Synthesis and Structure of Carboxyl-bonded Oxovanadium(v) Complexes incorporating α-Amino Acid Salicylaldiminates and Quinolin-8-olate

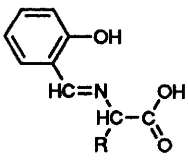
Sujit Mondal, Somnath Dutta and Animesh Chakravorty *
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

The complexes [VO(L^1)(hquin)] and [VO(L^2)(hquin)] incorporating *N*-salicylidene-glycinate and -L-phenylalaninate respectively have been synthesised in excellent yields from [V^{IV}O(L)(H$_2$O)] and quinolin-8-ol (Hhquin) in air which acts as the oxidant. The crystal structure of [VO(L^2)(hquin)] revealed tridentate ONO and bidentate ON binding by [L^2]$^{2-}$ and hquin$^-$ respectively. The V–O (carboxylate) bond length is longer than V–O (phenolate) by ≈0.1 Å. The CD spectrum of [VO(L^2)(hquin)] in the visible region revealed the composite nature of the phenolato→vanadium charge-transfer band. The absolute configuration of [VO(L^2)(hquin)] is *CS* both in the crystalline state and in solution. In CDCl$_3$ solution the ^{1}H NMR spectrum of the complex shows that the amino acid side chain has the same conformation as that in the crystal lattice. The complexes display the quasi-reversible one-electron couple [VO(L)(hquin)]–[VO(L)(hquin)]$^-$ near 0.0 V *vs.* saturated calomel electrode. Electrogenerated solutions of [VO(L)(hquin)]$^-$ are EPR-active corresponding to a d$_{xy}$^{1} configuration.

This work stems from our interest in the chemistry of new oxovanadium systems.[1–5] The binding of the monooxovanadium(v) motif, VO^{3+}, to carboxyl oxygen atoms is of current interest but authentic species having this structural feature are rare.[5–10] We have been searching for species of this category.[5] Herein salicylaldimines of α-amino acids are utilised as potential carboxyl-co-ordinating ligands. To assist stabilisation[4,5,11] of the oxovanadium(v) state, quinolin-8-ol (Hhquin) is chosen as the coligand. Complexes of type [VO(L)(hquin)] have been successfully assembled with salicylaldimines of glycine and L-phenylalanine. The crystal structure of the latter complex has been determined. The choice of L-phenylalanine was motivated by several objectives: (*i*) to observe the extent of chiral selectivity imposed on the metal by the predetermined chirality of the amino acid residue; (*ii*) to examine the CD spectrum in the ligand-to-metal charge-transfer (l.m.c.t.) region; and (*iii*) to compare the conformation of the amino acid side chain in the solid state (X-ray diffraction) with that in solution (^{1}H NMR spectroscopy). The [VO(L)(hquin)] complexes undergo facile electroreduction to air-sensitive EPR-active oxovanadium(IV) congeners, [VO(L)(hquin)]$^-$.

Results and Discussion

Synthesis and Characterisation.—The salicylaldimines of glycine and L-phenylalanine are abbreviated as H$_2$L^1 and H$_2$L^2 respectively. Upon mixing [V^{IV}O(L)(H$_2$O)] precursors[12–14] with quinolin-8-ol in methanol under ambient conditions the violet [VO(L)(hquin)] complexes are afforded in excellent yields. The lowering of metal reduction potential (see below) due to hquin$^-$ chelation is a crucial factor which drives the synthesis *via* spontaneous oxidation of co-ordinated VO^{2+} to VO^{3+} by aerial oxygen.



R	
H	H$_2$L^1
CH$_2$Ph	H$_2$L^2

Selected spectral data for the complexes are collected in Table 1. The IR spectra display monooxovanadium and asymmetric monoco-ordinated carboxyl stretches as strong bands near 975 and 1620 cm^{-1} respectively. The complexes absorb strongly in the visible region with a band near 560 nm (Fig. 1) which is assigned to l.m.c.t. excitation of type p→d where p and d represent phenolato oxygen lone-pair and vanadium 3d orbitals respectively.[15] Bond-length data support the existence of V–O (phenolate) back bonding (see below).

In the CD spectrum of [VO(L^2)(hquin)] there is a strong positive peak at 625 nm and a weaker negative peak at 435 nm (Fig. 1). It seems likely that the p→d excitation has at least two components which are not resolved in absorption. An intraligand absorption shoulder near 325 nm becomes a well defined positive peak in the CD spectrum (Fig. 1).

