Oriental Journal of Chemistry Vol. **26**(3), 921-929 (2010)

Study of mixed-ligand hydrazonato-oxovanadium(V) complexes incorporating salicylaldehyde as co-ligand

NAUSHAD AHMAD

Department of Chemistry M.M.T.M., College, Darbhanga (India).

(Received: May 09, 2010; Accepted: June 23, 2010)

ABSTRACT

In the present paper $[V^{IV}O(acac)_2]$ reacts with an equimolar amount of tridentate dibasic ONO donor hydrazone ligand derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone (H_2L^1) or its para-substituted derivatives (H_2L^2) (general abbreviation H_2L), in the presence of excess amount of salicylaldehyde (Hsal) in methanol under aerobic conditions producing the mixed-ligand $[V^{V}O(L)(sal)]$, complexes (1)-(4) in good yields. The complexes are diamagnetic indicating the pentavalent state of vanadium and exhibit only LMCT transition band near 440 nm in addition to intra-ligand ($\pi \rightarrow \pi^*$) transition band near 330 nm in CH_2Cl_2 solution. IR spectra of these complexes in KBr disc and their ^1H NMR spectra in $CDCl_3$ solution indicate the presence of two isomeric forms for each of these complexes in different proportions. λ_{max} (for the LMCT transition) and redox potentials of these complexes are linearly related to the Hammett constants (σ) of the substituents in the aryloxy ring of the hydrazone ligands.

Key words: Mixed-ligand, Co-ligand & Hammett constants.

INTRODUCTION

The hard acidic nature of the two commonly occurring motifs of vanadium, viz. VO^{2+} and VO^{3+} is probably the main reason for their rich chemistry with O,N donor ligands. n this context, hydrazones derived from the condensation of aromatic 2- hyclroxycarbonyl compound with either aliphatic or aromatic acid hydrazide are important ligands for providing suitable coordination environment around the vanadium center and depending upon their basicity they stabilize selectively one of these two motifs. As a part of our studies on the hydrazone chemistry of vanadium[1-8], we report here the mixedligand oxovanadium(V) complexes incorporating tridentate dibasic ONO donor hydrazone ligands derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone (H_2L^1) and their parasubstituted derivatives (H_2L^{2-4}) (general abbreviation H_2L) (Scheme 1) as primary ligands and salicylaldehyde (Hsal), a bidentate monobasic OO donor species as co-ligand. The investigations were aimed at: (i) examining which of these two motifs be stabilized by this family of hydrazone ligands in the presence of a bidentate monobasic OO donor ligand, viz. salicylaldehyde; (ii) studying the electronic effect of para substituents in the aryloxy ring of these hydrazone ligands on the electronic properties of vanadium in its mixed-ligand complexes containing salicylaldehyde as co-ligand; and, (iii) to enrich the chemistry of mixed-ligand oxovanadium complexes incorporating hydrazone ligands. There are very few examples of such types of mixed-ligand hydrazone complexes in the literature[1-3,6-16] and particularly with salicylaldehyde as auxiliary ligand are very rare[1,3]. This study is important in connection with the various biochemical and physiological activities exhibited by such type of oxovanadium(IV/V) complexes such as haloperoxidation[17-20], phosphorylation[21], vanadium nitrogenases[22], a-olefin polymerization[23-27], insulin

mimicking[28-37], anticancer[38-39], antitumour[40] and antifungal/antibacterial[41] activities.

MATERIAL AND METHODS

2-Hydroxyacetophenone, 2-hydroxy-5-methylaceto-phenone, 2-hyclroxy-5-methoxyacetophenone and 5- chloro-2-hydroxyacetophenone were procured from Aldrich. Benzoyl hydrazine was purchased from E. Merck. Acetylacetone, vanadyl sulphate pentahydrate and salicylaldehyde were obtained from Loba Chemical Company (India). The procedures for the synthesis of H_2L^{1-4} ligands and their characterisation have been described elsewhere[6]. $[V^{IV}O(acac)_2]$[42] was synthesized by the reported method. All other reagents were of A.R. grade, obtained from commercial sources and used without further purification.

