Electrochemical Properties and ESR Characterization of Mixed Valence α-$[XMo_{3-x}V_xW_9O_{40}]^{n-}$ Heteropolyanions with X = P^V and Si^{IV}, $x = 1, 2,$ or 3

Emmanuel Cadot, Michel Fournier,[†] André Tézé, and Gilbert Hervé*

Laboratoire d'Electrochimie et Chimie de Solides Inorganiques, EP CNRS J0067, Université de Versailles Saint-Quentin, 45 Avenue des Etats-Unis, 78035 Versailles Cedex, France

Received August 3, 1994[⊗]

Electrochemical behavior of the α-$[SiMo_{3-x}V_xW_9O_{40}]^{(4+x)-}$ and α-$[PMo_{3-x}V_xW_9O_{40}]^{(3+x)-}$ anions with $x = 1$, 2, or 3 were studied. Electrochemical reduction of each compounds was consistent with its Mo/V ratio, reduction of vanadium and molybdenum atoms occurring in the +0.6 to −0.6 V potential range. The one-electron-reduced species were prepared by electrolysis and then characterized by ESR spectroscopy. The g and A values for V^{4+} ions appeared to depend on the nature of the surrounding atoms (Mo^{VI}, W^{VI}, and V^V). In solution at 330 K, the ESR spectrum of the protonated α-$H[SiMoV^{IV}VW_9O_{40}]^{6-}$ anion displayed 29 superhyperfine lines which were related to the partial localization of the electron on one vanadium nucleus. The ESR spectra at room temperature for the divanadium-substituted anions showed a strong anisotropy of the **A** tensor which would be related to the electron transfer along a preferential axis. An isolated V^{4+} signal was not observed, even at 12 K, indicating that the electron is never firmly trapped on one single vanadium atom.

Introduction

Heteropolyanions have won particular attention mainly because of their use in heterogeneous catalysis as well in oxidation[1] and acidic processes.[2] Oxovanadomolybdophosphate Keggin type compounds corresponding to the general formula α-$[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ with $x = 0$, 1, 2, or 3 as acid, alkali, or transition metal salts exhibit important catalytic activities for oxidation reactions, as in, for example, the oxidative dehydrogenation of isobutyric acid into methacrylic acid.[3−6] Vanadium atoms appear to display a crucial effect upon the redox properties of the catalysts. Actually, vanadium atoms have oxidation number IV in the steady state, and indeed they were initially vanadium(V) atoms in the fresh catalysts. ESR spectroscopy is then a suitable method of characterization of the catalysts in order to determine if the structure is preserved in the conditions of the reaction ($T = 570−600$ K) and to differentiate the roles of molybdenum and vanadium atoms. In other respects, α-$[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ compounds with $x = 2$ or 3 are mixtures of anions differing in the amounts of vanadium and, for a given Mo/V ratio, of geometrical isomers.[7] So, we have chosen to start from pure mixed Mo, V, and W species as models of the potential P/Mo/V catalysts. This paper deals with the redox properties in solution and the ESR characterization of the one-electron-reduced species of each pure anion α-$[SiMo_{3-x}V_xW_9O_{40}]^{(4+x)-}$ and α-$[PMo_{3-x}V_xW_9O_{40}]^{(3+x)-}$ with $x = 1$, 2, or 3. Information is obtained about the influence of the nature of the metallic surrounding (W^{VI}, Mo^{VI}, and V^V) of the V^{4+} center on its properties and on electron transfer and electron delocalization. This work is in keeping with the studies of So and Pope on the mixed valence vanadium anions.[8] In a previous work, we have reported syntheses and multinuclear NMR structural characterization (^{51}V, ^{29}Si, and ^{183}W) of the α-$[SiMo_{3-x}V_xW_9O_{40}]^{(4+x)-}$ anion[9] and showed that the MoO_6 and VO_6 octahedra are adjacent and share a corner oxygen atom (Figure 1).

Experimental Section

Preparations of Reduced Polyanions in Solution. The one-electron-reduced species were prepared from solutions of oxidized anions by electrochemical reduction at a controlled potential platinum electrode. The solutions, 1.33×10^{-3} M, were under nitrogen. A 0.5 M acetic acid−0.5 M sodium acetate buffer was used for α-$[SiMo_2VW_9O_{40}]^{5-}$, α-$[SiMoV_2W_9O_{40}]^{6-}$, α-$[PMoV_2W_9O_{40}]^{5-}$, and α-$[PV_3W_9O_{40}]^{6-}$. For α-$[PMo_2VW_9O_{40}]^{4-}$, the electrochemical reduction was performed in an aqueous solution of HCl (1 M)−NaCl (1 M) and for α-$[SiV_3W_9O_{40}]^{7-}$, in 1 M (hydroxymethyl)aminomethane aqueous buffer, at pH = 8.

Polycrystalline Samples Diluted in Diamagnetic Matrix. For α-$K_7[SiMoV^{IV}VW_9O_{40}]$ in α-$K_7[SiV_3W_9O_{40}]$, 0.1 mL of α-$[SiMoV^{IV}VW_9O_{40}]^{7-}$ solution (1.33×10^{-3} M in acetic buffer) was added to 15 mL of α-$[SiV_3W_9O_{40}]^{7-}$ solution (1.33×10^{-3} M in acetic buffer). Solid potassium carbonate was then added until a pH of *ca.* 8 was reached. Potassium chloride (2.8 g; 37.5 mmol) was added to the stirring solution. The α-$K_7[(SiMoV^{IV}VW_9O_{40})_\epsilon(SiV_3W_9O_{40})_{1-\epsilon}]$ mixture precipitated and was isolated by filtration and washed by a 2.5 M solution of potassium chloride.

For α-$K_6[PMoV^{IV}VW_9O_{40}]$ in α-$K_6[SiMoV_2W_9O_{40}]$, the procedure was the same, but the pH was maintained at around 4.5−4.7 by addition of sodium acetate.

[†] Laboratoire de Chimie des Métaux de Transition, URA CNRS 419, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex 05, France.

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1995.

(1) See, for example: (a) Akimoto, M.; Tsuchida, Y.; Sato, K.; Echigoya, E. *J. Catal.* **1983**, *72,* 83. (b) Mori, H.; Mizuno, N.; Misono, M. *J. Catal.* **1991**, *131,* 133 . For a review, see: (c) Misono, M. *Catal. Rev.-Sci. Eng.* **1987**, *29,* 269. (d) Jansen, R. J. J.; van Veldhuizen, H. M.; Schwegler, M. A.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1994**, *113,* 115.

(2) See, for example: (a) Ghosh, A. K.; Moffat, J. B. *J. Catal.* **1986**, *101,* 238. (b) Orita, H.; Hayakawa, T.; Shimizu, M.; Takehira, K. *Appl. Catal.* **1991**, *77,* 133. (c) Okuhara, T.; Aorai, T.; Ichiki, T.; Lee, K. Y.; Misono, M. *J. Mol. Catal.* **1989**, *55,* 393. (d) Nayak, V. S.; Moffat, J. B. *Appl. Catal.* **1991**, *77,* 251.

(3) Haeberle, T.; Emig, G. *Chem. Eng. Technol.* **1988**, *11,* 392.

(4) Watzenberger, A.; Emig, G.; Lynch, D. T. *J. Catal.* **1990**, *124,* 247.