Structure and Chiral Configuration of [VO(L^2)(hquin)].—The complex crystallizes in the polar space group *P*2$_1$ 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 2. The [L^2]$^{2-}$ ligand acts in the meridional tridentate fashion co-ordinating *via* carboxyl and phenolic oxygen atoms and the azomethine nitrogen atom.

In the VL^2 fragment, the V–O (carboxylate) bond length, 1.935(4) Å, is ≈0.1 Å longer than V–O (phenolate), 1.857(3) Å. Owing to the low basicity of carboxyl oxygen, O→V back bonding in the V–O (carboxyl) bond can at best be weak. On the other hand, the phenolate oxygen basicity ensures significant back bonding in the V–O (phenolate) bond as revealed by the bond-length data. The charge-transfer (O→V) spectra considered above are consistent with this.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Spectral and electrochemical data[a] at 298 K

Compound	UV/VIS[b] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	CD[b] λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1})	VO^{3+}–VO^{2+} couple[b] $E_{\frac{1}{2}}$[d]/V(ΔE_p[e]/mV), n[f]	IR data[c]/cm^{-1} VO, CO_2^-
[VO(L^1)(hquin)]	550(3620), 325[g](5700)	—	0.07(140), 0.98	965, 1610
[VO(L^2)(hquin)]	575(4570), 330[g](4860)	625(136), 435(−34), 340(206)	−0.06(120), 0.97	980, 1625

[a] At a platinum-disk electrode; supporting electrolyte NEt_4ClO_4 (0.1 mol dm^{-3}); scan rate 50 mV s^{-1}; reference electrode SCE; solute concentration $\approx 10^{-3}$ mol dm^{-3}. [b] In dichloromethane. [c] In KBr discs. [d] Calculated as the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [e] $\Delta E_p = E_{pa} - E_{pc}$. [f] $n = Q/Q'$ where Q is the observed coulomb count and Q' the calculated count for one-electron transfer. [g] Shoulder.

Table 2 Selected bond lengths (Å) and angles (°) for [VO(L^2)(hquin)]

V–O(1)	1.577(4)	V–O(5)	1.843(4)
V–O(2)	1.935(4)	V–N(1)	2.082(4)
V–O(4)	1.857(3)	V–N(2)	2.382(5)
O(2)–C(1)	1.315(7)	O(3)–C(1)	1.201(6)
O(4)–C(16)	1.340(7)	O(5)–C(24)	1.323(7)
N(1)–C(10)	1.278(6)		
O(1)–V–O(2)	100.3(2)	O(1)–V–O(4)	98.3(2)
O(2)–V–O(4)	155.5(2)	O(1)–V–O(5)	96.5(2)
O(2)–V–O(5)	90.5(2)	O(1)–V–O(5)	103.0(2)
O(1)–V–N(1)	98.6(2)	O(2)–V–N(1)	76.1(2)
O(4)–V–N(1)	85.5(2)	O(5)–V–N(1)	161.4(2)
O(1)–V–N(2)	171.8(2)	O(2)–V–N(2)	82.8(2)
O(4)–V–N(2)	81.0(2)	O(5)–V–N(2)	75.8(2)
N(1)–V–N(2)	89.5(2)		

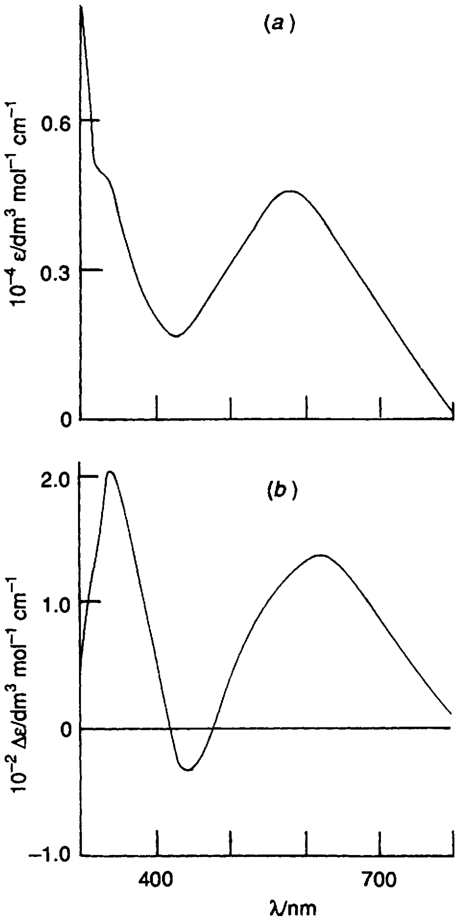


Fig. 1 Electronic (*a*) and CD spectra (*b*) of [VO(L^2)(hquin)] in dichloromethane solution