Electronic spectra (in CH_2C_{12}) were recorded on a Hitachi U-3501 spectrophotometer, JR spectra on a Perkin-Elmer 782 spectrophotometer and ^1H NMR spectra were recorded in $CDC1_3$ solution on a Brucker AM 300L (300 MHz) super conducting FT NMR spectrophotometer. Electrochemical measurements were performed at 298 K in CH_2C1_2 solution for ca. 1×10^{-3} mol dm^{-3} using Et_4NClO_4 as supporting electrolyte under a dry N2 atmosphere on a PC controlled PAR model 273A electrochemistry system. A Pt disk, Pt wire auxiliary electrode and an aqueous saturated calomel electrode (SCE) were used in a three-electrode configuration. All the potential values reported here are uncorrected for junction contribution. The $E_{½}$ for the ferrocinium-ferrocene couple under the experimental conditions was 0.39 V. Perkin-Elmer CHNS/O analyzer 2400 was used to obtain microanalytical (C, H, N) data. Mass spectral analysis was performed on Qtof Micro YA263 instrument.

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

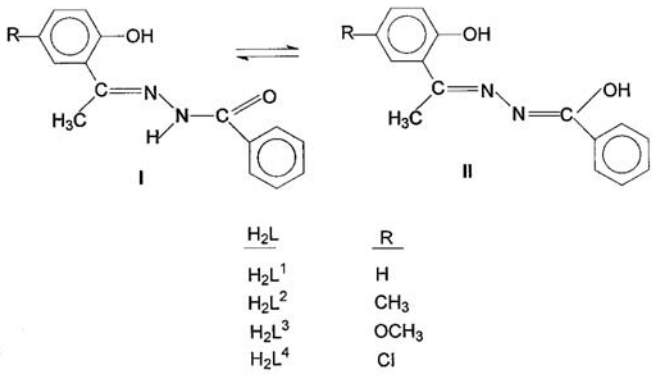
{2-[1(1_hydroxybenzylidenehydrazono] ethylphenolato(2-)}lsalicylaldehydato(1-)] oxovanadium(V), $IV^{V}O(L^1)$(sal)l

To a warm methanolic solution (20 cm^3) of H_2L^1 (0.254 g, 1 mmol) and about 0.5 cm^3 of salicylaldehyde was added a methanolic solution (10 cm^3) of $[V^{IV}O(acac)_2]$ (0.265 g, 1 mmol) with stirring whereby a reddish-brown solution was obtained. This mixture was then heated under reflux for 1 h and the resulting deep red solution was then allowed to evaporate slowly at room temperature. A black product was obtained after 4 days, which was filtered, washed with methanol and dried over silica gel. Yield: 0.29 g (66%). Mass: m/z 463 (M+Na).

Complexes 2-4 were synthesized following similar procedure in 62-70% yield.

RESULTS AND DISCUSSION

When a methanol solution of $[V^{IV}O(acac)_2]$ was added to an equimolar methanol solution of H_2L in presence of excess amount of salicylaldehyde, the pentavalent mixed-ligand complexes $[V^{V}O(L)(sal)]$, 1-4 were obtained in nearly 70% yield. Reactions can be represented as:



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

Fig. 1:

$2[V^{IV}O(acac)_2] + 2H_2L + 2Hsal + ½O_2 \rightarrow 2[V^{V}O(L)(sal)] + 4Hacac + H_2O$ ...(1)

where Hacac is the acetylacetone and the oxidising agent is most probably the aerial oxygen assisted by the lowering of the reduction potential at the vanadium center due to sal coordination (vide infra). These complexes have good solubility in common organic solvents. Elemental analysis and selected IR spectral data are presented in Table 1.

Table 1: Analytical and IR spectral data of the complexes

Compound	Found (Calc.) (%)				IR[a] (Cm^{-1})			
	C	H	N	V=O	N-N	C-O (enolic)	C=N[b]	CHO
$[VO(L^1)(sal)]$,1	59.8(60.0)	3.8(3.9)	6.3(6.4)	976(m),908(w)	1025	1282	1596	1656
$[VO(L^2)(sal)]$,2	60.6(60.8)	4.1(4.2)	6.1(6.2)	974(m),907(w)	1029	1287	1589	1655
$[VO(L^3)(sal)]$,3	58.6(58.7)	4.0(4.0)	5.9(6.0)	972(m),901(w)	1028	1277	1597	1653
$[VO(L^4)(sal)]$,4	55.6(55.6)	3.3(3.4)	5.9(5.9)	978(m),907(w)	1030	1281	1588	1652

