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SPECTROELECTROCHEMISTRY AND RESONANCE RAMAN SPECTRA OF VANADIUM(II) AND (III) COMPLEXES OF 2,2'-BIPYRIDINE

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The optical and redox properties of the $[\text{V}(\text{bipy})_3]^{2+}$ and $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complexes (bipy = 2,2'-bipyridine) were studied by resonance Raman and spectroelectrochemical techniques. Strong enhancement of the vibrational modes of bipy was observed in the Raman spectra of the $[\text{V}(\text{bipy})_3]^{2+}$ complex. In contrast, the Raman spectra of $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ exhibited pronounced enhancement of the vibrational modes of the V(III)-O-V(III) chromophore. Spectroelectrochemical measurements carried out for the $[\text{V}(\text{bipy})_n]^{2+}$ complexes showed that for $n = 1$ and 2, the oxidation process leads to oxo-bridged binuclear V(III) species, and for $n = 3$, the oxidation proceeds *via* two successive electron transfer steps, generating vanadium(IV) products.

Key words: vanadium, 2,2'-bipyridine, Raman, spectroelectrochemistry

INTRODUCTION

The redox behaviour of vanadium(II) complexes of 2,2'-bipyridine (bipy) and related ligands¹ has been a subject of current interest, because of their potential usefulness as multielectron transfer agents. Recently, Shah and Maverick,²⁻⁴ investigated the photophysics and photochemistry of the tris(2,2'-bipyridine)- and tris(1,10-phenanthroline)vanadium(II) complexes, in the presence of various electron acceptors. They observed that the photooxidation mechanism involves oxidative quenching of the $\text{V}(\text{NN})_3^{2+}$ excited state, followed by hydrolysis and dimerization of $\text{V}(\text{NN})_3^{3+}$. A binuclear V(III) product has also been detected in *Ascidacea* cells treated with bipy.⁵ Its structure was shown by X-ray diffraction to be $[\{\text{V}(\text{bipy})_2\text{Cl}\}_2\text{O}]^{2+}$, with a near linear VOV^{4+} unit.⁵ A similar V(III)-O-V(III) structure has been characterized in $[(\text{THF})_3\text{Cl}_2\text{VOVCl}_2(\text{THF})_3]$, where THF = tetrahydrofuran,⁶ and in $[\text{V}_2\text{O}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_4]$.⁷ It has been suggested that compounds of this type are useful models of vanadium polynuclear intermediates formed during the hydrodesulfurization of crude oils.⁷

This work deals with the spectroelectrochemistry and resonance Raman (RR) spectra of bipy-vanadium(II) and their corresponding binuclear vanadium(III) complexes in aqueous solution. These techniques have been particularly useful in the assignment of the electrochemistry and the electronic spectra of inorganic complexes, and to our knowledge, they have never been employed in the case of the bipy-vanadium species reported in this paper.

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EXPERIMENTAL

All manipulations were performed using standard inert-atmosphere techniques. Solvents were purified by distillation, and dried over molecular sieves. VCl_3 (Alpha), bipy (Aldrich), and other chemicals were of reagent grade and were used as supplied.

The tris(bipy)vanadium(II) complex was prepared by reacting 20 cm^3 of aqueous $V(\text{III})$ (2 mmol) generated from the electrolysis of VO^{2+} ions, with 2,2'-bipyridine (7.5 mmol) previously dissolved in 5 cm^3 of methanol. The dark blue complex precipitated on adding tetraethylammonium tetrafluoroborate or ammonium hexafluorophosphate (6 mmol). The solid was collected on a filter, washed with diethyl ether, and dried in a vacuum, in the presence of calcium chloride. Anal.; Calcd. for $[V(\text{bipy})_3](PF_6)_2$: C, 44.50; N, 10.38; H, 2.97%. Found: C, 43.90; N, 10.24; H, 2.93%. Calcd. for $[V(\text{bipy})_3](BF_4)_2 \cdot 3H_2O$: C, 48.19; N, 11.24; H, 4.01%. Found: C, 48.51; N, 11.28; H, 3.9%. The syntheses of the analogous perchlorate and trifluoromethanesulfonate salts have already been published.^{2,8}

