

Ligand controlled synthesis of mixed-ligand oxovanadium(V) and oxovanadium(IV) complexes

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Reaction of V^{IV}O(acac)₂ (where Hacac = acetylacetonate) with 2-hydroxybenzylalcohol (H₂L) produces [V^{VO}(L)(acac)(H₂O)], **1** but the above reaction mixture produces [V^{VO}(L)(hq)(CH₃OH)], **2** and [V^{IV}O(HL)(pa)(CH₃OH)], **3** in presence of 8-hydroxyquinoline(Hhq) and picolinic acid(Hpa), respectively.

Keywords: mixed-ligand complexes, oxovanadium(V) / oxovanadium(IV)

The recognition of involvement of VO²⁺ and VO³⁺ motifs in many important biochemical processes¹⁻⁶ has attracted considerable attention for the development of their chemistry. These two motifs have strong affinity towards N/O donor type of ligands due to their hard acidic nature and as a result of that many model complexes containing such type of donor ligands have been synthesised and characterised.⁷ The stability of either of these two motifs depends upon the basicity of the donor atoms of the ligand molecule. With a view to study the effect of auxiliary ligands on the metal valence in the mixed-ligand system containing a fixed primary ligand, we have selected 2-hydroxybenzylalcohol (H₂L), which acts as a mono or dinegative bidentate ligand) as such a ligand and acetylacetonate (Hacac) or 8-hydroxyquinoline (Hhq) or picolinic acid (Hpa) as auxiliary ligands. These auxiliary ligands are bidentate mononegative containing one negative O donor species (either enolate or phenolate or carboxylate moiety) and one neutral O or N donor atom.

H₂L binds with the metal in the bidentate dinegative fashion in complexes **1** and **2** but in a bidentate mononegative fashion in complex **3**. Hacac, Hhq and Hpa were used as coligand. Reaction of V^{IV}O(acac)₂ with H₂L (in equimolar ratio or in excess) in acetonitrile produces [V^{VO}(L)(acac)(H₂O)], **1**, whereas reaction with H₂L followed by the addition of Hhq in methanol produces [V^{VO}(L)(hq)(CH₃OH)], **2**. If Hhq is added first to a methanolic solution of V^{IV}O(acac)₂ followed by the addition of H₂L, then because of the strong coordination property of Hhq the [V^{VO}(hq)₂(OCH₃)] complex is formed to a greater extent rather than the formation of our desired complex **2**. V^{IV}O(acac)₂ on reaction with Hpa in methanol followed by the addition of H₂L (or vice-versa) produces [V^{IV}O(HL)(pa)(CH₃OH)], **3**. The oxidising agent is aerial dioxygen for the formation of pentavalent complexes **1** and **2**. The reactions are:



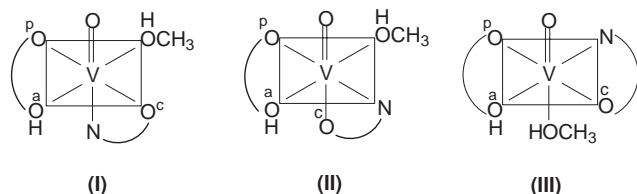
Table 1 Analytical, IR and magnetic moment data for the complexes

Compound	Found (Calcd.) (%)			IR ^a (cm ⁻¹) V=O	CO ₂ ⁻	μ _{eff} ^b (B.M.)
	C	H	N			
[VO(L)(acac)(H ₂ O)], 1	46.8(47.1)	4.7(4.9)	-	960	-	c
[VO(L)(hq)(CH ₃ OH)], 2	55.7(55.9)	4.3(4.4)	3.8(3.8)	953	-	c
[VO(HL)(pa)(CH ₃ OH)], 3	48.7(49.0)	3.8(4.1)	3.9(4.1)	967	1660, 1628	1.73

^aKBr discs; ^bat 298K; ^cdiamagnetic.

* Correspondence.