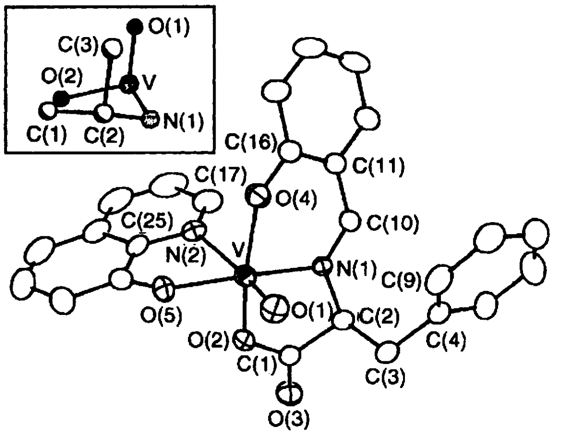


Fig. 2 An ORTEP[16] plot and atom-labelling scheme for [VO(L^2)(hquin)]. All non-hydrogen atoms are represented by their 30% probability ellipsoids. The *endo* configuration is shown in the inset

The [L^2]$^{2-}$ ligand is non-planar but the phenolate imine and the CCO_2 fragments constitute two good individual planes (mean deviation 0.03 Å) mutually rotated by 37.4° along the N(1)–C(2) bond. The metal atom is displaced from the phenolate imine chelate ring by ≈0.29 Å. The hquin$^-$ ligand is excellently planar but the metal atom is shifted from this plane by ≈0.24 Å. All the chelate rings in the structure are thus non-planar and the VO_4N_2 co-ordination sphere is a severely distorted octahedron. The N (hquin$^-$) atom lies *trans* to the oxo oxygen O(1) as in other cases,[4,5,11] and a possible reason for this is that if O (hquin$^-$) were placed in this position it would have competed with O(1) in O→V back bonding. The V–O (phenolate) lengths corresponding to [L^2]$^{2-}$ and hquin$^-$ are closely similar.

The V=O bond length, 1.577(4) Å, is unexceptional[4,5,17,18] and the V–N (hquin) bond lying *trans* to it is weak. The metal atom is shifted towards the oxo oxygen atom by 0.28 Å from the plane (mean deviation 0.02 Å) defined by the three co-ordinated oxygen atoms and the nitrogen atom of [L^2]$^{2-}$.

The absolute configuration of L-phenylalanine is *S* and it is logical to assume that in the synthesis of [VO(L^2)(hquin)] this configuration is conserved. The signs of the atomic co-ordinates of [VO(L^2)(hquin)] were chosen to conform to the *S* configuration of the phenylalanine residue. The chiral configuration of the metal centre was then viewed down the unique V=O axis. The priority sequence[19] [O(2) > O(5) > O(4) > N(1)] of the four atoms on the equator is found in a clockwise manner. The absolute configuration of the vanadium co-ordination sphere is thus *C*.[19] In this configuration the V=O axis lies *endo* to the C(2)–C(3) bond (inset in Fig. 2). The structurally characterised [VO(L^2)(hquin)] complex therefore has *CS* configuration. We have not found any concrete evidence for the presence of the possible *AS* diastereoisomer [V=O and C(2)–C(3) configured oxo] either in the solid state or in solution (see below).

Table 3 Proton NMR spectral data[a] in $CDCl_3$ at 298 K

Proton	δ(J/Hz) $[VO(L^1)(hquin)]$	 $[VO(L^2)(hquin)]$
H(2)	4.78 (d, 14.0)	4.70 (dd, 11.1,[b] 3.4[c])
H(2A)	5.32 (d, 14.0)	—
H(3)	—	3.69 (dd, 13.7,[d] 11.2[b])
H(3A)	—	3.76 (dd, 13.7,[d] 3.5[c])
H(4)–H(9)	—	7.30 (cm)
H(10)	8.79 (s)	7.47 (s)
H(12)	7.59 (d, 7.6)	7.13 (d, 7.7)
H(13)	6.99 (t, 7.4)	6.80 (t, 7.4)
H(14)	7.63 (t, 8 0)	7.59 (t, 8.0)
H(15)	6.74 (d, 8.4)	6.60 (d, 8.4)
H(17)	7.84 (d, 4.8)	7.61 (d, 5.0)
H(18)	7.26 (dd, 8.3,[e] 4.5[f])	7.08 (dd, 8.2,[e] 4.6[f])
H(19)	8.14 (d, 8.1)	8.0 (d, 8.2)
H(21)	7.47 (d, 8.4)	7.40 (d, 8.3)
H(22)	7.50 (t, 7.7)	7.37 (t, 7.8)
H(23)	7.13 (d, 7.7)	7.02 (d, 7.8)