(5) Akimoto, M.; Ikeda, H.; Otake, A.; Echigoya, E. *J. Catal.* **1984**, 89, 196.

(6) Cadot E.; Marchal, C.; Fournier, M.; Tézé, A.; Hervé, G. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; p 315.

(7) Leparulo-Loftus, M. A.; Pope, M. T. *Inorg. Chem.* **1987**, *26,* 2112−2120.

(8) So, H.; Pope, M. T. *Studies in Physical and Theorical Chemistry*; Elsevier Science Publishers B.V.: Amsterdam 1992; Vol. 78, p 71.

(9) Cadot, E.; Thouvenot, R.; Tézé, A.; Hervé, G. *Inorg. Chem.* **1992**, *31,* 4128.

0020-1669/96/1335-0282$12.00/0

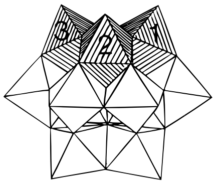

Figure 1. Polyhedral representation of the Keggin anions α-$[XMo_{3-x}V_xW_9O_{40}]^{n-}$. The Mo and V atoms are located in positions 1, 2, and 3.

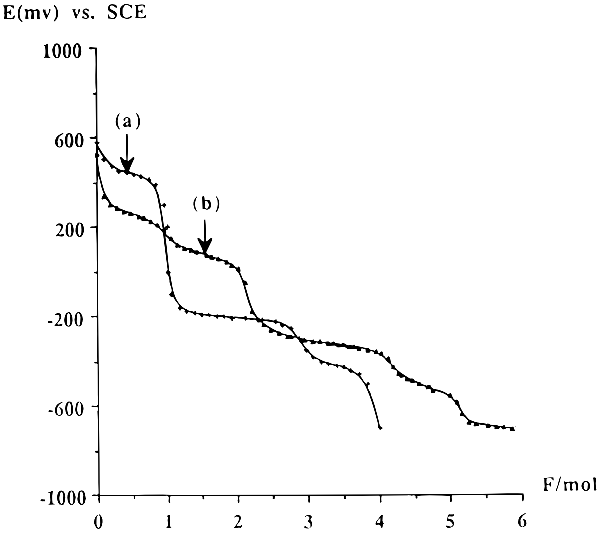

Figure 2. Electrochemical reduction of silicic compounds, potentiometric curves: (a) α-$[SiMo_2VW_9O_{40}]^{5-}$ (pH = 4.7) and (b) α-$[SiMoV_2W_9O_{40}]^{6-}$ (pH = 4.7).

In order to obtain samples for recording the Q-band ESR spectra, the lithium salts of oxidized anions α-$Li_7[SiV_3W_9O_{40}]$ and α-$Li_6[SiMoV_2W_9O_{40}]$ were added, respectively, to 2 mL of solutions (1.33 × 10^{-3} M) of α-$H[SiV_2V^{IV}W_9O_{40}]^{6-}$ and α-$[SiMoVV^{IV}W_9O_{40}]^{7-}$.

Apparatus. The X-band and Q-band spectra were recorded on a VARIAN CSE 109 spectrometer. The X-band ESR spectra measured between 300 and 12 K were recorded on a BRUKER 220D spectrometer.

Spectra Simulation. A computer program was used in order to simulate the ESR spectra of V^{4+} ions. The powder spectra were calculated by accumulating the spectra corresponding to different orientations of the magnetic field. These orientations were obtained by subdividing the triangular faces of a regular icosahedron into several triangles, giving 1329 orientations per octant. The line shape was taken as Gaussian, and the line width dependence on the orientation was taken as $\Delta H = f(3\cos^2\theta - 1)$.

Results

Electrochemical Behavior. The electrochemical reduction of the mixed α-$[XMo_{3-x}V_xW_9O_{40}]^{n-}$ with X = P^V or Si^{IV} occurs in successive steps which are characteristic of each polyanion. Assignments of the successive reduction steps are based on the consideration of decreasing oxidizing character following the sequence V > Mo > W and on the characterization of each reduced compound by vis–near-IR spectroscopy.

In the potential range +0.6 to −0.6 V, only vanadium and molybdenum atoms are involved in the reduction processes. Polarograms of these compounds show that reduction of tungsten atoms in the SiW_9O_{34} subunit occur at potentials lower than −0.8 V. Potentiometric curves drawn during the electrolysis of the mono- and divanadium-substituted anions are shown in Figures 2 and 3, respectively. Redox potentials of the different anions are reported in Table 1.

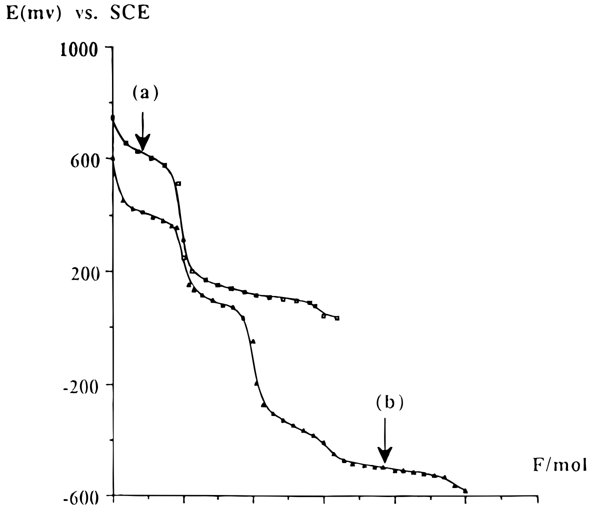

Figure 3. Electrochemical reduction of phosphoric compounds, potentiometric curves: (a) α-$[PMo_2VW_9O_{40}]^{4-}$ (pH = 1.0) and (b) α-$[PMoV_2W_9O_{40}]^{5-}$ (pH = 4.7).

Table 1. Redox Potentials of Mixed Mo–V–W Heteropolyanions[a]

anion	pH	redox potentials (volts vs SCE)
α-$[SiMo_2VW_9O_{40}]^{5-}$	4.7	+0.43 (1), −0.21 (2), −0.42 (1)
α-$[SiMoV_2W_9O_{40}]^{6-}$	4.7	+0.25 (1), +0.075 (1), −0.30 (2), −0.51 (1)
α-$[SiV_3W_9O_{40}]^{7-}$	8.0	+0.10 (1), −0.13 (1), −0.27 (1)
α-$[PMo_2VW_9O_{40}]^{4-}$	1.0	+0.61 (1), +0.13 (2)
	4.7	+0.61 (1), −0.20 (2), −0.51 (1)
α-$[PMoV_2W_9O_{40}]^{5-}$	4.7	+0.40 (1), +0.09 (1), −0.34 (1), −0.50 (2)

[a] The number of electrons involved in each step is indicated in parentheses.

(a) α-$[SiMo_2VW_9O_{40}]^{5-}$. The potentiometric curve of this compound in acetic buffer at pH 4.7 consists of three reduction steps at +0.43, −0.21, and −0.42 V, corresponding to 1, 2, and 1 electrons, respectively. The first reduction at +0.43 V is assigned to $V^V \rightarrow V^{IV}$.[10,11] The bielectronic reduction at −0.21 V concerns the two equivalent molybdenum atoms ($2Mo^{VI} \rightarrow 2Mo^V$). Then, the last monoelectronic step at −0.42 V before the reduction of tungsten corresponds to $V^{IV} \rightarrow V^{III}$.

