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Synthesis, structure and metal redox of alkoxide bound oxovanadium(V) complexes incorporating N-salicylidene/N-naphthalidene-α-aminoalcohols

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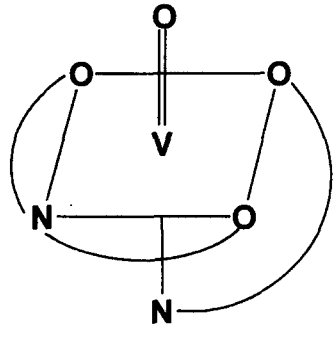
Abstract—In the title families the ONO ligands are deprotonated forms of N-(1-hydroxyethyl) salicylaldimine(H_2L^1), N-(1-hydroxy-2-methylpropyl)salicylaldimine (H_2L^2), N-(1-hydroxyethyl)naphthaldimine(H_2L^3), N-(1-hydroxy-2-methylpropyl) naphthaldimine(H_2L^4). The ON ligand is deprotonated 8-quinolinol(Hhq). The complexes VO(L)(hq) (L = L^1–L^4) have been synthesized in excellent yields from $\{VO(L)\}_x$ and 8-quinolinol in methanol (oxidant is aerial oxygen). The crystal structure of $VO(L^2)(hq)$ has revealed tridentate ONO and bidentate ON binding by $[L^2]^{2-}$ and hq^-, respectively. The V—O(phenolate) bond length is longer than V—O(alkoxidic) by ~0.09 Å. In $CDCl_3$ solution the ^1H NMR spectrum of the $VOL^2(hq)$ shows that the binding nature in solid state is also retained in solution. The complexes display the quasi-reversible one-electron couple VO(L)(hq)–$VO(L)(hq)^-$ near −0.43 V vs saturated calomel electrode. This lowering of potentials indicate considerable VO^{3+} stabilization due to alkoxide binding. Electrogenerated solution of $VO(L)(hq)^-$ are EPR-active corresponding to a d^1_{xy} configuration. © 1997 Elsevier Science Ltd

Keywords: oxovanadium(V) complexes; alkoxide complexes; oxine complexes; crystal structure.

The recognition that certain haloperoxidases [1–3], nitrogenases [4], and amavadin [5] isolated from *Aminata muscaria* contain the relatively uncommon monooxo pentavalent motif VO^{3+} set in non-porphyrinic O/N ligated environments [6–10] has motivated renewed search for complexes of VO^{3+} coordinated to ON ligands having at least some biomimetic features [11–14]. Some of our findings on carboxylate [15] and phenolate [16] bindings VO^{3+} complexes have been published during past few years. Increasing interest is being focused in the recent years on the vanadium(V)-bound alkoxides in view of their implications in vanadium-bromoperoxidase [9], potential utility as selective oxidants [17], bioinorganic linkages to processes such as phosphorylation [18] and insulin mimicking [19].

The present study concerns the complexes of coordination type $V^VO(ONO)(ON)$ based on tridentate ONO and bidentate ON donating ligands. The structure of the chelates shown as in **1** is probed with the help of single-crystal X-ray crystallography and ^1H NMR spectroscopy. Electronic spectra as well as the electrochemistry of the compounds are reported.



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The systematics of donor dependence of the VO^{3+}–VO^{2+} reduction potentials are scrutinized. The VO(L)(hq) complexes undergo facile electroreduction to air sensitive EPR-active oxovanadium(IV) congeners $[VO(L)(hq)]^-$.

EXPERIMENTAL

Materials

Electrochemical grade dichloromethane and tetraethylammonium perchlorate were obtained as before [20]. All other chemicals and solvents were of analytical grade and used as received.

Synthesis of the complexes

The complexes reported in this work were prepared by the same general method. Details are given for two representative cases only.

