Synthesis, Structure and Metal Redox of New VO^{3+} and VO^{2+} Complexes incorporating Mixed Tridentate–Bidentate Binding†

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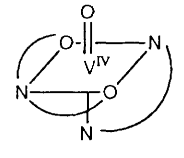
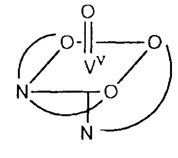
The reaction of bis(acetylacetonato)oxovanadium(IV) with a mixture of a tridentate ONO-co-ordinating hydrazone H_2L^1–H_2L^4 (general abbreviation H_2L; condensates of benzoylhydrazine with benzoylacetone, salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2-hydroxybutyrophenone respectively) and a bidentate compound 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) or quinolin-8-ol (Hquin) has afforded the complexes [V^{IV}O(L)(bipy)], [V^{IV}O(L)(phen)] and [V^{V}O(L)(quin)] in high yields. The crystal structure of [VO(L^1)(quin)] has been determined, revealing the distorted-octahedral VO(ONO)(ON) co-ordination sphere with the L^1 ligand spanning meridionally. The V=O distance is 1.592(3) Å and the atom lying *trans* to V=O is the quin nitrogen. There is a large decrease ($\approx$700 mV) in the VO^{3+}–VO^{2+} $E_{\frac{1}{2}}$ values between [VO(L)(bipy)] {or [VO(L)(phen)]} and [VO(L)(quin)]. The complex $[V^{IV}O(L)(quin)]^-$ was electrogenerated in solution but spontaneously reoxidized to [V^{V}O(L)(quin)] in air. For a given bidentate ligand, the VO^{3+}–VO^{2+} $E_{\frac{1}{2}}$ values follow the order $L^1 < L^4 < L^2 < L^3$. The ESR spectra of the VO^{2+} complexes correspond to an axially compressed $d_{xy}{}^1$ configuration. The ^{51}V hyperfine constants are slightly larger for $[VO(L)(quin)]^-$ than for [VO(L)(bipy)] and [VO(L)(phen)]. The $d_{xy} \longrightarrow d_{xz},d_{yz}$ transition of the tetravalent complexes occurs in the region 700–950 nm.

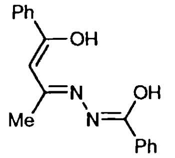
In vanadium chemistry the common monooxo motif is VO^{2+}. The less familiar[1–8] VO^{3+} is of current interest.[9–13] Certain haloperoxidases[14–16] are known to incorporate it (reducible to VO^{2+} by dithionite) in non-porphyrinic O/N environments.[17–21] In the present work we report examples of selective stabilization of the VO^{z+} moieties (z = 2 or 3) in a family of [VO(tridentate ligand)(bidentate ligand)] complexes. The tridentate ligand is dianionic and ONO-co-ordinating. The bidentate coligand is either NN- (electroneutral) or ON-co-ordinating (monoanionic). The stable combinations of z and co-ordination type are VO(ONO)(NN) **I** (z = 2) and VO(ONO)(ON) **II** (z = 3). The synthesis and characterization of the complexes are described along with the crystal structure of one member of the VO(ONO)(ON) group. Trends in the VO^{3+}–VO^{2+} reduction potentials are scrutinized.



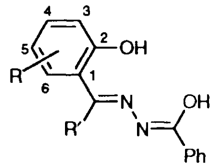
I



II



H_2L^1



H_2L^2 R = R′ = H
H_2L^3 R = 5,6-benzo, R′ = H
H_2L^4 R = H, R′ = Pr^n

Results and Discussion

Ligands and Complexes.—Four tridentate hydrazone ligands H_2L^1–H_2L^4 (general abbreviation H_2L) have been employed in the present work. The bidentate NN-co-ordinating ligands are 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) and the ON-co-ordinating ligand is quinolin-8-ol (Hquin). Both H_2L and Hquin bind in the deprotonated forms.

Upon treating a solution of bis(acetylacetonato)oxovanadium(IV) in methanol with an equimolar mixture of H_2L and a bidentate ligand, facile displacement of acetylacetone occurs at room temperature affording the electroneutral species [V^{IV}O(L)(bipy)], [V^{IV}O(L)(phen)] and [V^{V}O(L)(quin)]. In the formation of the last complex the metal is oxidized by aerial oxygen, see below. The complexes synthesized are listed in Table 1 along with selected characterization data. All are new. A few vanadium chelates of H_2L ligands have been reported,[8,22] but none belongs to the types described here. The V=O stretching frequencies of the present chelates appear in the region 950–990 cm^{-1} which is compatible with six-co-ordination.[4,23] Only the [V^{IV}O(L)(NN)] species are paramagnetic ($S = \frac{1}{2}$, Table 1).

