

Chemistry of Variable-Valence VO^{z+} (z = 2, 3) Complexes: Synthesis, Structure, and Metal Redox of New V^{VO}(ONO)(ON) and V^{IV}O(ONO)(NN) Families†

Joydip Chakravarty, Somnath Dutta, Swapan Kumar Chandra, Partha Basu, and Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Received February 24, 1993

In the title families the ONO ligands are deprotonated forms of *N*-(2-hydroxyphenyl)salicylaldehyde (H₂amp), 2,2'-dihydroxyazobenzene (H₂azp), *N*-(2-carboxyphenyl)salicylaldehyde (H₂amc), or 2-hydroxy-2'-carboxy-5-methylazobenzene (H₂azc). The ON ligand is deprotonated 8-quinolinol (Hhq), and the NN ligands are 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). Reaction of VO(acac)₂ with a mixture of H₂amp and bpy or Hhq in methanol affords V^{IV}O(amp)(bpy) or V^{VO}O(amp)(hq) (oxidant is aerial oxygen). Complexes of azp²⁻ and amc²⁻ are similarly made, while those of azc²⁻ are synthesized from preformed VO(acac)₂·3H₂O. In both VO(acac)(hq)·2MeOH and VO(acac)(bpy) the V(acac) and V(bidentate) fragments are respectively nonplanar and planar. The V–O distances within V(acac) are shorter in the former complex. Crystals of VO(acac)(hq)·2MeOH are triclinic, space group P $\bar{1}$, with *a* = 8.104(3) Å, *b* = 12.217(4) Å, *c* = 12.573(5) Å, α = 100.62(3)°, β = 92.26(3)°, γ = 105.81(3)°, *V* = 1176(1) Å³, *Z* = 2, *R* = 6.69%, and *R*_w = 6.69%. Crystals of VO(acac)(bpy) are monoclinic, space group P2₁/c, with *a* = 9.848(4) Å, *b* = 18.169(6) Å, *c* = 12.936(4) Å, β = 111.78(3)°, *V* = 2149(2) Å³, *Z* = 4, *R* = 6.25%, and *R*_w = 6.39%. In VO(ONO)(NN) and electrogenerated VO(ONO)(ON)⁻ the ⁵¹V EPR hyperfine constants (*A*_{av}) are slightly larger in the amc²⁻ and azc²⁻ (~102 G) than in the amp²⁻ and azp²⁻ (~99 G) complexes. The more nucleophilic phenolato function delocalizes electron density better. The VO³⁺–VO²⁺ *E*_{1/2} values shift considerably to more negative values when neutral NN is replaced by anionic ON, which also provides better VO³⁺ binding via phenolato oxygen. For a given bidentate ligand *E*_{1/2} increases in the order amp²⁻ < azp²⁻ < amc²⁻ < azc²⁻ and correlates linearly with $\sum pK_a$, which represents the sum of p*K*_a's of the variable N and O functions.

Introduction

Two dominant motifs in the coordination chemistry of vanadium are monooxo VO²⁺ for the tetravalent state and dioxo VO²⁺ for the pentavalent state. In contrast the monooxo pentavalent motif VO³⁺ has remained relatively uncommon.^{1–12} The recognition that certain haloperoxidases^{13–15} contain this motif (becomes VO²⁺ by dithionite reduction) set in nonporphyrinic ON ligated environments^{16–20} has motivated renewed search for complexes

of VO³⁺ vis-a-vis those of VO²⁺ coordinated to ON ligands having at least some biomimetic features.^{21–24} Herein we disclose some of our own findings in this area as part of a program on oxovanadium chemistry.^{25,26}

The syntheses of two families of complexes of coordination types V^{VO}O(ONO)(ON) and V^{IV}O(ONO)(NN) based on tridentate ONO and bidentate ON/NN donating ligands are described. The O-donor groups are carboxylate and/or phenolate, and the N-donor functions are pyridine and azo or azomethine. Carboxylate oxygen coordination has been implicated in bromoperoxidases,^{20,27} but very few structurally characterized VO³⁺ complexes with carboxylate binding are known.^{11,21} The X-ray structures of a pair of V^{VO}O(ONO)(ON) and V^{IV}O(ONO)(NN) complexes involving carboxylate coordination are reported in this work. The spectral and electrochemical features of the two families are enumerated. The systematics of donor dependence of the VO³⁺–VO²⁺ reduction potential are scrutinized.

† This work is dedicated to the memory of the late Professors P. Rây and N. K. Dutt on the occasion of the fiftieth anniversary of the Rây–Dutt twist mechanism.

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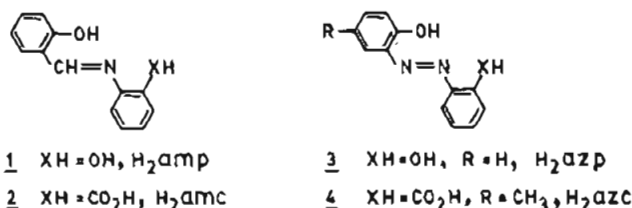
Table I. Characterization Data

compounds	UV-vis, ^b λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	IR data, ^d cm ⁻¹	μ_{eff} , ^c μ_B
VO(amp)(bpy)	850 (50), 460 (10 070), 400 ^c (6430)	960	1.65
VO(azp)(bpy)	1000 (74), 540 (13 020), 450 ^c (4880)	955	1.70
VO(amp)(bpy)	750 (27), 550 ^c (200), 410 (6080)	960, 1620	1.72
VO(azc)(bpy)	1000 (59), 515 (8130), 400 ^c (4390)	960, 1620	1.78
VO(azp)(phen)	1000 (73), 550 (14 120), 450 ^c (4960)	955	1.75
VO(azc)(phen)	1000 (70), 515 (8710), 390 ^c (5150)	960, 1620	1.76
VO(amp)(hq)	490 (7030), 375 (8650)	955	<i>e</i>
VO(azp)(hq)	530 (11 280), 350 (14 660)	970	<i>e</i>
VO(amp)(hq)	510 (4160), 390 ^c (5480)	955, 1650	<i>e</i>
VO(azc)(hq)	545 (10 290), 400 ^c (9910), 340 (25 350)	970, 1650	<i>e</i>
VO(amp)(hq) ^{-a}	850 (32), 440 (8630)		1.77
VO(azp)(hq) ^{-a}	1000 (40), 485 (8720), 425 ^c (5740)		1.69
VO(amp)(hq) ^{-a}	900 (30), 535 ^c (620), 375 (4480)		1.71
VO(azc)(hq) ^{-a}	1050 (35), 500 (5460), 390 ^c (4690)		1.74

^a Electrogenerated in CH₂Cl₂ solution. ^b In CH₂Cl₂. ^c Shoulder. ^d In KBr disks. ^e Diamagnetic.

