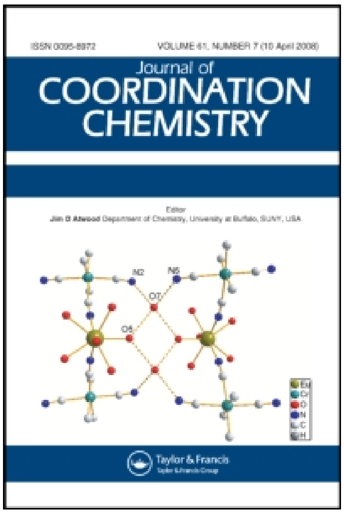

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METAL–LIGAND ELECTRON TRANSFERS IN VANADIUM COMPLEXES OF 11-TUNGSTOSILICATE ISOMERS

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$(VSiW_{11}O_{40})^{n-}$ complexes exhibit two kinds of redox systems, those of vanadium (V^{V}–V^{IV} and V^{IV}–V^{III}) and those of the ligand. Electron transfers between the vanadium and the ligand are observed by change in the pH. Electronic spectra are discussed with regard to two types of electronic transitions, intervalence transfers and d-d transitions.

The formation of pentadentate ligand isomers β_1, β_2, β_3 and α-$SiW_{11}O_{39}{}^{8-}$ has been previously reported[1] and their properties discussed with regard to their structure[2,3]. In this paper, we report the properties of some vanadium complexes which differ in the oxidation states of the metal or of the ligand as well as comment on the electron transfers between the vanadium and the tungsten atoms.

EXPERIMENTAL

Chemicals

Potassium salts of the ligands have been prepared as previously described[1].

$M_5(OV^{V}SiW_{11}O_{39})$, n H_2O, M = K^+ or Cs^+. 16g of ligand were added to a solution of 0.5 M $NaVO_3$ (15 ml) and 1M HCl (30 ml). Potassium salt of the α-isomer or cesium salts of the β_i-isomers were precipitated with KCl (5g) or CsCl (6g). Salts were recrystallized from water.

Analyses of W^{VI} and V^{V} were carried out by polarography in pyrocatechol + acetate buffer.

Physical Measurements

Polarograms were recorded on a PRG 3 Tacussel instrument using a rotating graphite electrode or a dropping mercury electrode. The concentration of the product was 10^{-4} M. Electrolyses were carried out at a controlled potential using a Tacussel PRT 20 potentiostat, the solutions, 5.10^{-3} or 10^{-2} M, were under nitrogen. The U.V. and visible spectra were recorded on a Beckmann DK 2a spectrophotometer.

RESULTS AND DISCUSSION

Electron Transfers in the Complexes

This work establishes the conditions of electron transfers in the complexes by polarography of the various reduced compounds obtained by controlled potential electrolyses. The half-wave potentials of the $SiW_{11}O_{39}^{8-}$ ligands do not change significantly when a metallic complex is formed, and this allows us to assign the tungsten reduction waves in polarograms of the vanadoundecatungstates isomers at the different pH values. New waves were assigned to the vanadium reductions. The four complexes have a similar behavior. Figure 1 shows the variation of the polarographic half-wave potentials of β_1-$VSiW_{11}$ versus pH. Two types of redox reactions can be considered: those involving the vanadium and those involving the polyanionic ligand.

a) Oxidation-reduction of the vanadium. It occurs through two monoelectronic steps. The first one does not depend on the pH and is only an electron exchange, the second is dependent upon the pH: the slope of the straight line $E_{1/2} = f(pH)$ is about 110 mV/pH unit (Figure 1, A), so, there is a simultaneous exchange of one electron and of two protons. The oxidation-reduction of the vanadium can be described by the following equations

(1) $(OV^{V}SiW_{11}O_{39})^{5-} + e \rightleftharpoons (OV^{IV}SiW_{11}O_{39})^{6-}$
(2) $(OV^{IV}SiW_{11}O_{39})^{6-} + e + 2H^+ \rightleftharpoons (H_2OV^{III}SiW_{11}O_{39})^{5-}$

which take account that the $SiW_{11}O_{39}^{8-}$ polyanion is a pentadentate ligand and, therefore, the sixth