Structure of [VO(L^1)(quin)].—Discrete molecules constitute the monoclinic lattice. A view of the complex is shown in Fig. 1 and selected bond parameters are listed in Table 2. The tri- and bi-dentate ligands are bonded respectively in the ONO and ON-modes providing (along with oxo oxygen) a severely distorted-octahedral N_2O_4 co-ordination sphere. The structure of only one other hydrazone complex of VO^{3+} is known, [VO(L^1)(OEt)] in which the metal is five-co-ordinated.[8] To our knowledge [VO(L^1)(quin)] is the first example of a six-co-ordinated hydrazone complex of VO^{3+}.

The entire V(quin) fragment is highly planar (mean deviation 0.02 Å) and the oxo oxygen atom, O(4), also lies on this plane.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: G = 10^{-4} T, $\mu_B = 9.274 \times 10^{-24}$ J T^{-1}.

Table 1 Characterization data

Compound	Analysis[a] (%) C	H	N	ν(V=O)[b]/ cm^{-1}	μ_{eff}[c]/ μ_B
[VO(L^1)(bipy)]	64.5 (64.6)	4.2 (4.3)	11.0 (11.1)	950	1.72
[VO(L^2)(bipy)]	62.4 (62.5)	3.8 (3.9)	12.0 (12.1)	965	1.73
[VO(L^3)(bipy)]	65.9 (65.7)	3.8 (3.9)	10.8 (10.9)	970	1.72
[VO(L^4)(bipy)]	64.3 (64.4)	4.6 (4.7)	11.3 (11.1)	960	1.74
[VO(L^1)(phen)]	66.3 (66.2)	4.1 (4.2)	10.5 (10.6)	960	1.73
[VO(L^2)(phen)]	64.2 (64.3)	3.6 (3.7)	11.4 (11.5)	965	1.75
[VO(L^3)(phen)]	67.4 (67.3)	3.6 (3.7)	10.5 (10.4)	970	1.74
[VO(L^4)(phen)]	66.1 (66.0)	4.4 (4.5)	10.5 (10.6)	960	1.76
[VO(L^1)(quin)]	63.7 (63.8)	4.1 (4.3)	8.5 (8.6)	960	*d*
[VO(L^2)(quin)]	61.3 (61.4)	3.5 (3.3)	9.2 (9.3)	975	*d*
[VO(L^3)(quin)]	64.7 (64.9)	3.5 (3.6)	8.5 (8.4)	990	*d*
[VO(L^4)(quin)]	63.6 (63.5)	4.5 (4.4)	8.4 (8.5)	980	*d*

[a] Calculated values in parentheses. [b] In KBr discs. [c] At 298 K. [d] Diamagnetic.

Table 2 Selected bond lengths (Å) and angles (°) for [VO(L^1)(quin)]

V–O(1)	1.896(3)	V–O(2)	1.931(3)
V–O(3)	1.852(2)	V–O(4)	1.592(3)
V–N(1)	2.060(3)	V–N(3)	2.350(3)
O(1)–C(7)	1.303(4)	O(2)–C(11)	1.308(4)
O(3)–C(25)	1.338(4)	N(1)–N(2)	1.410(4)
O(1)–V–O(2)	156.0(1)	O(1)–V–O(3)	100.1(1)
O(2)–V–O(3)	93.9(1)	O(1)–V–O(4)	97.9(1)
O(2)–V–O(4)	98.8(1)	O(3)–V–O(4)	99.9(1)
O(1)–V–N(1)	84.7(1)	O(2)–V–N(1)	75.4(1)
O(3)–V–N(1)	158.5(1)	O(4)–V–N(1)	100.1(1)
O(1)–V–N(3)	83.0(1)	O(2)–V–N(3)	81.7(1)
O(3)–V–N(3)	75.3(1)	O(4)–V–N(3)	175.3(1)
N(1)–V–N(3)	84.6(1)		