$\{VO(L^1)\}_x$. To a solution of ethanolamine (0.305 g, 0.005 mol) in ethanol (5 cm^3) were added successively a solution of salicylaldihyde (0.61 g, 0.005 mol) in ethanol (7.5 cm^3) and a solution of sodium acetate (0.82 g, 0.01 mol) in water (10 cm^3). An aquous solution of $VOSO_4 \cdot 5H_2O$(1.265 g, 0.005 mol) in water (4 cm^3) was then added dropwise to the stirring mixture. A deep brown coloured solution initially formed and immediately turned to a heavy grey precipitate which was filtered after stirring the solution for one and half hour at room temperature. It was washed thoroughly with water, 50% EtOH and diethyl ether and dried over P_4O_{10}. Yield: 1.09 g (95%).

$VO(L^1)(hq)$. To a methanolic suspension (30 cm^3) of $\{VO(L^1)\}_x$ (0.182 g, 7.9×10^{-4} mol) was added 8-hydroxy quinoline (0.115 g, 7.9×10^{-4} mol). After stirring the reaction mixture for some time a deep coloured solution was formed. The black precipitate was obtained after 4 h with continuous stirring, which was filtered and dried over P_4O_{10}. Yield: 0.22 g (75%).

Electrogeneration of $VO(L)(hq)^-$ *species*. The representative example of $VO(L^1)(hq)$ is described. A solution of 11.22 mg (0.03 mmol) of $VO(L^1)(hq)$ in 15 cm^3 of dry dichloromethane (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) was reduced at -0.63 V *vs* SCE in a nitrogen atmosphere. Electrolysis stopped when 2.837 C had passed. The calculated one-electron coulomb count was 2.895. The reduced solution was used for spectral and electrochemical measurements.

Crystal structure determination

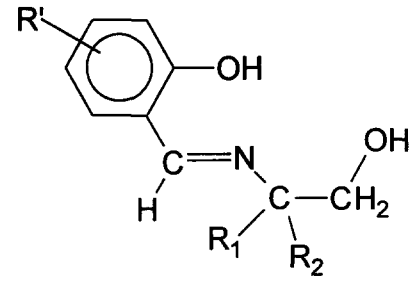
Single crystals of $VO(L^2)(hq)$ ($0.25 \times 0.30 \times 0.34$ mm) were grown by slow evaporation of a methanolic solution. The cell parameters were determined by a least-squares fit of 30 machine centred reflections ($2\theta = 15$–$30°$). Data were collected by the ω-scan method in the range $2\theta = 3$–$55°$ on a Siemens R3m/V diffractometer with graphite-monochromated Mo–Kα radiation ($\lambda = 0.710\ 73$ Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction. Data were corrected for Lorentz-polarization effects. An empirical absorption correction was made on the basis of azimuthal scans [22].

All calculation for data reduction, structure solution and refinement were done on a Micro VaxII computer with the program SHELXTL-PLUS [23] and crystal structure plots were drawn using ORTEP [24]. The structure was solved by direct methods and refined by full-matrix least-squares procedure. All non-hydrogen atoms were made anisotropic. All the hydrogen atoms were located in Fourier-difference maps. Significant crystal data are listed in Table 1.

RESULTS AND DISCUSSION

Synthesis and characterization

Four tridentate Schiff base ligands H_2L^1–H_2L^4 (general abbreviation H_2L, **2**) have been employed in the present work. The bidentate ON coordinating ligand is 8-quinolinol (Hhq). Both H_2L and Hhq bind in the deprotonated form.



