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Note

Valence Delocalization in a Mixed-Oxidation Divanadium (IV, V) Complex Electrogenerated from Its Structurally Characterized Divanadium (V) Analogue with a Tridentate (ONO) Ligand

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Introduction

Coordination chemistry of vanadium with multidentate ligands is receiving special attention in the past decade because of its catalytic[1,2] and medicinal[3−5] importance. Structural and/or functional models for vanadate-dependent haloperoxidases, vanadium nitrogenases, and other biologically active vanadium compounds have further stimulated research efforts on vanadium coordination chemistry.[6] The study of mixed-valence vanadium chemistry is an area of contemporary research interest.[7,8] Over the past few years, our group has been working on the coordination chemistry of vanadium and has reported the synthesis, characterization, chemical and electrochemical properties of V(III) and V(IV) complexes[9−14] along with biological activity of some of them.[15,16] In the present work, we report the synthesis, characterization, and crystal structure of a new complex containing the $\{OV^{v}(\mu\text{-}O)\ V^{v}O\}^{4+}$ unit which exhibits the following characteristics. (i) The bridging O atom does not lie on a 2-fold axis, and the two halves of the molecule are not crystallographically equivalent.[17−19] (ii) The V−O−V angle in this compound is quite small (112.06°), and only two other molecules of similar type are known[19,20] where the V−O−V angles are still smaller. (iii) It is the stablest of the reported complexes[18,21] containing the $V_2O_3^{4+}$ core as evidenced by the highly negative potentials at which the V^V centers undergo successive reduction. (iv) The two V^V centers of the $V_2O_3^{4+}$ core are found to undergo electrochemical reduction in two distinctly separate steps which are not found in previous reports.[18,21] We also report here a mixed-oxidation state species $[L(O)V^{IV}OV^{V}(O)L]^-$ electrogenerated from its divanadium(V) analogue in solution and characterized by IR, EPR, and electronic spectroscopy. To our knowledge, it is a rare example of a mixed-oxidation $[L(O)V^{IV}OV^{V}(O)L]^-$ species electrogenerated from its divanadium(V) analogue in which the two VOL units are crystallographically nonequivalent.

Results and Discussion

Synthesis. The Schiff base of anthranilhydrazide and 2-hydroxy acetophenone is used as the ligand (H_2L) in this work. Trioxidic binuclear vanadium (V) species $V_2O_3L_2$ (**1**) is obtained by stirring stoichiometric amounts (1:1 mol ratio) of $VO(acac)_2$ and the tridentate ONO ligand H_2L in ethyl alcohol medium in open air (Scheme 1). During this reaction, vanadium is oxidized from its initial +IV state to the +V state. Magnetic susceptibility and molar conductivity data indicate that $V_2O_3L_2$ is diamagnetic and electrically nonconducting in solution.

The mixed-valence vanadium (IV,V) species $V_2O_3^{3+}$ is generated in solution by constant potential electroreduction (at −1.3 V) of the corresponding $V_2VO_3^{4+}$ species (eq 1).

$$V_2O_3L_2 + e^- \rightleftharpoons V^VV^{IV}O_3L_2^- \tag{1}$$

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Scheme 1. Reaction Diagram for the Isolation of Mixed-Valence V(IV, V) Complex

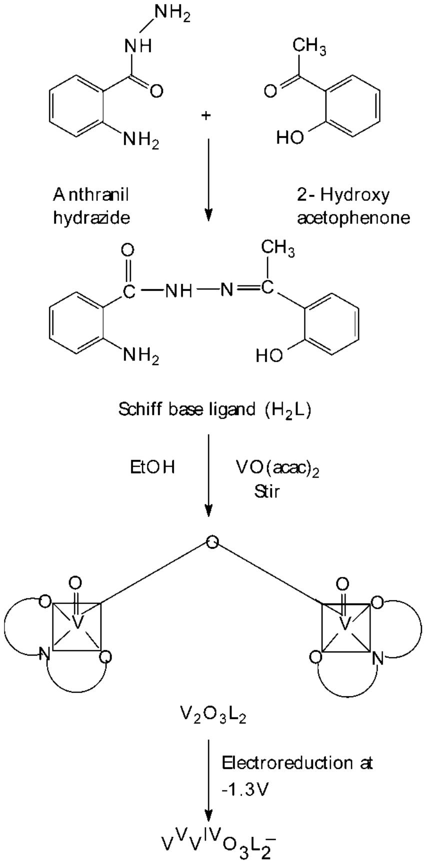

Table 1. IR, Electronic Spectral, and Cyclic Voltammetric Data

complex	V−O str, cm^{-1}	V−O−V str, cm^{-1}	UV−vis^b λ_{max}, nm (ϵ, M^{-1}cm^{-1})	$E_{1/2}{}^c$ ($\Delta E_p{}^d$)/ V(mv)
$V_2O_3L_2$	1016, 979^a	856^a	418 (16170), 324 (31807), 281 (41039)	−0.96 (230), −1.68 (200)
$V_2O_3L_2^-$	1001, 918^b	860^b	979(454), 675(626)	

[a] In KBr pellet. [b] In CH_2Cl_2. [c] At a platinum electrode; supporting electrolyte, tetrabutylammonium perchlorate (TBAP; 0.1 M); reference electrode, SCE; scan rate, 50 mV s^{-1}; $E_{1/2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [d] $\Delta E_p = E_{pa} - E_{pc}$.

