

Article

Synthesis and Spectroscopic Behavior of Some Oxovanadium(IV) and Oxovanadium(V) Complexes of 7-Iodo-8-Hydroxyquinoline-5-Sulfonate

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O complexo de oxovanádio(IV) $[\text{VOL}_2].5\text{H}_2\text{O}$ (**1**) e os complexos de oxovanádio(V) $\text{K}[\text{VOL}_2\text{O}].4\text{H}_2\text{O}$ (**2**), $[\text{VOL}_2\text{OH}]$ (**3**) e $[\text{VOL}_2\text{OCH}_3]$ (**4**) (L = sal de potássio do ácido 7-iodo-8-hidroxiquinolina-5-sulfônico) foram preparados e caracterizados. Os espectros no infravermelho dos sólidos foram discutidos e comparados com os de outros compostos semelhantes. Os espectros eletrônicos, obtidos em diferentes solventes, também foram analisados. Medidas de Raman pré-ressonante dos dois primeiros compostos mencionados acima fortalecem algumas das atribuições espectroscópicas.

The oxovanadium (IV) complex $[\text{VOL}_2].5\text{H}_2\text{O}$ (**1**) and the oxovanadium(V) complexes $\text{K}[\text{VOL}_2\text{O}].4\text{H}_2\text{O}$ (**2**), $[\text{VOL}_2\text{OH}]$ (**3**) and $[\text{VOL}_2\text{OCH}_3]$ (**4**) (L = potassium salt of 7-iodo-8-hydroxyquinoline-5-sulfonic acid) were prepared and characterized. The IR spectra of the solids were recorded and discussed in comparison with those of other similar compounds. The electronic absorption spectra, in different solvents, were also analyzed. Pre-resonance Raman measurements, performed with the first two mentioned complexes, reinforce some of the spectroscopic assignments.

Keywords: oxovanadium(V), oxovanadium(IV), IR spectra, electronic spectra, pre-resonance Raman spectra.

Introduction

As part of a series of model studies related to vanadium biochemistry¹, we have recently investigated the structural, spectroscopic, magnetic, electrochemical and thermal behavior of a number of oxovanadium complexes with halogenated derivatives of 8-hydroxyquinoline (*oxine*) as ligands²⁻⁶, which normally produce complexes containing VN_2O_2 environments. Coordination spheres with nitrogen and oxygen donors are found, for example, in the active site of vanadium-depending haloperoxidases and in other natural systems¹. These studies have also been extended to other related ligands^{7,8} and in this paper we present results on the spectroscopic behavior of a series of oxovanadium(IV) and oxovanadium(V) complexes with 7-iodo-8-hydroxyquinoline-5-sulfonate as a ligand.

Among the *oxine* derivatives used as analytical reagents, the 5-sulfonic acids have an important hydrophilic character conferring to its metal complexes an unusually high water solubility⁹. On the other hand, the 7-substituted-8-hydroxyquinoline-5-sulfonic acids, developed also as analytical reagents, present a higher selectivity at the expense

of their sensitivity¹⁰. One of these reagents is the 7-iodo substituted acid, usually known as *ferron* (Figure 1), due to its excellent and almost specific capacity of coloration of the Fe(III) ion¹¹. It appears as an interesting ligand for our model studies, as it coordinates the vanadium *via* the nitrogen of the heterocycle and *via* the phenolic oxygen atom, keeping the sulfonate group uncoordinated. This is the general behavior of *oxine* (QH) and some of its derivatives, which were previously studied¹²⁻²⁰.

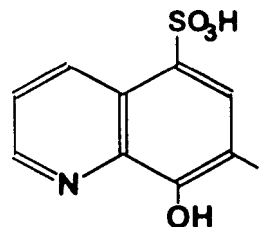


Figure 1. Structure of the 7-iodo-8-hydroxyquinoline-5-sulfonic acid (*ferron*).

Even though it is present as the potassium salt, containing the $-\text{SO}_3^-/\text{K}^+$ moiety, in the vanadium complexes described in this paper, we will maintain the nomenclature *ferron* for simplicity.