$[V_2O(\text{bipy})_4Cl_2]X_2$ ($X = BF_4^-$, PF_6^-) was prepared by reacting 10 cm^3 of an aqueous solution of vanadium(III) trichloride (7 mmol) with 2,2'-bipyridine (16 mmol) previously dissolved in 10 cm^3 of ethanol. The mixture was kept at 50°C for 30 minutes and 10 cm^3 of an aqueous solution of $LiBF_4$ or NH_4PF_6 (16 mmol) were added very slowly. The hexafluorophosphate complex precipitated immediately. In the case of the tetrafluoroborate complex, the volume was reduced under vacuum to approximately 6 cm^3 . After one night at 0°C , the resulting solid was collected on a filter, washed with diethyl ether, and dried in a vacuum, in the presence of calcium chloride. Anal.; Calcd. for $[V_2O(\text{bipy})_4Cl_2](PF_6)_2$: C, 43.53; N, 10.16; H, 2.93; Cl, 6.42%. Found: C, 43.15; N, 9.95; H, 2.95; Cl, 6.30%. Calcd. for $[V_2O(\text{bipy})_4Cl_2](BF_4)_2 \cdot 3H_2O$: C, 46.14; N, 10.76; H, 3.69%. Found: C, 46.01; N, 10.82; H, 3.57%.

Cyclic voltammetry measurements were carried out with a Princeton Applied Research instrument, consisting of a 173 potentiostat and a 175 universal programmer. A platinum electrode was employed for the measurements, along with the conventional Luggin capillary with the $Ag/AgCl$ (1 M KCl) reference electrode. The auxiliary electrode was a platinum wire dipped into the electrolyte solution (0.5 M KCl) in a small compartment separated from the working solution by a fine glass frit. The temperature for all experiments was 25°C . The measured potentials were converted to the normal hydrogen electrode (NHE) scale by adding 0.222 V.

The electronic spectra of the complexes were recorded on a Cary 17 or a Hewlett-Packard 8451-A diode array spectrophotometer. Magnetic susceptibility measurements were carried out in acetone solutions, based on the method described by Evans.⁹ Infrared spectra were recorded on a Perkin Elmer 283 spectrophotometer, with the solids dispersed in KBr pellets. Resonance Raman (RR) spectra were recorded on a Jarrell-Ash instrument, using Spectra Physics argon and krypton ion lasers. The measurements were carried out with use of a spinning cell, with the solids dispersed in compressed pellets with a supporting medium of sodium sulfate. The intensities were measured as peak heights relative to the sulfate Raman band at 980 cm^{-1} . Spectroelectrochemical measurements were carried out with the PARC potentiostat attached to the diode-array spectrophotometer. A three electrode system was designed for a thin layer cell of 0.028 cm internal optical pathlength. A gold minigrad was used as transparent working electrode, in the presence of a small $Ag/AgCl$ (1 M KCl) reference electrode and of a platinum auxiliary electrode. All the experiments were performed at 25°C under semi-infinite diffusion conditions, as described by Kuwana and Winograd.¹⁰

RESULTS AND DISCUSSION

The electronic spectrum of the $[V(\text{bpy})_3]^{2+}$ complex consists of strong absorption bands at 645 ($6900 \text{ M}^{-1} \text{ cm}^{-1}$) and 400 nm ($4100 \text{ M}^{-1} \text{ cm}^{-1}$), (Figure 1) which has been assigned^{8,11} to charge-transfer transitions (MLCT) from the metal d_π orbitals to π^* orbitals localized on bpy. König and Herzog⁸ have shown that the ${}^4A_2 \rightarrow {}^4T_2$ and ${}^4A_2 \rightarrow {}^4T_1$ ligand field bands occur superimposed to the MLCT bands, with an estimated $10 Dq = 16,150 \text{ cm}^{-1}$.