Results and Discussion

A. Ligands and Synthesis of Complexes. The tridentate diphenolic and phenolic-carboxylic ligands used in the present work and their abbreviations are shown in 1–4. These coordinate



in the deprotonated dianionic form through O⁻, N, and X⁻. The NN ligands are 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen), and the ON ligand is 8-quinolinol (Hhq), which binds in the deprotonated hq⁻ form. The known vanadium coordination chemistry of 1–3 consists of binuclear complexes of H₂amp and some reactions thereof,^{28–30} the complex³¹ V^{IV}O(amp)₂·1/2H₂O, and the species²⁶ V₂O₃(azp)₂ and VO₂(azp)⁻. No studies on H₂azc complexes appear to have been made.

When bis(acetylacetonato)oxovanadium(IV), VO(acac)₂, is treated with an equimolar mixture of a tridentate diphenolic ligand (1 or 3) and an ON or NN bidentate ligand in methanol under ambient conditions, acetylacetonate is smoothly displaced affording V^{VO}(ONO)(ON) or V^{VO}(ONO)(NN) in excellent yields. The complexes incorporating the phenolic-carboxylic ligand H₂amc, 2, are similarly made, but here it is necessary to boil the reaction mixture. On the other hand, the synthesis of the complexes of H₂azc, 4, is best achieved via VO(azc)·3H₂O, which can be isolated by treating VO(acac)₂ with H₂azc in methanol. Since the starting vanadium complex is always tetravalent, the formation of the pentavalent complexes of type VO(ONO)(ON) involve metal oxidation. The oxidizing agent is aerial oxygen; *vide infra*. The chelates synthesized in the present work are listed in Table I along with selected characterization data which will be scrutinized in later sections.

B. Structure. So far we have succeeded in growing good single crystals of only VO(azc)(hq) and VO(azc)(bpy)—the former as a methanol adduct which rapidly loses the solvent along with crystallinity in the open. The crystals are however stable when sealed with mother liquor.

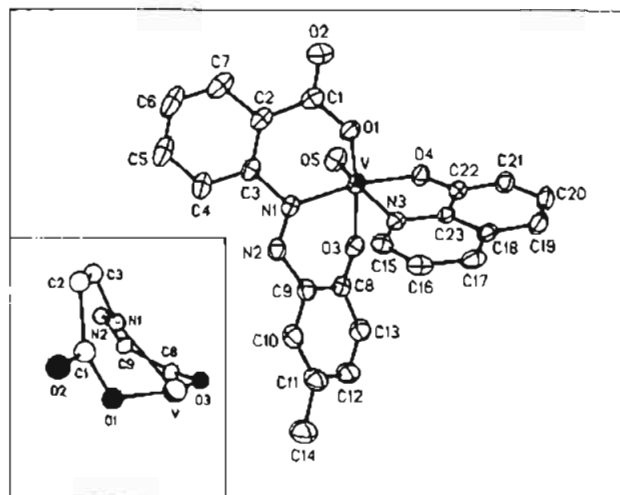
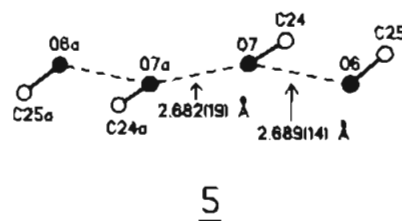


Figure 1. ORTEP plot and atom-labeling scheme for VO(azc)(hq)·2MeOH. All non-hydrogen atoms are represented by their 30% probability ellipsoids. The nonplanarity of the V(azc) chelate rings is shown in the inset.

Table II. Selected Bond Lengths (Å) and Angles (deg) for VO(azc)(hq)·2MeOH

Distances			
V–O(1)	1.892(4)	V–O(3)	1.895(5)
V–O(4)	1.841(4)	V–O(5)	1.579(4)
V–N(1)	2.098(5)	V–N(3)	2.387(4)
O(1)–C(1)	1.303(8)	O(2)–C(1)	1.218(10)
O(3)–C(8)	1.298(8)	O(4)–C(22)	1.350(6)
O(6)–C(25)	1.233(14)	O(7)–C(24)	1.280(19)
N(1)–N(2)	1.271(8)		
Angles			
O(1)–V–O(3)	158.2(2)	O(1)–V–O(4)	95.5(2)
O(3)–V–O(4)	95.3(2)	O(1)–V–O(5)	99.1(2)
O(3)–V–O(5)	97.7(2)	O(4)–V–O(5)	99.9(2)
O(1)–V–N(1)	81.7(2)	O(3)–V–N(1)	81.8(2)
O(4)–V–N(1)	160.4(2)	O(5)–V–N(1)	99.6(2)
O(1)–V–N(3)	79.7(2)	O(3)–V–N(3)	84.5(2)
O(4)–V–N(3)	76.3(2)	O(5)–V–N(3)	175.8(2)
N(1)–V–N(3)	84.2(2)		

a. VO(azc)(hq)·2MeOH. The lattice consists of discrete VO(azc)(hq) molecules and centrosymmetric linear methanol tetramers assembled via hydrogen bonding. A view of the VO(azc)(hq) molecule is shown in Figure 1, and the (MeOH)₄ tetramer is depicted in structure 5. Selected bond parameters



are listed in Table II. The oxo, azc²⁻, and hq⁻ ligands together provide a severely distorted octahedral N₂O₄ coordination sphere. Structurally authenticated V^V–N(azo) binding is very rare,^{26,32} and the present complex is the only example of azo binding to VO³⁺.