The complexes **1–3** exhibited a strong V=O stretching absorption in the 953–967 cm⁻¹ region (Table 1) indicating the hexacoordinated environment around the metal centre.⁸ Two bidentate ligands and one oxo group provide penta-coordination to the metal and the sixth coordination site is occupied either by H₂O (in **1**) or by solvent CH₃OH (in **2** and **3**). The coordination of H₂O in complex **1**, may be due to the higher affinity of the hard VO³⁺ motif towards the oxygen-containing ligand. The appearance of one band near 3396 cm⁻¹ in **1** and near 3430 cm⁻¹ in **2** and **3** indicated the presence of a coordinated H₂O molecule⁹ and a coordinated CH₃OH molecule (also indicated in the NMR spectra of **1** and **2**, *vide infra*), respectively. A band at 3100 cm⁻¹ in **3** indicated the existence of a bonded CH₂OH group.^{8,10,11} The presence of one symmetric (1348 cm⁻¹) and two asymmetric (1628 cm⁻¹ and 1660 cm⁻¹) stretching modes is in favour of monodentate coordination nature of the carboxylate group¹² in **3**. The coordination of pyridine ring nitrogen is indicated by the red-shift of the pyridine ring in-plane deformation vibration¹³ (observed at 695 cm⁻¹ in **3** and at 676 cm⁻¹ in free Hpa) by 19 cm⁻¹. Bidentate coordination of the H₂L ligand with deprotonation of both of the two OH groups exists in **1** and **2**, but bidentate coordination without deprotonation of the alcoholic OH group occurs in **3**. This type of binding nature is confirmed from the disappearance of OH stretching frequencies of the phenolic and alcoholic moieties at 3162 and 3444 cm⁻¹, respectively, and from the shifting of the C-O stretching band of the phenolic and alcoholic moieties at 1460 and 1260 cm⁻¹ towards higher frequency in the complexes by 35–70 cm⁻¹ for phenolic C–O and by 25–55 cm⁻¹ for alcoholic C–O moieties. A band appearing at 1234 cm⁻¹ in **1** is assigned to ν(C–O) (enolate mode) of the bonded acetylacetonate moiety⁹ (also confirmed by the NMR spectra, *vide infra*).



Magnetic susceptibility measurements indicate that **1** and **2** are diamagnetic while **3** is paramagnetic ($\mu_{\text{eff}}=1.73$ B.M.) at room temperature. The complex **3** is EPR active and exhibits an axial EPR spectrum in DMSO at 77K. The parameters calculated from this spectrum are: $g_{\parallel} = 1.930$, $g_{\perp} = 1.975$ and $A_{\parallel} = 176.4 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 65.0 \times 10^{-4} \text{ cm}^{-1}$. The $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\perp}$ relationships are characteristic of an axially compressed d_{xy}^1 configuration.^{14,15} The presence of two bidentate ligands, one oxo group and one solvent molecule indicate that three structures **I**, **II** and **III** (the superscripts a, c and p stand for alcoholic, carboxylic and phenolic oxygen moieties, respectively) are possible. At this stage the EPR data provide important information about the groups coordinated to the metal in the equatorial positions. The value of A_{\parallel} can be estimated ($A_{\parallel}^{\text{est}}$) on the basis of additivity relationship presented by Chasteen¹⁶ (with estimated accuracy $\pm 3 \times 10^{-4} \text{ cm}^{-1}$) for the individual structures **I–III** with a specific equatorial donor set by the eqn (1)

$$A_{\parallel}^{\text{est}} = \sum_{i=1}^4 A_{\parallel, i} / 4 \quad (1)$$

The $A_{\parallel}^{\text{est}}$ value for **I** with two protonated alcoholic oxygens and two deprotonated phenolic and carboxylic oxygens in the equatorial positions is $176.1 \times 10^{-4} \text{ cm}^{-1}$, for **II** with two protonated alcoholic oxygens, one deprotonated phenolic oxygen and one pyridine nitrogen is $173.6 \times 10^{-4} \text{ cm}^{-1}$ and for **III** with one protonated alcoholic oxygen, two deprotonated phenolic and carboxylic oxygens and one pyridine nitrogen this value is $170.0 \times 10^{-4} \text{ cm}^{-1}$. So a comparison with the observed and with these calculated values indicate that the most probable gross structure of **3** is as designated by **I**.

¹H NMR spectral data suggest the binding nature of the ligands with the metal in the complexes **1** and **2**. The 300 MHz NMR spectra of **1** and **2** were recorded in dry CDCl₃. Signals