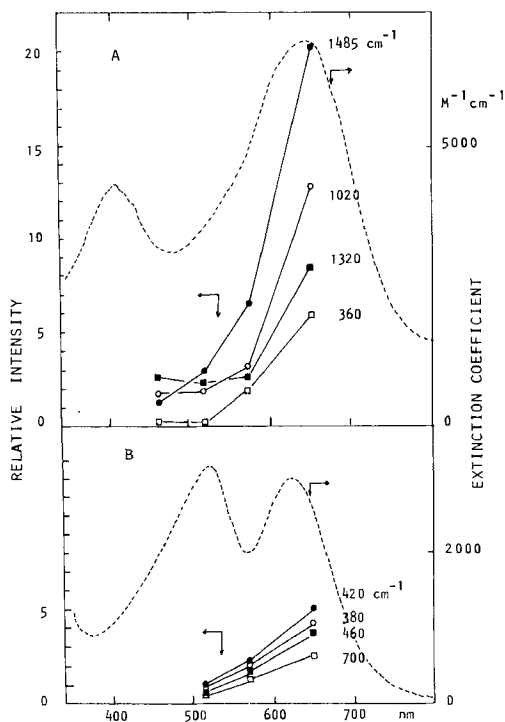


FIGURE 1 Electronic spectra and typical resonance Raman excitation profiles of (A) $[V(\text{bpy})_3]^{2+}$ and (B) $[V_2O(\text{bipy})_4Cl_2]^{2+}$ complexes.

Typical Raman spectra of $[V(\text{bpy})_3](\text{PF}_6)_2$ are shown in Figure 2. The assignment of the vibrational bands of the aromatic ligand can be discussed based on the normal modes of biphenyl or bpy, which have been analysed in detail by Zerbi and Sandroni,^{12,13} and Strukl and Walter.¹⁴ The available data on the infrared spectra of bpy complexes are also quite useful.¹⁵⁻¹⁹ In general, the ring stretching frequencies of aromatic compounds fall in the region of $1600\text{--}1400 \text{ cm}^{-1}$. According to the potential energy distribution for bpy,¹⁴ the vibrational frequencies near 1600 cm^{-1} involve a high contribution of CC and CN stretching, while those near 1400 cm^{-1} involve equivalent contributions of CC, CN stretching and CCH deformation vibrations. The vibrational frequencies around 1300 cm^{-1} are associated with composite CC, CN stretch and HCC bending modes. The inter-ring stretching vibration

is expected to occur in this region. The peaks in the region of $1200\text{--}1000\text{ cm}^{-1}$ can be ascribed to ring vibrations, as well as to ring-H in-plane bending vibrations. The out-of-plane ring-H bending vibrations are expected to occur in the region $900\text{--}750\text{ cm}^{-1}$. The ring torsion and ring bending modes occur below 700 cm^{-1} .

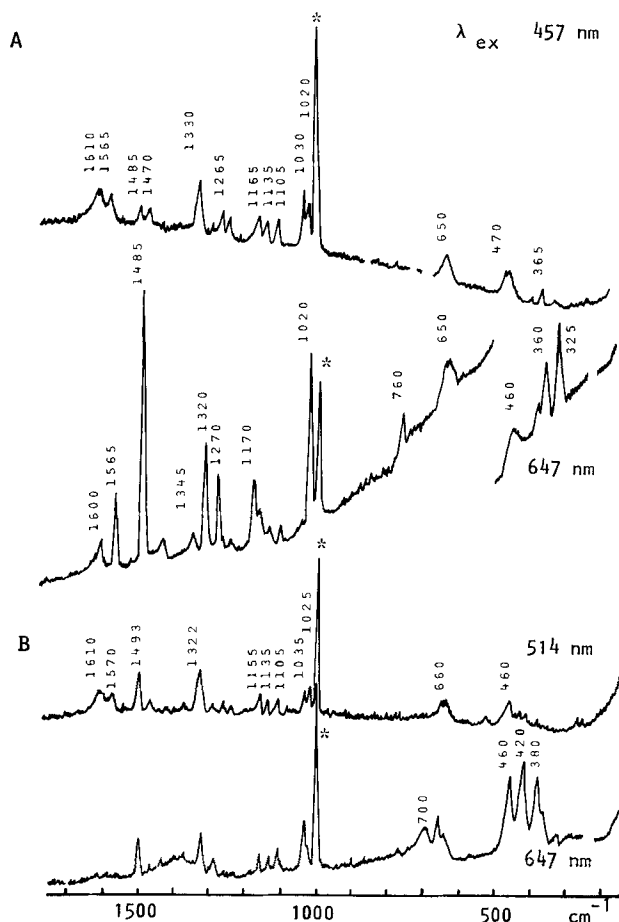


FIGURE 2 Resonance Raman spectra of (A) $[\text{V}(\text{bipy})_3]^{2+}$ and (B) $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complexes, at several excitation wavelengths. The internal sulfate reference is indicated by an asterisk.