[a]Kbr discs; [b]this band may be associated with the aromatic C=C stretching band; m= medium; w=weak;s=strong

Table 2: ^1H NMR spectral date[a] of complexes 1-4 in $CDCl_3$ at 298 K

Complex	Isomar	H (14)	H (17-CH_3)	H (17-OCH_3)	H (28-CHO)	Aromatic hydrogen
1	A	3.04(s)	-	-	9.46(s)	6.99-7.95(13H)
1	B	3.02(s)	-	-	9.91(s)	6.99-7.95(13H)
2	A	3.00(s)	2.25(s)	-	9.44(s)	6.92-7.89(12H)
2	B	3.00(s)	2.25(s)	-	9.89(s)	6.92-7.89(12H)
3	A	3.03(s)	-	3.80(s)	9.46(s)	6.90-7.65(12H)
3	B	3.00(s)	-	3.91(s)	9.91(s)	6.90-7.65(12H)
4	A	2.98(s)	-	-	9.45(s)	6.98-7.89(12H)
4	B	3.02(s)	-	-	9.90(s)	6.98-7.89(12H)

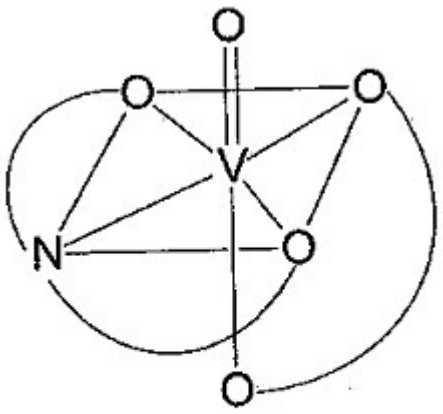
Table 3: Electronic spectral and electrochemical[a] data of the complexes 1-4 at 298 K

Compound	UV - vis[b] λmax / nm (ε/dm^3 mol^{-1} cm^{-1})	$E½^{b,c}$ (V)$(E½)^I$ (ΔE_p[d]/mV)	$(E½)^{II}$ (ΔE_p/mV)
$[VO(L^1)(sal)]$,1	438(3751); 326(11,226)	0.09(70)	0.36(70)
$[VO(L^2)(sal)]$,2	430(6600); 330(16870)	0.06(60)	0.33(80)
$[VO(L^3)(sal)]$,3	425(6722); 340(12,404)	0.03(70)	0.29(80)
$[VO(L^4)(sal)]$,4	452(14,209); 330(25,585)	0.13(80)	0.40(80)

[a]At a Pt disc electrode; supporting electrolyte; Et_4NClO_4 (TEAP, ~ 0.1M); scan rate 50 mV sec^{-1}; reference electrode SEC; solute concentration ca. 10^{-3} M; [b]in CH_2Cl_2; [c]$E_{½}$ is calculated as the average of anodic (E_p^a) and cathodic (E_p^a) peak potentials, [d]$\Delta E_p = E_p^a - E_p^C$

IR spectra and probable gross structure of the complexes

The ligand characteristic bands in the 1646-1651, 2924-2989 and 32 15-3240 cm^{-1} regions due to v(C=O), v(N-H) and v(O-H) stretches respectively (I), disappear in the IR spectra of their vanadium complexes 1-4 indicating the transformation of C=O and N-H groups into their enolic forms (II) followed by their binding with the vanadium through deprotonation. The formation of enolic moiety is further confirmed from the appearance of a new band in the 1277-1287 cm^{-1} region, which is assigned to the v(C-O) (enolate) mode[2,6,15,16]. The v(C=N) (azomethine) stretch of the ligands appearing in the 1603-1605 cm^{-1} region is shifted to lower wave number by 8-15 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 v(N-N) stretching undergoes a 93-128 cm^{-1} shift to a higher wave number on complexation due to diminished repulsion between the lone pairs of adjacent