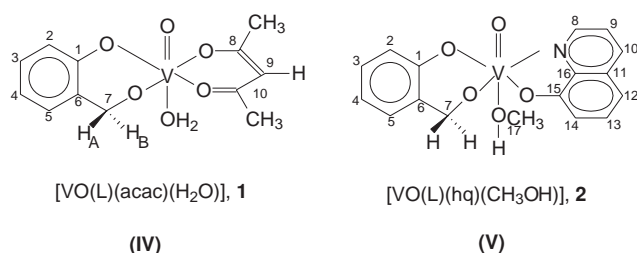


Table 2 ¹H NMR spectral data^a of complexes **1** and **2** in CDCl₃ solution

Complex 1		Complex 2	
Proton	δ (J/Hz)	Proton	δ (J/Hz)
H(2)	6.76(1H,dd,8.1,1.5)	H(ArH)	7.13–7.25(5H,m)
H(3,5)	7.17–7.21(2H,m)	H(7)	3.49(2H,s)
H(4)	7.03(1H,m)	H(8)	8.58(1H,dd,4.2,1.5)
H(7A)	5.64(1H,d,15.8)	H(9)	7.54(1H,dd,8.0,1.5)
H(7B)	6.48(1H,d,15.8)	H(10)	8.46(1H,dd,8.0,1.5)
H(8-CH ₃)/H(10-CH ₃)	2.00(3H,s)/1.93(3H,s)	H(ArH)	8.02–8.11(2H,m)
H(9)	5.61(1H,s)	H(17-CH ₃)	5.56(3H,s)
H(H ₂ O)	15.47(brs)	H(CH ₃ OH)	10.8(brs)

^aThe numbering system corresponds to that in **IV** and **V**, e.g., H(2) represents proton attached to C(2); s = singlet; d = doublet; dd = double doublet; m = multiplet; brs = broad singlet.

were assigned (Table 2) on the basis of intensity, spin-spin structure and chemical shift.

In the ¹H NMR spectra of **1**, the enolic proton H(9) is a singlet and the two methyl signals of the coordinated acetylacetonate moiety appear at δ 1.93 and 2.00 ppm. The methylene protons of the L²⁻ moiety are non-equivalent^{17,18} (**IV**). The pair of signals $\sim \delta$ 5.64 and δ 6.48 ppm are assigned to CH₂OV protons. The aromatic protons appear in the δ 6.76–7.21 ppm region. The protons of coordinated water appear as a broad singlet at δ 15.47 ppm and are exchangeable with D₂O.

The ¹H NMR spectra of **2** indicates that the methylene protons of the L²⁻ moiety are equivalent¹⁹ and appear at δ 3.49 (**V**). The methyl protons of the coordinated CH₃OH molecule²⁰ appear at δ 5.56 ppm and OH appears as a broad signal at δ 10.80 ppm. The aromatic protons appear at δ 7.13–8.58 ppm.

The pentavalent complexes **1** and **2** are shiny black in the solid state but in CH₂Cl₂ are intense blue and red respectively, and exhibit only strong LMCT transitions at 590 nm and 490 nm, respectively, due to O(phenolic)→V⁵⁺(3d) transition. The greenish-yellow tetravalent complex **3** displays three ligand-field transitions in the visible region (Table 3) at 742, 551 and 370 nm due to $d_{xy} \rightarrow d_{xz}$, d_{yz} ; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{z^2}$ transitions, respectively.²¹

The complexes **1** and **2** displayed an irreversible reduction peak near –0.43 V and –0.60 V vs SCE respectively, while the complex **3** exhibited a quasi-reversible one electron oxidation peak near +0.37 V. The irreversible nature of the reduction peaks is probably due to the decomposition of the complexes on reduction. The higher basic acac⁻ and hq⁻ moieties on coordination decreases the reduction potential value of the metal to such an extent so that spontaneous aerial oxidation occurs but this is not possible in case of the less basic pa⁻ moiety.

Comparison of redox potential values (Table 3) reveals the order: **2** < **1** < **3**. Such an order can be explained by considering the overall basicity of the combined ligand system. Hhq is more basic than Hacac and it is more basic than Hpa. Moreover, in **3** the H₂L ligand binds the metal in the mononegative fashion whereas in **1** and **2** it binds in the

Table 3 Spectral and electrochemical data^a at 298K for the complexes

Compound	UV-VIS ^{b,c} $\lambda_{\text{max}}/\text{nm}(\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$	$E_{1/2}^d/\text{V}$ ($\Delta E_p/\text{mV}$)
[VO(L)(acac)(H ₂ O)], 1	590 ^b (1272)	–0.43 ^{b,e}
[VO(L)(hq)(CH ₃ OH)], 2	490 ^b (4585); 378(6256)	–0.60 ^{b,e}
[VO(HL)(pa)(CH ₃ OH)], 3	742 ^c (47); 551(36); 370(534)	+0.37 ^c (100)

^aAt a Pt disk electrode; supporting electrolyte Bu₄NClO₄ (TBAP, 0.1M), scan rate 50 mVs⁻¹, reference electrode SCE, solute concentration ca. 10⁻³ M; ^bin CH₂Cl₂; ^cin DMSO; ^d $E_{1/2}$ is calculated as the average of anodic(E_p^a) and cathodic(E_p^c) peak potentials; ^e E_p^c values only; ΔE_p = difference of cathodic and anodic peak potential values.

dinegative fashion. As a result of that the basicity of this ligand molecule is lower in **3** than in **1** and **2**.