Strong enhancement of bipy vibrational modes has been observed, leading to excitation profiles which follow the visible absorption spectrum, as shown in Figure 1B. According to Caswell and Spiro²⁰ the a_{1g} and b_{2u} vibrational modes of biphenyl (D_{2h}) are correlated with the enhanced Raman peaks of a_1 symmetry in $[\text{Ru}(\text{bpy})_3]^{2+}$, assuming a local C_{2v} symmetry for bipy. If a similar approach is employed for the tris(bipy)vanadium(II) complex, a good correlation is also observed, as shown in Table I.

TABLE I
Comparison of RR frequencies (cm^{-1}) for bipyridine (L) vibrations, and correlation with biphenyl.

Symm D_{2h}	biphenyl ^a	Symm C_{2v}	RuL_3^{2+b}	VL_3^{2+}	$\text{V}_2\text{OL}_4\text{Cl}_2^{2+}$
A_g	1612	A_1	1605	1610	1620
B_{2u}	1571	A_1	1560	1565	1570
A_g	1507	A_1	1489	1485	1493
B_{2u}	1432	A_1	1448	1470	1432
B_{2u}	1383	A_1		1345	1370
A_g	1285	A_1	1317	1320	1322
B_{2u}	1272	A_1	1264	1270	1285
A_g	1190	A_1	1173	1170	1155
B_{2u}	1156	A_1	1109	1135	1135
B_{2u}	1074	A_1	1067	1105	1105
A_g	1030	A_1	1041	1030	1035
A_g	1003	A_1	1027	1020	1025
A_g	742	A_1	766	760	770
B_{2u}	629	A_1	663	650	660
A_g	315	A_1		325	315

^a Ref. 12 ^b Ref. 20.

A strong enhancement is also observed for the vibrational band at 360 cm^{-1} (Figures 1, 2). This band does not occur in the vibrational spectra of bipy (Table I) and by analogy to related examples in the literature²¹ it can be assigned to the V(II)-N stretching mode.

In the case of the binuclear $[\text{V}_2\text{O}(\text{bpy})_4\text{Cl}_2]^{2+}$ complex, the electronic spectrum exhibits two strong absorption bands at 525 ($3 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$) and 625 nm ($3 \times 10^3\text{ M}^{-1}\text{ cm}^{-1}$), as shown in Figure 1C. This species was also studied by Murray and Sheahan,²² who proposed an intervalence transfer assignment for the visible spectra, based on a mixed-valence V(II)/V(III) description. Recently, however, Shah and Maverick^{2,3} demonstrated that the binuclear complex consists of vanadium(III) ions, and the crystal structure was solved by Hawkins,⁵ indicating the existence of a near linear VOV^{4+} unit in the complex. Many other complexes containing linear M-O-M bridges are known in transition metal chemistry,^{6,7} and the short M-O bond lengths compared to single-bond values support a multiple bonding character, involving π -bonding interactions.

Molecular orbital calculations for the $[\text{VOV}]^{4+}$ unit in the $[\text{V}_2\text{O}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_4]$ complex have been reported by Money *et al.*⁷ The V-O-V σ -framework consists of overlap between the metal d_z^2 and oxygen p_z orbitals. The V-O-V π -bonding framework consists of overlap of metal d_{xz} , d_{yz} and oxygen p_y and p_x orbitals to yield two degenerate three-center bonding molecular orbitals (π_1 , π_2), and the corresponding set of antibonding orbitals (π_3^* , π_4^*). The metal d_{xy} orbitals possess δ -symmetry with respect to the VOV axis, but are quite remote for an effective interaction. The antisymmetric combination of the d_{xz} , or d_{yz} orbitals of the two vanadium(III) ions leads to another degenerate pair of non-bonding orbitals.

Magnetic susceptibility measurements ($\mu = 2.82\text{ BM/V}^{3+}$) carried out at room temperature for the $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complex, were consistent with the existence of four unpaired electrons in the binuclear complex. This means that the energy of the d_{xy} orbitals of δ -symmetry and the pair of non-bonding d_{xz} and d_{yz} molecular

orbitals are indeed very close. For this reason, the several half-filled non-bonding orbitals will be considered as a single group.