H_2L^1 $R_1=R_2=R'=H$

H_2L^2 $R_1=R_2=CH_3$; $R'=H$

H_2L^3 $R_1=R_2=H$; R'=5,6-benzo

H_2L^4 $R_1=R_2=CH_3$; R'=5,6-benzo

2

By applying a procedure used earlier for making aquo species [25] we get the $\{VO(L)\}_x$ species in the case of aminoalcohols in much better yield than reported [26]. This polymerization may be due to strong alkoxide binding. The compounds are characterized by elemental analysis and their magnetic moments are very low (Table 2) due to strong coupling of vanadium atoms [26]. Upon treating a suspension of $\{VO(L)\}_x$ in methanol with an equimolar mixture of Hhq, facile formation of mononuclear electroneutral species $V^{V}O(L)(hq)$ takes place at room

Table 1. Crystal, data collection and refinement parameters for $VO(L^2)(hq)$

Formula	$C_{20}H_{19}N_2O_4V$
Formula weight	402.3
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	12.323(6)
b (Å)	11.673(5)
c (Å)	12.977(8)
β (°)	97.90(4)
V (Å^3)	1849(1.5)
Z	4
D_c (g cm^{-3})	1.445
μ (Mo–Kα)(cm^{-1})	5.65
Temp (°C)	22
Transm. coeff.	0.7005–0.8014
Total no. of reflections	2797
No. of unique reflections	2428
No. of observed reflections [$I > 3.0\sigma(I)$]	1913
No. of parameters refined	244
Final R^a	0.0384
Final $R_w{}^b$	0.0398
Goodness of fit (GOF)^c	1.17

$^a R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$.
$^b R_w = [\Sigma w(\| F_o| - |F_c\|)^2 / \Sigma w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2|F_o| + g|F_o|^2$; $g = 0.0008$.
^{c} The GOF is defined as $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

Table 2. Characterization data

Compounds	Analysis (%)^a C	H	N	IR data^b (cm^{-1}) V=O	C=N	μ_{eff}^c (μ_B)
$\{VO(L^1)\}_x$	46.90 (46.96)	3.84 (3.91)	6.16 (6.09)	960	1625	1.10
$\{VO(L^2)\}_x$	51.10 (51.16)	5.12 (5.04)	5.38 (5.43)	1000	1615	1.15
$\{VO(L^3)\}_x$	55.78 (55.71)	3.87 (3.93)	4.94 (5.00)	970	1625	1.21
$\{VO(L^4)\}_x$	58.41 (58.44)	4.95 (4.87)	4.48 (4.54)	980	1620	1.16
$VO(L^1)(hq)$	57.81 (57.75)	4.00 (4.01)	7.42 (7.49)	962	1630	^{d}
$VO(L^2)(hq)$	59.64 (59.70)	4.80 (4.73)	6.90 (6.96)	952	1620	^{d}
$VO(L^3)(hq)$	62.22 (62.26)	4.08 (4.01)	6.54 (6.60)	962	1620	^{d}
$VO(L^4)(hq)$	63.67 (63.72)	4.59 (4.65)	6.25 (6.19)	962	1615	^{d}

^{a} Calculated values in parentheses.
^{b} In KBr discs.
^{c} At 298 K
^{d} Diamagnetic.

temperature (similar treatment with bipyridyl was failed). The metal is oxidized by aerial oxygen, see below.

Selected characterization data of the complexes are listed in Table 2. The $V^VO(L)(hq)$ complexes display a strong V=O stretch in the region 950–990 cm^{-1} which is suggestive of hexacoordination [13,16b,27]. The complexes have well-defined band near 1620 ± 5 cm^{-1} (Table 2) assigned to $\nu_{C=N}$, also indicating V—N binding. Absence of free ν_{O-H} stretching indicate the vanadium–alkoxy binding.

The d^0 $V^VO(L)(hq)$ complexes are violet and exhibit only intense transitions, the one at lowest energy lying around 500 nm which is assigned to l.m.c.t. excitation of type $p \rightarrow d$ where p and d represent phenolato oxygen lone pair and vanadium $3d$ orbitals, respectively [28]. Intraligand transition ($\pi \rightarrow \pi^*$) were observed near 325 nm. Spectral data were tabulated in Table 3 and representative spectra are display in Fig. 1. The shoulder at ~410 nm for complexes $VO(L^3)(hq)$/