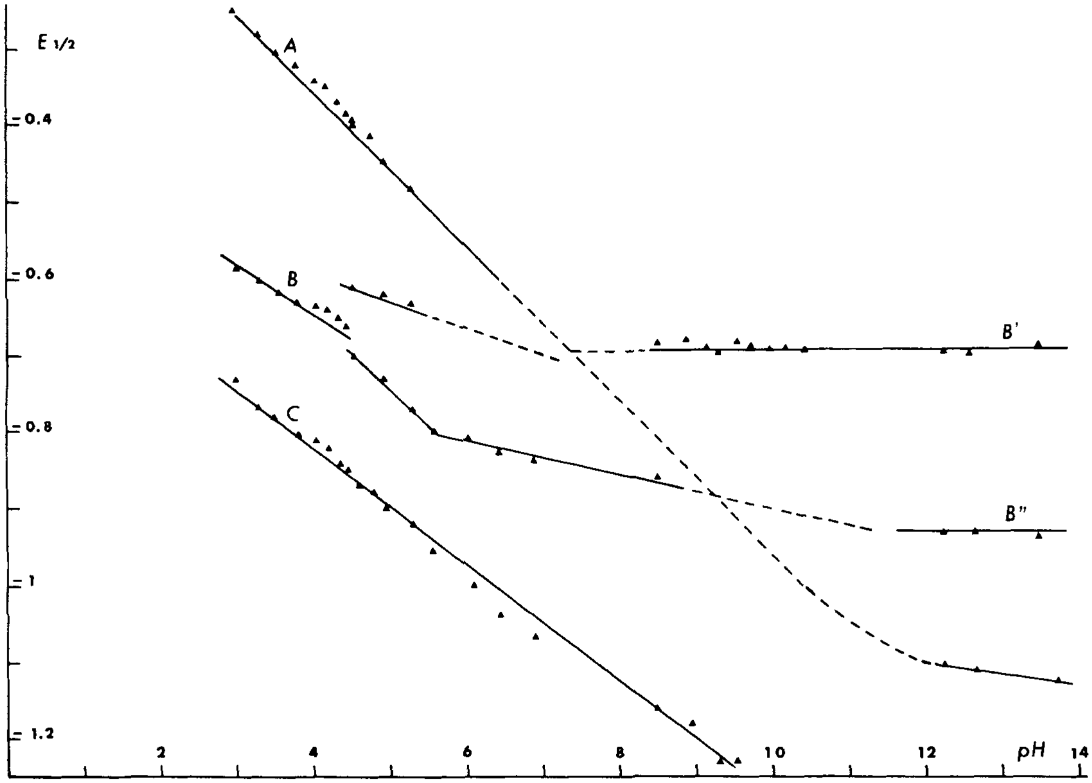

FIGURE 1 Half-wave potentials of β_1-VSiW$_{11}$ complexes (vs SCE) versus pH. A, one-electron wave ($V^{IV/III}$); B, C, two-electron waves (W). Above pH 5, B splits into two one-electron waves B' and B". Broken lines denote regions where waves overlap and precise half-wave potentials cannot be measured.

coordination position of the vanadium is occupied either by an oxygen atom in the V^V and V^{IV} complexes or by a molecule of water in the V^{III} complex. Oxidation-reduction potentials of the vanadium do not depend at all (with regard to V^{IV}/V^{III}) or do not largely depend (with regard to V^V/V^{IV}) on the complexing isomer.

b) Oxidation-reduction of the ligand. At pH < 5, two successive steps of two electrons are involved (Figure 1, B, C) and the relative polarographic half-wave potentials decrease as the pH increases. This is due to the protonation of the various reduced forms of the ligand[4]. At pH > 5, the first wave splits into two waves of one electron (Figure 1, B', B") which are not dependent upon the pH when the reduced species are not protonate. Therefore, the ligand can have three oxidation states by fixing 1, 2 or 4 electrons.

Table I shows that the oxidation-reduction potentials of the unprotonated ligand β-isomer are the same while the α-isomer is less reducible.

TABLE I
Half-wave potentials (±0.01 V) of unprotonated VSiW$_{11}$ isomers;
L: SiW^{VI}_{11}, L_I: $SiW^{VI}_{10}W^V$, L_{II}: $SiW^{VI}_9W^V_2$

	$V^VL/V^{IV}L$	$V^{IV}L/V^{IV}L_I$	$V^{IV}L_I/V^{IV}L_{II}$	$V^{IV}L_{II}/V^{III}L_{II}$
β_1	0.31	−0.69	−0.92	−1.12
β_2	0.36	−0.70	−0.90	−1.12
β_3	0.39	−0.71	−0.91	−1.12
α	0.38	−0.80	−1.00	−1.12

