoulders in the optical spectrum at 12 and 14.5 kK are almost certainly due to d-d transitions and correspond to so-called bands I and II in normal oxovanadium complexes.[17] The absorption bands at 20 and 25 kK that are responsible for the intense color of the anion are assigned as "heteronuclear intervalence charge-transfer (IVCT) transitions,"[18] V(IV) → W(VI). We have demonstrated elsewhere that the lowest energy for such a transition should be at about 20 kK.[15] The complex can thus be regarded as a heteropoly "blue"[9] and is isoelectronic with $PW^VW_{11}O_{40}{}^{4-}$, the spectrum of which shows three IVCT bands separated by about 5 kK. A discussion of heteropoly blue spectra will appear in a later paper.

The *g* values for $PVW_{11}O_{40}{}^{5-}$ are unusually low[19] for an oxovanadium(IV) complex (normal ranges: $g_\parallel = 1.92\text{-}1.97$; $g_\perp = 1.98\text{-}2.00$). The esr parameters for such a complex with the unpaired electron in the d_{xy} orbital are expressed approximately as[20]

$$g_\parallel = 2.0023 - \frac{8\alpha^2\gamma^2\lambda}{\Delta E(x^2-y^2 \leftarrow xy)} \tag{6}$$

$$g_\perp = 2.0023 - \frac{2\alpha^2\gamma^2\lambda}{\Delta E(xz, yz \leftarrow xy)} \tag{7}$$

$$A = P\left[-\frac{4}{7}\alpha^2 - \kappa + g_\parallel - 2.0023 + \frac{3}{7}(g_\perp - 2.0023)\right] \tag{8}$$

$$B = P\left[\frac{2}{7}\alpha^2 - \kappa + \frac{11}{14}(g_\perp - 2.0023)\right] \tag{9}$$

where α^2, β^2, and γ^2 are the fractional contributions of d_{xy}, $d_{x^2-y^2}$, and d_{xz}, d_{yz} orbitals, respectively, to the ligand field molecular orbitals; λ is the spin-orbit coupling constant for the metal ion; κ is the isotropic Fermi contact term; and P is $2.0023\beta_e g_N \beta_N \langle r^{-3}\rangle$.

The above expressions have been quite successfully used to interpret esr parameters for most vanadyl complexes but prove to be inadequate in the present case. Equations 8 and 9 can be rearranged to give values for α^2 and κ, provided a suitable value for P is available. If we use $P = 0.0128$ cm^{-1} (for V^{2+})[21] we obtain $\alpha^2 = 0.890$ and $\kappa = 0.691$. These values are not unreasonable, but it must be remembered that their magnitudes depend upon the value chosen for P and hence the charge assumed to be on the vanadium atom.[22]

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(17) J. Selbin, *Coord. Chem. Rev.*, 1, 293 (1966).

(18) N. S. Hush, *Progr. Inorg. Chem.*, 8, 391 (1967).

(19) We have checked our measurements using DPPH. Also, the calculated average *g* agrees with the measured isotropic value.

(20) See, for example, B. R. McGarvey, *Transition Metal Chem.*, 3, 89 (1966).

(21) B. R. McGarvey, *J. Phys. Chem.*, 71, 51 (1967).

Table II. Orientations of Metal–Terminal Oxygen Vectors

Crystal	Space group	Angles,[a] deg		Method	Ref
		η_3	η_6		
$PVW_{11}O_{40}{}^{5-}$ in $K_5BW_{12}O_{40}\cdot 20H_2O$	$P6_222$	45 ± 2	80 ± 2	Esr	This work
$K_4SiW_{12}O_{40}\cdot 17H_2O$	$P6_222$	48.1[b]	80.8	Neutron diffraction	*c*
$H_3PW_{12}O_{40}\cdot 5H_2O$	*Pn*3*m*	46	89	X-Ray	*d*
$H_3PW_{12}O_{40}\cdot 29H_2O$	*Fd*3*m*	48	71	X-Ray	*e*

[a] Angles are defined in Figure 5; for the cubic groups, the angles are measured with reference to the normal from a rectangular face of the cuboctahedron formed by the 12 tungsten atoms. [b] Average of two crystallographically independent values. [c] P. M. Smith, Ph.D. Thesis, Georgetown University, 1971. [d] J. F. Keggin, *Proc. Roy. Soc., Ser. A*, 144, 75 (1934). [e] A. J. Bradley and J. W. Illingworth, *ibid.*, 157, 113 (1936).