[a] The numbering system corresponds to that in Fig. 1, *e.g.*, H(3) and H(3A) represent protons attached to C(3); cm = complex multiplet; d = doublet; s = single; t = triplet. [b] ^3J[H(2)–H(3)]. [c] ^3J[H(2)–H(3A)]. [d] ^2J[H(3)–H(3A)]. [e] ^3J[H(18)–H(19)]. [f] ^3J[H(17)–H(18)].

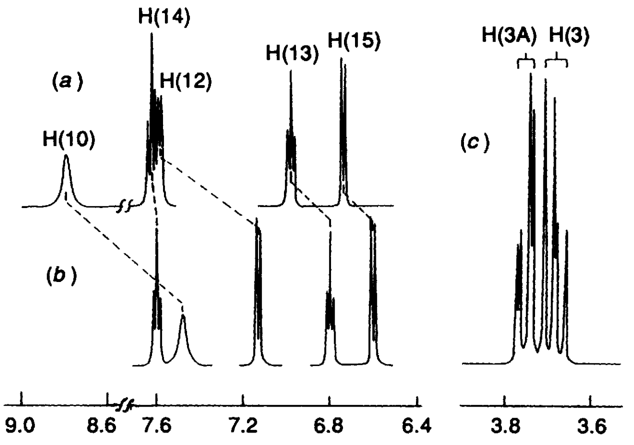
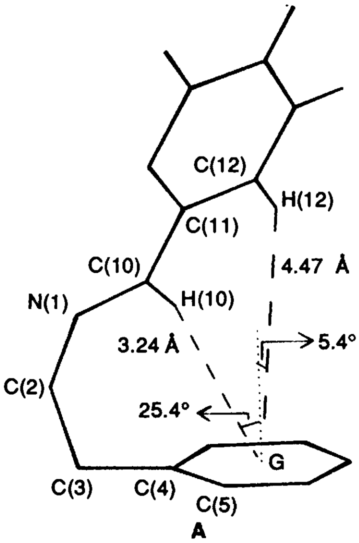


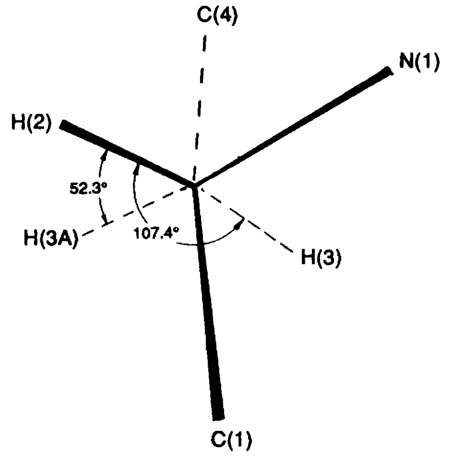
Fig. 3 Proton NMR spectra (in $CDCl_3$) of the azomethine and salicyl protons of (*a*) $[VO(L^1)(hquin)]$, (*b*) $[VO(L^2)(hquin)]$ and of the methylene protons of (*c*) $[VO(L^2)(hquin)]$

Solution Structure.—Proton chemical shifts due to ring currents of the CH_2Ph phenyl group have provided a unique opportunity to define the side-chain conformation in solution. The 500 MHz ^1H NMR spectra of the complexes have been examined in $CDCl_3$. Spectral data are listed in Table 3. While the azomethine proton, H(10), is a singlet, the aliphatic [H(2), H(3)] and aromatic [H(5), H(23)] protons mostly appear as a series of well resolved multiplets. The salicylaldimine protons H(10), H(12)–H(15) in $[VO(L^2)(hquin)]$ are systematically shifted upfield [(Fig. 3(*a*) and 3(*b*)] relative to those of $[VO(L^1)(hquin)]$. The shifts are: H(10), 1.32; H(12), 0.46; H(13), 0.19; H(14), 0.04 and H(15), 0.14 ppm. The shift pattern provides a clue to the solution conformation of the coordinated L^2 fragment.