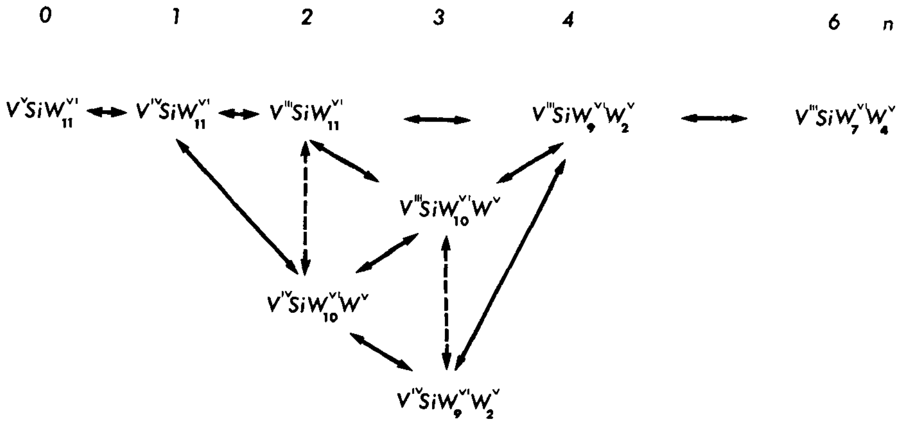

FIGURE 2 Redox behavior of $VSiW_{11}$ complexes; n: number of electrons added; ⟷: reversible oxidation reduction; ←---→: electron transfer between vanadium and ligand

c) Metal-ligand electron transfers. Figure 1 shows the inversion of oxidation-reduction potential values of the vanadium and of the ligand as the pH increases, thus, with the β_1 isomer, the first step of the ligand reduction at pH > 7.5, the two steps at pH > 9.5, occur before the vanadium reduction V^{IV}/V^{III}. Because of this particular behavior, different redox complexes can be obtained according to the pH (Figure 2) and electron transfers between the vanadium and the ligand are observed by change in the pH. Two redox reactions may be observed.

$$(3)\quad [H_2OV^{III}SiW^{VI}_{11}O_{39}]^{5-} \rightleftharpoons [OV^{IV}SiW^{VI}_{10}W^{V}O_{39}]^{7-} + 2H^+$$

$$(4)\quad [H_2OV^{III}SiW^{VI}_{10}W^{V}O_{39}]^{6-} \rightleftharpoons [OV^{IV}SiW^{VI}_{9}W^{V}_{2}O_{39}]^{8-} + 2H^+$$

These metal-ligand electron transfers involve an inner sphere mechanism through oxygen bridges between the vanadium and the tungstens of the polyanionic ligand. They are observed for pH values depending on the isomers according to the individual redox

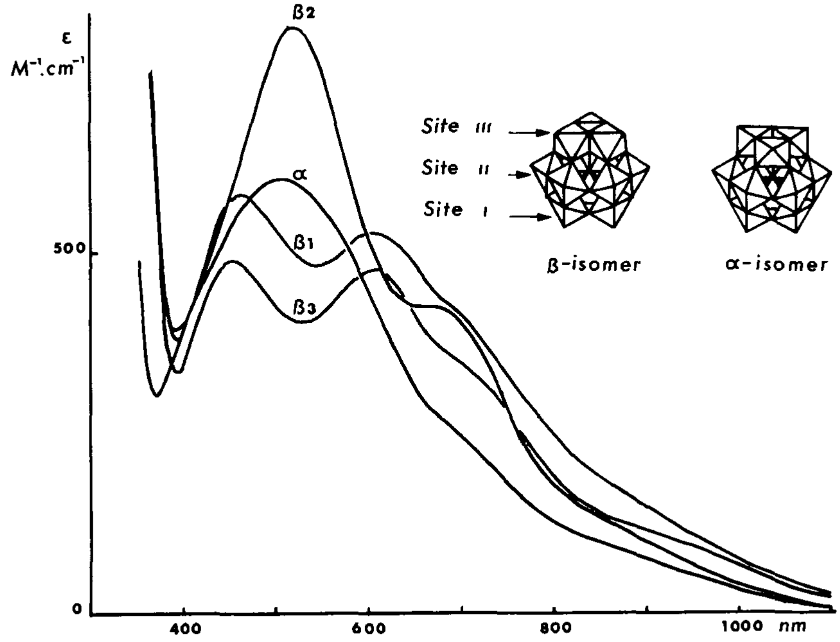

FIGURE 3 Electronic spectra and idealized structures of $VSiW_{11}$ complexes; in β_1, β_2 and β_3 isomers, the vanadium is respectively in site I, II and III

behavior of each isomer at a given pH. Let us take the β_1-isomer as example: the reaction (3) occurs at $6.5 < \mathrm{pH} < 8.5$ and the reaction (4) at $8.5 < \mathrm{pH} < 10.5$. For the α-isomer, reaction (4) is never complete even in strongly basic medium owing to the vicinity of the oxidation-reduction potentials of both vanadium and ligand (Table I).