If the optical bands at 12.0 and 14.5 kK are assigned as $x^2 - y^2 \leftarrow xy$ and $xz, yz \leftarrow xy$, respectively, eq 6 and 7 do not yield consistent results. Equation 6 gives $\alpha^2\beta^2\lambda = 166$ cm^{-1} and hence $\lambda \geqslant 166$ cm^{-1}; eq 7 gives $\alpha^2\gamma^2\lambda = 221$ cm^{-1}, thus $\lambda \geqslant 221$ cm^{-1}. The free-ion value of λ for V^{4+} is 248 cm^{-1},[23] so that besides being inconsistent, the second of the experimentally derived values for λ is unacceptably high. The assignments of the optical bands are not certain of course. In terms of satisfying eq 6 and 7 either band could be due to $x^2 - y^2 \leftarrow xy$, but the transition $xz, yz \leftarrow xy$ should occur below 10 kK (*e.g.*, at 9.2 kK if $\alpha^2\gamma^2\lambda = 170$ cm^{-1}). We have carefully searched the spectrum between 12 and 8 kK and found no other bands.

It could be argued that the failure of eq 6 and 7 and the very low *g* values are somehow due to a contribution from the low-lying intervalence charge-transfer excited state. Although the local symmetry around the vanadium in $PVW_{11}O_{40}{}^{5-}$ is C_{4v}, the symmetry is reduced to C_1 when the VO_6 group and four adjacent WO_6 groups are considered together. Thus the charge-transfer excited state can mix with the ground state *via* spin–orbit coupling. Since the excited state is only 20 kK above the ground state, the effect may be appreciable. In this connection we note that the esr spectrum of a mixed-valence vanadium complex of unknown structure, "$V^{IV}{}_2V^{V}{}_4O_{20}H_{12}$," has been reported with $g_{\parallel} = 1.920$ and $g_{\perp} = 1.970$.[24] No optical spectral data are available for this material however, nor could hyperfine lines be observed in the polycrystalline esr spectrum.

Whatever the reason, the usual expressions for *g* values are not satisfactory for this quasi mixed-valence complex. If, instead of using explicit ligand field orbitals, one starts with wave functions for the ground state Kramers doublet, one can derive expressions for *g* values and hyperfine parameters and then determine *P* and κ from these equations.[25] It turns out that the results are essentially the same as those derived from eq 8 and 9 when $\alpha^2 = 1.0$. We have calculated *P* and κ for $PVW_{11}O_{40}{}^{5-}$ and for VO^{2+} doped into zinc Tutton salt[26] for comparison, using eq 8 and 9 with $\alpha^2 = 1.0$. The results are as follows: for the heteropoly anion, $P = 0.0115$ cm^{-1}, $\kappa = 0.78$; for $VO(H_2O)_5{}^{2+}$, $P = 0.0121$ cm^{-1}, $\kappa = 0.86$. Since *P* is a direct measure of $\langle r^{-3}\rangle$ and κ is a measure of the polarization of the inner s electrons by interaction with the unpaired electron, reduction in both of these parameters could have resulted from delocalization of the unpaired electron in the heteropoly complex. We are determining esr parameters of several other vanadium(IV) polyanions to test the validity of this conclusion.

Registry No. $PV^{IV}W_{11}O_{40}{}^{5-}$, 12412-86-1; $K_5PV^{IV}W_{11}O_{40}$, 37234-37-0; $Na_3PW_{12}O_{40}$, 12026-98-1; $VOSO_4$, 27774-13-6.

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(22) If, for example, *P* for V^{4+} (172×10^{-4} cm^{-1}) is used, $\alpha^2 = 0.638$.

(23) T. M. Dunn, *Trans. Faraday Soc.*, 57, 1441 (1961).

(24) J. Bernard, F. Theobald, and J. G. Theobald, *C. R. Acad. Sci.*, 260, 873 (1965).

(25) J. D. Swalen, B. Johnson, and H. M. Gladney, *J. Chem. Phys.*, 52, 4078 (1970).

(26) R. H. Borcherts and C. Kikuchi, *J. Chem. Phys.*, 40, 2270 (1964).