Based on this localized MO approach, one would expect two strong absorption bands associated with the $[\text{VOV}]^{4+}$ chromophore, arising from the excitation of the (π_1, π_2) electrons to the non-bonding orbitals, and to the (π^*_3, π^*_4) orbitals. This simple model would explain the two absorption bands observed in the $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complex, at 625 and 525 nm, respectively, as well as the strong bands at 463 and 324 nm for the $[\text{V}_2\text{O}(\text{SCH}_2\text{CH}_2\text{NMe}_2)_4]$ complex.⁷ The bathochromic shift observed for the $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complex may be due to the presence of the bipy ligand, which has a strong field strength, stabilizing the metal d_π orbitals.

The assignment of the visible bands in the $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complex to charge-transfer transitions from the bipy or chloride orbitals to the metal d_π orbitals is another interesting point to be examined. Usually, the chloride(π)-V(d_π) charge transfer bands in vanadium(III) chloride complexes occur in the ultraviolet region, below 350 nm. Fowles and Greene²³ have reported that a yellow-brown solid of composition $[\text{VCl}_2(\text{bipy})_2]\text{Cl}$ is produced by reacting $\text{VCl}_3 \cdot 2\text{NMe}_3$ with bipy in excess, in benzene. The electronic spectrum of this product in the solid state exhibited three shoulders at 485, 434 and 410 nm, and a very weak band at 735 nm. We obtained a similar species by reacting VCl_3 with bipy in dimethylformamide (DMF) solution. However, when a small amount of water was added to the DMF solution, the yellow-brown colour changed rapidly to deep-violet, and the characteristic bands of $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$, at 525 and 625 nm appeared in the electronic spectra. It seems possible that the chloride ions in $[\text{V}_2\text{O}(\text{bipy})_2\text{Cl}_2]^{2+}$ undergo solvation, since a similar spectrum was obtained by reacting bipy with aqueous V(III) ions generated from the electrochemical reduction of $[\text{VO}(\text{H}_2\text{O})_4](\text{SO}_4)$. Therefore, one can conclude that the strong absorption bands in the visible region belong to the $[\text{V}^{\text{III}}-\text{O}-\text{V}^{\text{III}}]$ chromophore.

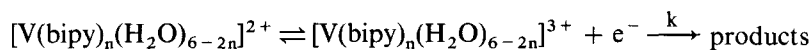
Typical Raman spectra of the $[\text{V}_2\text{O}(\text{bipy})_4\text{Cl}_2]^{2+}$ complex are illustrated in Figure 2. A substantial resonance Raman enhancement is observed for the vibrational peaks at 700, 460, 420 and 380 cm^{-1} , using an exciting wavelength of 647.1 nm. The corresponding excitation profiles can be seen in Figure 1B. These peaks are not present in the spectra of bipy complexes, and can be ascribed to the $[\text{V}-\text{O}-\text{V}]^{4+}$ chromophore. The vibrational peaks at 690 and 460 cm^{-1} seem to correspond to the V-O-V antisymmetric and symmetric vibrations, respectively, and the vibrational peaks at 420 and 380 cm^{-1} would be better assigned to V-O-V bonding modes. In contrast to the strong enhancement observed at 647 nm, only a weak resonance Raman effect occurs at 514 nm. According to current theories, this might be due to a great similarity of the potential energy coordinates of the ground state and those of the corresponding excited state.²⁴

The vibrational peaks of the *N*-heterocyclic ligands (Table I) are also slightly enhanced at 647.1 and 514.5 nm, becoming, however, extremely weak at 457.9 nm. Therefore, the low lying electronic levels cannot be exclusively ascribed to the V-O-V center, but should also involve some mixture of the vanadium(III) d_π orbitals and bipy p_π orbitals.