It is well known that a black, water insoluble, complex of stoichiometry $[Q_2VO(OH)]$ is generated by reaction of vanadium(V) with 8-hydroxyquinoline (QH)¹²⁻¹⁴, which according to a suggestion of Giacomelli *et al.* may be considered as an inorganic analog of a carboxylic acid^{3,15}. According to this proposal, species of the types $[Q_2VOO]^-$ and $[Q_2VO(OR)]$ can be considered as salts and esters, respectively. Concerning the vanadium(V)/ferron system, the *acid*, the *potassium salt* and the *methoxo complex* have been briefly described in the literature, but have been scarcely characterized¹⁶. These three compounds, together with a vanadium(IV) complex of stoichiometry $[VO(ferron)_2]$, were prepared and spectroscopically characterized in this study.

Experimental

Syntheses

$[VO(ferron)_2] \cdot 1.5H_2O$ (**1**). This complex was obtained adapting procedures described in the literature for the preparation of complexes with other derivatives of *oxine* as ligands^{2,17}. 2.00 g (5.7 mmol) of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Sigma) were dissolved in 50 cm³ of distilled water containing a few KOH platelets. To the resulting orange-red solution, 1.5 cm³ of a 50% $VOCl_2$ solution (Carlo Erba) were added dropwise, under continuous stirring. A green solid precipitates immediately. The mixture was held in digestion over a water bath during 3 h and finally the product was filtered by suction through a fritted glass funnel, washed several times with water and dried in vacuum over P_4O_{10} . The elemental analysis agrees with the proposed stoichiometry (Found: C, 23.05; H, 2.1; N, 2.97; S, 7.03; V, 5.5. Calc. for $C_{18}H_{18}O_{14}N_2S_2I_2K_2V$: C, 23.14; H, 1.94; N, 3.00; S, 6.87; V, 5.45%).

$K[VO(ferron)_2O] \cdot 4H_2O$ (**2**). This and the other oxovanadium (V) complexes were prepared following general procedures described in the literature¹⁶.

1.54 g (4.4 mmol) of the sulfonic acid and 0.20 g (1 mmol) of V_2O_5 (Merck) were dissolved in 5 cm³ of a KOH (2 mol dm⁻³) solution, keeping the system over a boiling water bath, until a brownish colored solution is obtained. After cooling to room temperature, and addition of 40 cm³ of acetone, a yellow suspension was immediately obtained. The solid was separated by centrifugation and washed twice with 10 cm³ of acetone. After rapid evaporation of the remnant acetone *in vacuum*, the product was dried in an oven at 105° C, turning to a brownish-yellow coloration. The composition was confirmed by the analytical results (Found: C, 21.98; H, 1.67; N, 2.85; S, 6.60; V 5.3. Calc. for $C_{18}H_{16}O_{14}N_2S_2I_2K_3V$: C, 22.25; H, 1.65; N, 2.88; S, 6.61; V, 5.25%).

$[VO(ferron)_2OH]$ (**3**). 0.15 g (0.15 mmol) of compound **2** were mixed with 2 cm³ of glacial acetic acid to form a paste to which 10 cm³ of acetone were immediately added. The obtained black suspension was centrifuged and the separated solid washed several times with acetone. The remnant acetone was eliminated *in vacuum* and the final drying was performed by warming the product during 30 min over a water bath. The composition was confirmed by chemical analysis (Found: C, 24.95; H, 1.12; N, 3.22; S, 7.40; V, 6.0. Calc. for $C_{18}H_9O_{10}N_2S_2I_2K_2V$: C, 25.11; H, 1.05; N, 3.25; S, 7.45; V, 5.92 %).

$[VO(ferron)_2OCH_3]$ (**4**). 0.15 g (0.17 mmol) of **3** were dissolved at room temperature, with stirring, in 12 cm³ of methanol. The undissolved solid was separated from the reddish solution by centrifugation. The methoxo complex was precipitated by addition of 30 cm³ of benzene to the solution, and separated by centrifugation. After several washings with benzene it was dried *in vacuum* and characterized by chemical analysis (Found: C, 26.00; H, 1.28; N, 3.24; S, 7.30; V, 5.9. Calc for $C_{19}H_{11}O_{10}N_2S_2I_2K_2V$: C, 26.08; H, 1.26; N, 3.20; S, 7.33; V, 5.82%). The potassium salt of the ligand, prepared for comparative purposes, was obtained by mixing hot aqueous solutions of the *acid* and KOH in a 1:1 molar ratio. The salt precipitated after cooling²².