We first consider the cases of H(10) and H(12) for which the shifts are particularly large. In the crystal structure these protons lie at distances of 3.24 and 4.47 Å respectively from the centroid (G) of the CH_2Ph phenyl ring, as in **A**. The H(12) ··· G and H(10) ··· G lines are tilted from the normal (dotted line in **A**) to this phenyl ring at G by 5.4 and 25.4° respectively. The two protons thus lie well within the ring-current shielding cone of the CH_2Ph aromatic ring. Assuming crystal coordinates to apply and using the available isoshielding ρ *vs.* z plots (where ρ and z are the usual cylindrical coordinates)[20] constructed with the help of free-electron theory, it is estimated that the upfield shifts due to the ring current should be 1.3 for H(10) and 0.6 ppm for H(12). The H(13)–H(15) protons also lie within the shielding cone but their location corresponds to much lower estimated shifts (0.1–0.2 ppm). In view of the many approximations inherent in the theory used[20,21] the agreement between the calculated shifts and those observed with reference to $[VO(L^1)(hquin)]$ which has no corresponding ring current is indeed very satisfactory. Thus the conformation of the amino acid side chain of $[VO(L^2)(hquin)]$ is virtually unaffected in going from the solid to the solution phase.



A



B

This is also consistent with the spectrum of the ethane fragment, $CHCH_2$ (Table 3), the CH_2 region of which is displayed in Fig. 3(*c*). The CH_2 protons [H(3), H(3A)] are inequivalent (^2J 13.7 Hz) and their vicinal couplings (^3J) to H(2) are 11.2 and 3.5 Hz respectively. Vicinal couplings are sensitive to dihedral angles.[22,23] In crystalline $[VO(L^2)(hquin)]$ the dihedral angles corresponding to H(2)–H(3) and H(2)–H(3A) ^3J couplings are respectively 170.4 and 52.3° as depicted in **B**, which shows a view down the C(2)–C(3) bond. The corresponding ^3J values computed from a modified Karplus equation[22] are 13.3 and 3.0 Hz respectively. The agreement with the experimental values is satisfactory.

The ^1H NMR spectra of solutions prepared from discrete crystals of $[VO(L^2)(hquin)]$ and from bulk samples (isolated in

Table 4 Characterisation data for electrogenerated [VO(L)(hquin)]$^-$ species in CH_2Cl_2

Compound	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)(hquin)]$^-$	840(30), 390(4450)	1.951(163.8)	1.985(57.7)
[VO(L^2)(hquin)]$^-$	830(44), 370(4635)	1.955(165.5)	1.984(58.1)

≈90% yield in synthesis) gave rise only to the lines stated in Table 3. The CD spectra of solutions of crystals and bulk samples were also superposable. Evidently we are able to observe only the *CS* configuration of the complex as identified in the crystal lattice. The *AS* diastereoisomer is at best a minor constituent in synthesis and we have not succeeded in isolating it.

This finding can be contrasted with two reported results both involving complexes of the salicylaldimine (H_2L^3) of L-alanine. In the case of [V^{V}O(L^3)(OMe)(MeOH)], whereas a crystal containing a single diastereoisomer was identified, solution NMR results of bulk samples were consistent with the presence of two diastereoisomers in 3:4 ratio.[9] On the other hand in the VO^{2+} complex [V^{IV}O(L^3)(bipy)] (bipy = 2,2′-bipyridine) the two diastereoisomers coexist in equal proportions within the crystal lattice.[24] Diastereoisomeric stability is evidently variable in these systems and more systems need to be examined in order to define the controlling factors.

Metal Redox.—The [VO(L)(hquin)] complexes display a quasi-reversible one-electron cyclic voltammetric response in dichloromethane near 0.0 V *vs.* the saturated calomel electrode (SCE) (Table 1). Coulometric reduction at −0.30 V leads to quantitative transfer of one electron affording a green solution which has the same voltammogram (initial scan anodic) as the parent solution (initial scan cathodic). Upon reoxidation at +0.25 V the parent [VO(L)(hquin)] complex (violet) is fully regenerated. The electrogenerated green solutions contain [V^{IV}O(L)(hquin)]$^-$ and the observed voltammetric response is due to the couple [VO(L)(hquin)]–[VO(L)(hquin)]$^-$. The reduced complex is air-sensitive, being rapidly transformed into [V^{V}O(L)(hquin)]. This is consistent with the low reduction potential of the [VO(L)(hquin)]–[VO(L)(hquin)]$^-$ couple and explains the synthesis of [VO(L)(hquin)] from [V^{IV}O(L)(H$_2$O)] and Hhquin.