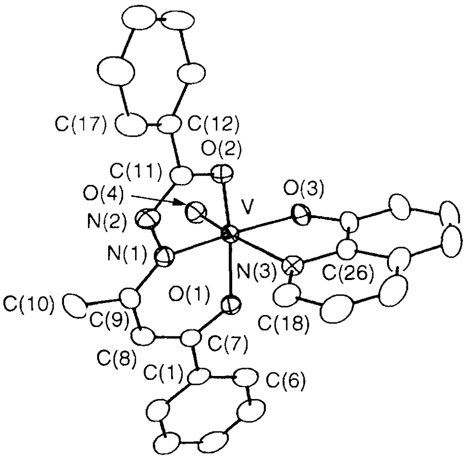

Fig. 1 The ORTEP plot and atom labelling scheme for [VO(L^1)(quin)]. All atoms are represented by their 30% probability ellipsoids

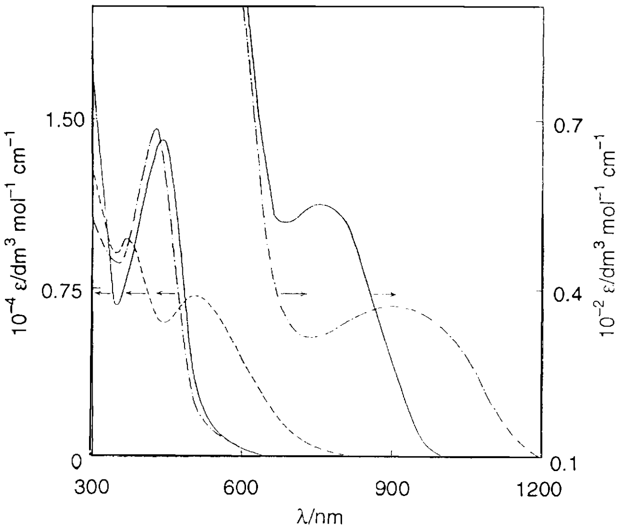

Fig. 2 Electronic spectra of [VO(L^1)(bipy)] (——), [VO(L^1)(quin)] (– – –) and electrogenerated [VO(L^1)(quin)]$^-$ (– · · · –) in dichloromethane solution at 298 K

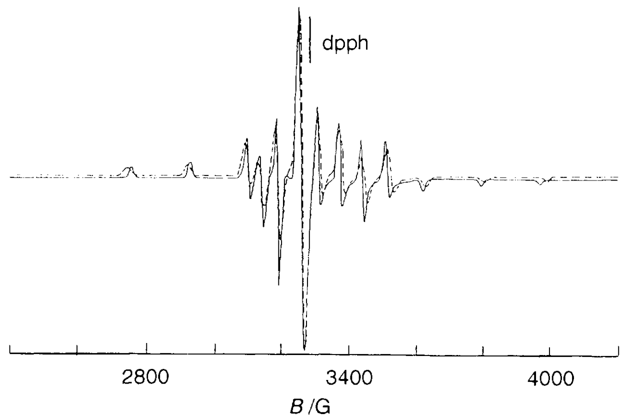

Fig. 3 The ESR spectra at X-band of [VO(L^1)(bipy)] (——) and electrogenerated [VO(L^2)(quin)]$^-$ (– – –) in dichloromethane–toluene glass at 77 K

Atoms O(1), N(1), O(2) and O(3) constitute a very good plane (mean deviation 0.03 Å) from which the metal atom is shifted towards the oxo oxygen atom O(4) by 0.31 Å. The five-membered chelate ring formed by the hydrazone ligand is almost perfectly planar (mean deviation 0.01 Å) but the six-membered ring is non-planar. The V=O distance, 1.592(3) Å lies within the range (1.55–1.60 Å) characterizing most VO^{3+} complexes.[1–13] The quin nitrogen atom N(3) lies *trans* to V–O, and the V–N(3) distance is relatively long.[2,24] The V–O-(phenolate) length in the V(quin) fragment is significantly shorter than the V–O lengths in the VL^1 fragment, 1.852(2) *versus* 1.896(3), 1.931(3) Å.

The other complexes reported in this work did not afford X-ray-quality single crystals. However, the above structure taken collectively with spectral, magnetic and electrochemical properties provides a firm basis for assuming that the complexes generally belong to the structural types **I** and **II**.

