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A study on the electronic effect of *para* substituents in the aryloxy ring of the hydrazone ligands on the vanadium centre in a family of mixed-ligand [$V^VO(ONO)(OO)$] complexes

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Abstract

[$V^{IV}O(acac)_2$] reacts with the methanolic solutions of tridentate dibasic ONO donor hydrazone ligands derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone (H_2L^1) or its *para*-substituted derivatives ($H_2L^{2–4}$) (general abbreviation H_2L), in the presence of vanillin (Hvan) in equimolar ratio under aerobic conditions generating the mixed-ligand oxovanadium(V) complexes of the type [$V^VO(L)(van)$], *(1)–(4)* in good yield. All the complexes are diamagnetic and exhibit only ligand-to-metal charge transfer (l.m.c.t.) band near 510 nm in addition to intra-ligand ($\pi \rightarrow \pi^*$) transition band near 330 nm in CH_2Cl_2 solution. ^{1}H-n.m.r. spectra of the complexes in $CDCl_3$ solution indicate the presence of two isomeric forms [*(1A)*, *(1B)*; *(2A)*, *(2B)*; *(3A)*, *(3B)* and *(4A)*, *(4B)*] in different ratios, which is explained by the interchange of the two binding sites of van$^-$ motif between its coordinated equatorial and axial positions. Complexes display two quasi-reversible one electron reduction peaks near $+0.10$ V and near $+0.30$ V *versus* s.c.e. in CH_2Cl_2 solution which are attributed to the successive reduction of $V^V \rightarrow V^{IV}$ and the $V^{IV} \rightarrow V^{III}$ motifs, respectively. λ_{max} (for l.m.c.t. transition), and the two reduction potential values $(E_{1/2})^I$ (average of the first step anodic and first step cathodic peak potentials) and $(E_{1/2})^{II}$ (average of the second step anodic and second step cathodic peak potentials) of the complexes, are found to be linearly related to the Hammett constants (σ) of the substituents in the aryloxy ring of the hydrazone ligands. λ_{max}, $(E_{1/2})^I$ and $(E_{1/2})^{II}$ values show large dependence: $d\lambda_{max}/d\sigma = 37.29$ nm, $d(E_{1/2})^I/d\sigma = 0.21$ V and $d(E_{1/2})^{II}/d\sigma = 0.21$ V, respectively, on σ.

Introduction

In vanadium chemistry, two commonly occurring motifs, *viz.*, VO^{2+} and VO^{3+}, have attracted special attention after the discoveries of their involvements in many biochemical and physiological processes such as haloperoxidation [1–4], phosphorylation [5], vanadium nitrogenases [6], α-olefin polymerization [7–11], insulin mimicking [12–21], anticancer [22, 23], antitumour [24] and antifungal/antibacterial [25] activities. Due to hard acidic nature of these two motifs, they have strong affinity towards the hard basic O, N-donor ligands. Hydrazone ligands derived from both aliphatic and aromatic acid hydrazides with aromatic 2-hydroxycarbonyl compounds are important tridentate O, N-donor ligands containing two basic groups, viz., phenolic and amide groups and one neutral imine moiety. With a view to studying the electronic effect of *para* substituents in the aryloxy ring of the hydrazone ligands on the vanadium center in a family of mixed-ligand oxovanadium(V) complexes of the type [V^VO-(ONO)(OO)], we have used benzoyl hydrazones of 2-hydroxyacetophenone (H_2L^1) and its *para* substituted derivatives ($H_2L^{2–4}$) as tridentate dibasic ONO donor primary ligands and vanillin (Hvan) as a bidentate monobasic OO donor auxiliary ligand. In fact, such types of mixed-ligand complexes containing hydrazone ligands are very rare [26, 27].

Experimental

Materials

2-Hydroxyacetophenone, 2-hydroxy-5-methylacetophenone, 2-hydroxy-5-methoxyacetophenone and 5-chloro-2-hydroxyacetophenone were procured from Aldrich. Benzoyl hydrazine was purchased from E. Merck. Acetylacetone, vanadyl sulphate pentahydrate and vanillin were obtained from Loba Chemical Company (India). The procedure for the synthesis of $H_2L^{1–4}$ ligands and their characterization have already been described elsewhere [28]. [$V^{IV}O(acac)_2$] [29] was synthesized by the reported method. All other reagents were

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Table 1. Analytical and i.r. data of the complexes