The atoms O(1), N(1), O(3), and O(4) define a good plane (mean deviation ~ 0.03 Å) from which the metal atom is shifted away toward the oxo atom O(5) by 0.30 Å. The V(hq) fragment along with O(5) and N(1) constitute an excellent plane (mean

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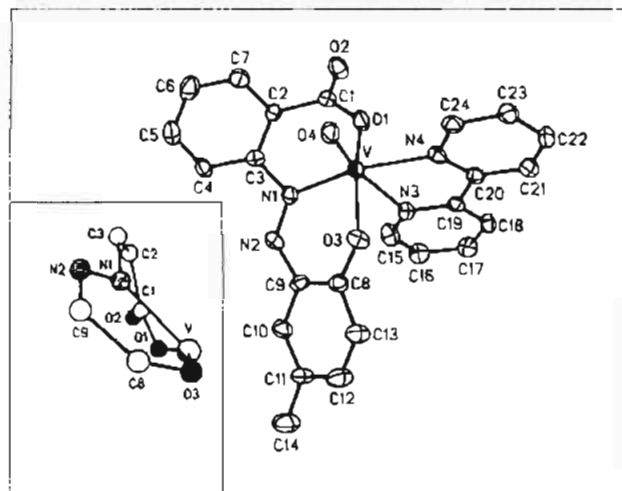


Figure 2. ORTEP plot and atom-labeling scheme for VO(azc)(bpy). All non-hydrogen atoms are represented by their 30% probability ellipsoids. The nonplanarity of the V(azc) chelate rings is shown in the inset.

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for VO(azc)(bpy)

Distances			
V—O(1)	1.955(5)	V—O(3)	1.954(4)
V—O(4)	1.583(5)	V—N(1)	2.094(7)
V—N(3)	2.323(6)	V—N(4)	2.137(7)
O(1)—C(1)	1.278(11)	O(2)—C(1)	1.237(8)
O(3)—C(8)	1.306(8)	N(1)—N(2)	1.288(8)
Angles			
O(1)—V—O(3)	157.2(2)	O(1)—V—O(4)	101.5(2)
O(3)—V—O(4)	101.2(2)	O(1)—V—N(1)	86.1(2)
O(3)—V—N(1)	87.0(2)	O(4)—V—N(1)	101.1(3)
O(1)—V—N(3)	77.6(2)	O(3)—V—N(3)	80.9(2)
O(4)—V—N(3)	167.7(3)	N(1)—V—N(3)	91.1(2)
O(1)—V—N(4)	90.9(2)	O(3)—V—N(4)	89.7(2)
O(4)—V—N(4)	95.3(3)	N(1)—V—N(4)	163.6(2)
N(3)—V—N(4)	72.5(2)		

deviation ~ 0.02 Å). The phenolic O(1) and O(3) atoms of azc²⁻ span trans positions on two sides of this plane.

The six-membered azc²⁻ chelate rings are highly nonplanar; *vide inset* in Figure 1. The dihedral angle between the two benzene rings of azc²⁻ is 54.6°, and that between the carboxyl group and the benzene ring to which it is attached is 10.2°. This configuration suits an unhindered tridentate approach of azc²⁻ to the planar VO(hq) fragment.

The V=O distance is 1.579(4) Å, which lies well within the range (1.55–1.60 Å) defined by most other VO³⁺ complexes.^{1–12,21–24} The long bond trans to V=O is formed with the hq⁻ nitrogen N(3) as expected.^{2,33,34} The V–O(phenolate) lengths follow the order azc²⁻ > hq⁻ (1.895(5), 1.841(4) Å). The opposite is expected and found to be true for C–O(phenolic) lengths, azc²⁻ < hq⁻ (1.298(8), 1.350(6) Å).

To our knowledge VO(azc)(hq)·2MeOH is the only structurally characterized VO³⁺ complex incorporating aromatic carboxylate coordination. The V–O(carboxylate) distance in it, 1.892(4) Å, is shorter than the corresponding distances (1.95–2.08 Å, excluding trans labilized bonds) in the two other structurally known VO³⁺ carboxylate (both aliphatic) complexes.^{11,21}

b. VO(azc)(bpy). A perspective view of the molecule is shown in Figure 2, and selected bond distances and angles are collected in Table III. Here the coordination sphere is of the type N₃O₃. The gross geometrical features of the structure are similar to those of VO(azc)(hq). The metal atom is shifted toward the oxo atom by 0.34 Å from the plane (mean deviation ~ 0.04 Å) of

O(1)N(1)O(3)N(4). The VO(4)N(1)(bpy) fragment is planar (mean deviation ~ 0.04 Å), but the V(azc) chelate rings are severely distorted from planarity (inset in Figure 2). The dihedral angles between the two benzene rings of azc²⁻ and that between the carboxyl group and the benzene ring to which it is attached are 48.3 and 21.0°, respectively.

The bpy ligand is unsymmetrically bound, the V–N distance trans to V=O being ~ 0.2 Å longer than the other V–N distance. The V–N(4) length is normal for bpy complexes of VO²⁺ (observed range, 2.10–2.14 Å).^{25,35,36} The azo nitrogen binds VO²⁺ better than bpy nitrogen, the V–N(azo) length being significantly shorter than V–N(4).

The V=O distance, 1.583(5) Å, lies near the lower limit of the usual VO²⁺ values (observed range, 1.59–1.62 Å)^{35,37–41} and is virtually equal to that in VO(azc)(hq)·2MeOH. The different metal oxidation states of the two complexes are however reflected in the phenolic and carboxylic V–O distances of the V(azc) fragment. The distances in VO(azc)(bpy) are longer than those in VO(azc)(hq)·2MeOH by ~ 0.06 Å.

c. Other Complexes. On the basis of spectral, magnetic, and electrochemical results (see below), it has been concluded that the gross structures of all the VO(ONO)(ON) and VO(ONO)(NN) complexes are similar to those of VO(azc)(hq)·2MeOH and VO(azc)(bpy). The ONO binding of amp²⁻ and azp²⁻ to oxovanadium(V) moieties (VO₂⁺, V₂O₃⁴⁺) has been demonstrated by structure determinations.^{26,30}

C. IR and Electronic Spectra. The V=O stretching frequency of the complexes occur (Table I) as a strong band in the 950–970 cm⁻¹ region, which is in accord with hexacoordination.^{6,42} Like the V=O bond length, the frequency is insensitive to metal valence. Strong bands at 1620 cm⁻¹ in VO(ONO)(NN) and 1650 cm⁻¹ in VO(ONO)(ON) are assigned to the antisymmetric stretch of the monodentate carboxyl function.⁴³ The symmetric ν_{COO} expected⁴³ near 1350 cm⁻¹ could not be identified unambiguously due to the presence of other strong bands in the same region.