Spectroelectrochemical behaviour

In the presence of 7 to 70 mM of bipy, vanadium(II) ions (7 mM) form a mixture of 1:1, 1:2 and 1:3 successive complexes, which can be detected by cyclic voltammetry, as shown in Figure 3. The stepwise stability constants are $K_1 = 8.1 \times 10^4 \text{ M}^{-1}$,

$K_2 = 4.7 \times 10^4 \text{ M}^{-1}$ and $K_3 = 7.1 \times 10^3 \text{ M}^{-1}$, respectively.²⁵ The redox waves of the 1:1 complex are almost reversible, exhibiting anodic and cathodic peaks separated by 60–90 mV, with corresponding current ratios slightly lower than unity. The estimated $E_{1/2}$ is -0.15 V vs NHE, in comparison to -0.25 V for the $\text{V}(\text{H}_2\text{O})_6^{3+/2+}$ couple in aqueous solution. As the concentration of bipy increases, the waves around 0 V, corresponding to the $[\text{V}(\text{bipy})_2(\text{H}_2\text{O})_2]^{3+/2+}$ couple, grow in intensity as shown in Figure 3. The electrochemical behaviour of the 1:2 complex is much less reversible. The anodic and cathodic peak separation, and the current ratios increase as a function of the potential scan rates. The analysis of the data for the 1:1 and 1:2 complexes based on the formalisms proposed by Nicholson,²⁶ were consistent with a scheme involving a reversible monoelectronic electrochemical step followed by an irreversible chemical reaction²⁷ as shown below



The values of the kinetic constant k for the mono and disubstituted complexes were estimated as 7×10^{-2} and $1.2 \times 10^{-1} \text{ s}^{-1}$, respectively.

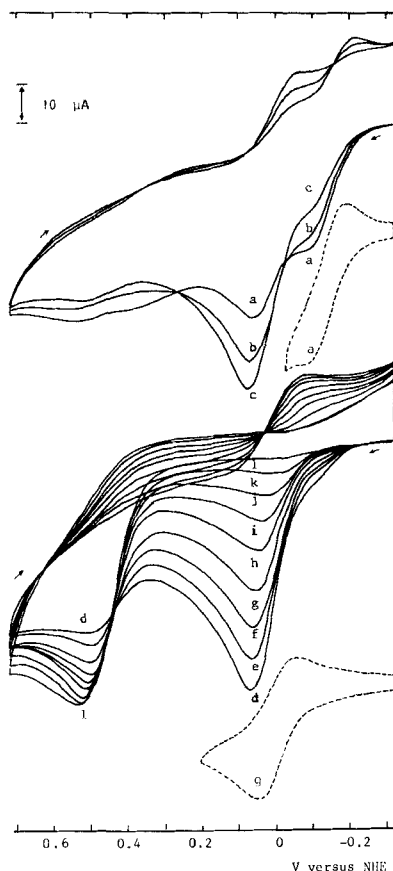


FIGURE 3 Cyclic voltammograms of vanadium(II) ions (7 mM) in the presence of bipy (a) 7, (b) 16, (c) 20, (d) 27, (e) 31, (f) 35, (g) 39, (h) 42, (i) 47, (j) 51, (k) 55, and (l) 59 mM, 25°C, lithium trifluoroacetate 0.1 M, gold working electrode, scan rate 100 mV s^{-1} . The waves corresponding to the 1:1, 1:2 (see dotted lines) and 1:3 complexes are located at -0.1 , 0.05 and 0.5 V versus NHE, respectively.

At bipy concentrations above 10^{-2} M, $[\text{V}(\text{bipy})_3]^{2+}$ is the major species in solution. The electrochemical behaviour of the $[\text{V}(\text{bipy})_3]^{2+}$ complex is irreversible, exhibiting only an anodic wave at 0.5 V, with no corresponding cathodic wave, as shown in Figure 3. In acetonitrile solutions however, the electrochemical behaviour of the tris-substituted complex has been reported to be almost reversible,² with anodic and cathodic peak potentials at 0.57 and 0.47 V vs ferrocene, and a corresponding current ratio of about 1.7.

According to Bennett and Taube,¹ the electron transfer reactions involving $[\text{V}(\text{bipy})_3]^{2+}$ yield vanadium(IV) products. The $[\text{V}(\text{bipy})_3]^{3+}$ intermediate formed after the first monoelectronic electron transfer step loses a bipy ligand very rapidly, forming V(III) species which undergo further electron transfer, leading to vanadium(IV) products. A similar mechanism, involving a monoelectronic electrochemical step followed by an irreversible chemical reaction and by a second monoelectronic electrochemical step, would explain the cyclic voltammograms of $[\text{V}(\text{bipy})_3]^{2+}$ observed in this work. In order to elucidate this point, we investigated the spectroelectrochemical behaviour of the vanadium(II) bipy complexes.

