A study on the electronic effect of *para*-substituents in the aryloxy ring of the hydrazone ligands on the vanadium centre in the mixed-ligand [$V^{IV}O(ONO)(NN)$] families

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The hyperfine coupling constant (A_{II}) and the redox potential ($E_{½}$) values of vanadium(IV) in its mixed-ligand hydrazone complexes [$V^{IV}O(L)(bipy)$], **1–4** and [$V^{IV}O(L)(phen)$], **5–8,** [which have been synthesised from the reaction of $V^{IV}O(acac)_2$ with the hydrazone ligand H_2L in the presence of equimolar amount of 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) in methanol], exhibit a linear relationship with the Hammett constant (σ) of the *para*-substituents in the aryloxy ring of the hydrazone ligands.

Keywords: mixed-ligand oxovanadium(IV) complexes, hydrazone complexes, redox potential values

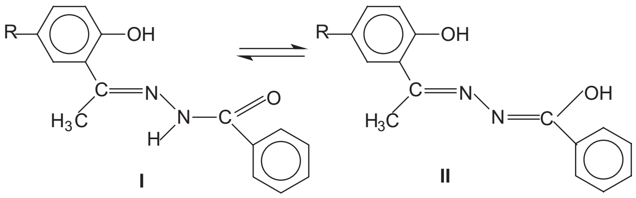
Vanadium chemistry is dominated by its two commonly-occurring monooxo motifs *viz*., VO^{2+} and VO^{3+}, probably due to their involvements in many biochemical and physiological processes, namely, haloperoxidation,[1-4] phosphorylation,[5] α-olefin polymerisation,[6-10] insulin mimicking,[11-20] anticancer,[21-22] antitumour,[23] and antifungal/antibacterial[24] activities. Mixed-ligand complexes containing hydrazone ligands are rare.[25-37] We are searching for new mixed-ligand oxovanadium complexes with hydrazone ligands containing these two motifs.[25-29] In this work we have used four tridentate, dinegative, ONO donor hydrazone ligands 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) as primary ligands. We have already seen that in the presence of a bidentate, mononegative ON donor ligand *viz*., 8-hydroxyquinoline, or a bidentate, mononegative OO donor ligand *viz*., vanillin, these ligands stabilise the VO^{3+} motif selectively.[28,29] This work was motivated by three objectives: (i) to examine whether these hydrazone ligands can selectively stabilise the VO^{2+} motif in the presence of a neutral bidentate NN donor ligand *viz*., 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) or not; (ii) to study 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 one neutral bidentate NN donor ligand as coligand and (iii) to enrich the chemistry of mixed-ligand oxovanadium(IV) complexes incorporating hydrazone ligands. In fact, mixed-ligand oxovanadium(IV) complexes containing aromatic acid hydrazides and bipy or phen are very rare.[25,27,30]

The H_2L ligands (**I**) bind the metal through the deprotonated phenolate-O, deprotonated amide-O and the imine-N atoms in their enol forms (**II**) (Scheme 1). When a methanolic solution of [$V^{IV}O(acac)_2$] was added to a methanolic solution of H_2L and bipy or phen (B) in equimolar ratio, the tetravalent mixed-ligand complexes [$V^{IV}O(L)(B)$], **1–8** were obtained in good yield. Reactions can be represented as in (1):

$$[V^{IV}O(acac)_2] + H_2L + B \rightarrow [V^{IV}O(L)(B)] + 2Hacac \qquad (1)$$

where Hacac is acetylacetone.