Frozen solutions (77 K) of electrogenerated [VO(L)(hquin)]$^-$ exhibit axial EPR spectra with well resolved ^{51}V hyperfine lines (Table 4). The $g_{\parallel} < g_{\perp}$ and $A_{\parallel} > A_{\perp}$ relationships are normal[1,4,5,25] for the axially compressed $d_{xy}{}^1$ configuration. Curiously, the *g* and *A* values lie close to those of reduced bromoperoxidase at low pH (citrate buffer).[26] The [VO(L)(hquin)]$^-$ species show a ligand-field band near 835 nm (Table 4) presumably due to $d_{xy} \longrightarrow d_{xz}, d_{yz}$ excitation.[27]

Conclusion

Mixed ligation of salicylaldimines of glycine/L-phenylalanine and quinolin-8-ol has afforded carboxyl-bonded VO^{3+} in the form of [VO(L)(hquin)] which displays a phenolate→V l.m.c.t. band which appears to be composite in the CD spectrum of [VO(L^2)(hquin)]. The absolute configuration of [VO(L^2)(hquin)] in the crystalline state and in solution is *CS* showing that the amino acid chirality controls the metal chirality. The [VO(L)(hquin)]–[VO(L)(hquin)]$^-$ couple has low $E_{\frac{1}{2}}$ values (0.0 V) and the EPR-active reduced complex is spontaneously oxidised by air to the parent [VO(L)(hquin)] complex.

The paucity of authentic carboxyl-co-ordinated VO^{3+} species is probably more due to the lack of research than to any inherent incompatibility. By choosing suitable coligands which lower the VO^{3+}–VO^{2+} reduction potential it should be possible to generate carboxyl-bonded VO^{3+} species in a systematic manner.

Experimental

Materials.—Electrochemical grade dichloromethane, methanol and tetraethylammonium perchlorate were obtained as before.[28] All other chemicals and solvents were of analytical grade used as received.

Physical Measurements.—Electronic spectra were recorded with a Hitachi 330 spectrophotometer, CD spectra on a JASCO 500 spectropolarimeter, infrared spectra on a Perkin-Elmer 783 spectrophotometer, and EPR spectra at X-band on a Varian E-109C spectrometer equipped with a quartz Dewar for low-temperature (77 K) measurements. Diphenylpicrylhydrazyl (g = 2.0037) was used to calibrate the latter spectra. Electrochemical measurements were performed on a par Model 370–4 system as previously.[29] All potentials reported in this work are uncorrected for junction contribution. A Perkin-Elmer elemental analyzer was used to collect microanalytical data (C,H,N).

Preparations.—The complexes reported were prepared by the same general method using [VO(L)(H$_2$O)][13] as the starting material.

*Oxo(quinolin-8-olato)(*N*-salicylidene-*L*-phenylalaninato)vanadium(*V*)*, [VO(L^2)(hquin)]. A mixture of [VO(L^2)(H$_2$O)] (0.10 g, 0.28 mmol) and Hhquin (0.041 g, 0.28 mmol) was dissolved in methanol (10 cm^3). The resulting solution upon stirring for 0.5 h afforded a dark solid. It was filtered off, washed throughly with methanol and dried *in vacuo* over P_4O_{10}. Yield: 0.12 g (88%) (Found: C, 62.70; H, 3.90; N, 5.95. Calc. for $C_{25}H_{19}N_2O_5V$: C, 62.75; H, 3.95; N, 5.85%).

The compound [VO(L^1)(hquin)] was prepared similarly in 90% yield (Found: C, 55.75; H, 3.45; N, 7.15. Calc. for $C_{18}H_{13}N_2O_5V$: C, 55.65; H, 3.35; N, 7.20%).

Electrogeneration of [VO(L)(hquin)]$^-$.—The representative example of [VO(L^2)(hquin)]$^-$ is described. A solution of [VO(L^2)(hquin)] (24 mg, 0.05 mmol) in dry dichloromethane (15 cm^3, 0.1 mol dm^{-3} NEt$_4$ClO$_4$) was reduced at −0.30 V *vs.* SCE in a nitrogen atmosphere. Electrolysis stopped when 4.71 C had passed. The calculated one-electron coulomb count is 4.85. The reduced solution was used for spectral measurements.