Electronic spectral data of the complexes in the visible region are given in Table I, and representative spectra of selected complexes are displayed in Figure 3. In the VO(ONO)(NN) species the lowest energy ligand field transition ($d_{xy} \rightarrow d_{xz}, d_{yz}$) is observed in the region 750–1000 nm but the remaining transitions⁴⁴ are obscured by an intense absorption around 500 nm. The VO(ONO)(ON) complexes (d⁰) display only strong bands, the one at lowest energy lying in the region 450–550 nm. Upon electroreduction to VO(ONO)(ON)⁻ (*vide infra*) the expected ligand field transition becomes observable near 1000 nm (Table I and Figure 3).

D. Magnetism and EPR Spectra. The VO(ONO)(NN) species have magnetic moments corresponding to the d¹ configuration, and the diamagnetic VO(ONO)(ON) complexes afford one-electron paramagnetic VO(ONO)(ON)⁻ upon electroreduction (Table I). In frozen dichloromethane solution (77 K) the complexes ($S = 1/2$) display axial EPR spectra with well-resolved ⁵¹V ($I = 7/2$) hyperfine structure. Spectra of two representative

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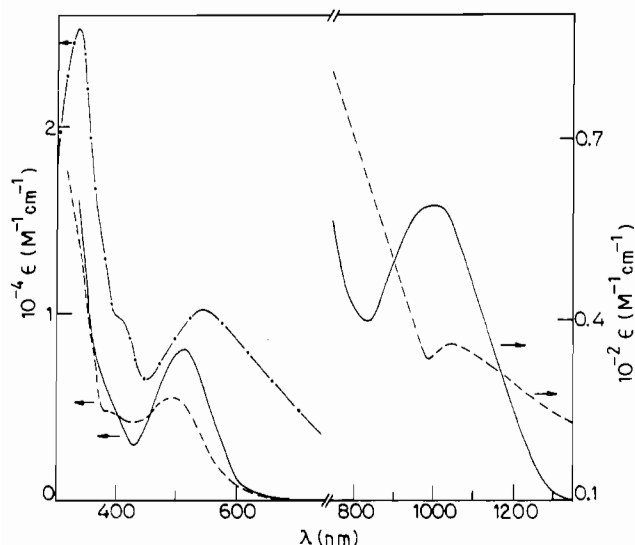


Figure 3. Electronic spectra of VO(azc)(bpy) (—), VO(azc)(hq) (---), and electrogenerated VO(azc)(hq)⁻ (- · -) in dichloromethane solution at 298 K.

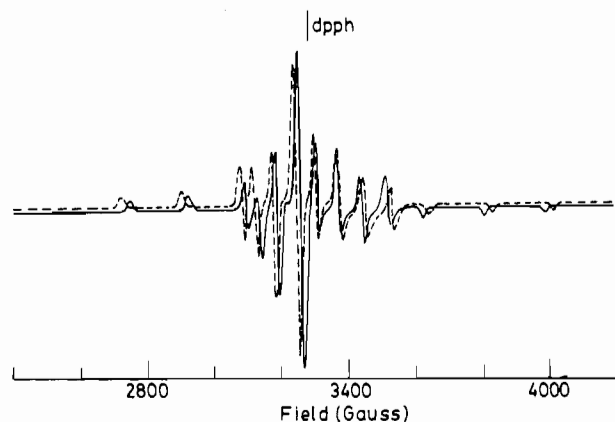


Figure 4. EPR spectra at X-band of VO(amp)(bpy) (—) and electrogenerated VO(amp)(hq)⁻ (---) in dichloromethane at 77 K. Instrument settings are as follows: power, 30 dB; modulation, 100 KHz; sweep center, 3200 G; sweep width, 2000 G; sweep time, 240 s.

Table IV. EPR Data^a at 77 K

compounds	g_{\parallel}	g_{\perp}	g_{av}^b	A_{\parallel} , G	A_{\perp} , G	A_{av}^c , G
VO(amp)(bpy)	1.953	1.986	1.975	175.7	60.0	98.6
VO(azp)(bpy)	1.953	1.986	1.975	174.3	59.7	97.9
VO(amp)(bpy)	1.951	1.985	1.974	179.3	63.1	101.9
VO(azc)(bpy)	1.952	1.984	1.974	177.4	62.9	101.1
VO(azp)(phen)	1.955	1.986	1.976	173.6	59.7	97.7
VO(azc)(phen)	1.955	1.986	1.976	178.0	63.1	101.4
VO(amp)(hq) ^{-d}	1.953	1.986	1.974	178.6	61.9	100.8
VO(azp)(hq) ^{-d}	1.952	1.985	1.974	178.6	61.1	100.3
VO(amp)(hq) ^{-d}	1.944	1.978	1.967	182.9	63.6	103.3
VO(azc)(hq) ^{-d}	1.949	1.982	1.971	181.7	63.6	103.0

^a In CH₂Cl₂. ^b $g_{av} = 1/3[2g_{\perp} + g_{\parallel}]$. ^c $A_{av} = 1/3[2A_{\perp} + A_{\parallel}]$. ^d Electrogenerated in CH₂Cl₂ solution.

complexes are shown in Figure 4, and spectral parameters are listed in Table IV. The usual^{25,40,41} $g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\perp}$ relationships corresponding to the axially compressed d_{xy}^1 configuration are present.