Characteristic ligand bands in the region 1646–1651, 2924–2989 and 3215–3240 cm^{-1} due to C=O, N–H and O–H stretches respectively, are not observed in their corresponding vanadium complexes, indicating the transformation of C=O and N–H groups to the enolic form (Scheme 1) and their subsequent coordination to vanadium through the deprotonation of the phenolic and enolic hydrogens. A new band appearing in the 1214–1242 cm^{-1} region in the metal complexes was assigned to the ν(C–O) (enolate) mode (Table 1). The shifting of the (C=N) (azomethine) band of the ligands to a lower wave number by 23–36 cm^{-1} in the metal complexes indicates the coordination of azomethine nitrogen to the metal. The characteristic ν(N–N) value of the free ligands (observed at 902–932 cm^{-1}) underwent a 137–168 cm^{-1} shift towards higher wave number upon complexation due to diminished repulsion between the lone pairs of adjacent nitrogen atoms.[25,28,38] A strong band in the 1352–1365 cm^{-1} region is associated with the stretching frequency of the V–O (phenolic) bond.[25,28,39] The strong band, appearing in the 939–961 cm^{-1} region in all the complexes is attributed to V=O stretching, indicating the hexacoordinated environment around the metal centre.[25,28,30,39] An analysis of the V=O stretching frequency data indicates that ν(V=O) values for phen complexes **5–8** are significantly lower than for the corresponding bipy complexes **1–4**. This trend is quite expected from the basicity point of view of these two ligands. Such a trend is also observed in their A_{II} and $E_{½}$ values (*vide infra*).



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

Scheme 1

In spite of our best efforts, none of the complexes reported in this work afforded X-ray quality single crystals. However, we have already established the meridional disposition of $(L^4)^{2-}$ species by X-ray crystallography[28] in complex [$V^{V}O(L^4)(hq)$] [where hq^- is the deprotonated form of 8-hydroxyquinoline (Hhq)] and extending this behaviour to the present compounds, the most probable gross structure of these complexes will be as designated by (**III**). The dissimilar binding nature of the two nitrogen atoms of bipy or phen moieties in the proposed structure (**III**) is not unusual because such a type of binding is crystallographically well established.[40,41]

Complexes are one electron paramagnetic and display axial EPR spectra [in frozen CH_2Cl_2-toluene (1 : 1, V/V), 77 K] with well-resolved ^{51}V (I = 7/2) hyperfine lines. Parameters are collected in Table 2. An analysis of the EPR

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Table 1 Analytical and IR spectral data of the complexes

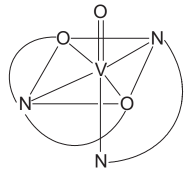
Compound	Found (Calcd.) (%)			IR[a] (cm^{-1})			
	C	H	N	V=O	N–N	C–O(enolic)	C=N[b]
[VO(L^1)(bipy)], **1**	62.9(63.2)	3.8(4.2)	11.7(11.8)	957	1069	1226	1577
[VO(L^2)(bipy)], **2**	63.4(63.8)	4.3(4.5)	11.4(11.5)	958	1060	1232	1580
[VO(L^3)(bipy)], **3**	61.2(61.8)	4.2(4.4)	10.9(11.1)	950	1069	1242	1582
[VO(L^4)(bipy)], **4**	58.7(58.9)	3.5(3.7)	11.0(11.0)	961	1070	1229	1580
[VO(L^1)(phen)], **5**	64.2(64.9)	3.8(4.0)	11.0(11.2)	940	1070	1242	1575
[VO(L^2)(phen)], **6**	65.0(65.5)	4.5(4.3)	10.7(10.9)	954	1071	1230	1580
[VO(L^3)(phen)], **7**	63.1(63.5)	4.4(4.2)	10.4(10.6)	939	1073	1228	1569
[VO(L^4)(phen)], **8**	60.2(60.7)	3.5(3.6)	10.4(10.5)	951	1068	1214	1580

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

Table 2 Magnetic moment (at room temperature) and EPR spectral data[a] [at 77 K in CH_2Cl_2–toluene (1:1, V/V)] of the complexes **1–8**