(b) α-$[SiMoV_2W_9O_{40}]^{6-}$. This anion undergoes four successive reduction steps at +0.25, +0.07, −0.30, and −0.51 V, corresponding to 1, 1, 2, and 1 electrons, respectively. The two first steps correspond to the successive reduction of the two vanadium(V) atoms ($2V^V \rightarrow 2V^{IV}$). As shown by Pope *et al.*, the divanadium α-$[PV_2W_{10}O_{40}]^{6-}$ anion has an analogous behavior in the same range of potential.[12] The third reduction at −0.30 V involves two electrons and is attributed to the simultaneous reduction of the two vanadium(IV) atoms ($2V^{IV} \rightarrow 2V^{III}$). In order to explain the bielectronic reduction, it can be recalled that the reduction of vanadium(IV) in vanadium(III) is accompanied by the diprotonation of the anion, which induces a decrease in the charge of the anion.[13] The decrease in the ionic charge of the divanadium anion during the first electron transfer on V^{IV} atom must strongly enhance the oxidizing character of the second V^{IV}. Then, reduction at −0.51 V involves the single molybdenum atom ($Mo^{VI} \rightarrow Mo^V$).

(c) α-$[SiV_3W_9O_{40}]^{7-}$. The reduction of this anion at pH = 8 consists of three monoelectronic steps at +0.10, −0.13, and

---

(10) Contant, R.; Fruchart, J. M.; Hervé, G.; Tézé A. *C. R. Seances Acad. Sci., Ser. C* **1974**, *t278*, 199.

(11) Fruchart, J. M.; Hervé,G.; Launay, J. P.; Massart, R. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1627.

(12) Smith, D. P.; Pope, M. T. *Inorg. Chem.* **1973**, *12*, 331.

(13) Hervé, G.; Tézé, A.; Leyrie, M. *J. Coord. Chem.* **1979**, *9*, 245.

Table 2. Characteristics of Electronic Spectra of Reduced Anions[a]

α-$[PMo_2VW_9O_{40}]^{4-}$

reduction states	position, 10^3 cm^{-1} (ϵ, M^{-1} cm^{-1})	
I	16.0 (810)	20.9 sh[b] (500)
III	20.4 (4070)	
IV	20.4 (3730)	25.2 sh (1570)

α-$[PMoV_2W_9O_{40}]^{5-}$

reduction states	position, 10^3 cm^{-1} (ϵ, M^{-1} cm^{-1})			
0	21.8 (1750)	26.6 sh (4150)		
I	9.0 (510)	11.4 (620)	14.1 (610)	25.5 sh (850)
II	12.0 (430)	14.4 (540)	19.0 (910)	22.5 sh (785)
III	20.6 (2820)	24.8 sh (1650)		
V	20.4 (1920)			

α-$[SiMoV_2W_9O_{40}]^{6-}$

reduction state	position, 10^3 cm^{-1} (ϵ, M^{-1} cm^{-1})			
0	22.2 sh (1360)	27.2 (3100)		
I	9.2 (340)	11.3 (420)	13.7 (460)	17.5 (350)
	22.0 sh (460)	26.3 sh (890)		
II	12.3 (235)	14.5 (420)	19.0 (653)	21.6 sh (624)
IV	23.2 (603)			
V	20.5 (785)	24.0 sh (660)		

[a] The state of reduction (I, II ...) refers to the number of electrons introduced in the oxidized polyanion. [b] sh = shoulder.

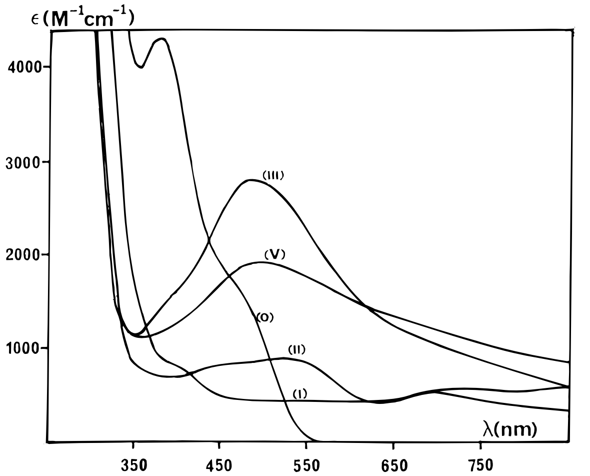

Figure 4. UV−vis spectra of the α-$[PMoV_2W_9O_{40}]^{5-}$ reduced forms. Roman numerals correspond to the number of electrons introduced.

−0.27 V, which are due to the successive reduction of the three vanadium atoms ($V^V \rightarrow V^{IV}$).

(d) α-$[PMo_2VW_9O_{40}]^{4-}$. This anion shows in acid solution (pH = 1) the same electrochemical behavior as that of the homologous Si compound. A one-electron reduction at +0.61 V ($V^V \rightarrow V^{IV}$) is observed, followed by a two-electron exchange at +0.13 V ($2Mo^{VI} \rightarrow 2Mo^V$).

(e) α-$[PMoV_2W_9O_{40}]^{5-}$. The potentiometric curve of reduction of this compound at pH 4.7 shows four steps at +0.40 (1e), +0.09 (1e), −0.34 (1e), and −0.50 (2e) V. The number of electrons involved in each step and the electronic spectra lead to the proposal that, in a behavior opposite to that of the homologous Si compound, reduction of the single Mo^{VI} (−0.34 V) occurs before those of the two vanadium(IV) atoms (−0.50 V).

Electronic Spectra. Energies and extinction coefficients of the electronic transitions of some representative species are collected in Table 2, and spectra corresponding to the different states of reduction of α-$[PMoV_2W_9O_{40}]^{5-}$ are shown in Figure 4.

(a) α-$[PMo_2VW_9O_{40}]^{4-}$. The electronic spectrum of the one-electron-reduced anion shows two bands in the visible region at 16 000 and 20 900 cm^{-1}. In comparison with α-$[PMo_{11}V^{IV}O_{40}]^{5-}$ and α-$[PW_{11}V^{IV}O_{40}]^{5-}$, which exhibit intense intervalence transitions at 15 200 and 20 000 cm^{-1}, respectively,[14] both absorptions can be attributed to intervalence charge transfers (IVCTs) $V^{IV} \rightarrow Mo^{VI}$ and $V^{IV} \rightarrow W^{VI}$, respectively. The three-electron-reduced state is characterized by a strong absorption at 20 400 cm^{-1} (ϵ = 4070 M^{-1} cm^{-1}), likely due to intervalence transitions $Mo^V \rightarrow W^{VI}$ which are expected in this region (20 000 cm^{-1} for α-$[PMo^VW_{11}O_{40}]^{5-}$).[14] The introduction of a fourth electron induces a decreasing of the 20 400 cm^{-1} maximum from ϵ = 4070 to 3730 M^{-1} cm^{-1}. This result can be qualitatively related to the reduction of the single V^{IV} atom into V^{III} that induces changes of the $V^{IV} \rightarrow W^{VI}$ intervalence transition.