Analysis of NMR Spectra.—Measurements were made on a 500 MHz Bruker FT spectrometer in CDCl$_3$ solution at room temperature. The signals were assigned to individual protons on the basis of chemical shifts, spin–spin structure, substituent effects and comparison with other complexes, *e.g.* [VO(L)(OCH$_2$CH$_2$OH)].[30] The ring-current shifts were estimated as follows. The crystal coordinates were first transformed into an orthogonal coordinate system with the origin at the centroid (G in A) of the CH$_2$Ph benzene ring. These were then further transformed into the corresponding cylindrical coordinate system[31] which is normally used in ring-current theories.[20,21] The cylindrical ρ and z parameters were expressed in units of C–C distance (1.39 Å) and the shifts were estimated from interpolation of the isoshielding ρ *vs.* z plots.[20] The calculated

Table 5 Crystal data for [VO(L^2)(hquin)]

Formula	$C_{25}H_{19}N_2O_5V$
M	478.4
Crystal size/mm	0.12 × 0.26 × 0.64
Crystal system	Monoclinic
Space group	$P2_1$ (no. 4)
a/Å	11.870(7)
b/Å	6.632(3)
c/Å	13.932(9)
β/°	102.21(5)
U/Å^3	1072(1)
Z	2
D_c/g cm^{-3}	1.482
μ(Mo-Kα)/cm^{-1}	5.04
F(000)	492
2θ range/°	3–55
Total number of reflections	2828
Number of unique reflections	2699
Number of observed reflections [$I > 2\sigma(I)$]	1850
g in $w = 1/[\sigma^2(\|F\|) + g\|F\|^2]$	0.0007
Number of refined parameters	297
R	4.36
R'	4.59
Goodness of fit	1.07
Maximum and mean Δ/σ	0.001, 0.000
Data-to-parameters ratio	6.2:1
Maximum, minimum difference peaks/e Å^{-3}	0.31, −0.27

Table 6 Atomic coordinates (× 10^4) for [VO(L^2)(hquin)]

Atom	x	y	z
V	−2312(1)	0	−2101(1)
O(1)	−1131(3)	1110(6)	−2071(3)
O(2)	−2027(3)	−1134(6)	−792(2)
O(3)	−1193(3)	−3457(8)	266(3)
O(4)	−2860(3)	6(8)	−3452(2)
O(5)	−3062(3)	2165(6)	−1689(3)
N(1)	−1783(3)	−2938(6)	−2293(3)
N(2)	−4214(4)	−1209(8)	−2153(3)
C(1)	−1429(4)	−2795(9)	−554(4)
C(2)	−1036(4)	−3767(9)	−1409(3)
C(3)	240(4)	−3190(9)	−1378(3)
C(4)	608(4)	−3797(11)	−2305(4)
C(5)	967(5)	−5730(12)	−2429(5)
C(6)	1263(6)	−6335(15)	−3284(6)
C(7)	1188(5)	−4965(23)	−4037(5)
C(8)	837(6)	−3017(18)	−3938(5)
C(9)	543(5)	−2432(13)	−3057(4)
C(10)	−2034(4)	−4033(9)	−3064(3)
C(11)	−2738(4)	−3393(8)	−3984(3)
C(12)	−2990(5)	−4800(13)	−4749(3)
C(13)	−3669(6)	−4247(12)	−5642(4)
C(14)	−4085(5)	−2332(13)	−5778(4)
C(15)	−3834(5)	−915(11)	−5052(4)
C(16)	−3142(4)	−1426(9)	−4140(4)
C(17)	−4805(5)	−2832(11)	−2455(4)
C(18)	−5967(6)	−3111(16)	−2353(6)
C(19)	−6461(6)	−1645(18)	−1887(6)
C(20)	−5863(5)	100(18)	−1562(4)
C(21)	−6305(7)	1675(18)	−1054(6)
C(22)	−5637(8)	3252(18)	−754(5)
C(23)	−4504(7)	3492(13)	−933(4)
C(24)	−4072(5)	2022(10)	−1436(4)
C(25)	−4729(5)	286(13)	−1723(3)

vicinal coupling constants for the ethane protons correspond to the relation $^3J = 11.0 \cos^2 \varphi - 2.3 \cos \varphi + 0.3$.[22]

Crystal Structure Determination.—A single crystal of [VO(L^2)(hquin)] grown by slow evaporation of a methanolic solution was used. The cell parameters were determined by a least-squares fit of 30 machine-centred reflections (2θ 15–30°). Data were collected by the ω-scan method in the range 2θ 3–55° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Two check reflections measured after every 98 showed no significant intensity reduction during the 25.07 h of exposure to X-rays. Data were corrected for Lorentz and polarisation effects. Systematic absences led to the identification of the space group as $P2_1$ or $P2_1/m$. The structure was successfully solved in $P2_1$ only.