Compound	Found (Calcd.) (%)			I.r.[a] (cm^{-1})				
	C	H	N	V=O	N–N	C–O(enolic)	C=N[b]	CHO
[VO(L^1)(van)], (1)	58.3(58.7)	3.7(4.0)	5.8(6.0)	988	1025	1269	1590	1686
[VO(L^2)(van)], (2)	59.2(59.5)	4.2(4.3)	5.7(5.8)	997	1024	1274	1584	1686
[VO(L^3)(van)], (3)	57.1(57.6)	3.9(4.2)	5.4(5.6)	994	1025	1276	1585	1684
[VO(L^4)(van)], (4)	54.4(54.7)	3.4(3.6)	5.5(5.6)	1000	1029	1276	1584	1690

[a] KBr discs; [b] This band may be associated with the aromatic C=C stretching band.

of A. R. grade and were obtained from commercial sources and used without further purification.

Preparation of the metal complexes

The complexes were prepared by the same general method. Details are given for one representative case.

[$V^VO(L^1)(van)$], (1)

To a warm methanolic solution (20 cm^3) of H_2L^1 (0.254 g, 1 mmol was added a methanolic solution (10 cm^3) of [$V^{IV}O(acac)_2$] (0.265 g, 1 mmol) with stirring whereby a brown solution was obtained. To this brown solution was added a methanolic solution (5 cm^3) of vanillin (0.152 g, 1 mmol) with continuous stirring at room temperature. Immediately the colour of the solution changed to reddish-violet. This mixture was then heated under reflux for 1 h and then kept for slow evaporation at room temperature. A black poppy-like product was obtained after 4 days, which was filtered, washed with methanol and dried over silica gel. Yield: 0.34 g (72%).

Physical measurements

Electronic spectra in CH_2Cl_2 were recorded on a Hitachi U-3501 spectrophotometer and i.r. spectra on a Perkin-Elmer 782 spectrophotometer. ^{1}H-n.m.r. spectra were recorded in $CDCl_3$ on a Brucker AM 300L (300 MHz) super conducting FT n.m.r. spectrophotometer. Electrochemical measurements were performed at 298 K in CH_2Cl_2 solution for *ca.* 1×10^{-3} mol dm^{-3} using Et_4NClO_4 as supporting electrolyte under a dry N_2 atmosphere on a PC controlled PAR model 273A electrochemistry system. A Pt disk, Pt wire auxiliary electrode and an aqueous saturated calomel electrode (s.c.e.) were used in a three-electrode configuration. All the potential values reported are uncorrected for junction contribution. The $E_{1/2}$ for the ferrocinium–ferrocene couple under the experimental conditions was 0.39 V. A Perkin-Elmer CHNS/O analyzer 2400 was employed to obtain the microanalytical data.

Results and discussion

Four hydrazone ligands (H_2L^{1-4}, I) derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone (H_2L^1) and its *para* substituted derivatives (H_2L^{2-4}) (general abbreviation H_2L; two H's representing the dissociable phenolic and amide protons) were used as primary ligands in the present study, while, the vanillin (Hvan) was used as coligand. These hydrazone ligands coordinate the vanadium through their deprotonated phenolate-O, deprotonated amide-O and the imine-N atoms in their enol forms (II) (Scheme 1), whereas, Hvan binds with the vanadium through its deprotonated phenolate-O and the methoxy-O atoms.

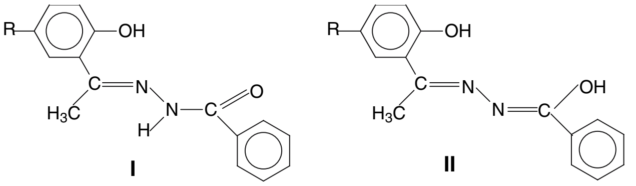
[$V^{IV}O(acac)_2$] reacts with H_2L and Hvan in equimolar ratios in methanol under aerobic conditions yielding the mixed-ligand oxovanadium(V) complexes of the type [$V^VO(L)(van)$], *(1)–(4)* in nearly 70% yield. Reactions can be represented as:

$$2[V^{IV}O(acac)_2] + 2H_2L + 2Hvan + 1/2O_2 \rightarrow [V^VO(L)(van)] + 4Hacac + H_2O \quad (1)$$

where Hacac is the acetylacetone and the oxidising agent is most probably the aerial oxygen associated with the lowering of the reduction potential at the vanadium center due to van$^-$ coordination (*vide infra*). Characteristic data are given in Table 1.