(b) α-$[PMoV_2W_9O_{40}]^{5-}$. The reduction of one vanadium atom is characterized by the presence of a $V^{IV} \rightarrow V^V$ IVCT band at 9000 cm^{-1}, ϵ = 510 M^{-1} cm^{-1}, which disappears with the reduction of the second V atom. Simultaneously, a large band at about 19 000 cm^{-1}, ϵ = 910 M^{-1} cm^{-1}, grows. It should be due to the increase of the $V^{IV} \rightarrow Mo^{VI}$ and $V^{IV} \rightarrow W^{VI}$ IVCT intensities. The third reduction state obtained by one additional electron causes the apparition of a novel strong absorption at 20 600 cm^{-1}, ϵ = 2820 M^{-1} cm^{-1}. For the monovanadium α-$[PMo_2VW_9O_{40}]^{4-}$ anion, such a band characterizes the presence of Mo^V atoms. As a confirmation of this assumption, two more electrons lead to a significant decreasing of the intensity of this band from 2820 to 1920 M^{-1} cm^{-1}, likely due to the presence of two V^{III} atoms, which causes the disappearance of the $V^{IV} \rightarrow W^{VI}$ IVCT.

(c) α-$[SiMoV_2W_9O_{40}]^{6-}$. A $V^{IV} \rightarrow V^V$ IVCT is observed at 9200 cm^{-1} for the one-electron-reduced state. The reduction of the second vanadium(V) gives an absorption band at 19 000 cm^{-1} and a shoulder at 21 600 cm^{-1}, likely due to the $V^{IV} \rightarrow Mo^{VI}$ and $V^{IV} \rightarrow W^{VI}$ IVCTs. The third reduction step involves two electrons, and all absorptions disappear in the visible region while an absorption band at 23 200 cm^{-1} arises which agrees with a $V^{III} \rightarrow W^{VI}$ IVCT.[15] The four-electron-reduced compound is characterized by a maximum at 20 500 cm^{-1}, which likely corresponds to the $Mo^V \rightarrow W^{VI}$ IVCT.

pH Dependence of the First Monoelectronic Transfer (V^V/V^{IV}). The variations of the apparent standard potential $E°$ with pH for P and Si compounds are shown in parts a and b of Figure 5, respectively. For each anion with the exception of the less-charged α-$[PMo_2VW_9O_{40}]^{4-}$, a slope of −60 mV per pH unit is observed, which means that a simultaneous exchange of one electron and one proton occurs. α-$[SiMo_2V^{IV}W_9O_{40}]^{6-}$ exhibits a weak acidity (p$K \approx 1.5$). Both divanadium anions have a weak acidity (p$K \approx 2$ for α-$[PMoV^{IV}VW_9O_{40}]^{6-}$, and p$K \approx 4$ for α-$[SiMoV^{IV}VW_9O_{40}]^{7-}$). For the trivanadium compound α-$[SiV_3W_9O_{40}]^{7-}$, the curve can be interpreted as follows: (i) at pH > 9.5, the redox potential does not depend on the pH so no protonation transfer occurs during the reduction process. (ii) At 4 < pH < 9.5, the −60 mV/pH unit slope shows a simultaneous exchange of one proton and one electron. The pK of this weak acidity of the reduced anion is about 9.5. (iii) In the 3−4 pH range, a decrease in the slope near zero is due to the protonation of the oxidized form of α-$[SiV_3W_9O_{40}]^{7-}$ and the redox equilibrium does not involve the proton. Below 3, a slope of −60 mV/pH unit is observed again and indicates a novel proton exchange during the reduction (p$K \approx 3$).

For α-$[PV_3W_9O_{40}]^{6-}$, the variation of the redox potential with the pH does not reveal the same features. This difference is

---

(14) Altenau, J. J.; Pope, M. T.; Prados, R. A.; So, H. *Inorg. Chem.* **1975**, *14*, 417.

(15) Tézé, A.; Hervé, G. *J. Inorg. Nucl. Chem.* **1977**, *39*, 2151.

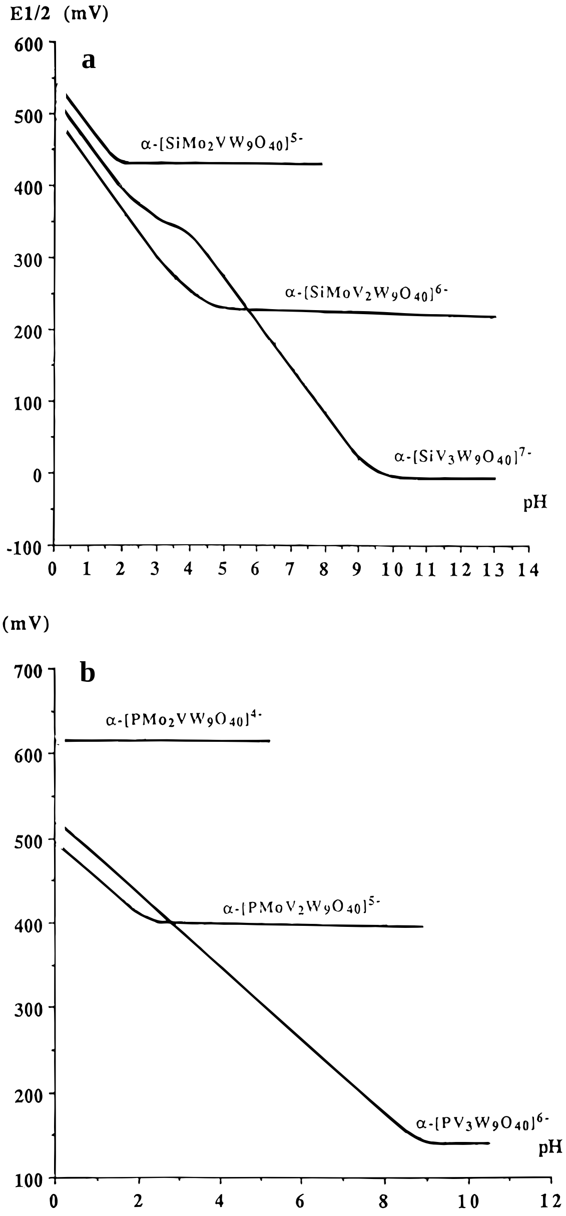

Figure 5. Variation of the first redox potentials ($V^V \rightarrow V^{IV}$) (vs SCE) with pH: (a) α-[SiMo$_{3-x}$V$_x$W$_9$O$_{40}$]$^{(4+x)-}$ and (b) α-[PMo$_{3-x}$V$_x$W$_9$O$_{40}$]$^{(5+x)-}$.

likely due to the strength of the first acidities of the oxidized (p$K \approx 1.5$) and the reduced anion. The protonation of both forms should occur in a narrow range of pH. The value of the pK of the first weak acidity of the reduced α-H[PV^{IV}V$_2$W$_9$O$_{40}$]$^{6-}$ is 8.5.

The narrow range of extrapolated redox potential at pH = 0 (0.50-0.52 V) for all compounds but one seems to indicate that protonations of the different compounds then give isocharged oxidized complexes: α-[SiMo$_2$VW$_9$O$_{40}$]$^{5-}$, α-H[SiMoV$_2$W$_9$O$_{40}$]$^{5-}$, α-H$_2$[SiV$_3$W$_9$O$_{40}$]$^{5-}$, α-[PMoV$_2$W$_9$O$_{40}$]$^{5-}$, and α-H[PV$_3$W$_9$O$_{40}$]$^{5-}$. The monovanadium α-[PMo$_2$VW$_9$O$_{40}$]$^{4-}$ anion exhibits a highest potential at pH = 0 (+0.61 V) because of its lower charge. The first redox potential of anions (V^V/V^{IV}) determined for unprotonated species depends on the anionic charge with a variation of about −0.21 V per charge unit, in agreement with Pope *et al.*,[16] who have noted an analogous trend for α-[XW$_{12}$O$_{40}$]$^{n-}$ and α-[PV$_x$W$_{12-x}$O$_{40}$]$^{(3+x)-}$ anions and proposed an electrostatic model in order to explain such a correlation.