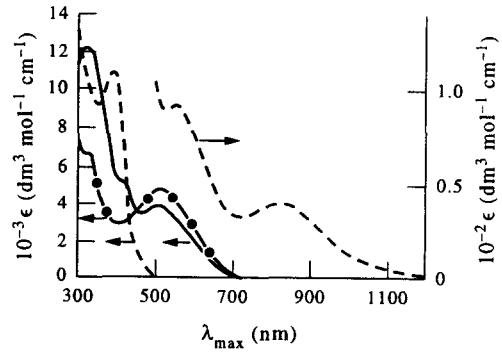


Fig. 1. Electronic spectra of $VO(L^2)(hq)$ (-·-·), $VO(L^4)(hq)$ (—) and $VO(L^2)(hq)^-$ (- - -) in dichloromethane at 298 K.

Table 3. Spectral and electrochemical data[a] at 298 K

Compounds	UV–vis[b] λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1})	VO^{3+}–VO^{2+} couple[b] $E^c_{1/2}$/V (ΔE^d_p/mV), $n^{e,f}$
$VO(L^1)(hq)$	515(4230); 320(6020)	−0.43(150); 0.98
$VO(L^2)(hq)$	515(4800); 325(6590)	−0.43(160); 0.97
$VO(L^3)(hq)$	515(4420); 415[g](4240) 330(12,370)	−0.41(150); 0.98
$VO(L^4)(hq)$	510(3800); 410[g](5250) 320(12,240)	−0.41(100); 0.96

[a] At a platinum disk electrode; supporting electrolyte tetraethylammonium perchlorate (TEAP, 0.1 M); scan rate 50 mV s^{-1}; reference electrode SCE; solute concentration $\sim 10^{-3}$ M.

[b] In dichloromethane.

[c] $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials.

[d] $\Delta E_p = E_{pa} - E_{pc}$.

[e] Constant-potential coulometric data $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated count for one-electron transfer.

[f] Electrolysis performed at 200 mV below E_{pc} for reduction and 200 mV above E_{pa} for oxidation.

[g] Shoulder.

$VO(L^4)(hq)$ are in line with the results described earlier [16c].

Structure and chelate ring planarity of $VO(L^2)(hq)$

The complex crystallizes in the space group $P2_1/n$ and the asymmetric unit consists of a single molecule, a view of which is shown in Fig. 2. Selected bond distances and angles are listed in Table 4. The $[L^2]^{2-}$ ligand acts in the meridional tridentate fashion coordinating *via* alkoxidic and phenolic oxygen atoms and the azomethine nitrogen atom.

In the VL^2 fragment the phenolate imine group is almost perfectly planar (mean deviation ~0.02 Å) and the metal atom is displaced from this plane by ~0.48 Å. The entire V(hq) fragment is highly planar (mean deviation ~0.01 Å) and the oxo oxygen atom also lies on this plane. These two excellent individual planes are inclined to each other by 85.5° to minimize steric interaction. The five-membered ring of the VL^2 fragment is non-planar. This non-planarity may support the inequivalency of the two methyl groups at C(2) atom (*vide infra*).

Table 4. Selected bond distances (Å) and bond angels (°) and their estimated standard deviations for $VO(L^2)(hq)$

V—O(1)	1.594(3)	V—O(2)	1.825(3)
V—O(3)	1.892(3)	V—O(4)	1.863(3)
V—N(1)	2.126(3)	V—N(2)	2.385(4)
O(2)—C(1)	1.392(5)	O(3)—C(11)	1.312(5)
O(4)—C(19)	1.338(5)	N(1)—C(5)	1.283(5)

O(1)—V—O(2)	100.5(1)	O(1)—V—O(3)	98.6(1)
O(1)—V—O(4)	98.2(1)	O(1)—V—N(1)	98.5(1)
O(1)—V—N(2)	173.1(1)	O(2)—V—O(3)	155.0(1)
O(2)—V—O(4)	96.9(1)	O(2)—V—N(1)	78.0(1)
O(2)—V—N(2)	83.5(1)	O(3)—V—O(4)	96.3(1)
O(3)—V—N(1)	83.3(1)	O(3)—V—N(2)	79.3(1)
O(4)—V—N(1)	163.2(1)	O(4)—V—N(2)	75.7(1)
N(1)—V—N(2)	87.8(1)		