I.r. spectra of the complexes

Disappearance of the ligand characteristic bands in the 1646–1651, 2924–2989 and 3215–3240 cm^{-1} regions due to ν(C=O), ν(N–H) and ν(O–H) stretches respectively (I) in the i.r. spectra of their vanadium complexes indicate that C=O and N–H groups are transformed into their enolic forms (II) and their binding with the vanadium through deprotonation. A new band, appearing in the 1212–1245 cm^{-1} region, is assigned to the ν(C–O) (enolato) mode [28, 30, 31]. The ν(C=N) (azomethine)

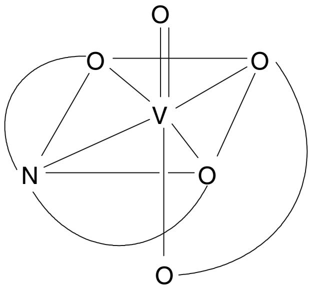


H_2L	R
H_2L^1	H
H_2L^2	CH_3
H_2L^3	OCH_3
H_2L^4	Cl

Scheme 1.

stretch of the ligands appearing in the 1603–1605 cm^{-1} region is shifted to lower wave number by 15–21 cm^{-1} in the complexes indicating the binding of azomethine nitrogen with the vanadium. The ligand band in the 902–932 cm^{-1} region due to ν(N–N) stretching undergoes a 93–127 cm^{-1} shift to a higher wave number on complexation due to diminished repulsion between the lone pairs of adjacent nitrogen atoms upon coordination [32]. The band appearing in the 1352–1360 cm^{-1} region for all the complexes has been assigned to ν(Ph–O) [33]. Complexes *(1)–(4)* exhibit a sharp band in the 988–1000 cm^{-1} region and a weak shoulder at *ca.* 910 cm^{-1}, which are attributed to ν(V=O) stretching indicating the presence of two isomeric forms in different proportions (also evident in their ^{1}H-n.m.r. spectra, *vide infra*). The strong band near 1685 cm^{-1} has been assigned to ν(C=O) of the uncoordinated aldehyde moiety of the coordinated van$^-$ ligand.

In spite of our best efforts, none of the four complexes reported here, afforded single crystals suitable for X-ray crystallographic study. However, the meridional disposition of $(L^4)^{2-}$ ligand has been characterized by X-ray crystallography [28]. Extending this behaviour to the present complexes, the most probable gross structure of the complexes *(1)–(4)* is as designated by structure (III).



III

^{1}H-n.m.r. spectra of the complexes (1)–(4)

^{1}H-n.m.r. spectral data suggest the binding nature of the ligands with the metal. We are considering the 300 MHz ^{1}H-n.m.r. spectra of the complexes separately recorded in CDCl$_3$ solvent. Signals are assigned (Tables 2–5) on the basis of intensity, spin–spin structure and chemical shift.

^{1}H-n.m.r. spectra of [VO(L^1)(van)], (1)

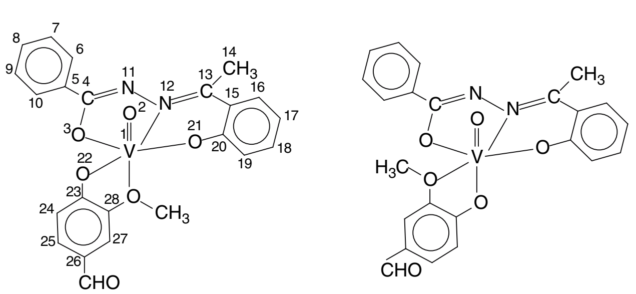
The ^{1}H-n.m.r. spectra of *(1)* in CDCl$_3$ solution indicate the presence of two isomeric compounds *(1A)* and *(1B)* in 3:2 ratio. The spectral data of *(1A)* and *(1B)* are collected in Table 2. The methyl protons H(14) appear as a singlet at δ3.06 p.p.m. for both the two isomers. The H(26-CHO) appears as a singlet at δ9.89 and δ9.83 p.p.m. for *(A)* and *(B)* isomers, respectively. Very small difference in the δ value for these two isomers indicates that they are not involved in bonding.

Table 2. ^{1}H-n.m.r. spectral data[a] of *(1A)* and *(1B)* in CDCl$_3$ at 298 K

Protons	δ/ p.p.m. (J/Hz) *(1A)*	*(1B)*
H(6,10)	7.93(d, 7.3)	
H(7,9,27)	7.29–7.38(m)	
H(8)	7.65(d, 8.1)	
H(14)	3.06(s)	
H(16)	7.43(dd, 7.8, 0.5)	
H(17)	7.13(dd, 7.8, 7.7)	
H(18)	7.47(dd, 7.7, 7.5)	
H(19)	7.04(d, 7.5)	
H(24)	7.08(d, 7.9)	
H(25)	7.61(dd, 7.9, 0.5)	
H(26-CHO)	9.89(s)	9.83(s)
H(28-OCH$_3$)	3.52(s)	3.98(s)

[a] The numbering system corresponds to that in (IV); e.g., H(6) represents the proton attached to C(6); s = singlet, d = doublet, dd = doublet of doublets, m = multiplet.