III

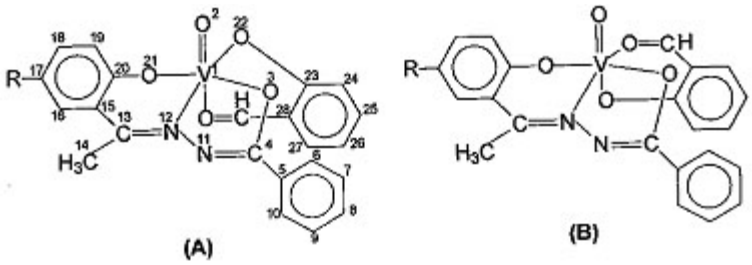
nitrogen atoms upon coordination[6,7,17,15]. The band appearing in the 1351-1361 cm^{-1} region for all the complexes has been assigned to v(Ph-O)[6,7,43]. Complexes 1-4 exhibit a sharp medium to strong intensity band in the 972-978 cm^{-1} region and a sharp weak to medium intensity band in the 901-908 cm^{-1} region, attributed to v(V=O) stretching indicating the presence of two isomeric forms in different proportions (also evident in their ^{1}H NMR spectra, vide infra). As the v(VO) stretching is greatly influenced by the basicity of the coordinating atom trans to the vanadyl oxygen, the formation of the two isomers probably arises from the interchange of the coordinating atoms (viz., phenolic-O and carbonyl-O atoms) of sal^- moiety between the axial and the equatorial positions. The sharp medium intensity band in the 1652-1656 cm^{-1} region has been assigned to v(C=O) of the coordinated aldehyde moiety of the bonded sal^- ligand[1,3] which is significantly lower (by~30 cm^{-1}) than the corresponding vanillin complexes[7] where the CHO group remained uncoordinated.

Two isomers of each of these complexes could not be separated chromatographically due to their almost identical R_f values. Moreover, there is no significant change in the ratio of the two isomers even if the heating time (during their synthesis) is increased to 3 h instead of 1 h (vide supra) in the attempts for almost full conversion of one of the two isomers selectively. In spite of our best efforts, none of the four complexes reported here, afforded single crystals suitable for X-ray crystallographic study. However, we have already established the meridional disposition of $(L^2)^{2-}$ ligand in $[V_2O_3(L^2)_2]$ complex[44] and also of $(L^4)^{2-}$ ligand in $[V^VO(L^4)(hq)]$ complex[6] [where hq^- is the deprotonated form of 8-hydroxyquinoline(Hhq)] by X-ray crystallography. Extending this behaviour to the present complexes, the most probable gross structure of the complexes 1-4 will be as designated by structure (111).

^{1}H NMR spectra of the complexes

The ^{1}H NMR spectra of 1 in $CDCl_3$ solution indicate the presence of two isomeric compounds 1 A and lB in ~ 4:1 ratio. The spectral data of 1A and lB are collected in Table 2. The methyl protons H(14) appear as a singlet at δ3.04 and δ3.02 ppm respectively for the two isomers. The H(28-CHO) appears as a singlet at δ9,46 and δ9.91 ppm for (A) and (B) isomers, respectively. Such a large difference in 6 values for these two isomers indicates that the CHO group is bonded with the vanadium and is more strongly bonded in the (B) isomer than in the (A) isomer. This is only possible if the CHO group exists in the axial position opposite to the vanadyl oxygen in the (A) isomer and in one of the four equatorial positions in the (B) isomer, as in the

former, the CHO 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 appear to be correct. The aromatic protons H(6, 10) and H(25) appear as doublet of doublets at δ7.95 and δ7.36 ppm, respectively while the aromatic proton H(8) appears as doublet at δ7.65 ppm. Other aromatic protons H(7,9,l7,26), H(16,18,27) and 11(19,24) appear as a multiplet at Ca. δ7.11 - δ7.29 ppm, Ca. δ7.42 - δ7.58 ppm and ca. δ6.99-δ7.07 ppm, respectively.



(A) (B)

R	Complex
H	1
CH_3	2
OCH_3	3
Cl	4

IV

The presence of two isomeric compounds 2A and 2B was also detected by 1H NMR spectroscopy and was found to be present in a nearly equimolar ratio in CDCI3 solution. The spectral data of 2A and 2B are collected in Table 2. The methyl protons H(14) and H(17-CH_3) appear as a singlet respectively at δ3.00 ppm and δ2.25 ppm for both the two isomers. Like the complex 1, the H(28-CHO) of this complex also appears as a singlet at δ9.44 and δ9.89 ppm, respectively for (A) and (B) isomers indicating its dissimilar binding nature in these two isomers. This observation is in favour of their gross structures (1V).