The hyperfine constants in the complexes incorporating carboxylate coordination (amp²⁻ and azc²⁻) are significantly larger than those in the diphenolic (amp²⁻ and azp²⁻) complexes. This suggests that the V–O(phenolic) interaction is more effective than the V–O(carboxylate) interaction in delocalization of the unpaired electron away from the metal. The unequal nucleophilicity of the coordinating atoms, viz., phenolate > carboxylate, can be one plausible reason.⁴⁵

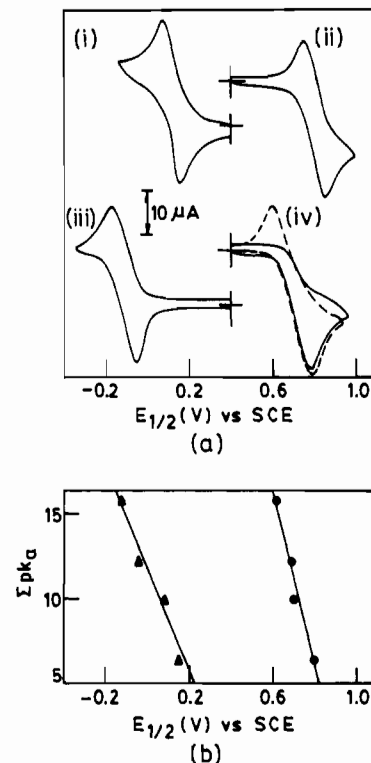


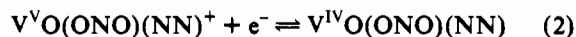
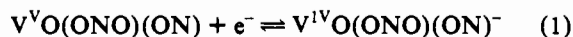
Figure 5. (a) Cyclic voltammograms (—, 298 K; - · -, 249 K) of $\sim 10^{-3}$ M solutions (0.1 M TEAP) of (i) VO(amp)(bpy), (ii) VO(azc)(hq), (iii) VO(amp)(bpy), and (iv) VO(azp)(bpy) in dichloromethane at a platinum electrode, scan rate 50 mV s⁻¹. (b) Least-squares plot of $E_{1/2}$, V vs $\sum \log K_a$ for the VO(ONO)(hq) (\blacktriangle) and VO(ONO)(bpy) (\bullet) complexes.

Table V. Electrochemical Data^a in CH₂Cl₂ at 298 K

compounds	$E_{1/2}^b$, V (ΔE_{pc}^c , mV); $n^{d,e}$	compounds	$E_{1/2}^b$, V (ΔE_{pc}^c , mV); $n^{d,e}$
VO(amp)(bpy)	0.61 (130)	VO(amp)(hq)	-0.12 (160); 0.97
VO(azp)(bpy)	0.69 ^f (150)	VO(azp)(hq)	-0.04 (140); 1.03
VO(amp)(bpy)	0.71 (100)	VO(amp)(hq)	0.09 (80); 0.95
VO(azc)(bpy)	0.80 (120); 1.01	VO(azc)(hq)	0.17 (90); 0.96
VO(azp)(phen)	0.69 ^f (180)		
VO(azc)(phen)	0.80 (180); 1.02		

^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 $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. ^c $\Delta E_p = E_{pa} - E_{pc}$. ^d Constant-potential coulometric data $n = Q/Q'$, where Q is the observed coulomb count and Q' is the calculated count for 1e transfer. ^e Electrolysis performed at 200 mV below E_{pc} for reduction and 200 mV above E_{pa} for oxidation. ^f At 249 K.

E. Electrochemistry. a. 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 VO³⁺–VO²⁺ couple, eqs 1 and 2. Representative voltammograms are displayed in Figure 5, and reduction potential data are set out in Table V.



The VO(ONO)(ON) complexes can be quantitatively reduced to VO(ONO)(ON)⁻ by constant potential coulometry: the color of the solution changes from violet to red and the coulomb count corresponds to one-electron stoichiometry (Table IV). The reduced solution has the same cyclic voltammogram (initial scan anodic) as the original solution (initial scan cathodic). Upon

coulometric reoxidation the parent VO(ONO)(ON) complex is quantitatively regenerated. Solutions prepared by coulometric reduction were used for magnetic and spectral characterization of the VO(ONO)(ON)⁻ species; *vide supra*. Upon exposure of such solutions to oxygen (or air), smooth oxidation occurs affording VO(ONO)(ON). This explains the formation of VO(ONO)(ON) from VO²⁺ precursors during synthesis.

Unlike hq⁻, which is compatible with both the V^{IV}O(ONO) and V^{VO}(ONO) states, the NN ligands bind well only to V^{IV}O(ONO). The VO(ONO)(NN)⁺ species are relatively unstable, and attempted generation in solution in bulk concentrations by coulometry have not been successful. In the case of VO(azp)(NN) the oxidized complex is unstable even on the cyclic voltammetric time scale at room temperature; better stability is achieved upon cooling to 274 K (Figure 5).

b. Trends of Reduction Potentials: E_{1/2}-pK Correlation. The VO³⁺ motif is stabilized by (ONO)(ON) ligation as opposed to VO²⁺ by (ONO)(NN) ligation. This is expressed in E_{1/2} of the couple of eq 1 being ~700 mV lower than that of the couple of eq 2 (for a given ONO ligand). The larger difference in E_{1/2} can be qualitatively understood in terms of charge types of the bidentate ligand (monoanionic ON versus neutral NN) and better vanadium(V) binding by phenolato oxygen (in ON) compared to pyridine nitrogen (in NN).

A more subtle variation of E_{1/2} is observed when the bidentate ligand is kept invariant. The E_{1/2} values follow the order OPⁿN^mOP^p(amp²⁻) < OPⁿN^aOP^p(azp²⁻) < OPⁿN^mO^c(amc²⁻) < OPⁿN^aO^c(azc²⁻), the difference between extreme members being (Table V) ~300 mV for hq⁻ and ~200 mV for bpy species (meaning of superscripts: p = phenolic, c = carboxylic, m = azomethine, a = azo). This trend can be rationalized by extending a thermodynamic model previously employed in the case of metal reduction potentials of manganese(IV) complexes.⁴⁶ The essential finding was that the E_{1/2}'s correlate with the pK_a's of the conjugate acids of coordinating groups.

The concerned pK_a values for the present purpose are PhOH, 10.0; PhCO₂H, 4.2; PhCH=NHPH⁺, 5.8; and PhN=NHPH⁺, 2.2.^{47,48} The sum of the two relevant pK_a's, ΣpK_a, will be used for each ONO ligand (the invariant phenolic oxygen merely adds a constant term and therefore need not be considered). The pK_a values for OPⁿN^mOP^p, OPⁿN^aOP^p, OPⁿN^mO^c, and OPⁿN^aO^c are 15.8, 12.2, 10.0, and 6.4, respectively. The plots of ΣpK_a against E_{1/2} are shown in Figure 5. The linearity is satisfactory for both series, the correlation constants being 0.96 and 0.98 for the couples of eqs 1 and 2, respectively. Whereas the goodness of the linearity could be partly fortuitous, we certainly have here a useful model for qualitative rationalization and for approximate prediction of oxovanadium reduction potentials within families of related complexes.