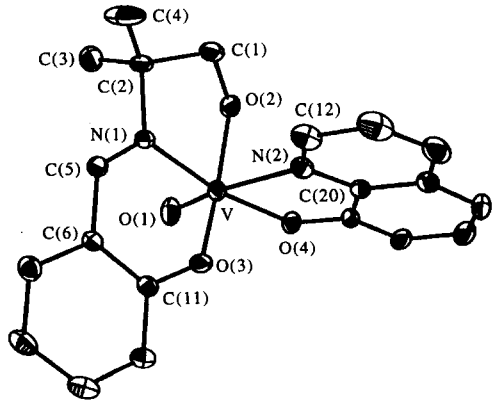


Fig. 2. An ORTEP plot and atom labelling scheme for $VO(L^2)(hq)$. All non-hydrogen atoms are represented by their 30% probability ellipsoids.

The VO_4N_2 coordination sphere is a severely distorted octahedron in which the vanadium atom is displaced by 0.30 Å from the equatorial plane (mean deviation ~0.008 Å) of O(2), O(3), O(4) and N(1) towards the oxo oxygen. The V=O bond length, 1.594(3) Å, is unexceptional and the N(hq) atom lies *trans* to the oxo oxygen O(1) as in other cases [15e, 16b, 16c], and a possible reason for this is that, if $O(hq^-)$ were placed in this position it would have competed with O(1) in $O \rightarrow V$ π-donation. The V—O(phenolate) length in V(hq) fragment is shorter

than the corresponding length in VL^2 fragment, 1.863(3) *vs* 1.892(3) Å. But in $[VO(L^2)(hquin)]$ [15c] these two lengths were comparable, 1.843(4) *vs* 1.857(3) Å. The variation in V—O(phenolate) bond length in VL^2 fragment is due to the *trans*-effect. In the present complex the strongly donating alkoxide oxygen rather than weakly donor carboxyl oxygen is placed *trans* to the phenolic oxygen. The V—O bond lengths of these two complexes also follow the order: alkoxidic ($V—O_{alk}$) < phenoxidic ($V—O_{phen}$) < carboxylic ($V—O_{carb}$). In each of the three cases, the oxygen function is monoanionic and the observed bond length trend is believed to reflect the $O \rightarrow V$ π donation (alkoxidic > phenoxidic > carboxylic). Interestingly it is noted that there is a parallel relationship obtained between the O—V length and acidity of the function concerned (carboxylic > phenolic > alcoholic).

Electrochemistry. Electrode reaction and stability of electrogenerated species

The complexes display a well defined cyclic voltammetric response in dichloromethane solution at platinum electrode due to the VO^{3+}–VO^{2+} couple, eq. (1). Representative voltammogram is displayed in Fig. 3, and reduction potential data are set out in Table 3.

$$V^{V}O(ONO)(ON) + e^- \rightleftharpoons V^{IV}O(ONO)(ON)^- \quad (1)$$

The VO(L)(hq) complexes display a quasi-reversible one-electron cyclic voltammetric response in CH_2Cl_2 near −0.43 V *vs* the SCE (Table 3). This value is much more negative than the carboxylate and phenolate bound VO^{3+} species [15c,16b]. This indicates that the alkoxo group favour V^V centre more than the carboxylate counterpart. Coulommetric reduction at −0.63 V leads to quantitative transfer of one-electron affording a yellowish green solution which has the same voltammogram (initial scan anodic) as the parent solution (initial scan cathodic). Upon reoxidation at −0.23 V the parent VO(L)(hq) complex (violet) is fully regenerated. The electrogenerated yellowish green solution contain $V^{IV}O(L)(hq)^-$ and the observed voltammetric response is due to the couple VO(L)(hq)–$VO(L)(hq)^-$. The reduced complex is air-sensitive, being rapidly transformed into $V^VO(L)(hq)$. This is consistent with the low reduction potential of the VO(L)(hq)–$VO(L)(hq)^-$ couple and explain the synthesis of VO(L)(hq) from VO^{2+} precursors.