The aromatic protons H(6,10) appear as a doublet of doublets at δ7.89 ppm, while H(16) appears as a doublet at δ7.65 ppm. Other aromatic protons H(7,9,25,26), H(8,18,27) and H(19,24) appear as a multiplet at Ca. δ7.18- δ7.41 ppm, δ7.51- δ7.57 ppm and δ6.92- δ7.07 ppm, respectively.

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 nearly 4:1 ratio in $CDCl_3$ solution. Spectral data for 3A and 3B are collected in Table 2 and their probable gross structures are shown in (IV). The methyl protons H(14) appear as a singlet at δ3.03 ppm and δ3.00 ppm, respectively for the two isomers. The singlet at δ3.80 ppm and δ3.91 ppm, respectively for the two isomers was assigned to 17-OCH_3 protons. The dissimilar binding nature of the 28-CHO group in the two isomers is indicated from its signal position appearing respectively at δ9.46 ppm and δ9.91 ppm which is in favour of their gross structures (IV). The aromatic protons H(6, 10), H(7,9), H(16) and H(26) appear as a doublet at δ7.65, δ7.08, δ7.32 and δ7.20 ppm respectively, while the aromatic proton H(18) appear as a doublet of doublets at d7.30 ppm. The other aromatic protons H(8,25,27) and H(19,24) appear as multiplet at Ca. δ7.42- δ7.60 ppm and Ca. δ6.90- δ7.05 ppm, respectively.

The ^{1}H NMR spectra of 4 also indicate the presence of two isomeric forms 4A and 4B in nearly 2:1 ratio in $CDCl_3$ solution. The methyl protons H(14) appear as a singlet for the two isomers respectively at δ2.98 ppm and δ3.02 ppm (Table 2). The axial position of the CHO 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 δ9.45 and δ9.90 ppm, respectively. So, the gross structures (IV) for 4A and 4B appear to be reasonably correct. The aromatic protons H(6,10), H(8), H(16), H(19), H(26) and H(27) appear as a doublet at δ7.89, δ7.64, δ7.81, d6.98, δ7.19 and δ7.69 ppm, respectively. The aromatic protons H(18) and H(25) appear as doublet of doublets respectively at δ7.41 and δ7.46 ppm, while the other aromatic protons H(7,9) and H(24) appear as multiplet at ca. δ7.30- δ7.35 ppm and Ca. δ7.07-δ7.12 ppm, respectively.

Electronic spectra of the complexes

Complexes 1-4 are orange-red in CH_2Cl_2 solution and exhibit only intense transitions. The lowest energy transition at ca. 440 nm (Table 3) is assigned to ligand to metal charge transfer (LMCT) transition of the type p→d (where p denotes the phenolic oxygen p orbital and d represents the metal d orbitals)[1-3,6,7] and these λ_{max} values are lower than the corresponding vanillin(Hvan) complexes[7] indicating the higher basicity of the sal^- motif over van^- motif. The intra-ligand ($\pi \rightarrow \pi^*$) transition was observed near 330 nm. A comparison of the spectral data indicates that the λ_{max} for the LMCT transition 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 at the para position. This is quite expected from the ligands' basicity point of view and such a trend is also reflected in their redox potential values (vide infra).

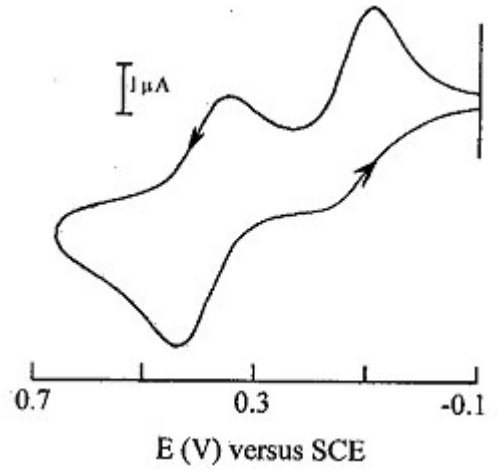


Fig. 1: Cyclic voltammogram of $[VO(L^4)(sal)]$, 4 in CH_2Cl_2 solution

Electrochemistry of the complexes

All these four complexes uniformly exhibit two one-electron quasi-reversible reduction peaks in CH_2Cl_2 solution near +0.10V and near +0.35V versus saturated calomel electrode (SCE), probably, due to successive reductions of the VO^{3+} motif, i.e. VO^{3+}-VO^{2+} and VO^{2+}-VO^{+} couples, respectively:

$$[V^{V}O(L)(sal)] + e \rightarrow [V^{IV}"O(L)(sal)]^- \quad ...(2)$$

$$[V^{IV}O(L)(sal)]^- + e \rightarrow [V^{III}"O(L)(sal)]^{2-} \quad ...(3)$$

$(E_{½})^{I}$ and $(E_{½})^{II}$ [where $(E_{½})^{I}$ and $(E_{½})^{II}$ represent the averages of the cathodic and anodic peak potential values for the first and second step reduction processes respectively] values are listed in Table 3 and representative spectra are displayed in Fig. 1. An analysis of the $E_{½}$ 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) compared to the unsubstituted species and all these values are relatively lower than the respective van^- complexes[7] indicating again the higher basic nature of the sal^- motif over van^- motif.

Influence of ligand substituents on the electronic aspects of the complexes

To study 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, four hydrazone ligands containing different substituents having different Hamrnett parameter[45] (σ) values [H (σ = 0.00), CH_3 (σ = -0.17), OCH_3 (σ -0.27) and Cl (σ = +0.23)] have been used in this work. For establishing the quantitative relation between the para substituents and their electronic effect on the vanadium nucleus, the λ_{max} values for the LMCT transition and the redox potential [$(E½)^{I}$ and $(E½)^{II}$]

values of these complexes are plotted against the value for the electronic influence of the substituents (s) (Fig. 2 and Fig. 3, respectively).

These two plots (Figs 2 and 3) show linear relations and statistical analysis gives the following relations describing the dependence on σ:

$$\text{UV-vis: } \lambda_{max}\ (nm) = 439.07 + 53.75\times\sigma \quad ...(4)$$

$$\text{CV:}(E½)^{I}(V) = 0.09 + 0.19\times\sigma \quad ...(5)$$

$$(E½)^{II}\ (V) = 0.36 + 0.21\times\sigma \quad ...(6)$$

Corresponding r values are 1.0, 0.99 and 0.98, respectively. The estimated error in $d\lambda_{max}/d\sigma$ $\delta(E½)^{I}/d\sigma$ and $d(E½)^{II}/d\sigma$ is 2.41, 0.015 and 0.027,

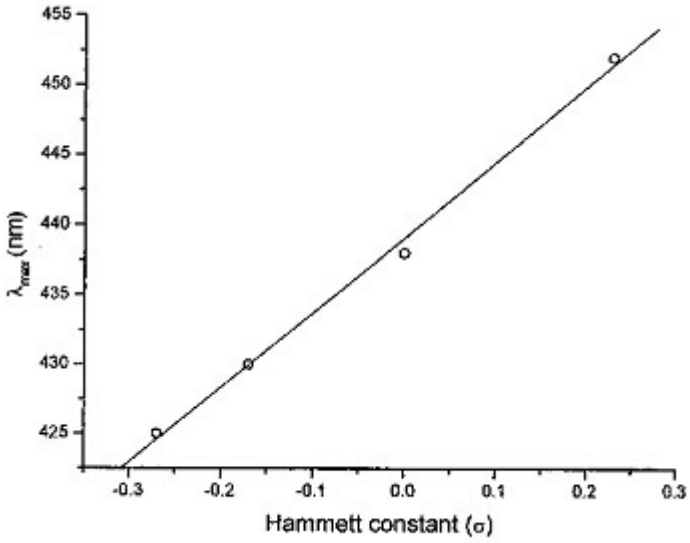


Fig. 2: Plot of λ_{max} (nm) versus Hammett constant (a)