The methyl protons of H(28-OCH$_3$) appear as a singlet at δ3.52 and δ3.98 p.p.m., respectively for *(A)* and *(B)* isomers. Such a large difference in δ values for these two isomers indicates that the OCH$_3$ group is bonded with the vanadium and this group is more strongly bonded in *(B)* isomer than in *(A)* isomer. This is only possible if the OCH$_3$ group is placed in the axial position opposite to the vanadyl oxygen in the *(A)* isomer and in the equatorial position in the *(B)* isomer, as in the former, the OCH$_3$ group is weakly bonded with the vanadium due to the *trans* influence of the vanadyl oxygen. So, the gross structures (IV) for *(1A)* and *(1B)* appears to be correct. The aromatic protons H(6,10), H(8), H(19) and H(24) appear as a doublet at δ7.93, δ7.65, δ7.04 and δ7.08 p.p.m. respectively, while the aromatic protons H(16), H(17), H(18) and H(25) appear as doublet of doublets respectively at δ7.43, δ7.13, δ7.47 and δ 7.61 p.p.m. Other aromatic protons H(7,9,27) appear as a multiplet at *ca.* δ7.29–δ7.38 p.p.m.



1A (60%) **IV** **1B** (40%)

^{1}H-n.m.r. spectra of [VO(L^2)(van)], (2)

The presence of two isomeric compounds *(2A)* and *(2B)* was also detected by ^{1}H-n.m.r. spectroscopy and was found to be present in a nearly equimolar ratio in CDCl$_3$ solution. The spectral data of *(2A)* and *(2B)*

Table 3. ^{1}H-n.m.r. spectral data[a] of *(2A)* and *(2B)* in $CDCl_3$ at 298 K

Protons	δ/ p.p.m. (J/Hz)		
	(2A)		*(2B)*
H(6,10)		7.92(d, 7.5)	
H(7,9,27)		7.32–7.36(m)	
H(8)		7.65(d, 8.0)	
H(14)		3.04(s)	
H(16)		7.40(d, 0.5)	
H(17-CH_3)	2.26(s)		2.44(s)
H(18)		7.44(dd, 7.7, 0.5)	
H(19)		7.01(d, 7.7)	
H(24)		7.05(d, 8.3)	
H(25)		7.61(d, 8.3)	
H(26-CHO)	9.88(s)		9.83(s)
H(28-OCH_3)	3.50(s)		3.98(s)

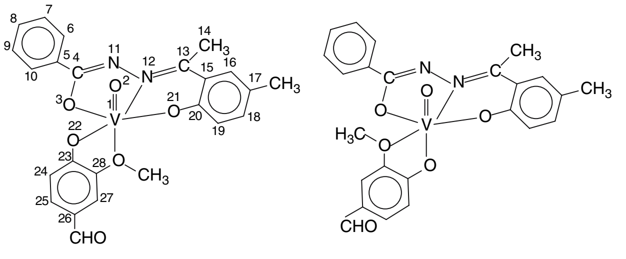
[a] The numbering system corresponds to that in (V).

Table 4. ^{1}H-n.m.r. spectral data[a] of *(3A)* and *(3B)* in $CDCl_3$ at 298 K

Protons	δ/p.p.m. (J/Hz)		
	(3A)		*(3B)*
H(6,10)		7.92(dd, 7.4, 0.5)	
H(7,9,27)		7.29–7.37(m)	
H(8)		7.65(d, 7.6)	
H(14)		3.03(s)	
H(16)		7.20(d, 1.0)	
H(17-OCH_3)		3.89(s)	
H(18)		7.43(dd, 9.0, 1.0)	
H(19)		7.05(d, 9.0)	
H(24)		7.12(d, 7.6)	
H(25)		7.60(dd, 7.6, 0.5)	
H(26-CHO)	9.87(s)		9.82(s)
H(28-OCH_3)	3.50(s)		3.96(s)

[a] The numbering system corresponds to that in (VI).