The electronic spectra of aqueous solutions containing vanadium(II) and bipy at molar ratios 1:1, 1:2 and 1:10 are shown in Figure 4A–C. In the first two cases, the spectra refer to a mixture of successive complexes where the 1:1 and 1:2 species are the major ones, respectively. In the last case, a high excess of ligand was employed to ensure the complete formation of the 1:3 complex.

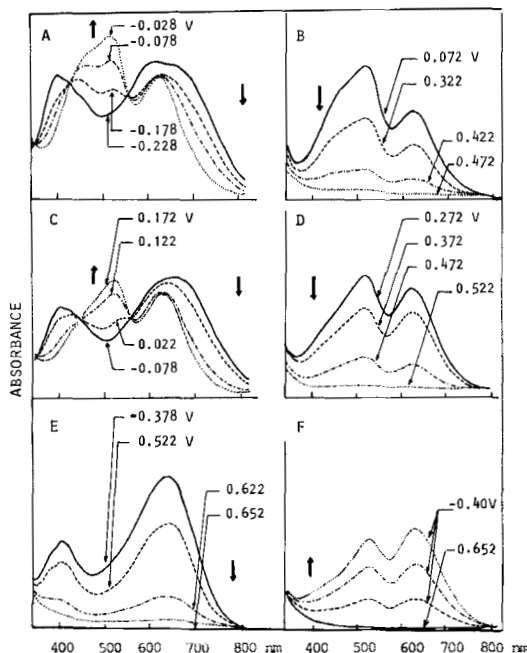


FIGURE 4 Spectroelectrochemistry of vanadium(II) ions (6 mM) in the presence of bipy (A) 5 mM, (C) 14 mM and (E) 60 mM, 25°C, lithium trifluoroacetate 0.1 M. The successive oxidation of the mononuclear $[\text{V}(\text{bipy})_n]^{2+}$ complexes ($n = 1, 2$) and of the corresponding binuclear V(III)–O–V(III) species are shown in (A, C) and (B, D), respectively. The oxidation of $[\text{V}(\text{bipy})_3]^{2+}$ leading to V(IV) species is illustrated in (E). Reduction of such species generating binuclear V(III)–O–V(III) products is shown in (F).

The electronic spectra of the 1:1 and 1:2 complexes remain practically unchanged at applied potentials more negative than -0.2 and -0.1 V, respectively. Above these values, the MLCT bands decay according to a non-Nernstian behaviour, in parallel with the rise of two new, strong absorption bands at 525 and 625 nm, with three simultaneous isosbestic points, as shown in Figure 4. The spectra of the oxidation products are similar to those previously reported for the binuclear $[V_2O(bipy)_4Cl_2]^{2+}$ species. The products can be further oxidized above 0.25 V, presumably to V(IV) species, leading to the decay of the strong visible absorption bands (Figure 4D–E).

In the case of the 1:3 complex, the spectroelectrochemical behaviour is completely different from that of the preceding cases as shown in Figure 4C. The oxidation of the tris-substituted complex starts above 0.4 V. The expected product was the $[V_2O(bipy)_4Cl_2]^{2+}$ ion, by analogy to the 1:1 and 1:2 complexes; however, at the applied potentials, this ion is completely oxidized to vanadium(IV) species. By reversing the potential to negative values, the binuclear V(III) complex can be detected spectroelectrochemically (Figure 4F).

According to these results, the chemical reaction succeeding the electron transfer step in the cyclic voltammograms corresponds to the formation of binuclear vanadium(III) products. In the case of the 1:3 complex, this process is preceded by the dissociation of a bipy ligand from the $[V(bipy)_3]^{3+}$ product. Our results confirm that the dissociation is complete within the time scale of the conventional techniques, and that the binuclear $[V_2O(bipy)_4]^{2+}$ product undergoes further electron transfer, leading to V(IV) species, with the involvement of two electrons, as proposed by Bennett and Taube.¹

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