Spectroscopic measurements

The infrared spectra were recorded with a Perkin Elmer 580 B spectrophotometer, using the KBr pellet technique. Raman spectra were obtained with a Jarrell-Ash 25-300 instrument equipped with a ITT-FW 130 photomultiplier. For the measurements, samples were dissolved in 1:1 DMF:H₂O solutions and excited with different Ar⁺ and Kr⁺ laser lines within the absorption ranges of the electronic spectra. The power ranged between 30 and 60 mW and the spectral width was 5 cm⁻¹. Excitation profiles were constructed with the relative line intensities, obtained by comparison of peak areas.

Electronic absorption spectra of the ligand and the complexes, in different solvents, were measured on a Hewlett-Packard 8452 A diode-array spectrophotometer, using 10 mm quartz cells.

Results and Discussion

Syntheses of the complexes

The oxovanadium(IV) complex, $[VO(ferron)_2] \cdot 1.5H_2O$ (**1**), could be obtained for the first time, using a similar procedure as that employed for the synthesis of VO^{2+} complexes with other *oxine* derivatives^{2,17}. The

oxovanadium(V) compounds $K[VO(\text{ferron})_2O] \cdot 4H_2O$ (**2**), $[VO(\text{ferron})_2OH]$ (**3**), and $[VO(\text{ferron})_2OCH_3]$ (**4**) were obtained adapting methods described in the literature¹⁶.

It is probable that in the case of compound **1**, one of the water molecules occupies the sixth coordination position around the metal, generating a monomeric hexacoordinated species, as suggested by its green coloration¹⁸.

Infrared spectra

The presence of a sulfonate group in the quinoline ring confers special characteristics to the ligand, introducing changes in spectroscopic and structural properties of the metallic complexes. A charge density redistribution through the ring, due to this negatively charged group, reinforces the ligand bonds counteracting, in some cases, the weakening effect generated after the coordination of the metal.

The positions of the most representative and characteristic bands of the investigated series of compounds are shown in Table 1. The proposed assignments are mainly based on comparisons with previously reported data for compounds of related ligands^{2,3,8,19,20}.

The band at 3484 cm^{-1} in the spectrum of the potassium salt of *ferron* can be assigned to the stretching mode of the phenolic OH-group, whereas those located at 1313 and 714 cm^{-1} are related to its "on plane" and "out of plane" deformational modes respectively. The absence of these three bands in all the investigated complexes confirms the

coordination of the metals *via* the oxygen atom of this deprotonated group, according with the general behavior of *oxine* and derived ligands.

The relatively strong bands found at 1050 and 1144 cm^{-1} in the free *ferron* molecule, assignable to the symmetric and antisymmetric stretching of the SO_3^- moiety²¹, are slightly displaced to somewhat higher frequencies in the V(IV) complex, but remain unaffected in the other species. As a consequence of the fact that the four donor atoms of the two ligands lie in the equatorial plane in the former compound, the effects on band positions are often different from those of the oxovanadium(V) complexes, in which these donors lie in different planes.

In the hydrated complexes, broad bands related to the water stretching modes appear around 3400 cm^{-1} , whereas the bending vibration is found at 1636 cm^{-1} . Also the rocking and wagging motions can be clearly seen at 790 and 640 cm^{-1} , respectively.

The apparent absence of the δ and wagging bands in the oxovanadium(IV) complex **1** can be explained by its overlap with the strong ligand bands found at 1624 and 633 cm^{-1} , respectively.

The displacement of the bands related to the $\nu_{C=N}$ vibrations, in complex **1**, also confirms the participation of the nitrogen atom of quinoline in bonding²². The shift in the oxovanadium(V) compounds is negligible, as a consequence of their different geometry, as mentioned above. The behavior of the $\nu_{C=C}$ vibrations is surely related to the presence of the sulfonate moiety, which probably

Table 1. Assignment of relevant IR bands of the potassium salt of the ligand and of the investigated *ferron* complexes.