Compound	ì$_{eff}$(B. M.)	$g_{\|\|}(10^4 A_{\|\|}/cm^{-1})$	$g_\perp$ $(10^4 A_\perp/cm^{-1})$	$10^4 A_{\|\|}^{est}$
[VO(L^1)(bipy)], **1**	1.72	1.952(172.4)	1.984(59.3)	169.3
[VO(L^2)(bipy)], **2**	1.73	1.949(171.2)	1.980(59.3)	169.3
[VO(L^3)(bipy)], **3**	1.72	1.951(170.1)	1.982(58.7)	169.3
[VO(L^4)(bipy)], **4**	1.72	1.950(173.8)	1.981(59.6)	169.3
[VO(L^1)(phen)], **5**	1.73	1.950(171.4)	1.985(58.1)	169.3
[VO(L^2)(phen)], **6**	1.74	1.952(170.2)	1.983(58.3)	169.3
[VO(L^3)(phen)], **7**	1.73	1.953(169.3)	1.984(57.1)	169.3
[VO(L^4)(phen)], **8**	1.75	1.951(173.2)	1.982(58.9)	169.3

[a]Estimated error in g values: 0.002 and A values: 3×10^4 cm^{-1}.



III

parameter data reveals the relationships: $g_{||} < g_\perp$ and $A_{||} >> A_\perp$, which are characteristic of an axially compressed $d_{xy}{}^1$ configuration.[25,30,42] According to the additivity relationship developed by Chasteen,[43] the value of $A_{||}$ can be estimated ($A_{||}^{est}$) (accuracy $\pm$ 3×10^{-4} cm^{-1}) for a specific equatorial donor set by the Eqn (2)

$$A_{||}^{est} = \sum_{i=1}^{4} A_{||}, i/4 \qquad (2)$$

The $A_{||}^{est}$ value for (**III**) with one deprotonated phenolic oxygen, one deprotonated enolic oxygen, one neutral imine nitrogen and one neutral pyridine nitrogen in the equatorial positions is 169.3×10^{-4} cm^{-1} and this is close to the experimentally observed values for **1–8**. The analysis of the EPR parameter data (Table 2) also indicates that phen slightly decreases $A_{||}$ and increases $g_{||}$ compared to bipy for an identical primary ligand and for an identical auxiliary ligand, the complexes with $(L)^{2-}$ species having an electron donating group in the *para*-position with respect to OH group in the aryloxy ring, have slightly lower $A_{||}$ values compared to unsubstituted species, and the reverse is true for the presence of an electron withdrawing group (*vide infra*).

The orange to orange-red tetravalent complexes **1–8** display two ligand-field transitions (Table 3) in the near IR-visible region: one near 840 nm and other at around 696–775 nm region due to $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions respectively.[44] The expected third band due to $d_{xy} \rightarrow d_{z^2}$ transition is probably masked by the strong charge transfer band at lower energies. The strong absorption at around 400 nm may be due to charge transfer transition of the type O(phenolic) → V^{4+}. The intra-ligand $\pi \rightarrow \pi^*$ (of the C=N bond) transition is observed at *ca* 322 nm.

Complexes uniformly exhibit a quasi-reversible one-electron oxidation peak near + 0.70 V *versus* SCE for bipy complexes and near + 0.60 V *versus* SCE for phen complexes due to the VO^{2+}–VO^{3+} couple, Eqn (3).

$$[V^{IV}O(L)(B)] \rightarrow [V^{V}O(L)(B)]^+ + e \qquad (3)$$

$E_{1/2}$ values *versus* SCE are listed in Table 3. Analysis of the electrochemical data indicates a decrease in $E_{1/2}$ values by *ca* 70 mV for [V^{IV}O(L)(phen)], **5–8** complexes compared to [V^{IV}O(L)(bipy)], **1–4** complexes, which can be explained by considering the higher basicity of phen compared to bipy, as was explained for the trend of ν(V=O) and $A_{||}$ values for these complexes (*vide supra*). For a given bidentate ligand,

Table 3 Electronic spectral and electrochemical[a] data at 298 K of the complexes **1–8** in CH_2Cl_2 solution