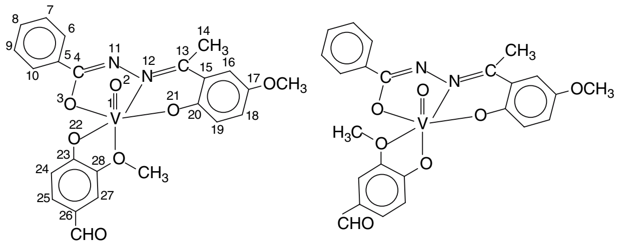
are collected in Table 3. The methyl protons H(14) appear as a singlet at δ3.04 p.p.m. for both the two isomers, while, the methyl protons H(17-CH_3) also appear as a singlet respectively at δ2.26 and δ2.44 p.p.m. for the isomers *(A)* and *(B)*. Like the complex *(1)*, the H(26-CHO) of this complex also appears as a singlet at δ9.88 and δ9.83 p.p.m. respectively for *(A)* and *(B)* isomers indicating their noninvolvement in metal ion coordination. The dissimilar binding nature of the OCH_3 group in the two isomers is evident from the large difference of the δ value corresponding to 28-OCH_3 protons as they appear as a singlet at δ3.50 and δ3.98 p.p.m., respectively for *(A)* and *(B)* isomers. This observation is in favour of their gross structures (**V**). The aromatic protons H(6,10), H(8), H(16), H(19), H(24) and H(25) appear as a doublet at δ7.92, δ7.65, δ7.40, δ7.01, δ7.05 and δ7.61 p.p.m. respectively, while H(18) appears as doublet of doublets at δ7.44 p.p.m. Other aromatic protons H(7,9,27) appear as a multiplet at *ca.* δ7.32–δ7.36 p.p.m.



2A (55%) **V** **2B** (45%)

^{1}*H-n.m.r. spectra of [VO(L*^{3}*)(van)], (3)*

As in the previous cases, the presence of two isomeric forms *(3A)* and *(3B)* was also observed for complex *(3)* and was found to be present in a 3:1 ratio in $CDCl_3$ solution. Spectral data for *(3A)* and *(3B)* are collected in Table 4 and the probable structures of the two isomers are shown in (VI). The methyl protons H(14) appear as a singlet at δ3.03 p.p.m. for both the two isomers. The singlet at δ3.89 p.p.m. was assigned to 17-OCH_3 protons, while the singlets at δ3.50 and δ3.96 were assigned to 28-OCH_3 protons for the isomers *(3A)* and *(3B)*, respectively. These observations indicate that 17-OCH_3 group is not involved in coordination, while, the 28-OCH_3 group is bonded with the vanadium atom but in different environment in the two isomers which is also in favour of their gross structures (VI). The signal corresponding to H(26-CHO) for the isomers *(3A)* and *(3B)* was observed respectively at δ9.87 and δ9.82 p.p.m. The aromatic protons H(8), H(16), H(19) and H(24) appear as a doublet at δ7.65,δ7.20, δ7.05 and δ7.12 p.p.m. respectively. The aromatic protons H(6,10), H(18) and H(25) appear as doublet of doublets respectively at δ7.92, δ7.43 and δ7.60 p.p.m., while the other aromatic protons H(7,9,27) appear as a multiplet at *ca.* δ7.29–δ7.37 p.p.m.



3A (75%) **VI** **3B** (25%)

^{1}*H-n.m.r. spectra of [VO(L*^{4}*)(van)], (4)*

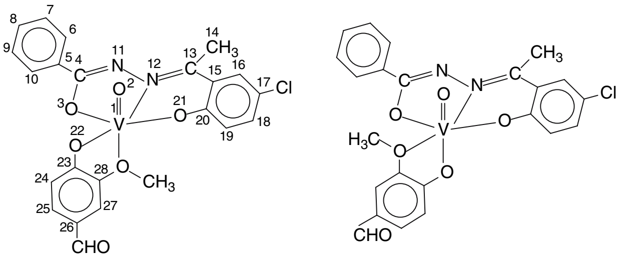
The ^{1}H-n.m.r. spectra of *(4)* also indicates the presence of two isomeric forms *(4A)* and *(4B)* in 4:1 ratio in $CDCl_3$ solution. Spectral data of these two isomers are collected in Table 5 and their probable structures are shown in (VII). The methyl protons H(14) appear as a singlet at δ3.02 p.p.m. for both the two isomers. The H(26-CHO) appears as a singlet at δ9.89 and δ9.83 p.p.m. for *(A)* and *(B)* isomers, respectively. Such a small difference in the δ value is an indication for their noninvolvement in coordination with vanadium. The