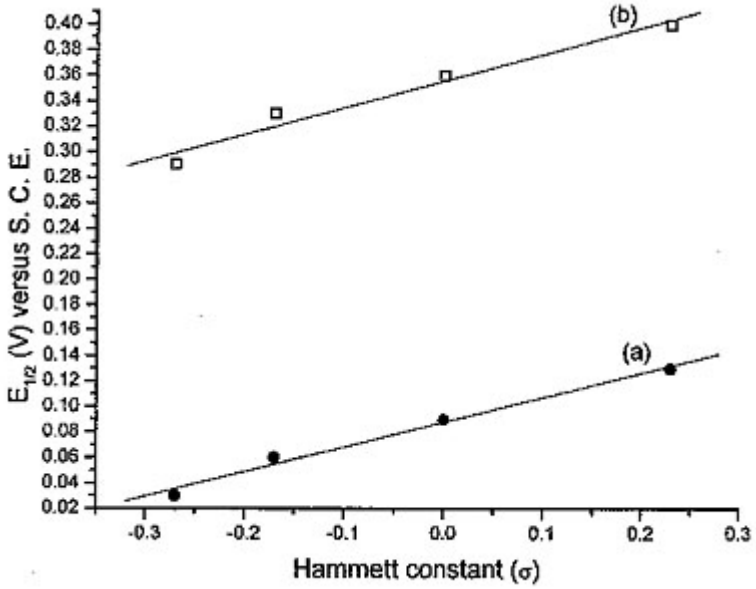


Fig. 3: Plots of: (a) $(E½)^{I}$ versus Hammett constant (σ); and (b) $(E½)^{II}$ versus Hammett constant (σ)

respectively. Similarly, the estimated error in the intercept of Fig. 2, Fig. 3(a) and Fig. 3(b) is 0.47, 0.003 and 0.005, respectively.

All these relations indicate the sensitivity of the vanadium electron density on the s of the R substituent. The three relations (4), (5) and (6) also indicate that there should be direct relation between λ_{max} and $(E½)^{I}$ and also between λ_{max} and $(E½)^{II}$. Eliminating s from the Eqs (4) and (5) and also from the Eqs (4) and (6), one can obtain Eqs (7) and (8) correlating λ_{max} respectively with $(E½)^{I}$ and $(E½)^{II}$

λ_{max} (nm) = 413.61 + 282.89×$(E½)^{I}$ ...(7)
λ_{max} (nm) = 346.93 + 255.95×$(E½)^{II}$ ...(8)

CONCLUSIONS

This study shows that in the presence of a bidentate niononegative unsymmetrical OO donor ligand like salicylaldehyde, these tridentate dinegative ONO donor hydrazone ligands selectively stabilize the VO^{3+} motif and in these complexes they are coordinated with the vanadium meridionally in their fttlly deprotonated enol forms. The IR spectra of the complexes in the solid state and their ^{1}H NMR spectra in $CDCl_3$ solution indicate the presence of two isomeric forms [i.e., (A) and (B)] in different ratios, which can best be explained by considering the interchange of the positions of the two donor sites of coordinated sal^{-} motif between axial and equatorial positions. The formation of the (A) isomer to a greater extent in comparison to the (B) isomer is usual from the bond strength point of view because in the former the phenolic oxygen moiety is present in the equatorial position of the vanadium and in this position stronger binding is possible than at the vacant axial position trans to vanadyl oxygen as in the (B) isomer. This study also show that there are linear relations between the λ_{max}, $(E½)^{I}$ and $(E½)^{II}$ values with the Hammett constant (s) and these three parameters show large dependence on a.

REFERENCES

1. Ghosh T, Bandyopadhyay C, Bhattacharya S & Mukherjee G, *Trans Met Chem*, **29**: 444 (2004).
2 Ghosh T, Bhattacharya S, Das A, Mukherjee G & Drew M G B, *Inorg Chim Acta*, 358: 989 (2005).
3 Ghosh T, Roy A, Bhattacharya S & Banerjee S, *Trans Met Chem*, **30**: 419 (2005).
4 Ghosh T, *Trans Met Chem*, **31**: 560 (2006).
5 Ghosh T & Sur K R, *J Ind Chem Soc,* **83**: 888 (2006).
6 Ghosh T, Mondal B, Ghosh T, Sutracihar M, Mukherjee G & Drew M 0 B, *Inorg Chim Acta*, **360**: 1753 (2007).
7 Ghosh T, Mondal B & Patra R, *Trans Met Chem*, **32**: 468 (2007).
8 Ghosh T & Mondal B, *J Chem Res*, 410 (2007).
9 Rath S P. Rajak K K & Chakravorty A, *Inorg Chem*, **38**: 4376 (1999).
10 Rath S P, Rajak K K, Mondal S & Chakravorty A, *J Chem Soc Dalton Trans*, 2097 (1998).
11 Rath S P, Mondal S & Chakravorty A, *Inorg Chiin Acta*, **263**: 247 (1997).
12 Nica S, Pohlmann A & Plass W, *Eur J Inorg Chem*, 2032 (2005).
13 Plass W, Pohlmann A & Yozgatli H - P, *J Inorg Biochem*, **80**: 181 (2000).
14 Maurya M R, Agarwal S, Bader C, Ebel M & Rehder D, *Dalton Trans*, 537 (2005).
15 Maurya M R, Khurana S, Zhang W & Rehder D, *J Chem Soc Dalton Trans*, 3015 (2002).
16 Maurya M R, Khurana S, Schulzke C & Rehder D, *Eur J Inorg Chem,* 779 (2001).
17 Weyand M, Hecht H J, Kiess M, Liaud M F, Vitler H & Schomburg D, *J Mol Biol*, **293**: 595 (1999).
18 Plass W, Angew Chem, *Int Edn Engl*, **38**: 909 (1999).
19 Carter-Franklin J N, Parrish J D, Tchirret-Guth R A, Little R D & Butler A, *Jam Chem Soc*, **125**: 3688 (2003).
20 Rehder D, Antoni G, Licini G M, Schulzke C & Meier B, *Coord Chem Rev*, **237**: 53 (2003).
21 (a) Crans D C, Felty R A & Miller M M, *J Am Chem Sac*, **111**: 265 (1991); (b) Hillerns F, Olbrich F, Behrens U & Rehder D, *Angew Chem, Int Edn Engl*, **31**: 447 (1992).
22 Eady R R, *Coord Chem Rev*, **237**: 23 (2003).
23 Coates G W, Hustad P D & Reinartz S,