Table 3. ESR Parameters of the One-Electron-Reduced Anion at 77 K Under Trapped Electron Conditions

anion	$g_\perp$	$g_\parallel$	$A_\perp$(G)	$A_\parallel$ (G)
α-[SiMo$_2$VW$_9$O$_{40}$]$^{6-\,a}$	1.973	1.940	68.0	170.0
α-[SiMoV$_2$W$_9$O$_{40}$]$^{7-\,b}$	g_2 = 1.9710 g_3 = 1.9745	1.939	A_2 = 60.0 A_3 = 57.1	167.5
α-[SiV$_3$W$_9$O$_{40}$]$^{8-\,b}$	g_1 = 1.9875 g_2 = 1.9815	1.9370	A_1=60.0 A_2 = 59.0	184.0
α-[PMo$_2$VW$_9$O$_{40}$]5− a	1.975	1.935	61.0	168.0

[a] X-band recording. [b] Q-band recording.

Table 4. Isotropic ESR Parameters of the Anions at 330 K

anion	pH	$\langle g \rangle$	$\langle A \rangle$ (G)
α-[SiMo$_2$VW$_9$O$_{40}$]$^{6-}$	4.7	1.960	96.0
α-[SiMoV$_2$W$_9$O$_{40}$]$^{7-}$	>4.5	1.959	50.5
	<3.5	1.962	75.0 25.0
α-[SiV$_3$W$_9$O$_{40}$]$^{8-}$	5−12	1.960	68.0 17.0
α-[PMo$_2$VW$_9$O$_{40}$]$^{5-}$	1.0	1.961	95.7
α-[PMoV$_2$W$_9$O$_{40}$]$^{6-}$	2−6	1.959	53.0
α-[PV$_3$W$_9$O$_{40}$]$^{7-}$	5−11	1.954	~72.0 ~18.0

ESR Spectra. The values of the isotropic and anisotropic g and A parameters are reported in Tables 3 and 4, respectively.

(a) α-[SiMo$_2$V^{IV}W$_9$O$_{40}$]$^{6-}$ and α-[PMo$_2$V^{IV}W$_9$O$_{40}$]$^{5-}$. The ESR spectra of the monovanadium anions recorded in solution at 330 K reveal a typical V^{4+} signal and exhibit the eight hyperfine lines due to the coupling of the unpaired electron ($S = {}^1/_2$) with the nuclear spin ($I = {}^7/_2$) of the 100% abundance ^{51}V isotope. The frozen solution or powder spectra of both anions recorded at 77 K exhibit the perpendicular and parallel components characteristic of the V^{4+} ion in an axially distorted ligand field. No orthorhombic feature can be seen on the spectra, showing that the orthorhombic component of the ligand field must be smaller than the experimental line width. The symmetry around the V^{4+} ions can be approximated to C_{4v}.

(b) α-[SiMoV^{IV}VW$_9$O$_{40}$]$^{7-}$. The ESR spectra of this anion in solution at 330 K and in dilute polycrystalline mixture between 300 and 12 K are presented in Figures 6 and 7. The isotropic X-band ESR spectrum of the unprotonated anion in aqueous buffer (pH = 5.0) at room temperature (Figure 6a) consists of 15 equally spaced lines ($\langle A \rangle$ = 50.5 G, $\langle g \rangle$ = 1.959), showing that the unpaired electron interacts with the two equivalent vanadium nuclei. The feature of the spectrum is unchanged from pH ≈ 4.5 to pH ≈ 9. At pH ≈ 3, protonation of the compound (p$K \approx 4$) leads to a more complex spectrum consisting of 29 experimental lines each spaced by about 25 G. Spectra recorded at pH = 3 and pH = 5 were found to be reproducibly interconverted (the polarographic study of α-[SiMoV^{IV}VW$_9$O$_{40}$]$^{7-}$ has revealed that this compound is stable in acidic medium at pH > 2). The proposed interpretation will be discussed below in the Discussion Section. The ESR spectrum of the dilute polycrystalline K$_7$[SiMoV^{IV}VW$_9$O$_{40}$] in K$_6$[HSiV$_3$W$_9$O$_{40}$] (Figure 7) recorded at room temperature displays complex sets of lines. The experimental spectrum is in good agreement with three sets of 15 lines (g_1 = 1.942, A_1 = 86.0 G; g_2 = 1.966, A_2 = 42.5 G; g_3 = 1.972, A_3 = 24.5 G), showing that the unpaired electron interacts with two equivalent vanadium nuclei (I = 7). The temperature dependence of the ESR spectrum has been studied. It appears that the spectrum is strongly changed between 300 and 80 K. At the present time, the variation of the g and A parameters with temperature could not be extracted from our simulation program. Then, from 80 to 12 K, the spectrum does not vary significantly. In this temperature range, the complexity of the spectrum seems to

---

(16) Pope, M. T.; Varga, G. M. *Inorg. Chem.* **1966**, *5*, 1249.

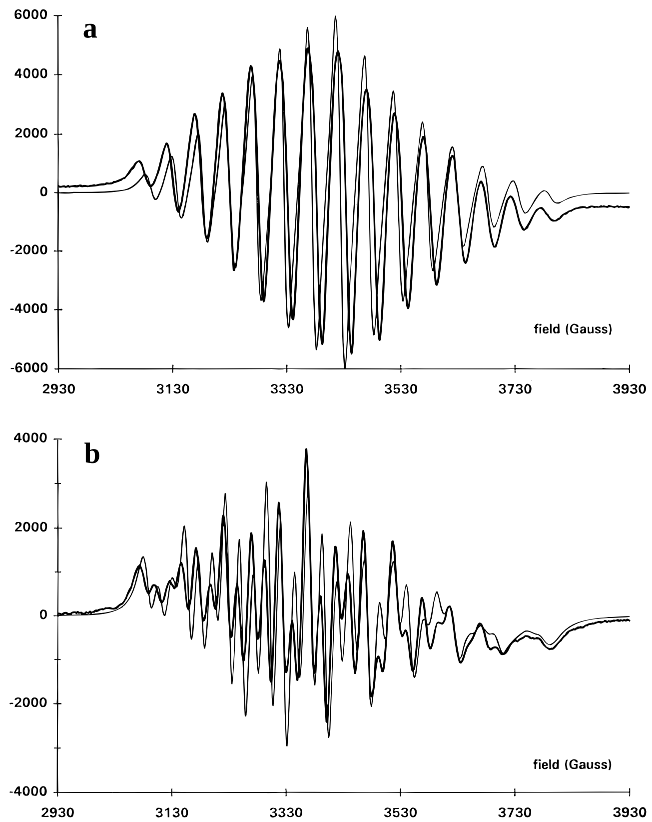

Figure 6. Measured (bold line) and calculated (normal line) X-band ESR spectrum of α-$[SiMoV^{IV}VW_9O_{40}]^{7-}$, in solution at 330 K: (a) at pH = 5 (deprotonated anion) and (b) at pH = 3 (monoprotonated anion); power, 10 mW; amplitude modulation, 10 G; frequency modulation, 100 kHz.

indicate that the electron still interacts with the two vanadium even at 12 K. In contrast, the Q-band spectrum recorded at 77 K on dilute frozen solution of lithium salts consists of three sets of eight lines, indicating that the electron is firmly trapped on one vanadium atom in an orthorhombic ligand field (g_1 = 1.939, A_1 = 167.5 G; g_2 = 1.971, A_2 = 60.0 G; g_3 = 1.974, A_3 = 57.1 G).