Assignment	Wavenumber/ cm^{-1}				
	K-ferron	$[VO(\text{ferron})_2] \cdot 5H_2O$ (1)	$K[VO(\text{ferron})_2O] \cdot 4H_2O$ (2)	$[VO(\text{ferron})_2OH]$ (3)	$[VO(\text{ferron})_2OMe]$ (4)
$\nu[Ar]O-H$	3454 w,b				
	1652 w	1624 w	1655 w	1651 w	1645 w
$\nu_{C=N}$	1643 w	1617 w		1647 w	1636 w
		1576 w	1570 vw	1626 w	
$\nu_{C=C}$	1567 w	1563 m	1557 m	1576 w	1574 w
			1532 m	1558 m	1558 m
	1490 s	1490 vs	1487 vs	1574 sh	
ν_{ring}	1463 w	1456 s	1447 s	1487 vs	1488 m
	1398 m	1375 m	1368 m	1448 s	1448 s
	1367 m			1371 m	1370 s
δ_{OH} in plane	1313 w				
ν_{C-O}	1200 s	1119 m	1107 m	1109 m	1109 m
ν_{R-SO_3}	1144 s	1155 s	1143 m	1145 m	1145 m
	1050 s	1059 s	1057 s	1054 s	1056 sh
$\nu_{V=O}$		984 vs	908 s	965 m	950 m
			890 s		
δ_{V-OH}				919 m	
δ_{OH} out of pl.	713 s				
$\nu_a V-O$		546 w	547 w	544 w	544 w
ν_{C-S}	600 vs	600 s	612 s	613 s	613 s
$\nu_s \nu_a V-O$		480 m	463 m	471 m	473 m
ν_{V-N}		373 w	369 m	384 w	385 w
				373 w	374 w

counteracts the weakening effects of the coordination, by donation of electronic density to the ring.

The C-O bond suffers also reinforcement in the free *ferron*, compared to other related ligands¹⁹, due to the presence of the SO₃⁻ group. After complexation the ν_{C-O} band shifts from 1200 cm⁻¹ to lower frequencies.

Although a reinforcement of the V=O bonds may be expected with an increase in the oxidation state of vanadium, the inverse trend is observed in the present cases. This behavior can be explained on the basis of geometric factors, which favors a better charge delocalization from the vanadium over the ring π -system, and consequently the O_p π →V_d π interaction, reinforcing the VO bond, in the case of the VO²⁺ complex. A similar behavior can also be observed for the V-O(ligand) modes.

In the case of compound **2** a VO₂⁻ group is present, and the two bands found in this region (908 and 890 cm⁻¹) are assigned to the symmetric and antisymmetric stretching modes of this moiety, respectively²⁰.

Electronic spectra

As previously mentioned, the presence of the sulfonate group on the ligand ring allows the dissolution of the complexes in water. The positions of the absorption maxima of the spectra measured in this solvent are shown in Table 2. As in the complexes the potassium salt of *ferron* is present, we have measured its spectrum at pH = 4.5, a pH-value at which only the sulfonate group is deprotonated (pK₁ = 2.5; pK₂ = 7.4 at $\mu = 0$)²³. Notwithstanding, the spectrum obtained

was rather similar to that of pure *ferron*, dissolved in water. Therefore, in Table 2, we have presented directly the values obtained with the pure acid. The spectra were also measured in N,N'-dimethylformamide (DMF) solution. These data are also included in Table 2. The two sets of spectra are presented in Figure 2. In all cases, the estimated molar extinction coefficients were of the order of 10³ to 10⁴ dm³ mol⁻¹ cm⁻¹ and, consequently, highly diluted solutions were used for the measurements (approximately 10⁻⁵ mol dm⁻³).

Obviously, the spectrum of the methoxo complex **4** could not be measured in water, due to its strong hydrolytic tendency. It was recorded in methanol, together with that of pure *ferron*. The data obtained are shown in Table 2.

The assignment of these spectra has been attempted from the DMF data, due to its simplicity. The intra ligand bands, located at 268 and 316 nm in the free *ferron* molecule, do not experience important modifications after complexation. The ligand → metal charge transfer bands were assigned in comparison with the results obtained for the [VO₂Q₂]⁻ anion²⁰. The band with maxima at 384 nm and the “tail” near 500 nm for the VO²⁺ complex, and the bands at 340 and 386 nm, in the case of the vanadium (V) species, are assigned to these transitions. The band located at 650 nm in the spectra of the acid and the methyl ester can be attributed to a charge transfer from a delocalized ring π -orbital to the metal center²⁰. Besides, its origin could also be a consequence of the formation of adducts between the complexes and the solvent, which produces band displacements in the electronic spectra²⁴. The existence of such interactions is evident from the

Table 2. Electronic absorption spectra of *ferron* and its complexes in aqueous, DMF and methanol solutions (absorption maxima in nm)