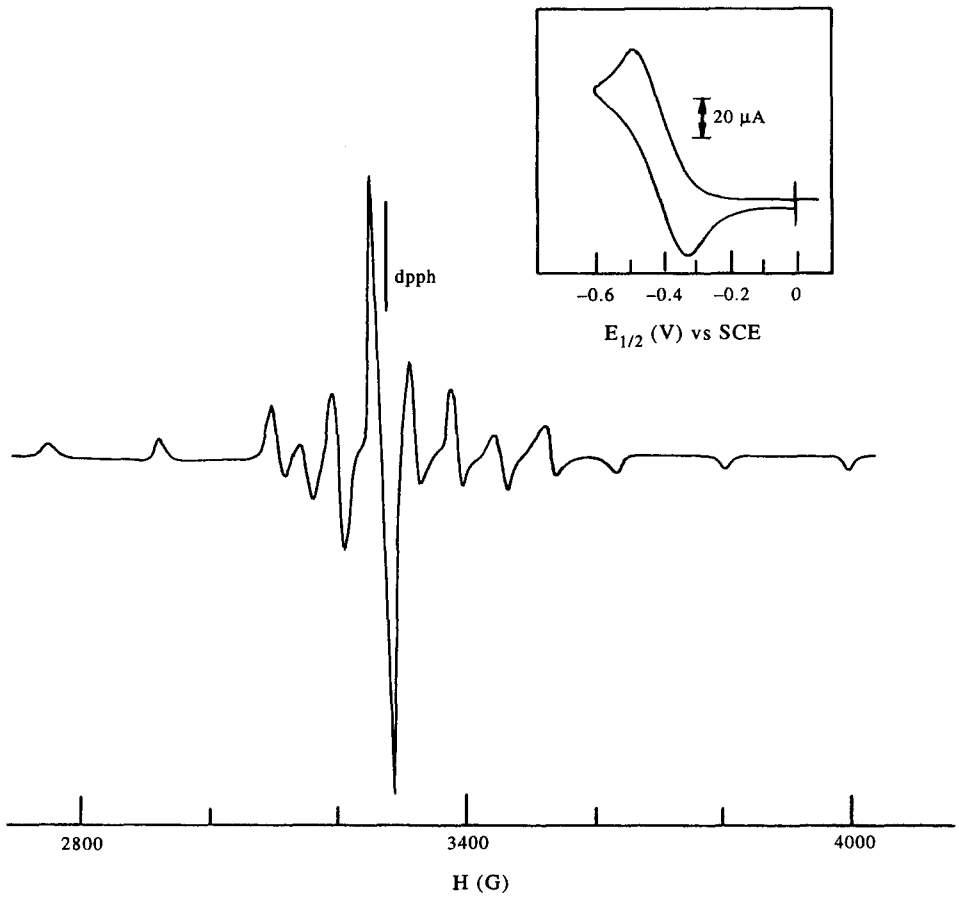


Fig. 3. X-Band EPR spectra of electrogenerated $VO(L^2)(hq)^-$ in dichloromethane at 77 K; dpph = diphenylpicrylhydrazyl. Cyclic voltammogram of $VO(L^2)(hq)$ in dichloromethane (0.1 mol dm^{-3} Et_4NClO_4) at 298 K is shown in the inset.