(c) α-$[PMoV^{IV}VW_9O_{40}]^{6-}$. In solution at room temperature and pH 4.7, the isotropic X-band ESR spectrum of this compound shows 15 equally spaced lines ($\langle A\rangle$ = 53 G, $\langle g\rangle$ = 1.959). Recording of the spectrum of the monoprotonated compound is not possible because α-$H[PMoV^{IV}VW_9O_{40}]^{5-}$ decomposes in vanadyl cation and unknown species at a pH of around 1. At room temperature, the dilute polycrystalline potassium salt α-$K_6[PMoV^{IV}VW_9O_{40}]$ gives the same behavior as the analogous divanadium silicic anion (g_1 = 1.940, A_1 = 87.5 G; g_2 = 1.963, A_2 = 45.7 G; g_3 = 1.973, A_3 = 24.4 G). At 77 K, the X-band anisotropic spectrum of the frozen solution gives a complicated spectrum which could not be simulated.

(d) α-$[SiV^{IV}V_2W_9O_{40}]^{8-}$. The isotropic X-band spectrum of the trivanadium-substituted anion in solution at pH 5.0 and T = 360 K has been recorded by Mossoba *et al.*[17] We obtained a similar spectrum which consists of more than 40 equally spaced lines. The spectrum pattern remains unchanged from pH = 2 to pH = 12. The anisotropic Q-band spectrum of the lithium salt of this anion as recorded in frozen solution at 77 K shows three sets of eight well-resolved lines characteristic of one V^{4+} center located in a orthorhombic ligand field (g_1 = 1.937, A_1 = 184.0 G; g_2 = 1.9875, A_2 = 60.0 G; g_3 = 1.9815, A_3 = 59.0 G).

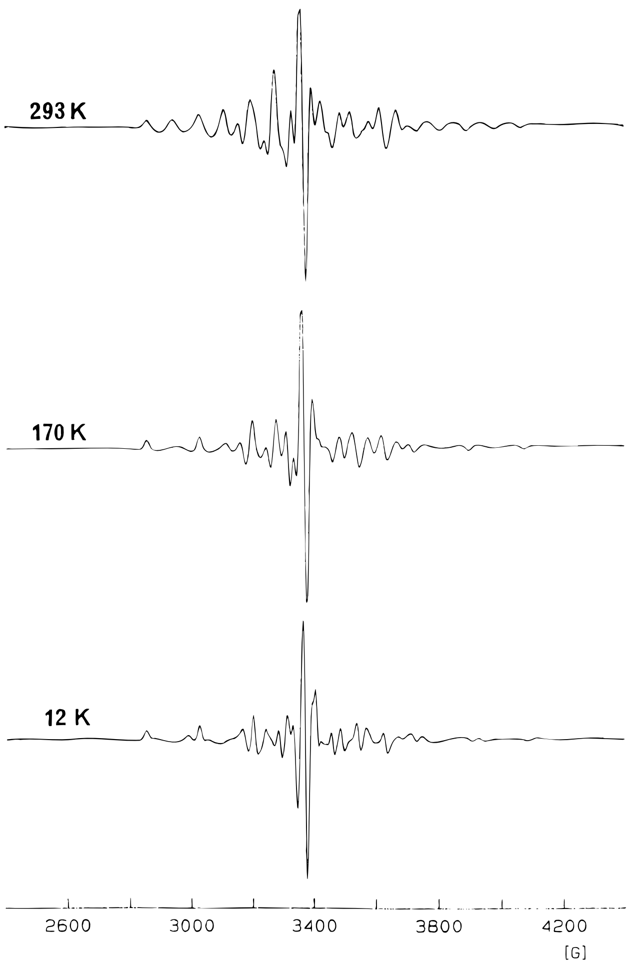

Figure 7. X-band ESR powder spectrum of α-$K_7[SiMoV^{IV}VW_9O_{40}]$ at different temperatures.

Table 5. $\Delta g = g_{\perp} - g_{\parallel}$, $\Delta A = A_{\parallel} - A_{\perp}$ (Gauss), and α^2 Values for the Monovanadium Compounds

anion	Δg	ΔA	α^2	ref
α-$[SiMo_2VW_9O_{40}]^{6-}$	0.033	102	0.80	*a*
α-$[SiVW_{11}O_{40}]^{6-}$	0.048	118	0.92	19
α-$[PMo_2VW_9O_{40}]^{5-}$	0.040	102	0.84	*a*
α-$[PVW_{11}O_{40}]^{5-}$	0.056	122	0.89	18

[a] This work.

Discussion

Symmetry of the V^{4+} Sites. The undecatungstovanado(IV) phosphate and silicate, previously investigated by Pope *et al.*[8] and Sanchez *et al.*[18] give some reference data for V^{4+} ions surrounded by four tungsten atoms. In such a surrounding, the vanadium(IV) atom appears approximately in the C_{4v} symmetry instead of the formal C_s expected one. The replacement of two tungsten(VI) by two molybdenum(VI) atoms gives the α-$[XMo_2VW_9O_{40}]^{n-}$ in which V(IV) and Mo(VI) are located in the positions 1, 2, or 3 (Figure 1), but does not modify the symmetry of the vanadyl group. However, the axial distortion of V^{4+} appears reduced: Δg varies from 0.048 to 0.033 and ΔA from 118 to 102 G when α-$[SiV^{IV}W_{11}O_{40}]^{5-}$ is changed into α-$[SiMo_2V^{IV}W_9O_{40}]^{5-}$ (Table 5). A similar variation is observed for the phosphoric anions. In addition, according to classical results, the unpaired electron lies in the b_2 molecular orbital, which in a LCAO-MO approach could be

---

(17) Mossoba, M.; O'Connor, C.; Pope, M. T.; Sinn, E.; Hervé, G.; Tézé, A. *J. Am. Chem. Soc.* **1980**, *102*, 6864.