Electronic and ESR Spectra.—The red [VO(L)(NN)] and the electrogenerated (see below) green [VO(L)(quin)]$^-$ species display one ligand-field transition[25] ($d_{xy} \longrightarrow d_{xz},d_{yz}$) in the region 700–950 nm (Table 3). Strong absorptions at lower energies preclude observations of other possible ligand field bands. The d^0 [VO(L)(quin)] complexes are violet and exhibit only intense transitions, the one at lowest energy lying around 500 nm. Representative spectra are displayed in Fig. 2.

The tetravalent vanadium complexes are ESR-active displaying axial spectra [frozen dichloromethane–toluene (1 : 1), 77 K] with well resolved ^{51}V ($I = \frac{7}{2}$) hyperfine lines. Parameters for selected complexes are collected in Table 4 and representative spectra are shown in Fig. 3. The $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\perp}$ relationships are characteristic of an axially compressed $d_{xy}{}^1$ configuration.[26–28] The ^{51}V hyperfine splittings (Table 4, Fig. 3) are slightly larger in [VO(L)(ON)]$^-$ (VO_4N_2 co-ordination) as compared to those in [VO(L)(NN)] (VO_3N_3 co-ordination). The V–N(bipy/phen) interaction causes greater delocalization of the unpaired electron compared to the V–O(quin) interaction. The greater nucleophilicity of the

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

Compound	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	$E_{\frac{1}{2}}{}^c$/V($\Delta E_p{}^d$/mV)
[VO(L^1)(bipy)]	760 (55), 440 (14 100)	+0.54 (110)
[VO(L^2)(bipy)]	700 (42), 400[e] (6370), 360[e] (11 500), 325[e] (17 300)	+0.70 (110)
[VO(L^3)(bipy)]	825 (52), 425 (12 260), 325 (15 280)	+0.74 (100)
[VO(L^4)(bipy)]	770 (50), 395 (10 070), 320[e] (12 450)	+0.62 (110)
[VO(L^1)(phen)]	775 (57), 440 (13 500), 330[e] (6750)	+0.64 (100)
[VO(L^2)(phen)]	725 (39), 410 (8880), 385[e] (7850), 320[e] (16 000)	+0.76 (120)
[VO(L^3)(phen)]	850 (46), 440 (14 500), 330 (13 050)	+0.82 (110)
[VO(L^4)(phen)]	890 (62), 400 (10 490), 325 (14 420)	+0.65 (110)
[VO(L^1)(quin)]	500 (7250), 370 (9900)	−0.17 (100)
[VO(L^2)(quin)]	525 (5090), 320[e] (18 000)	−0.05 (100)
[VO(L^3)(quin)]	490 (6670), 420[e] (9000), 330 (19 960)	+0.07 (100)
[VO(L^4)(quin)]	525 (3100), 325[e] (10 500)	−0.11 (100)
[VO(L^1)(quin)]$^-$ [f]	900 (37), 425 (14 600)	−0.16 (110)
[VO(L^2)(quin)]$^-$ [f]	800 (70), 380 (8200)	−0.05 (100)
[VO(L^3)(quin)]$^-$ [f]	930 (45), 410 (14 000), 325 (14 650)	+0.07 (100)
[VO(L^4)(quin)]$^-$ [f]	875 (41), 380 (7250)	−0.12 (100)

[a] In CH_2Cl_2. [b] Supporting electrolyte, [NEt$_4$][ClO$_4$] (0.1 mol dm^{-3}), platinum working electrode, SCE reference electrode, solvent for vanadium complexes dichloromethane, solute concentration 10^{-3} mol dm^{-3}. [c] Calculated as the average of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [d] $E_{pa} - E_{pc}$. [e] Shoulder. [f] Electrogenerated in CH_2Cl_2 solution by exhaustive coulometry at −0.45 V [ratio of observed and calculated (for one electron) coulomb counts in the range 0.92–0.98].

Table 4 The ESR spectra of selected complexes in dichloromethane–toluene (1 : 1) solution (77 K)

Compound	$g_{\parallel}(A_{\parallel}/G)$	$g_{\perp}(A_{\perp}/G)$	$g_{av}{}^a(A_{av}{}^b/G)$
[VO(L^1)(bipy)]	1.951 (174.6)	1.984 (59.3)	1.973 (97.7)
[VO(L^2)(bipy)]	1.946 (175.0)	1.979 (59.7)	1.968 (98.1)
[VO(L^1)(phen)]	1.947 (174.3)	1.979 (59.3)	1.968 (97.6)
[VO(L^3)(phen)]	1.951 (174.3)	1.984 (59.3)	1.973 (97.6)
[VO(L^1)(quin)]$^-$ [c]	1.953 (177.8)	1.983 (60.7)	1.973 (99.7)
[VO(L^2)(quin)]$^-$ [c]	1.949 (180.4)	1.982 (61.4)	1.971 (101.0)
[VO(L^3)(quin)]$^-$ [c]	1.953 (179.3)	1.986 (61.4)	1.975 (100.7)