Table 5. Characterization data for electrogenerated $VO(L^2)(hq)^-$ species in CH_2Cl_2

Compounds	UV–vis λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	EPR at 77 K $g_\parallel$ (10^4 $A_\parallel$/cm^{-1})	$g_\perp$ (10^4 $A_\perp$/cm^{-1})
$VO(L^1)(hq)^-$	820(60), 550(160), 360(10,000)	1.954(156.9)	1.977(56.0)
$VO(L^2)(hq)^-$	825(40), 555(85), 390(10,850)	1.953(163.1)	1.983(56.1)
$VO(L^3)(hq)^-$	825(90), 550(390), 370(15,000)	1.950(161.1)	1.983(54.2)
$VO(L^4)(hq)^-$	850(60), 545(245), 370(16,000)	1.953(162.7)	1.983(55.5)

Frozen solutions (77 K) of electrogenerated $VO(L)(hq)^-$ exhibit axial EPR spectra with well resolved ^{51}V hyperfine lines. Spectral parameters of the complexes are listed in Table 5 and representative spectra is displayed in Fig. 3. The $g_\parallel < g_\perp$ and $A_\parallel \gg A_\perp$ relationships are normal [29] for the axially compressed d^1_{xy} configuration. Curiously the g and A values lie close to those of reduced bromoperoxidase at low pH (citrate buffer) [30]. The $VO(L)(hq)^-$ species show a ligand-field band near 820 nm (Table 5) presumably due to $d_{xy} \rightarrow d_{xz}$, d_{yz} excitation and representative spectra is displayed in Fig. 1.

Trends of reduction potentials: $E_{1/2} - pK_a$ correlation

The $E_{1/2}$ values are much lower than the corresponding phenolate [16b] and carboxylate [15c,16b] binding complexes due to alkoxide binding. A more subtle variation of $E_{1/2}$ is observed when the bidentate ligand is kept invariant(hq^-). The $E_{1/2}$ values follow the order $O^aN^mO^p < O^pN^mO^p < O^cN^mO^p$ and the values are respectively around -430 mV, -120 mV and 70 mV and the difference between the $O^aN^mO^p - O^cN^mO^p$ is 500 mV for hq^- (meaning of superscripts: a = alkoxidic, p = phenoxidic, c = carboxylic, m = azomethine). This trend can be rationalized by extending a thermodynamic model previously employed in the case of metal reduction potential of Mn^{IV} [32] and V^V [16b] complexes. The essential findings was that the $E_{1/2}$'s correlate with the pK_a's (related to σ-donating strength) of coordinating groups.

The concerned pK_a values for the present purpose are EtOH, 15.9; PhOH, 10.0; PhCOOH, 4.2 and CH_3COOH, 4.75 [33,34]. Indeed the plot of above pK_a's *vs* the vanadium(V)–vanadium(IV) formal potentials of various complexes: VO(amc)(hq) [16b], $VO(L^1)$(hquin) [15c], VO(amp)(hq) [16b] and $VO(L^1)(hq)$ is satisfactorily linear. The correlation constant being 0.99 for the couple of eq. (1). For this qualitative rationalization and for approximate prediction of reduction potentials within families of related complexes we extend our study to V^V-bound alkoxide complexes.

Solution stability

^1H NMR spectral data suggest the binding nature observed in single crystal X-ray study also retained in solution. We consider the 300 MHz ^1H NMR spectra in dry $CDCl_3$ solvent in which the $VO(L^2)(hq)$ complex have good solubility. Signals were assigned (Table 6) on the basis of intensity, spin–spin structure and chemical shift. Some selected peak positions are displayed in Fig. 4. The azomethine proton, H(5), is a singlet, the two protons of—CH_2O fragment on five-membered ring (H(1), H(1A)) and aromatic protons (H(7)—H(18)) mostly appear as a series of well resolved multiplets. The down field shift and coupling between the two non-equivalents protons of the —CH_2O group of aminoalcohol represent its binding with VO^{3+} species.