Compound	Electronic spectral data λ_{max}/nm(ε/dm^3 mol^{-1} cm^{-1})	Electrochemical data $E_{1/2}{}^b$/V(ΔE_p/mV)
[VO(L^1)(bipy)], **1**	839(54); 698(58); 402(9118); 322^{sh}(13,270)	+ 0.73(100)
[VO(L^2)(bipy)], **2**	839(50); 696(54); 410(9745); 322^{sh}(16,638)	+ 0.70(100)
[VO(L^3)(bipy)], **3**	847(51); 765(49); 427(7599); 321^{sh}(8,329)	+ 0.68(110)
[VO(L^4)(bipy)], **4**	838(47); 719(45); 410(9719); 322^{sh}(13,963)	+ 0.78(110)
[VO(L^1)(phen)], **5**	847(36); 775(33); 401(9188); 322^{sh}(9,214)	+ 0.65(100)
[VO(L^2)(phen)], **6**	856(36); 763(10); 410(8332); 323(14,145)	+ 0.62(110)
[VO(L^3)(phen)], **7**	847(54); 765(53); 432(7923); 328(7466)	+ 0.60(110)
[VO(L^4)(phen)], **8**	839(54); 698(58); 402(9118); 322^{sh}(13,270)	+ 0.71(100)

[a]At a Pt disk electrode; supporting electrolyte: Et_4NClO_4 (TEAP, 0.1 M), scan rate 50 mVs^{-1}, reference electrode SCE., solute concentration *ca* 10^{-3} M; [b]$E_{1/2}$ is calculated as the average of anodic ($E_p{}^a$) and cathodic ($E_p{}^c$) peak potential values; ^{sh}shoulder.

the trend in the $E_{1/2}$ values with respect to L is: $L^3<L^2<L^1<L^4$ and this trend can qualitatively be explained by considering the normal substituent effect on the aryloxy ring of the hydrazone ligands, because an electron donating group at the *para*-position with respect to the OH group in the benzene ring increases its electron donor ability, while an electron withdrawing group decreases it. The $E_{1/2}$ values are substantially lower than for the similar complexes with the hydrazone ligand derived from the condensation of benzoyl hydrazine with salicylaldehyde[30] and higher than for the hydrazone complexes derived from the condensation of benzoyl hydrazine with 2-hydroxybutyrophenone.[30] This is most likely due to the higher basicity of the present hydrazone ligands over the salicylaldehyde family, owing to the presence of a CH_3 group in place of the azomethine H in the salicylaldehyde family, while the presence of the more electron releasing Pr^n substituent in the 2-hydroxybutyrophenone family makes it more basic than the present family.

To demonstrate the quantitative relation between *para*-substituents and their effect on the vanadium nucleus, the hyperfine coupling constant ($A_{||}$) and the redox potential ($E_{1/2}$) values are plotted against the value for the electronic influence of the substituents (σ, the Hammett parameter[45]) [H ($\sigma = 0.00$), CH_3 ($\sigma = -0.17$), OCH_3 ($\sigma = -0.27$) and Cl ($\sigma = +0.23$)] (Figs 1 and 2 respectively).

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

$$\textbf{EPR: } A_{||}\ (\text{cm}^{-1}) = 172.25 + 7.22 \times \sigma \text{ for bipy complexes} \quad (4)$$

$$A_{||}\ (\text{cm}^{-1}) = 171.43 + 7.70 \times \sigma \text{ for phen complexes} \quad (5)$$

The respective r values are 0.99 and 1.0 and the estimated error in $dA_{||}/d\sigma$ value is 0.61 for bipy complexes and 0.18 for phen complexes. Similarly, the estimated error in the intercept of Fig. 1(a) and Fig. 1(b) is 0.11 and 0.03 respectively.

$$\textbf{CV: } E_{1/2}\ (\text{V}) = 0.73 + 0.20 \times \sigma \text{ for bipy complexes} \quad (6)$$

$$E_{1/2}\ (\text{V}) = 0.66 + 0.22 \times \sigma \text{ for phen complexes} \quad (7)$$

Corresponding r values are 1.0 and 0.99 respectively and the estimated error in $dE_{1/2}/d\sigma$ value is 0.006 for bipy complexes and 0.01 for phen complexes. The estimated error in the intercept of Fig. 2(a) and Fig. 2(b) is 0.001 and 0.002 respectively. All these relations indicate the sensitivity of the vanadium electron density to substituent as indicated by the Hammett parameter of the substituent.