All calculations for data reduction, structure solution, and refinement were done on a MicroVAX II computer with the programs of SHELXTL PLUS.[32] The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at calculated positions with a fixed U value (0.08 Å^2). Significant crystal data are listed in Table 5, Atomic coordinates in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 P. Basu, S. Pal and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1991, 3217.

2 J. Chakravarty, S. Dutta and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1993, 2857.

3 S. Dutta, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 5343.

4 J. Chakravarty, S. Dutta, A. Dey and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, 1994, 557.

5 J. Chakravarty, S. Dutta, S. K. Chandra, P. Basu and A. Chakravorty, *Inorg. Chem.*, 1993, **32**, 4249; J. Chakravarty, S. Dutta and A. Chakravorty, *J. Chem. Soc., Chem. Commun.*, 1993, 1091.

6 H. Vitler and D. Rehder, *Inorg. Chim. Acta*, 1987, **136**, L7; D. Rehder, C. Weidemann, A. Duch and W. Priebsch, *Inorg. Chem.*, 1988, **27**, 584.

7 R. Wever and K. Kustin, *Adv. Inorg. Chem.*, 1990, **35**, 81; A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61; D. Rehder, *Angew. Chem,, Int. Ed. Engl.*, 1991, **30**, 148.

8 D. Rehder, W. Priebsch and M. V. Oeynhausen, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1221.

9 K. Nakajima, M. Kojima, K. Toriumi, K. Saito and J. Fujita, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 760.

10 M. J. Clague, N. L. Keder and A. Butler, *Inorg. Chem.*, 1993, **32**, 4754.

11 W. R. Scheidt, *Inorg. Chem.*, 1973, **12**, 1758.

12 A. K. Mukherjee and P. Ray, *J. Indian Chem. Soc.*, 1955, **32**, 505; R. Hamalainen, U. Turpeinen and M. Ahlgren, *Acta Crystallogr., Sect. C*, 1985, **41**, 1726.

13 L. J. Theriot, G. O. Carlisle and H. J. Hu, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2841.

14 J. J. R. Frausta da Silva, R. Wooton and R. D. Gillard, *J. Chem. Soc. A*, 1970, 3369.

15 J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, 1986, **108**, 4088.

16 C. K. Johnson, ORTEP Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

17 C. R. Cornman, G. J. Colpas, J. D. Hoeschele, J. Kampf and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1992, **114**, 9925.

18 D. C. Crans, H. Chen, O. P. Anderson and M. M. Miller, *J. Am. Chem. Soc.*, 1993, **115**, 6769.

19 G. J. Leigh, (Editor) *Nomenclature of Inorganic Chemistry*, Blackwell Scientific Publications, Oxford, 1990, p. 186.

20 C. E. Jr. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

21 J. S. Waugh and R. W. Fessenden, *J. Am. Chem. Soc.*, 1957, **79**, 846.

22 M. Barfield and W. B. Smith, *J. Am. Chem. Soc.*, 1992, **114**, 1574.
23 M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.
24 I. Cavaco, J. C. Pessoa, D. Costa, M. T. Durate, R. D. Gillard and P. Matias, *J. Chem. Soc., Dalton Trans.*, 1994, 149.
25 C. R. Cornman, J. Kampf, M. S. Lah and V. L. Pecoraro, *Inorg. Chem.*, 1992, **31**, 2035; G. R. Hausan, T. A. Kabanos, A. D. Keramidas, D. Mentzafos and A. Terris, *Inorg. Chem.*, 1992, **31**, 2587.
26 E. de Boer, K. Boon and R. Wever, *Biochemistry*, 1988, **27**, 1629.
27 C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, 1962, **1**, 111.
28 D. Dutta, P. K. Mascharak and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 1673.
29 S. K. Chandra, P. Basu, D. Ray, S. Pal and A. Chakravorty, *Inorg. Chem.*, 1990, **29**, 2423.
30 S. Mondal, S. Dutta, T. Ghosh and A. Chakravorty, unpublished work.
31 H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry*, Van Nostrand, Princeton, NJ, 1956, p. 178.
32 G. M. Sheldrick, SHELXTL PLUS 88, Structure Determination Software Programs, Nicolet Instrument Corp., Madison, WI, 1988.

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