[a] $g_{av} = \frac{1}{3}(2g_{\perp} + g_{\parallel})$. [b] $A_{av} = \frac{1}{3}(2A_{\perp} + A_{\parallel})$. [c] Electrogenerated in CH_2Cl_2 solution.

amine nitrogen (in bipy/phen) compared to phenolic oxygen (in quin) is a plausible reason.[26,29]

The VO^{3+}–VO^{2+} *Couple: Trends in Reduction Potentials.*— The complexes uniformly exhibit a quasi-reversible cyclic voltammetric response in dichloromethane solution due to the couple (1) or (2). Selected voltammograms are shown in Fig. 4

$$[V^VO(L)(ON)] + e^- \rightleftharpoons [V^{IV}O(L)(ON)]^- \quad (1)$$

$$[V^VO(L)(NN)]^+ + e^- \rightleftharpoons [V^{IV}O(L)(NN)] \quad (2)$$

and $E_{\frac{1}{2}}$ values [*versus* saturated calomel electrode (SCE)] are listed in Table 3.

There is a large (≈700 mV) decrease in $E_{\frac{1}{2}}$ between [VO(L)(NN)] and [VO(L)(ON)] species signifying superior stability of the pentavalent state in the latter. A major factor contributing to the decrease in $E_{\frac{1}{2}}$ is no doubt the monoanionic nature of quin as opposed to the neutral bipy/phen. For a given bidentate ligand, the trend in $E_{\frac{1}{2}}$ with respect to L is $L^1 < L^4 < L^2 < L^3$. The main difference between L^1 and the other L ligands is that the former binds through an enolic (alkoxidic) oxygen and the latter through a phenolic oxygen. As in the case of manganese,[30] alkoxidic binding stabilizes the higher oxidation states better than does phenolic binding. The trend within the triad L^2, L^3 and L^4 can be qualitatively explained in terms of normal substituent effects. Thus L^3 has the more electron-withdrawing naphthalene ring in place of the benzene ring of L^2 while L^4 has an electron-releasing Pr^n substituent in place of the azomethine H of L^2.

The complexes of type [V^{IV}O(L)(quin)]$^-$ can be quantitatively generated in solution *via* coulometry (Table 3) of [V^{V}O(L)(quin)]. The reduced solutions have the same cyclic voltammograms (initial scan anodic) as those of the original solutions (initial scan cathodic). The parent [VO(L)(quin)] complex can be quantitatively regenerated by coulometric oxidation of [VO(L)(quin)]$^-$. The low reduction potential of the VO^{3+}–VO^{2+} couple (Table 3) ensures that [VO(L)(quin)]$^-$ is spontaneously oxidized in solution by air to [VO(L)(quin)]. The successful synthesis of [VO(L)(quin)] from starting materials containing only VO^{2+} (see above) is thus understandable.

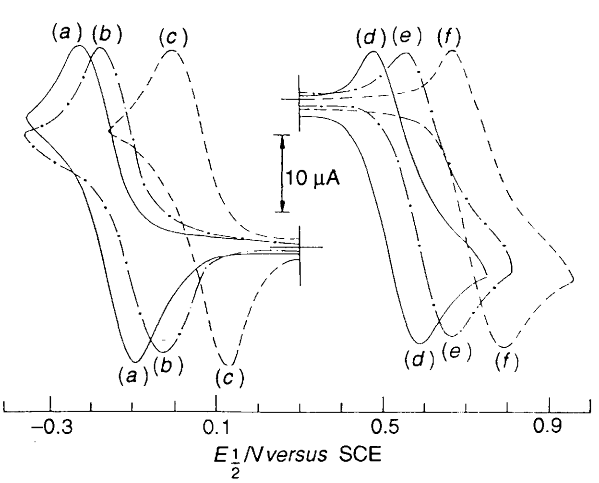

Fig. 4 Cyclic voltammograms (platinum electrode, 298 K) of (*a*) [VO(L^1)(quin)], (*b*) [VO(L^2)(quin)], (*c*) [VO(L^3)(quin)], (*d*) [VO(L^1)(bipy)], (*e*) [VO(L^2)(bipy)] and (*f*) [VO(L^3)(bipy)] in dichloromethane (10^{-3} mol dm^{-3}, 0.1 mol dm^{-3} [NEt$_4$][ClO$_4$])