F. Concluding Remarks. The main findings of this work will now be summarized. Mixed complexation by tridentate dianionic ONO (deprotonated 1-4) and bidentate neutral NN (e.g., bpy) or monoanionic ON (hq⁻) ligands have successfully afforded two new families of VO²⁺ (z = 2, 3) complexes: V^{IV}O(ONO)(NN) and V^{VO}(ONO)(ON).

The first structural characterization of O^c and N^a ligation to VO³⁺ is reported in a VO(OPⁿN^aO^c)(ON) complex, and the structure of the corresponding VO(OPⁿN^aO^c)(NN) complex is also reported. The V-O^p and V-O^c bonds in the former are shorter by ~0.06 Å. In VO(ONO)(NN) and electrogenerated VO(ONO)(ON)⁻, more nucleophilic O^p is more effective than O^c in delocalizing electron density away from the metal leading to smaller EPR hyperfine constants.

Due to the anionic nature of hq⁻ and the strong affinity of VO³⁺ for the phenolato function, the E_{1/2} values of the VO³⁺-VO²⁺ couple in VO(ONO)(ON) are much lower (by ~700 mV) than those in VO(ONO)(NN). In effect VO³⁺ is stabilized by (ONO)(ON) and VO²⁺ by (ONO)(NN) environments.

For fixed bidentate ligation, the E_{1/2} value increases significantly when, in ONO, N^m is replaced by N^a and/or O^p is replaced by O^c. The increments are approximately additive, and the E_{1/2} values correlate linearly with the pK_a sums of the variable coordination sites. The maximum spread of E_{1/2} due to combined variations in bidentate and tridentate ligands is ~900 mV. We are exploring the feasibility of assembling other VO²⁺ (z = 2, 3) families using the lessons of the present work.

Experimental Section

Materials. VO(acac)₂ was prepared as reported.⁴⁹ Electrochemically pure methanol, dichloromethane, and tetraethylammonium perchlorate (TEAP) were obtained as before.⁵⁰ All other chemicals and solvents were of analytical grade and used as obtained.

Physical Measurements. Electronic spectra were recorded with a Hitachi 330 spectrophotometer. Infrared spectra were taken on a Perkin-Elmer 783 spectrometer. EPR spectra were measured in the X-band on a Varian E-109C spectrometer equipped with a quartz Dewar for low-temperature (77 K) measurements. DPPH (g = 2.0037) was used to calibrate the spectra. Magnetic susceptibilities for solid VO(ONO)(NN) complexes were measured by using a PAR Model 155 vibrating-sample magnetometer fitted with a Walker Scientific L 75 FB AL magnet, and those for VO(ONO)(ON)⁻ complexes were determined in dichloromethane solution using the Evans method.⁵¹ The shift of ¹H signal of CH₂Cl₂ was measured in a Bruker 270 MHz spectrometer at 298 K. Electrochemical measurements were performed on a PAR Model 370-4 electrochemistry system as reported earlier.⁵² All potentials reported in this work are uncorrected for junction contribution. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (C, H, N).

Preparation of Compounds. The ligands 2-hydroxy-2'-carboxy-5-methylazobenzene (H₂azc), N-(2-carboxyphenyl)salicylaldehyde (H₂amc), 2,2'-dihydroxyazobenzene (H₂azp), and N-(2-hydroxyphenyl)salicylaldehyde (H₂amp) were prepared by reported procedures.⁵²⁻⁵⁴

(2,2'-Bipyridine)(2,2'-dihydroxyazobenzene)oxovanadium(IV), [VO(azp)(bpy)]. To a solution of VO(acac)₂ (0.125 g, 0.47 mmol) in 20 mL of methanol was added 0.075 g (0.47 mmol) of 2,2'-bipyridine. Addition of H₂azp (0.1 g, 0.47 mmol) to this solution resulted in immediate precipitation of a deep brown solid. It was filtered out, washed thoroughly with methanol, and finally dried in vacuo over P₂O₁₀. Yield: 0.18 g (87.7%). Anal. Calcd for VC₂₂H₁₆N₄O₃: C, 60.69; H, 3.68; N, 12.87. Found: C, 60.54; H, 3.52; N, 12.73.

The compounds VO(azp)(phen), VO(amp)(bpy), VO(azp)(hq), and VO(amp)(hq) were prepared similarly in excellent yields. Anal. Calcd for VO(azp)(phen), VC₂₄H₁₆N₄O₃: C, 62.75; H, 3.49; N, 12.20. Found: C, 62.59; H, 3.28; N, 12.02. Anal. Calcd for VO(amp)(bpy), VC₂₃H₁₇N₃O₃: C, 63.59; H, 3.92; N, 9.68. Found: C, 63.48; H, 3.79; N, 9.51. Anal. Calcd for VO(azp)(hq), VC₂₁H₁₄N₃O₄: C, 59.57; H, 3.31; N, 9.93. Found: C, 59.42; H, 3.21; N, 9.79. Anal. Calcd for VO(amp)(hq), VC₂₂H₁₅N₂O₄: C, 62.56; H, 3.55; N, 6.64. Found: C, 62.48; H, 3.43; N, 6.54.

(2,2'-Bipyridine)[N-(2-carboxyphenyl)salicylaldehyde]oxovanadium(IV), [VO(amc)(bpy)]. A mixture of 0.1 g (0.38 mmol) of VO(acac)₂ and 0.09 g (0.38 mmol) of H₂amc was dissolved in 20 mL of methanol and heated to reflux for 2 h. Then 0.6 g (0.38 mmol) of 2,2'-bipyridine was added and heating was continued for a further period of 1 h. The resulting solution on standing in air afforded brown crystals. Yield: 0.12 g (68.8%). Anal. Calcd for VC₂₄H₁₇N₃O₄: C, 62.34; H, 3.68; N, 9.09. Found: C, 62.20; H, 3.58; N, 8.95.