Angew Chem, Int Edn Eng, **41**: 2236 (2002).
24 Hagen H, Boersma J & Koten G Van, *Chem Soc Rev*, **31**: 357 (2002).
25 Lorber C, Choukroun R & Donnadieu B, *Inorg Chem*, **42**: 673 (2003).
26 Wolff F, Lorber C, Choukroun R & Donnadieu B*, Inorg Chem,* **42**: 7839 (2003).
27 Gambarrotta S, *Coord Chem Rev*, **237**: 229 (2003).
28 Tapscott RE & Bel ford R L, *Inorg Chem,* **6**: 735 (1967).
29 Sakurai H, Tsuchiya K, Nukatsuka M, Kawada J, Ishikawa S, Yoshida H & Komatsu M, *J Clin Biochem Nuir*, **8**: 193 (1990).
30 McNeill J H, Yuen V G, Hoveyda H R & Orvig C, *J Med Chem*, **35**: 1489 (1992).
31 Crans D C, Mahroof-Tahir M, Shin P K & Keramidas A D, *Mol Cell Biochem*, **153**: 17 (1995).
32 Thompson K H & Orvig C, *Coord Chem Rev*, **219-221**: 1033 (2001).
33 Sakurai H, Kojima M, Yoshikawa Y, Kawabe K & Yasui H, *CoordChem Rev,* **226**: 187 (2002).
34 Dikanov S A, Liboiron BD & Orvig C, *J Am Chem Sac*, **124**: 2969 (2002).
35 Song B, Aebischer N & Orvig C, *Inorg Chem*, **41**: 1357 (2002).
36 Rehder D, Pessoa J C & Geraldes C F, *J Bial Inorg Chem,* **7**: 675 (2002).
37 Crans D C, Yang L, Alfano J A, Chi L H, Jin W, Mahroof-Tahir M, Robins K, Tolouc M M, Chan L K, Plante A J, Grayson R Z & Willsky G R, Coord Chem Rev, 237 (2003)
38 Liasko R, Kabanos T A, Karkabounus 5, Malamas M, Tasiopoulos J A, Stefanou D, Collery P & Evangelou A, *Anticancer Res*, **18**: 3609 (1998).
39 Evangelou A, *Crit Rev Oncol Hematol*, **42**: 249 (2002).
40 Butler A & Walker J V. *Chem Rev*, **93**: 1937 (1993).
41 Campbell M J M, *Coord Chem Rev*, **15**: 279 (1975).
42 Rowe R A & Jones M M, *Inorg Synth*, **5**: 113 (1957).
43 Vergopoulos V. Priebsch W, Fritzsche M & Rehder D*, Inorg Chem*, **32**: 1844(1993).
44 Ghosh T, Mondal B, Sutradhar M, Drew M G B, Ghosh T & Mukherjee G, communicated.
45 Hammett L P. Physical Organic Chemistry, 2nd Edn (McGraw-Hill, New York) (1970).