A. Water					
Ferron	[VO(<i>ferron</i>) ₂].5H ₂ O (1)	K[VO(<i>ferron</i>) ₂ O](2)	[VO(<i>ferron</i>) ₂ OH](3)	[VO(<i>ferron</i>) ₂ OCH ₃](4)	
198	198	206	202		
230 sh	220 sh	224 sh	224 sh		
250	270	262	264		
286	316 sh	316 sh	316 sh		
328		332 sh	330 sh		
344	382	372	372		
438					
B. DMF					
268	274	272	274	270	
316	322 sh	328 sh	328 sh	324 sh	
		340	340	340	
	384	386	386	386	
	500(*)		650	650	
C. Methanol					
218				206	
252				252	
314				270 sh	
328 sh				322	
372				388	
				488	

sh: shoulder; (*) absorption “tail”

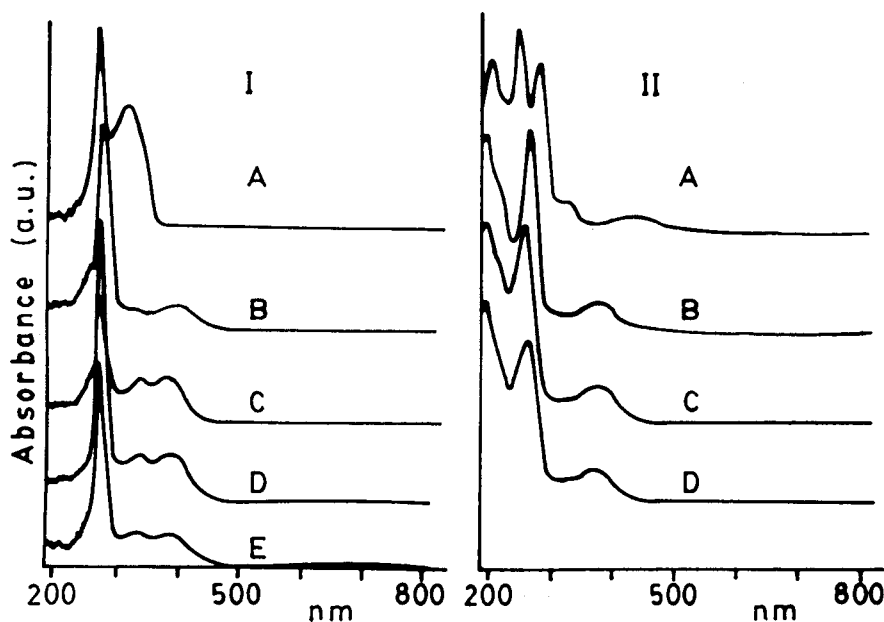


Figure 2. Electronic spectra of the free ligand and the vanadium complexes. I: in N-N-dimethylformamide (DMF); II: in aqueous solution. A: ferron; B: $[\text{VO}(\text{ferron})_2]$ (1); C: $\text{K}[\text{VO}(\text{ferron})_2\text{O}]$ (2); D: $[\text{VO}(\text{ferron})_2\text{OH}]$ (3); E: $[\text{VO}(\text{ferron})_2\text{OCH}_3]$ (4)

spectral behavior in the different investigated solvents.

In water, the shoulder found at 316 nm in all the complexes, together with the lower energy bands, can be ascribed to the ligand \rightarrow metal charge transfer, whereas for the methyl ester in CH_3OH solution these transitions are probably represented by the shoulder found at 270 nm and the band located at 488 nm.

As the substituents on the ring introduce important modifications on the MO energies of the ligand system it is not possible to make a direct comparison of our results with those of the $[\text{VO}_2\text{Q}_2]^-$ species²⁰. It is also impossible to assign with certainty which band corresponds to the $\text{N} \rightarrow \text{V}$ and which one corresponds to the $\text{O} \rightarrow \text{V}$ charge transfers. However, the pre-resonance Raman measurements, discussed in the next section, allows to assign the bands at longer wavelength to the $\text{N} \rightarrow \text{V}$ transition and that at higher energy to the $\text{O} \rightarrow \text{V}$ transition.

As a consequence of the extremely high extinction coefficients, due to the charge transfer processes, the bands related to d-d transitions in the VO^{2+} complex could not be visualized.

Pre-resonance Raman studies

To attain a wider insight into the spectroscopic behavior of these compounds, we have investigated the pre-resonance Raman spectra of salt 2 and of the oxovanadium(IV) complex 1. Measurements were performed in solution, using different excitation energies within the absorption range of the electronic spectra. For both complexes an intensity increase of some Raman lines

was observed when the wavelength of the excitation lines got closer to values of maxima in the electronic spectra.