VO(amc)(hq) was prepared in a similar manner in 94.2% yield. Anal. Calcd for VC₂₃H₁₅N₂O₅: C, 61.33; H, 3.33; N, 6.22. Found: C, 61.18; H, 3.12; N, 6.11.

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Table VI. Crystallographic Data for VO(azc)(hq)-2MeOH and VO(azc)(bpy)

	VO(azc)(hq)-2MeOH	VO(azc)(bpy)
empirical formula	C ₂₅ H ₂₄ N ₃ O ₇ V	C ₂₄ H ₁₈ N ₄ O ₄ V
fw	529.4	477.4
space group	P $\bar{1}$	P2 ₁ /c
a, Å	8.104(3)	9.848(4)
b, Å	12.217(4)	18.169(6)
c, Å	12.573(5)	12.936(4)
α , deg	100.62(3)	
β , deg	92.26(3)	111.78(3)
γ , deg	105.81(3)	
V, Å ³	1176(1)	2149(2)
Z	2	4
T, °C	22	22
λ , Å	0.710 73	0.710 73
ρ_{calc} , g cm ⁻³	1.495	1.475
μ , cm ⁻¹	4.76	5.02
R, %	6.69	6.25
R _w , %	6.69	6.39
GOFC	1.47	1.24

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|]^2$, $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$; $g = 0.00005$ for VO(azc)(hq)-2MeOH and 0.0007 for VO(azc)(bpy). ^c The goodness of fit is defined as $[\sum w(|F_o| - |F_c|)^2 / (n_o - n_v)]^{1/2}$, where n_o and n_v denote the numbers of data and variables, respectively.

Table VII. Atomic Coordinates ($\times 10^4$) and Equivalent^a Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for VO(azc)(hq)-2MeOH

	x	y	z	U(eq)
V	-460(1)	-2205(1)	-3166(1)	46(1)
O(1)	-1255(5)	-3621(3)	-2687(3)	55(2)
O(2)	-1010(7)	-4836(5)	-1647(4)	90(3)
O(3)	-517(5)	-776(3)	-3528(3)	52(1)
O(4)	-88(4)	-2874(3)	-4539(3)	51(1)
O(5)	1443(5)	-1793(4)	-2604(3)	68(2)
O(6)	6419(7)	2334(8)	10658(7)	120(4)
O(7)	5338(7)	3974(7)	9914(5)	114(3)
N(1)	-1740(6)	-1619(4)	-1858(3)	45(2)
N(2)	-2742(6)	-976(4)	-1821(3)	50(2)
N(3)	-3278(5)	-2933(4)	-4108(3)	41(2)
C(1)	-1079(7)	-3873(6)	-1734(5)	56(2)
C(2)	-1067(7)	-2960(5)	-775(5)	54(2)
C(3)	-1442(7)	-1921(5)	-827(4)	50(2)
C(4)	-1504(8)	-1140(6)	116(5)	62(2)
C(5)	-1127(10)	-1370(7)	1112(5)	80(3)
C(6)	-724(11)	-2366(8)	1171(6)	89(4)
C(7)	-724(9)	-3157(7)	257(6)	75(3)
C(8)	-1753(7)	-286(5)	-3448(4)	47(2)
C(9)	-2934(7)	-434(5)	-2677(4)	50(2)
C(10)	-4277(8)	78(5)	-2635(5)	59(2)
C(11)	-4471(9)	767(6)	-3354(6)	67(3)
C(12)	-3229(10)	966(6)	-4073(6)	71(3)
C(13)	-1903(8)	492(6)	-4131(5)	61(3)
C(14)	-5972(11)	1271(7)	-3360(7)	90(4)
C(15)	-4858(7)	-2997(5)	-3877(5)	45(2)
C(16)	-6316(7)	-3530(5)	-4639(5)	53(2)
C(17)	-6078(7)	-4008(5)	-5666(5)	53(2)
C(18)	-4442(7)	-3994(5)	-5946(4)	45(2)
C(19)	-4037(9)	-4483(6)	-6972(5)	59(3)
C(20)	-2396(9)	-4435(6)	-7161(5)	62(3)
C(21)	-1027(7)	-3896(6)	-6350(5)	55(2)
C(22)	-1347(7)	-3394(5)	-5356(4)	45(2)
C(23)	-3053(6)	-3429(4)	-5131(4)	39(2)
C(24)	6401(17)	3386(14)	9647(14)	168(9)
C(25)	6297(11)	1378(11)	10080(7)	94(4)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(2-Hydroxy-2'-carboxy-5-methylazobenzenato)oxovanadium(IV) Trihydrate, VO(azc)-3H₂O. A mixture of 0.24 g (0.94 mmol) of H₂azc and 0.25 g (0.94 mmol) of VO(acac)₂ was dissolved in 20 mL of methanol, and the resulting solution was heated to reflux for 3 h. The solvent was stripped off under reduced pressure. The dried solid was treated with dichloromethane to remove soluble impurities, and the residue was dried in vacuo over P₄O₁₀. Yield: 0.28 g (79%). Anal. Calcd for VC₁₄H₁₆N₂O₇: C, 44.8; H, 4.27; N, 7.35. Found: C, 44.62; H, 4.17; N,

Table VIII. Atomic Coordinates ($\times 10^4$) and Equivalent^a Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for VO(azc)(bpy)