Table 5. ^{1}H-n.m.r. spectral data[a] of *(4A)* and *(4B)* in $CDCl_3$ at 298 K

Protons	δ/p.p.m. (J/Hz) *(4A)*		*(4B)*
H(6,10)		7.93(d, 7.3)	
H(7,9)		7.33–7.38(m)	
H(8,27)		7.60–7.65(m)	
H(14)		3.02(s)	
H(16)		7.84(d, 1.9)	
H(18)		7.45(dd, 7.3, 1.9)	
H(19)		7.05(d, 7.3)	
H(24)		7.12(d, 8.4)	
H(25)		7.51(dd, 8.4, 2.2)	
H(26-CHO)	9.89(s)		9.83(s)
H(28-OCH_3)	3.51(s)		3.97(s)

[a]The numbering system corresponds to that in (VII).

axial position of the OCH_3 group *trans* to the vanadyl oxygen in the *(A)* isomer, and one of the four equatorial positions in the *(B)* isomer, are evident from the large difference in its proton signal positions at δ3.51 and δ3.97 p.p.m., respectively. So, the gross structures (VII) for *(4A)* and *(4B)* appears to be reasonably correct. The aromatic protons H(6,10), H(16), H(19) and H(24) appear as a doublet at δ7.93, δ7.84, δ7.05 and δ7.12 p.p.m., respectively. The aromatic protons H(18) and H(25) appear as doublet of doublets respectively at δ7.45 and δ7.51 p.p.m., while the other aromatic protons H(7,9) and H(8,27) appear as multiplet at *ca.* δ7.33–δ7.38 p.p.m. and *ca.* δ7.60–δ7.65 p.p.m. respectively.



4A (80%) **VII** **4B** (20%)

Electronic spectra of the complexes

Complexes *(1)–(4)* are reddish-violet in CH_2Cl_2 solution and exhibit only intense transitions. The lowest energy transition at *ca.* 510 nm (Table 6), which is assigned to ligand to metal charge transfer (l.m.c.t.) transition of the type p $\rightarrow$ d (where p denotes the phenolic oxygen and d represents the metal d orbitals) [28, 30, 34]. Representative spectra are displayed in Figure 1. The intra-ligand ($\pi \rightarrow \pi^*$) transition was observed near 330 nm. A comparison of the spectral data indicates that the wavelength for the l.m.c.t. transition (λ_{max} value) increases with the increase of electron withdrawing property of the *para* substituent with respect to the phenolic OH group in the aryloxy ring of the hydrazone ligand in comparison to the unsubstituted species and the reverse is true if an electron donating group is present in the *para* position. This is to be quite expected from the ligands' basicity point of view, which is also reflected in their redox potential values (*vide infra*).

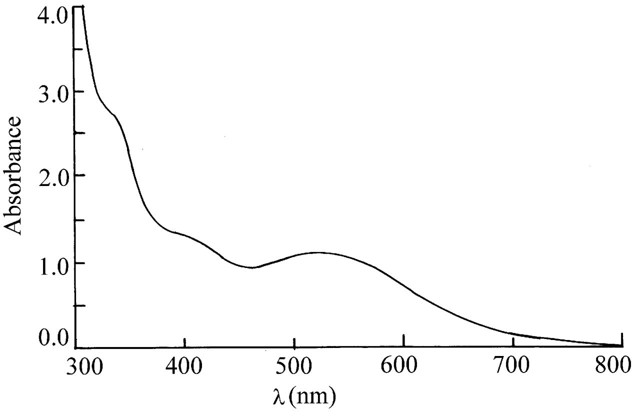


Fig. 1. Electronic spectra of [VO(L^4)(van)], *(4)* in CH_2Cl_2 solution, concentration = 1.703 × 10^{-4} mol. dm^{-3} at 298 K.

Electrochemistry of the complexes

Complexes *(1)–(4)* uniformly exhibit two one electron quasi-reversible reduction peaks in CH_2Cl_2 solution near +0.15 V and near +0.35 V *versus* saturated calomel electrode (s.c.e.), probably, due to successive reductions of the VO^{3+} motif i.e., VO^{3+}–VO^{2+} and VO^{2+}–VO^{+} couples respectively: Equations (2) and (3).

$$[V^{V}O(L)(van)] + e \rightarrow [V^{IV}O(L)(van)]^{-} \qquad (2)$$

$$[V^{IV}O(L)(van)]^{-} + e \rightarrow [V^{III}O(L)(van)]^{2-} \qquad (3)$$

$(E_{1/2})^{I}$ and $(E_{1/2})^{II}$ [where $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$ represent the averages of the cathodic and anodic peak potential

Table 6. Electronic spectral and electrochemical[a] data of the complexes *(1)–(4)* at 298 K