The chemical shift value of the singlet azomethine proton, doublet and triplet nature of aromatic salicylaldimine protons also support their binding. The inequivalency of the two methyl groups on C(2) atom

Table 6. Proton NMR spectral data[a] in $CDCl_3$ at 298 K

	δ/ppm (J/Hz)
Protons	$VO(L^2)(hq)$
H(1)	4.54 (d, 9.2)
H(1A)	5.01 (d, 9.2)
H(5)	8.59 (s)
H(7)	7.45 (d, 7.7)
H(8)	6.81 (t, 7.5)
H(9)	7.56 (t, 8.0)
H(10)	6.65 (d, 8.5)
H(12)	7.84 (d, 4.5)
H(13)	7.21 (dd, 8.1[b], 4.5[c])
H(14)	8.11 (d, 8.6)
H(16)	7.33 (d, 8.5)
H(17)	7.35 (t, 7.8)
H(18)	7.17 (d, 7.6)

[a] The numbering system corresponds to that in Fig. 3 e.g., H(1) and H(1A) represents proton attached to C(1); s = singlet; d = doublet; t = triplet.

[b] ^3J[H(13)–H(14)].

[c] ^3J[H(12)–H(13)].

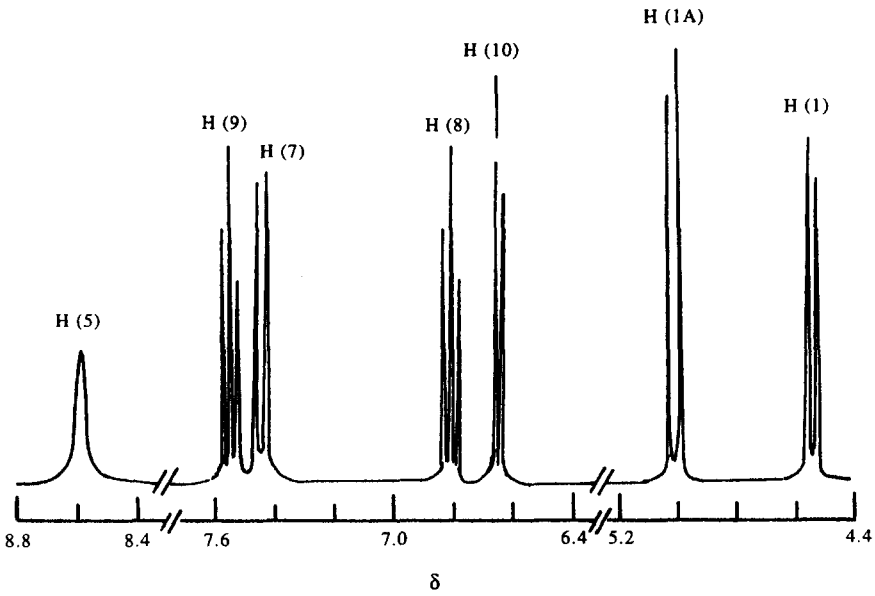


Fig. 4. Proton NMR spectra (in $CDCl_3$) of the H(5), H(7)–H(10) and H(1)–H(1A) of $VO(L^2)(hq)$. The numbering system corresponds to that in Fig. 3, e.g. H(1) and H(1A) represent protons attached to C(1).

is also retained in solution giving rise to two methyl signals at 1.79 and 1.58 ppm. The resonances of the protons followed the same pattern as in [VO(L)(hquin)] [15c] complexes.

CONCLUSION

The lowering of $E_{1/2}$ values indicate the alkoxide bound VO^{3+} stabilization. The stability difference is reflected in the large difference (500 mV) of $E_{1/2}$ values of the VO^{3+}–VO^{2+} couples between alkoxidic and carboxylic binding complexes. The EPR spectra of the electrogenerated $VO(L)(hq)^-$ corresponds to the axially compressed d^1_{xy} configuration. In accordance with our previous work [15c,16b] it is noted that for fixed bidentate ligation, the $E_{1/2}$ value increases significantly when O^a is replaced by O^p and O^p is replaced by O^c in ONO types tridentate ligand. The increments are approximately additive and the $E_{1/2}$ values correlate linearly with the pK_a of the variable coordination sites.

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