Thus the ligand combination [L(quin)]$^{4-}$ can sustain both VO^{2+} and VO^{3+} but only the latter is stable in air. On the other hand [L(NN)]$^{3-}$ makes the VO^{3+} state too oxidizing and unstable. Attempts to generate bulk concentrations of [V^{V}O(L)(NN)]$^+$ by coulometric oxidation of [V^{IV}O(L)(NN)] have not been successful.

Conclusion

The VO^{2+} and VO^{3+} motifs have been selectively stabilized in a family of electroneutral complexes of type [VO(tridentate ligand)(bidentate ligand)], the respective co-ordination spheres being $V^{IV}O(ONO)(NN)$ and $V^{V}O(ONO)(ON)$. Authentication has been achieved by a crystal structure determination, together with spectral, magnetic and electrochemical data.

The clue to selective stabilization lies in the VO^{3+}–VO^{2+} $E_{\frac{1}{2}}$ values which logically show a large increase ($\approx$700 mV) on going from the (ONO)(ON) environment of five anionic charges to (ONO)(NN) of four.

The $[VO(ONO)(ON)]^-$ species can be electrogenerated in solution, aerial oxygen rapidly oxidizing them to [VO(ONO)(ON)]. Both [VO(ONO)(NN)] and $[VO(ONO)(ON)]^-$ display axial ESR spectra corresponding to the $d_{xy}{}^1$ configuration.

Experimental

Materials.—The ligands H_2L^1–H_2L^4[31,32] and $[VO(acac)_2]$[33] were prepared by reported methods. Electrochemically pure dichloromethane and tetraethylammonium perchlorate were obtained as before.[34] All other chemicals and solvents were of analytical grade used as obtained.

Physical Measurements.—Electronic spectra were recorded with a Hitachi 330 spectrophotometer, infrared spectra on a Perkin Elmer 783 spectrometer, and ESR spectra in the X-band on a Varian E-109C spectrometer equipped with a quartz Dewar flask for low-temperature (77 K) measurements. Diphenylpicrylhydrazyl (dpph) ($g = 2.0037$) was used to calibrate the spectra. Magnetic susceptibilities for [VO(L)(NN)] species were measured by using a PAR model 155 vibrating-sample magnetometer fitted with a Walker Scientific L 75 FB AL magnet. Electrochemical measurements were performed on a PAR model 370-4 electrochemistry system as reported earlier.[35] All potentials reported in this work are uncorrected for junction contribution. A Perkin Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N).

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

Table 5 Crystal data for $[VO(L^1)(quin)]$

Formula	$C_{26}H_{20}N_3O_4V$
M	489.4
Crystal size/mm	0.64 × 0.44 × 0.45
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	12.895(5)
b/Å	9.634(4)
c/Å	18.854(9)
β/°	98.47(3)
U/Å^3	2318(2)
Z	4
D_c/g cm^{-3}	1.403
μ(Mo-Kα)/cm^{-1}	0.710 73
F(000)	1008
2θ range/°	3–50
Total number of reflections	4585
Number of unique reflections	4034
Number of observed reflections [$I > 3\sigma(I)$]	2801
g in $w = 1/[\sigma^2(\lvert F\rvert) + g\lvert F\rvert^2]$	0.000 01
Number of refined parameters	307
R	4.37
R'	4.61
Goodness of fit	1.13
Maximum and mean Δ/σ	0.001, 0.000
Data to parameter ratio	9:1
Maximum, minimum difference peaks/e Å^{-3}	0.65, −0.26

(Oxo)(4-phenylbutane-2,4-dione α-hydroxybenzylidenehydrazonato)(quinolin-8-olato)vanadium(V), $[VO(L^1)(quin)]$. To a solution of $[VO(acac)_2]$ (0.10 g, 0.38 mmol) in methanol (20 cm^3) was added H_2L^1 (0.11 g, 0.38 mmol). Addition of quinolin-8-ol (0.055 g, 0.38 mmol) to this solution followed by stirring for 10 min resulted in the precipitation of a dark crystalline solid. It was filtered off, washed thoroughly with methanol and dried *in vacuo* over P_4O_{10}; yield 0.155 g (84%).