	x	y	z	U(eq)
V	608(1)	1586(1)	2250(1)	34(1)
O(1)	-1306(5)	1226(3)	1267(4)	50(2)
O(2)	-3696(6)	1129(3)	522(4)	59(2)
O(3)	2567(5)	1535(3)	3401(3)	42(2)
O(4)	441(6)	2443(3)	2021(4)	51(2)
N(1)	-192(6)	1483(3)	3536(5)	38(3)
N(2)	490(6)	1255(3)	4539(5)	39(2)
N(3)	983(6)	323(3)	2249(4)	34(2)
N(4)	1508(6)	1360(3)	1012(4)	34(2)
C(1)	-2576(9)	1333(4)	1293(6)	39(3)
C(2)	-2731(8)	1710(3)	2286(6)	36(3)
C(3)	-1632(7)	1754(3)	3345(6)	35(3)
C(4)	-1932(9)	2073(4)	4217(6)	43(3)
C(5)	-3257(9)	2373(5)	4036(7)	55(4)
C(6)	-4364(9)	2345(5)	2990(8)	65(4)
C(7)	-4099(9)	2009(5)	2123(7)	54(4)
C(8)	2950(8)	1226(4)	4379(6)	39(3)
C(9)	1953(7)	1072(4)	4910(6)	38(3)
C(10)	2448(9)	719(4)	5966(6)	46(3)
C(11)	3889(9)	510(4)	6480(6)	52(3)
C(12)	4851(8)	698(5)	5949(7)	61(4)
C(13)	4419(8)	1046(4)	4954(6)	52(3)
C(14)	4422(10)	118(5)	7578(7)	76(4)
C(15)	641(8)	-181(4)	2866(6)	51(4)
C(16)	807(9)	-924(4)	2777(7)	49(4)
C(17)	1317(9)	-1165(4)	1975(7)	51(4)
C(18)	1666(8)	-663(4)	1313(6)	40(3)
C(19)	1471(7)	85(4)	1467(5)	32(3)
C(20)	1828(7)	668(4)	810(5)	33(3)
C(21)	2451(8)	526(4)	32(6)	45(3)
C(22)	2740(8)	1106(5)	-549(6)	54(4)
C(23)	2389(8)	1798(4)	-360(6)	48(3)
C(24)	1801(8)	1912(4)	431(6)	41(3)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

7.35. $\mu_{\text{eff}} = 1.74 \mu_B$. UV-vis spectral data in methanol (λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 900 (41), 500 (6110), 340 (12 230).

(8-Quinolino)(2-hydroxy-2'-carboxy-5-methylazobenzenato)oxovanadium(V), [VO(azc)(hq)]. To a solution of VO(azc)-3H₂O (0.15 g, 0.40 mmol) in 20 mL of methanol was added 8-quinolinol (0.058 g, 0.40 mmol). The resulting solution upon evaporation on a water bath yielded a black solid. It was dried in vacuo over P₄O₁₀. Yield: 0.16 g (86%). Anal. Calcd for VC₂₃H₁₆N₃O₆: C, 59.35; H, 3.44; N, 9.03. Found: C, 59.18; H, 3.34; N, 8.93.

The compounds VO(azc)(bpy) and VO(azc)(phen) were prepared in the same way in excellent yields. Anal. Calcd for VO(azc)(bpy), VC₂₄H₁₈N₄O₄: C, 60.38; H, 3.77; N, 11.74. Found: C, 60.10; H, 3.56; N, 11.58. Anal. Calcd for VO(azc)(phen), VC₂₆H₁₈N₄O₄: C, 62.27; H, 3.59; N, 11.18. Found: C, 62.08; H, 3.49; N, 11.02.

All compounds described above were isolated, after drying, in pure forms and without any solvent of crystallization. Crystals of VO(azc)(hq) grown from a dichloromethane-methanol (1:1) solvent mixture were isolated as a crystalline methanol adduct which rapidly lost the solvent and crystallinity on exposure to air.

Electrosynthesis of [VO(ONO)(hq)]⁻ Species. The representative example of [VO(azp)(hq)]⁻ is described. A solution of 21 mg (0.05 mmol) of VO(azp)(hq) in 20 mL of dry dichloromethane (0.1 M TEAP) was reduced at -0.35 V vs SCE in nitrogen atmosphere. Electrolysis stopped when 4.93 C has passed. The calculated one-electron coulomb count is 4.79. The reduced solution was used for spectral and magnetic measurements.

X-ray Structure Determination. A single crystal of VO(azc)(hq)-2MeOH (0.32 \times 0.43 \times 0.56 mm³) grown by slow diffusion of methanol into a dichloromethane solution was sealed in a capillary containing the mother liquor. In the absence of mother liquor the crystal deteriorated quickly. Crystals of VO(azc)(bpy) (0.14 \times 0.24 \times 0.35 mm³) were grown by slow diffusion of hexane into a dichloromethane solution. For both complexes cell parameters were determined by a least-squares fit of 30 machine-centered reflections (2θ , 15–30°). Data were collected by the ω -scan method in the 2θ range 3–50° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.710 73 \text{ Å}$). Two check reflections measured after every 98 reflections

showed no significant intensity reduction during the 41.68 h (VO(azc)(hq)·2MeOH) and 35.63 h (VO(azc)(bpy)) of exposure to X-rays. Data were corrected for Lorentz-polarization effects. Systematic absences (or lack of it) led to the identification of the space group as $P1$ or $P\bar{1}$ for VO(azc)(hq)·2MeOH and $P2_1/c$ for VO(azc)(bpy). For VO(azc)(hq)·2MeOH, 4668 reflections were collected; 4250 were unique and 2605 satisfying $I > 3.0\sigma(I)$ were used for structure solution which could be achieved only in the space group $P\bar{1}$. In the case of VO(azc)(bpy) the corresponding numbers are 4198, 3813, and 1890 (satisfying $I > 2.0\sigma(I)$), respectively.

All calculations for data reduction, structure solution, and refinement were done on a MICROVAX II computer with the programs of SHELXTL-PLUS.⁵⁵ The structure of VO(azc)(hq)·2MeOH was solved by direct method, and that of VO(azc)(bpy), by the heavy-atom method.

(55) Sheldrick, G. M. SHELXTL-PLUS 88, *Structure Determination Software Programs*; Nicolet Instrument Corp.: Madison, WI, 1988.

Both structures were refined by full-matrix least-squares procedures making all non-hydrogen atoms anisotropic. Hydrogen atoms were included in calculated positions with fixed U ($=0.08 \text{ \AA}^2$). The highest difference Fourier peaks were 0.76 and 0.15 e/ \AA^3 for VO(azc)(hq)·2MeOH and VO(azc)(bpy), respectively. Significant crystal data are listed in Table VI. Atomic coordinates with isotropic thermal parameters are collected in Tables VII and VIII.

Acknowledgment. Financial supports received from the Department of Science and Technology, New Delhi, and Council of Scientific and Industrial Research, New Delhi, are acknowledged.

Supplementary Material Available: Tables SI–SVIII, listing anisotropic thermal parameters, complete bond distances and angles, and hydrogen atom positional parameters (11 pages). Ordering information is given on any current masthead page.