Compound	u. v.–vis[b] λ_{max} /nm(ε/dm^3 mol^{-1} cm^{-1})	$E_{1/2}$[b,c] (V) values $(E_{1/2})^{I}$(ΔE_p[d]/mV)	$(E_{1/2})^{II}$(ΔE_p/mV)
[VO(L^1)(van)], *(1)*	516(8736); 407(8359); 336(17,362)	0.17(100)	0.37(70)
[VO(L^2)(van)], *(2)*	510(6971); 424(5855); 332(12,605)	0.15(90)	0.34(80)
[VO(L^3)(van)], *(3)*	505(8441); 430(8222); 334(14,253)	0.11(90)	0.30(80)
[VO(L^4)(van)], *(4)*	524(6632); 403(7656); 330(16,327)	0.22(120)	0.41(60)

[a]At a Pt disc electrode; supporting electrolyte: Et_4NClO_4 (TEAP, ~ 0.1 M); scan rate 50 mV s^{-1}; refer electrode s.c.e.; solute concentration *ca.* 10^{-3} M; [b]in CH_2Cl_2; [c]$E_{1/2}$ is calculated as the average of anodic (E_p^a) and cathodic (E_p^c) peak potentials; [d]$\Delta E_p = E_p^a - E_p^c$.

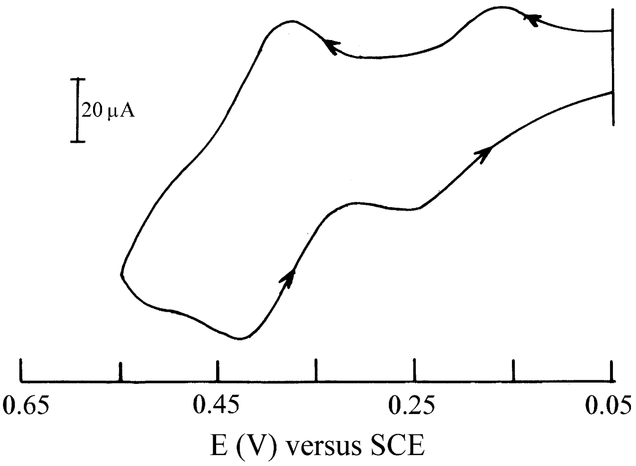


Fig. 2. Cyclic voltammogram of [VO(L^4)(van)], *(4)* in CH_2Cl_2 solution.

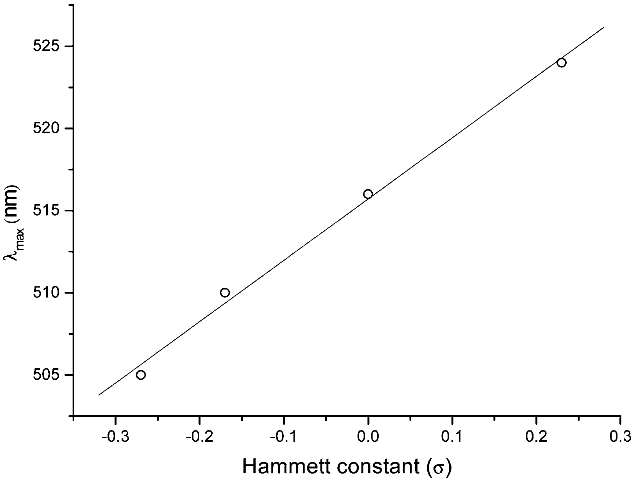


Fig. 3. A plot of λ_{max} (nm) *versus* Hammett constant (σ).

values for the first and second step reduction processes respectively] values are listed in Table 6 and representative spectra are displayed in Figure 2. An analysis of the $E_{1/2}$ values indicates that it increases with the decrease of basicity of the primary ligand due to the presence of an electron withdrawing group at the *para* position with respect to the phenolic OH group in the aryloxy ring of the hydrazone ligands [as in the case of complex *(4)*] and it decreases with the increase of basicity of the primary ligand due to the presence of an electron donating group at the *para* position [as in the case of complexes *(2)* and *(3)*].

Influence of ligand substituents on the electronic aspects of the complexes

With a view to studying the substituent effect in the *para* position with respect to the phenolic OH group in the aryloxy ring of the hydrazone ligands on the electronic property of vanadium, ligands containing three substituents of different Hammett parameter (σ) values [H ($\sigma = 0.00$), CH_3($\sigma = -0.17$), OCH_3($\sigma = -0.27$) and Cl ($\sigma = +0.23$)] have been used in this work. To find out the quantitative relation between *para* substituents and their effect on the vanadium nucleus, the λ_{max} values for the l.m.c.t. transition and the redox potential [$(E_{1/2})^{I}$ and $(E_{1/2})^{II}$] values are plotted against the value for the electronic influence of the substituents (σ) (Figures 3 and 4 respectively).