The pre-resonance excitation profiles of some of the most affected vibrational modes of both complexes are depicted in Figure 3.

The analysis of these profiles shows that the $\text{C}=\text{C}$ and $\text{C}=\text{N}$ stretchings, located in the $1550\text{--}1590\text{ cm}^{-1}$ range, and the characteristic ring stretching line found at around 1370 cm^{-1} are the most affected modes. These results show that from the two electronic transitions assignable to metal-to-ligand charge transfers, the one at longer wavelength is originated from a transition that involves mainly the MO localized over the N atom of the ligand.

The enhancement experienced by the 1370 cm^{-1} band suggests that this mode is not a pure ring stretching vibration. It is surely coupled to some extent with V-ligand modes. This speculation is also in agreement with the shift to lower energies observed for this band after complexation, in the IR spectra of all the investigated complexes (see Table 1).

Enhancement of band intensities is less important for other modes, suggesting their participation in electronic transitions of higher energies. An interesting behavior is found for the two VO stretching vibrations in salt 2. The lower frequency band related to these stretchings (882 cm^{-1}) shows a clear pre-resonance effect (see Figure 3) and has always a higher intensity than the second one, located at 903 cm^{-1} , which does not experience any resonance enhancement. On the basis of this behavior these two bands can be assigned to the ν_s and ν_{as} modes of this moiety,

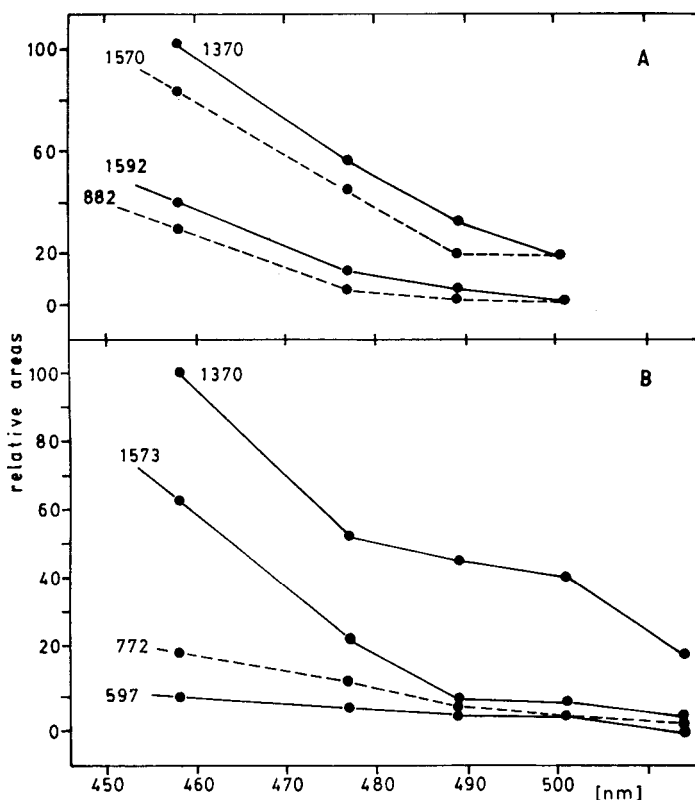


Figure 3. Pre-resonance-Raman excitation profiles of (A): $K[VO(ferroin)_2O]$ (2) and (B): $[VO(ferroin)_2]$ (1).

respectively. These results contrast with those found in the analogous $Na[VO(oxine)_2O]$ salt, for which $\nu_s > \nu_{as}$ ²⁰. These differences may be related to differences in the VO_2 angles, because the relative energies of these stretching modes are strongly dependent on this magnitude, as shown by the spectroscopic behavior of related systems²⁵⁻²⁹.

From the analysis of the excitation profiles, it was also possible to discriminate among the bending modes of the ligand, because those corresponding to in-plane vibrations show pre-resonance enhancement. Based on this criterion, bands located at 722 and 597 cm^{-1} in the oxovanadium(IV) complex 1 and at 843 and 728 cm^{-1} in the oxovanadium(V) salt 2 may be assigned to this type of bendings.

It is usually expected that bands corresponding to the symmetric stretching modes of the metal-ligand vibrations present important enhancement effects. Unfortunately, in the present case, this spectral region could not be explored due to the presence of solvent bands.

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