In conclusion, this study indicates that in the presence of a neutral NN donor ligands, *viz,* bipy or phen, these tridentate, dinegative, ONO donor hydrazone ligands stabilise the VO^{2+} motif selectively and in these complexes they are coordinated with the vanadium meridionally in their fully deprotonated enolic forms. This study also indicates that the *para*-substituents with respect to the phenolic OH group in the hydrazone ligands have a large effect on the electronic properties of vanadium, particularly on its $A_{||}$ and $E_{1/2}$ values.

Experimental

Electronic spectra (in CH_2Cl_2) were recorded on a Hitachi U-3501 spectrophotometer, IR spectra on a Perkin-Elmer 782 spectrophotometer and EPR spectra (X-band) on a E-112 Century series Varian E-102 Microwave bridge spectrometer. Tetracyanoethene (tcne) ($g = 2.0027$) was used to calibrate the EPR spectra. 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 (SCE) were used in a three-electrode configuration. All the potential values reported here are uncorrected for junction contribution. The $E_{1/2}$ for the ferrocinium–ferrocene couple under the experimental conditions was 0.39 V. Magnetic susceptibilities were measured using a PAR model 155 vibrating sample magnetometer fitted with a Walker Scientific L75 FBAL magnet using $Hg[Co(SCN)_4]$ as the calibrant. A Perkin-Elmer CHNS/O analyser 2400 was employed to obtain microanalytical (C, H, N) data.

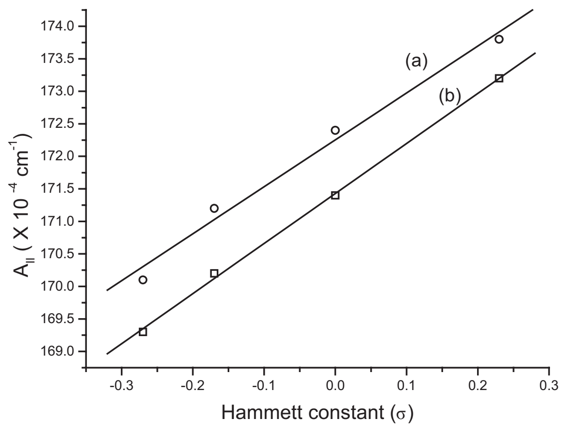


Fig. 1 Plot of $A_{||}$ *versus* Hammett constant (σ); (a) for bipy complexes and (b) for phen complexes.

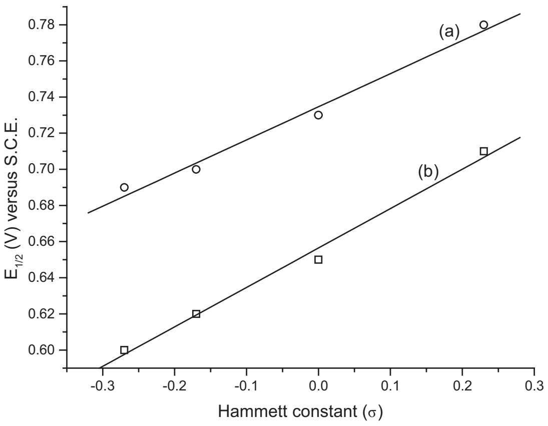


Fig. 2 Plot of $E_{1/2}$ *versus* Hammett constant (σ); (a) for bipy complexes and (b) for phen complexes.

Synthesis of the ligands H_2L^{1-4}

All the hydrazone ligands were synthesised by the reported method.[28]

Preparation of the metal complexes $[V^{IV}O(L)(B)]$, **1-8**

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

$[V^{IV}O(L^1)(bipy)]$, **1**

To a methanolic solution (20 cm^3) of $[V^{IV}O(acac)_2]$ (0.265 g, 1 mmol) and bipy (0.156 g, 1 mmol) was added a warm methanolic solution (20 cm^3) of H_2L^1 (0.254 g, 1 mmol) dropwise. The reaction mixture was then stirred at room temperature for 2 h. A brown precipitate was obtained which was filtered, washed with methanol and dried over silica gel. Yield: 0.39 g (82%). Complexes **2**–**8** were synthesised following the similar procedure in 76–84% yield.

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