(18) Sanchez, G.; Michaud, M.; Livage, J.; Hervé, G. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2795.

expressed as:

$$|b_2\rangle = \alpha|d_{xy}\rangle + \alpha'|\phi_{b2}\rangle$$

The α^2 coefficient, which characterized the fractional contribution of the d_{xy} orbital to the ligand field b_2, can be extracted from the ESR parameters.[19] α^2 can be approximately expressed as

$$\alpha^2 = \frac{7}{6}\left[-\frac{A_{\|} - A_{\perp}}{P} + g_{\|} - 2.0023 - \frac{5}{14}(g_{\perp} - 2.0023)\right]$$

with $P = 0.0128$ cm^{-1} for V^{2+} ions. α^2 values decrease from 0.92 to 0.80 for the silicic anions and from 0.89 to 0.84 for the phosphoric ones when two tungsten atoms are replaced by two molybdenum atoms. The low value of α^2 for α-$[XMo_2VW_9O_{40}]^{n-}$ may be due to a partial delocalization of the unpaired electron into the 5d orbitals of the two MoO_6 groups that share a corner with the VO_6 octahedron. This result suggests that the presence of molybdenum atoms in the vicinity of the VO_6 enhances the covalency of the V−O bonds. In addition, the substitution of molybdenum atoms for tungsten atoms modified mainly the $g_{\|}$ component which depends on the d_{xy} and $d_{x^2-y^2}$ molecular orbitals. A variation of $g_{\|}$ indicates a modification of the metal−oxygen bond in the *xy* plane, perpendicular to the V═O distortion axis. The effect of the molybdenum−tungsten substitution on the covalency of the Mo^{V}−O and V^{IV}−O bonds has been previously reported by Pope *et al.*[8] For the unpaired electron trapped on the molybdenum atom, the values $\alpha^2 = 0.62$ and 0.76 were reported for α-$[PMo^{V}Mo_{11}O_{40}]^{4-}$ and α-$[PMo^{V}W_{11}O_{40}]^{4-}$, respectively.

The Q-band ESR experiments show that at 77 K the unpaired electron remains trapped on a single vanadium atom for the di- and trivanadium-substituted anions. Owing to the well-resolved Q-band spectra of the di- and trivanadium anions as Li^+ salts, a slight discrepancy from the usual axial symmetry can be revealed; a third component for the expression of the **g** and **A** tensors is pointed out when molybdenum atoms are replaced by vanadium(V) atoms. The orthorhombic symmetry can be qualitatively explain by changes in the charge density of some oxygen atoms linked to the vanadium(IV) atom in *xy* plane. The replacement of a molybdenum(VI) atom for vanadium(V) increases the charge of the anion that induces an increase of the charge density on oxygen atoms of the V^{IV}−O−M oxo bridge. Consequently, the presence of the V^{IV}−O−V^{V} oxo bridge with respect to V^{IV}−O−M^{VI} (M = Mo or W) induces some distortions in the *xy* plane of the V^{4+} center.

Electron Delocalization. (a) Dinuclear systems. In solution at 293 K, unprotonated α-$[XMoV^{IV}VW_9O_{40}]^{n-}$ anions give ESR spectra consisting of 15 equally spaced isotropic lines. The unpaired electron interacts with two equivalent vanadium nuclei ($I = 7$). The spectrum of α-$[SiMoV^{IV}VW_9O_{40}]^{7-}$ becomes more complex when the pH is less than the p*K* of the first acidity (p$K \approx 4$). At pH 3, the protonation of the anion leads to the emergence of 29 equally spaced lines. The resulting spectrum can be interpreted in accordance with two possibilities: (i) The delocalized electron interacts magnetically with the hydrogen nucleus, giving a 30-line spectrum related to the splitting of each of the 15 lines into two components. A similar experiment performed in deuterium oxide at pH 3 gives an identical 29-line spectrum that allows exclusion of this assumption. Furthermore, the simulated spectrum does not produce a correct intensity pattern. (ii) The electron is trapped on one vanadium atom but partially delocalized on the adjacent one. This interpretation assumes a spectrum of eight equally spaced lines (a_1), each one of which is split into eight equal parts (a_2). To produce the 29 lines, the ratio a_1/a_2 must fall near 3. The best fit of the calculated spectrum gives $a_1 = 75$ G, $a_2 = 25$ G, and $g = 1.962$. Such a result seems to indicate that protonation of the V−O−V bridge cancels or reduces strongly the electron motion at the ESR time scale and makes both vanadium nuclei inequivalent. Since the splitting pattern remains unchanged between 25 and 80 °C, we concluded that at these temperatures, the electron is trapped on one vanadium atom but partially delocalized by about 25% on the other one. We note that the weighted average of a_1 and a_2 is 50 G, which is the observed splitting when the electron interacts equally with both equivalent nuclei.

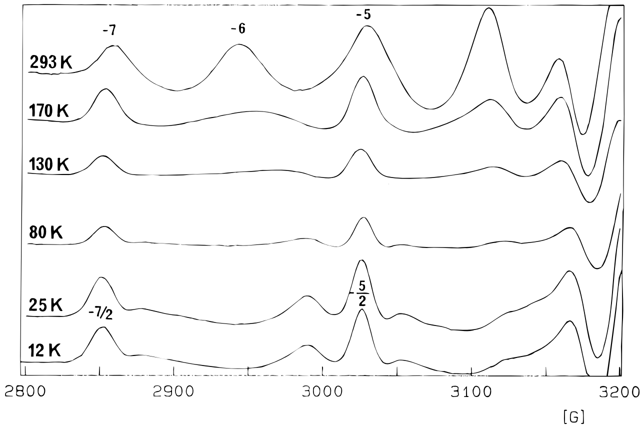

Figure 8. Expanded X-band ESR powder spectra of α-$K_7[SiMoV^{IV}VW_9O_{40}]$ at various temperatures.

At room temperature, the ESR of the diluted polycrystalline potassium salt α-$K_7SiMoV^{IV}VW_9O_{40}$ reveals a hyperfine structure which consists of three sets of 15 equally spaced lines. The simulation of the spectrum leads to the hyperfine constant values $A_1 = A_z = 86.0$ G, $A_2 = 42.5$ G, and $A_3 = 24.5$ G. It seems surprising that the *x*, *y* hyperfine components (A_2, A_3) would be so different, indicating that the site is strongly distorted in the *xy* plane. An explanation would be to consider the site as two corner-shared vanadium octahedra in which the main *z* axis of both tensors **g** and **A** is taken exactly halfway between the V═O vectors in the plane containing them. In the *xy* plane, the *y* axis would be directed along the V−O−V bridge and would correspond to the delocalization axis. The smaller hyperfine constant results from a lowest magnetic interaction of the unpaired delocalized electron with both vanadium atoms and then could be assigned to the component of the **A** tensor directed along the delocalization axis *y* ($A_3 = A_y = 24.5$ G). The remaining value is then attributed to the *x* component ($A_2 = A_x = 42.5$ G). The apparent orthorhombic ESR signal would not be mainly induced by geometric distortion of VO_6 octahedra but would be enhanced by a preferential axis for the electron delocalization. The ESR spectrum of the potassium salt of the divanadium anion has been recorded at different temperatures between 300 and 12 K. The behavior of this complex appears quite similar to those of $K_5H_2[PV^{IV}V_2W_9O_{40}]$ previously studied by So.[20] In order to understand the variation of the ESR spectrum with temperature, let us consider the lowest field lines corresponding to $m_I = -7$, -6, and -5 (m_I is the angular moment of nuclear spin), as shown in Figure 8. When the temperature decreases from 300 to 80 K, the odd lines get narrower gradually (from 30 to 16 G for $m_I = -7$). This can be explained by a decrease of the hopping rates of the electron between the two vanadium nuclei. As was shown for the mixed valence tungsten polyanions,[21] the line width is temperature dependent as a linear plot of log(δH_{pp}) = (1/*T*) (δH_{pp} is the

---

[19] McGarvey, B. R. *Transition Met. Chem.* **1966**, *3*, 89.