(2,2′-Bipyridine)oxo(salicylaldehyde α-hydroxybenzylidenehydrazonato)vanadium(IV), $[VO(L^2)(bipy)]$. Compound H_2L^2 (0.90 g, 0.38 mmol) dissolved in methanol (10 cm^3) was added to a stirred solution of $[VO(acac)_2]$ (0.10 g, 0.38 mmol) in methanol. After 15 min 2,2′-bipyridine (0.06 g, 0.38 mmol) was added and the resulting mixture stirred for 25 min when a snuff-coloured solid precipitated. It was filtered off, washed thoroughly with methanol and dried *in vacuo* over P_4O_{10}; yield 0.16 g (91%).

Electrogeneration of $[VO(L)(quin)]^-$ *in Solution.*—The representative example of $[VO(L^1)(quin)]^-$ is described. A solution of $[VO(L^1)(quin)]$ (25 mg, 0.05 mmol) in dry dichloromethane (20 cm^3) (0.1 mol dm^{-3} $[NEt_4][ClO_4]$) was reduced at −0.45 V *versus* SCE in a nitrogen atmosphere. Electrolysis stopped when 4.83 C had passed. The calculated one-electron coulomb count was 4.93. The reduced solution was used for spectral measurements.

Crystal Structure Determination.—Single crystals of $[VO(L^1)(quin)]$ were grown by slow diffusion of hexane into a dichloromethane solution. Cell dimensions were determined by a least-squares fit of 35 automatically centred reflections (2θ 15–30°). Data were collected at 296 K on a Nicolet R3m/V diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) by the ω-scan method. Two check reflections

Table 6 Atomic coordinates (× 10^4) for $[VO(L^1)(quin)]$

Atom	*x*	*y*	*z*
V	2 400(1)	1 494(1)	9 876(1)
O(1)	2 150(2)	920(3)	10 798(1)
O(2)	2 342(2)	2 733(3)	9 067(1)
O(3)	3 844(2)	1 307(2)	9 983(1)
O(4)	2 057(2)	97(3)	9 456(1)
N(1)	965(2)	2 462(3)	9 819(1)
N(2)	737(2)	3 473(3)	9 278(2)
N(3)	3 050(2)	3 499(3)	10 499(1)
C(1)	1 363(3)	−397(3)	11 629(2)
C(2)	474(3)	−887(5)	11 891(2)
C(3)	569(4)	−1 864(5)	12 441(2)
C(4)	1 545(5)	−2 346(5)	12 726(2)
C(5)	2 422(5)	−1 878(5)	12 481(3)
C(6)	2 388(3)	−911(4)	11 929(2)
C(7)	1 276(3)	609(3)	11 030(2)
C(8)	350(3)	1 197(4)	10 742(2)
C(9)	202(3)	2 176(4)	10 174(2)
C(10)	−845(3)	2 851(4)	9 990(2)
C(11)	1 499(3)	3 492(4)	8 906(2)
C(12)	1 397(3)	4 354(4)	8 245(2)
C(13)	2 035(3)	4 090(5)	7 735(2)
C(14)	1 902(4)	4 845(7)	7 098(2)
C(15)	1 147(5)	5 846(7)	6 973(3)
C(16)	524(5)	6 126(7)	7 486(3)
C(17)	638(4)	5 370(6)	8 117(3)
C(18)	2 620(3)	4 583(4)	10 772(2)
C(19)	3 207(4)	5 683(5)	11 099(3)
C(20)	4 261(4)	5 652(5)	11 152(3)
C(21)	4 774(3)	4 514(4)	10 886(2)
C(22)	5 857(4)	4 324(6)	10 929(3)
C(23)	6 249(3)	3 146(6)	10 668(3)
C(24)	5 595(3)	2 094(5)	10 345(3)
C(25)	4 530(2)	2 256(4)	10 283(2)
C(26)	4 103(3)	3 456(4)	10 560(2)

measured after every 98 showed no significant intensity reduction during 38 h of exposure to X-rays. Data were corrected for Lorentz-polarization effects.

The structure was solved by direct 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 fixed isotropic thermal parameters (0.08 Å^2). Crystal data and other details are collected in Table 5. Final fractional atomic coordinates are given in Table 6. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program system[36] and crystal structure plots were drawn using ORTEP.[37]

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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