These two plots show linear relations and statistical analysis gives the following relations describing the dependence on σ:

$$\text{UV}-\text{vis}: \lambda_{max}(\text{nm}) = 515.71 + 37.29 \times \sigma \quad (4)$$

$$\text{CV}: (E_{1/2})^{I}(\text{V}) = 0.17 + 0.21 \times \sigma \quad (5)$$

$$(E_{1/2})^{II}(\text{V}) = 0.37 + 0.21 \times \sigma \quad (6)$$

Corresponding r values are 1.0, 0.98 and 0.98 respectively.

All these relations indicate the sensitivity of the vanadium electron density on the Hammett (σ) parameter of the R substituent. These three Equations (4), (5) and (6) also indicate that there should be direct relation between λ_{max} and $(E_{1/2})^{I}$ and also between λ_{max} and $(E_{1/2})^{II}$. Eliminating σ from the Equations (4) and (5) and also from the Equations (4) and (6), one can obtain the following equations (7) and (8) correlating λ_{max} with $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$, respectively:

$$\lambda_{max}(\text{nm}) = 485.52 + 177.57 \times (E_{1/2})^{I} \quad (7)$$

$$\lambda_{max}(\text{nm}) = 450.01 + 177.57 \times (E_{1/2})^{II} \quad (8)$$

Equations (7) and (8) indicate the identical dependence of λ_{max} on both $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$.

Conclusion

The main findings of the work are summarized here. The study indicates that in the presence of a bidentate mononegative unsymmetrical OO donor ligand like

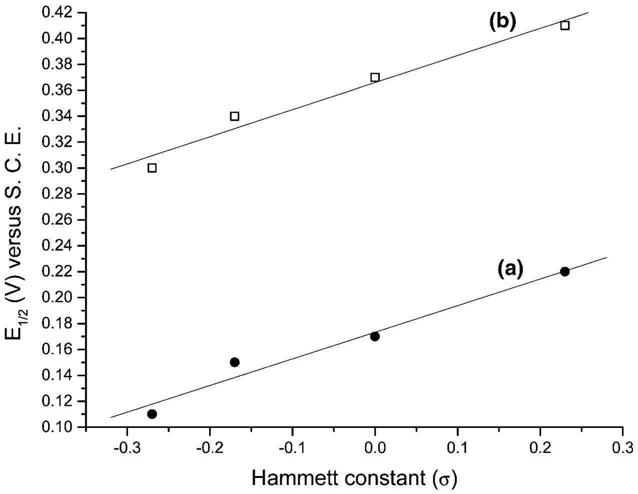


Fig. 4. A plot of (a) $(E_{1/2})^{I}$ (V) *versus* Hammett constant (σ) and (b) $(E_{1/2})^{II}$ (V) *versus* Hammett constant (σ).

vanillin, these tridentate dinegative ONO donor hydrazone ligands stabilize the VO^{3+} motif and in these complexes they are coordinated with vanadium meridionally in their fully deprotonated enolic forms. The i.r. spectra of the complexes in the solid state and their ^{1}H-n.m.r. spectra in $CDCl_3$ solutions indicate the presence of two isomeric forms [*i.e.*, *(A)* and *(B)*] in different ratios, which is explained by considering the interchange of the two donor sites of coordinated van^- motif between axial and equatorial positions. In complex *(4)*, the isomer *(4A)* is formed to a very significant extent in comparison to *(4B)* isomer while in the complexes *(1)* and *(2)* both these isomers [*i.e.*, *(A)* and *(B)*] are formed almost in equal proportions. This is probably due to the electron withdrawing property of the Cl atom, which decreases the basicity of the $(L^4)^{2-}$ motif and vanadium in its pentavalent state prefers more basic groups in the equatorial positions for its stabilization. This study also indicates that there are linear relations between the λ_{max}, $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$ values with the Hammett constant (σ) and these three parameters show large dependence on σ: $d\lambda_{max}/d\sigma = 37.29$ nm whereas, $d(E_{1/2})^{I}/d\sigma = 0.21$ V and $d(E_{1/2})^{II}/d\sigma = 0.21$ V, *i.e.*, both $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$ show similar dependence on σ. Equation (4) can be extensively used for the prediction of λ_{max} value and the Equations (5) and (6) for the prediction of $(E_{1/2})^{I}$ and $(E_{1/2})^{II}$ values for such type of mixed-ligand complexes provided the σ value of the respective substituent is known.

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