In conclusion, this study indicates that in the presence of a strong dibasic bidentate ligand (*e.g.*, 2-hydroxybenzylalcohol) enolate and phenolate moieties (*viz.*, acac^- and hq^-) have a tendency to stabilise the VO^{3+} motif, while the carboxylate moiety (*viz.*, pa^-) stabilises the VO^{2+} motif. This study also indicates that the deprotonation of the CH_2OH group of H_2L ligand in the complexes depends upon the oxidation state of the metal as this group is deprotonated if the metal is in pentavalent state (*e.g.*, in **1** and **2**) but it remains protonated if the metal is in the tetravalent state (*e.g.*, in **3**). Though there are very few examples containing acetylacetonate in the mixed-ligand oxovanadium(IV) complexes,^{22,23} to the best of our knowledge, no such example in the pentavalent state has been reported.

Experimental

Electronic spectra (in $\text{CH}_2\text{Cl}_2/\text{DMSO}$) 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. Tetracyanoethylene (TCNE) ($\epsilon = 2.0027$) was used to calibrate the EPR spectra. ^1H NMR spectra were recorded in CDCl_3 on a Bruker AM 300L (300 MHz) superconducting FT NMR spectrophotometer. Electrochemical measurements were performed at 298K in CH_2Cl_2 or in DMSO for a solute concentration $ca\ 1 \times 10^{-3}$ mol dm^{-3} using tetrabutylammonium perchlorate as supporting electrolyte under a dry nitrogen atmosphere on a PC-controlled PAR Model 273A electrochemistry system. A platinum disc, a platinum wire auxiliary electrode and an aqueous saturated calomel electrode (SCE) were used in a three-electrode configuration. The $E_{1/2}$ for the ferrocinium-ferrocene couple under the experimental condition was 0.39V. All the potentials reported here are uncorrected for junction contribution. Magnetic susceptibilities were measured using a PAR model 155 vibrating sample magnetometer fitted with Walker Scientific L75 FBAL magnet using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrant. A Perkin-Elmer CHNS/O analyzer 2400 was employed to obtain microanalytical (C, H, N) data.

Preparation of the metal complexes

$[\text{VO}(\text{L})(\text{acac})(\text{H}_2\text{O})]$, **1**: To an acetonitrile solution (20 ml) of $\text{VO}(\text{acac})_2$ [265mg, 1 mmol] was added dropwise acetonitrile solution (10ml) of 2-hydroxybenzylalcohol (124 mg, 1 mmol). The reaction mixture was then heated to reflux for 2h. The intense blue reaction mixture so obtained was then kept in the refrigerator for slow evaporation. A shiny black microcrystalline product was obtained after one week. It was then filtered and washed with acetonitrile and then dried over silica gel. Yield : 100 mg (33%).

$[\text{VO}(\text{L})(\text{hq})(\text{CH}_3\text{OH})]$, **2**: To a stirred methanolic solution (15ml) of $\text{VO}(\text{acac})_2$ (265 mg, 1 mmol) was added dropwise methanolic solution (10ml) of 2-hydroxybenzylalcohol (124mg, 1 mmol) at room temperature. The reaction mixture was then heated to reflux for 4h, then cooled and to this added dropwise methanolic solution (10ml) of 8-th methanol and dried over silica gel. Yield: 290mg (79%).

$[\text{VIVO}(\text{HL})(\text{pa})(\text{CH}_3\text{OH})]$, **3**: To a stirred methanolic solution (15 ml) of $\text{VO}(\text{acac})_2$ (265 mg, 1 mmol) was added dropwise a

methanolic solution (10 ml) of pyridine 2- carboxylic acid (123 mg, 1 mmol) at room temperature. The reaction mixture was then heated to reflux for 1h. then a methanolic solution (10 ml) of 2-hydroxybenzylalcohol (124 mg, 1 mmol) was added dropwise and the mixture again heated to reflux for 1h. The reaction mixture was then cooled and kept for slow evaporation at room temperature. A greenish-yellow product was obtained after one week. The product was filtered, washed with methanol and dried over silica gel. Yield : 175 mg (51%).

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