[20] Lee, W. C.; So, H. *Bull. Korean Chem. Soc.* **1986,** *7*, 318.

temperature dependent part of the line width). At the limit when the electron is trapped on one single vanadium atom, this line corresponds to $m_I = -7/2$ resonance. At the opposite end, as the temperature decreases from 300 to 80 K, the $m_I = -6$ line broadens and becomes asymmetric, and then splits into two components which move toward the $m_I = -7/2$ and $m_I = -5/2$ lines, respectively. This behavior can be explained by a progressive decrease of the hopping rate of the electron between two nuclei of $m_I = -7/2$ and $m_I = -5/2$. All lines for the $m_I = m_1 + m_2$ values with $m_1 \neq m_2$ have the same temperature dependence that explains the complexity of the whole spectrum. Below 80 K, the ESR spectrum appears nearly independent from temperature, and we never got an isolated V^{4+} signal. This observation would indicate that at 12 K, the transfer of the unpaired electron could still occur. Such results demonstrate that the activation energy for electron transfer is not fixed but decreases as the temperature falls to a near zero value. At low temperature, activationless electron transfer in the form of tunneling predominates. The comparison of Q-band and X-band spectra shows that the electron is trapped on a single atom for the 35 GHz frequency (Q-band) but always interacts with the two vanadium atoms at 9.5 GHz (X-band). This result can be related to the two different ESR time scales and suggests that the exchange frequency should be low enough to observe a localized electron at 35 GHz and high enough to visualize an electron motion at 9.5 GHz. The divanadium anion α-$K_6[PMoV^{IV}VW_9O_{40}]$, as a diluted polycrystalline sample, exhibits the same behavior as α-$K_7[SiMoV^{IV}VW_9O_{40}]$. At room temperature, the spectrum consists of three sets of 15 lines, which indicates that the delocalization of the electron generates three components for the **g** and **A** tensors ($A_z = 87.5$, $A_y = 24.4$, and $A_x = 45.7$ G). Therefore, the even transition at $m_I = -6$ or $m_I = +6$ appears substantially broadened with respect to the odd lines $m_I = -7$ or $+7$ at room temperature for the P compound but only at $T \approx 170$ K for Si compound. This observation is consistent with a lower transfer rate for the electron in α-$K_6[PMoV^{IV}VW_9O_{40}]$ than in α-$K_7[SiMoV^{IV}VW_9O_{40}]$.

(b) Trinuclear Systems. The α-$H[SiV^{IV}V_2W_9O_{40}]$ spectrum in solution at pH 5 has been reported and interpreted by Mossoba *et al.*[17]and correctly simulated by So *et al.*[22] They obtained more than 40 equally spaced hyperfine lines due to the interaction of the electron trapped on one vanadium atom with two equivalent vanadium nuclei. The theoretical spectrum would consist of 120 lines, but the overlapping of much of them gives only around 43 observed lines. Mossoba *et al.* concluded that the electron is partially localized on one vanadium atom (66%) and partially delocalized by about 17% on each of the other two. In order to explain the nonequivalence of the three vanadium atoms, the authors invoked the presence of one proton on a V−O−V bridge. However, we have observed that the feature of the spectrum was kept at whatever the pH conditions were ($5 < \mathrm{pH} < 12$). So, the partial delocalization of the unpaired electron does not appear to be dependent on the protonation of the V−O−V bridge. The α-$[PV^{IV}V_2W_9O_{40}]^{7-}$ anion gives a similar result in the 5−12 pH range and was previously interpreted by So *et al.*, who invoked the presence of protonated bridge.[22] Thus, in view of our results, the previous reported assumption seems dubious, and the nonequivalence of the three vanadium atoms may originate from another explanation.

A different behavior was observed on the mixed Dawson anion α-$[P_2V^{IV}V_2W_{15}O_{62}]^{10-}$. In this complex, the three addendum atoms form a metallic triad of three edge-shared octahedra and the electron is totally delocalized on the three equivalent vanadium atoms.[23−24] In such a structure, the extent of the V−O−V π bond, as a result of the ∼125° V−O−V bridge bond angle, is assumed to be lower than the extent of the V−O−V π bond (158°) in the α-(1,2,3)$[PV^{IV}V_2W_9O_{40}]^{7-}$, which would induce a more delocalized electron in the latter compound. Actually, an opposite trend is observed for both anions that would suggest two kinds of interaction between V centers depending on the arrangement of the three V centers. In a previous work, we suggested that increasing the vanadium atom number in the α-$[SiMo_{3-x}V_xW_9O_{40}]^{(4+x)-}$ induces a shortening of the V−V distances with respect to the V−W and V−Mo distances.[9] This assumption was based on some values of the homonuclear coupling constant $^2J_{W-O-W}$ determined by ^{183}W NMR and by the ^{51}V line width. We observed that the $^2J_{W-O-W}$ coupling constant involving tungsten atoms of the W−O−W bridge in the alignment of the V-O-V bridge decreased gradually as the vanadium atom number increased. We proposed that a concerted displacement of the metallic atoms leads to a successive alternation of short and long M−O bonds which originated from short V−V distances. In accordance with these conclusions, the decreasing of the relaxation times of the ^{51}V for the di- and trivanadium anions could be related to a greater distortion of the adjacent VO_6 octahedra, induced by the shortening of the V−V lengths. Such a shortening could close the V−O−V angle, to a great enough degree in α-$[SiV_3W_9O_{40}]^{8-}$ to cancel the electron transfer between the three vanadium centers. For the divanadium anion, α-$[SiMoV_2W_9O_{40}]^{7-}$, the 15-line spectrum interpreted as an electron hopping suggests a higher V−O−V angle than for α-$[SiV_3W_9O_{40}]^{8-}$. Under protonation conditions, the 29-line spectrum which would result from partial localization of the single electron on one vanadium nucleus (about 75%) and from delocalization of the adjacent other seems to indicate that the protonation of the V−O−V bridge destroys the dπ−pπ transfer to give rise to superhyperfine interactions. Such a conclusion fully agrees with those proposed by Pope and So from results obtained on analogous compounds. Then, such transfer should strongly depend on the π bond order of the V−O−V junctions. For the mixed Dawson α-$[P_2V^{IV}V_2W_{15}O_{62}]^{10-}$ anion, in spite of a lower angle value (∼120°), a complete electron delocalization is observed resulting in a characteristic 22-isotropic-line ESR spectrum. This result does not agree with an electron transfer through the V−O−V π bonds and needs other explanations. In such a system of three edge-sharing VO_6 octahedra, the electron delocalization could originate from direct overlap of the three d_{xy} orbitals. In such a case, the shortening of the V−V distance and the low V−O−V angle value would be favorable for d−d interactions. Then, we think that for trivanadium systems, the electron delocalization could occur through two kinds of interaction: (i) When the vanadium atoms share corners, the single electron could be transferred through the vanadium−oxygen dπ−pπ overlap. (ii) When the vanadium atoms share edges, the spin density could be transferred through direct V−V d_{xy} interactions.

Acknowledgment. We thank Bernard Morin for recording ESR spectra and Professor Didier Gourier and Professor Leonid Kazanskii for fruitful discussions. The research has been supported by CNRS and Elf-Atochem.

IC940908O

---

(21) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier M. *J. Am. Chem. Soc.* **1983**, *105*, 6817.

(22) So, H.; Lee, C. W. *Bull. Korean Chem. Soc.* **1990**, *11* (2), 115.

(23) Harmalker, S. P.; Leparulo, M. A.; Pope, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 4286.

(24) So, H.; Lee, C. W.; Lee, D. *Bull. Korean Chem. Soc.* **1987**, *8* (5), 384.