Electronic Spectra

The $V^{IV}SiW_{11}$ complexes can be considered as mixed valence compounds[5,6] and their spectra (fig. 3) discussed with regard to two types of electronic transfers: the intervalence transfers (IVT) $V^{IV} \rightarrow W^{VI}$ through oxygen bridges and the d-d transitions.[7,8] As we have previously reported[2], these latter do not depend on the ligand isomer in contrast to the IVT. Structural data (Figure 3) have led us to distinguish the IVT between atoms belonging to the $V^{IV}W_2O_{13}$ group ("intra group" IVT) from those between V^{IV} and W^{VI} of another W_3O_{13} group ("extra group" IVT).[9]

When the ligand is reduced, the added electrons are located on defined W atoms and the spectra can also be interpretated with IVT between W^V and W^{VI}. Until now, the proposed assignment correlated the bands of lower energy with the "intra IVT" and the bands of higher energy with "extra IVT"[9]. These correlations were supported by a structural hypothesis about the 9-tungstoheteropolyanions.[10] Actually, the resolution of the structure of the β-9-tungstosilicate sodium salt which is performed in our laboratory shows that this hypothesis is incorrect and, consequently, causes us invert the assignments. According to this scheme, the proposed assignments of $VSiW_{11}$ electronic spectra are recorded Table II. It can be pointed out that

a) in $V^{IV}SiW_{11}$ complexes, β_1, β_3 and α isomers show two IVT but β_2 only one, probably due to the vicinity of bands (two "intra IVT" and two "extra IVT" are expected when V^{IV} is in site II, Figure 3),

b) no significant changes occur in the absorption spectra of V^{III} or V^{IV} complexes when the ligand is

TABLE II
Proposed assignments of absorption bands of SiW_{11} complexes: band positions in kK (incertainties are given when the bands are poorly resolved), extinction molar coefficient in parentheses; [a]probably included in the 19.7 kK band; [b]according to ref. 7, 8 and 9; [c]possibility of two bands; [d]band hidden by the "intra IVT".

		d-d of V^{IV}	intra IVT $V^{IV} \rightarrow W^{VI}$	extra IVT $V^{IV} \rightarrow W^{VI}$
$V^{IV}SiW_{11}^{VI}$	β_1	11.5(170) 14.9(420)	22.3(520)	17.0(580)
	β_2	11.7(130) 15.0(420)	^{a}	19.7(780)
	β_3	11.5(130) 14.7(360)	22.9(470)	17.0(480)
	α^b	11.7(100) 14.8(280)	24.7(440)	20.3(600)
		d-d of $W^{V\,b}$	intra IVT $W^V \rightarrow W^{VI}$	extra IVT $W^V \rightarrow W^{VI}$
$V^{IV}SiW_{10}^{VI}W^V$	β_1	17.1(2600)	13.5(3400)	$9 \pm 1(2300)^c$
	β_2	19.0(1700)	13.9(2000) sh	$8.0 \pm 0.3(1900)$ 11.4(2700)
	β_3	19.0(1600)	13.5(2900)	$9.5 \pm 0.5(2600)$ 11.1(2800)
	α	d	$16.5 \pm 0.5(2200)$	$10.0 \pm 0.5(1800)$
$V^{III}SiW_9^{VI}W_2^V$	β_1	18.3(3300)	14.1(6400)	$10.0 \pm 0.2(4500)$
	β_2	18.2(4100)	14.3(5500)	$8.2 \pm 0.3(4300)$
	β_3	19.6(3100)	14.3(6000)	9.4(5400)
	α	d	16.9(4400)	9.8(4000)

reduced because IVT intensities $V^{III} \rightarrow W^{VI}$ [2] or $V^{IV} \rightarrow W^{VI}$ are similar and clearly weaker than $W^{V} \rightarrow W^{VI}$ ones, and

c) the $W^{V} \rightarrow W^{VI}$ "intra IVT" of the β_i complexes in a definite reduced state have practically the same energy; the related IVT of the α isomer is blue shifted of about 2.5 to 3 kK. The two "extra IVT" observed with the β_1 (?), β_2 or β_3 $V^{IV}SiW_{10}W^{V}$ are consistent with the location of the W^{V} in the site II of the ligand. In addition, "intra" and "extra IVT" observed in $V^{IV}SiW_9W_2^{V}$ suggest that the two W^{V} cannot both be in the immediate vicinity of the vanadium.

Although a more accurate location of the W^{V} cannot be derived from polarographic and spectroscopic data, it may be presumed that the electron transfers (3) and (4) occur through consecutive jumps via tungsten atoms.

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