Attempted isolation of the reduced complex, $V_2O_3L_2^-$, in the form of a pure salt has been unsuccessful.

Spectral Characteristics. Selected spectral data of the complex are summarized in Table 1. The IR spectrum of the complex does not exhibit the ligand bands at 3477 cm^{-1} [ν(OH)], 3209 cm^{-1} [ν(NH)], and 1640 cm^{-1} [ν(C=O)].[22,23] Characteristic strong bands in the spectra of both the ligand and the complex are located at 1600 and 1540 cm^{-1} because of ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand.[23,24] A pair of IR bands for the complex ($V_2O_3L_2$) are observed at 1016 and 979 cm^{-1} because of the terminal ν(V=O) stretching,[18−21,25−27] and a moderately strong band due to V−O−V asymmetric bridge vibration is located at 856 cm^{-1}.[25,27,28] After coulometric reduction, the terminal ν(V=O) and the asymmetric V−O−V stretching vibrations of the $V_2O_3L_2^-$ in CH_2Cl_2 solution appear at 1001, 918, and 860 cm^{-1}, respectively.

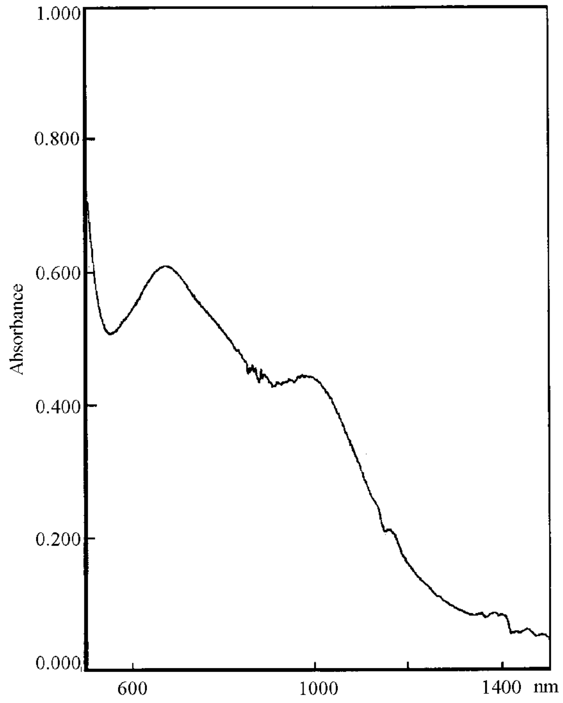

Figure 1. Electronic absorption spectra of electrogenerated [L(O)-$V^{IV}OV^{V}$(O)L]$^-$ in CH_2Cl_2.

The electronic absorption spectrum of complex **1** displays a shoulder in the 440−400 nm region followed by two strong absorptions in the 330−310 and 280−270 nm ranges which are assignable to L−V(dπ) LMCT and intraligand transitions, respectively.[18] The spectrum (Figure 1) of its electroreduced congener $V_2O_3L_2^-$ exhibits a new band of moderate intensity in the near-IR region at 979 nm. Absorption in this region is a characteristic feature of the $[V_2O_3]^{3+}$ core.[21,28−32]

The ^{1}H NMR (DMSO-d_6) spectral data of the free ligand and its divanadium (V) complex, **1**, are given in the Experimental Section. The spectrum of the free ligand exhibits an OH (phenolic) resonance at 13.4 ppm, CH_3 protons at 2.46 ppm, and aromatic protons at 7.64−6.57 ppm,

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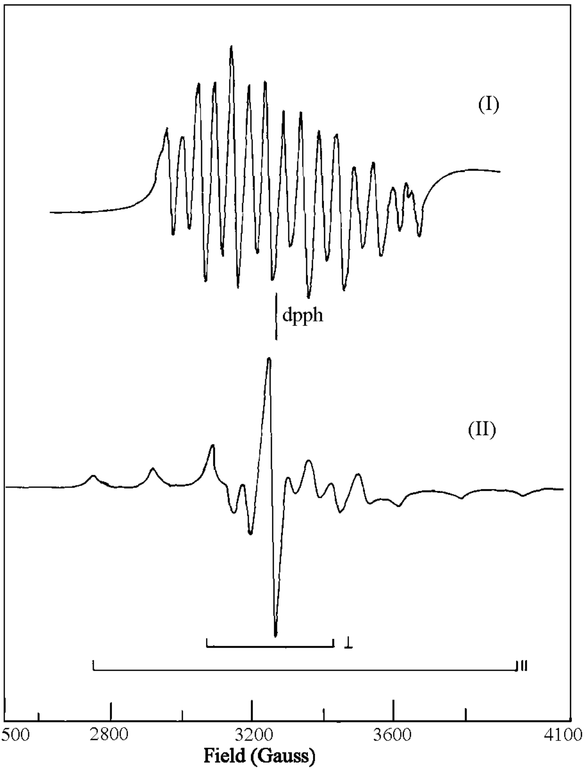

Figure 2. X-band EPR spectra of electrogenerated $[L(O)V^{IV}OV^{V}(O)L]^-$ in CH_2Cl_2/tolune (1:3 v/v) solution: (I) at 300 K; (II) at 77 K. Instrument settings: power, 30 dB; modulation, 100 kHz; sweep center, 3200 G; sweep time, 240 s; sweep width, 2000 G.

Table 2. X-band EPR Data for $V_2O_3L_2^-$ in CH_2Cl_2

300 K		77 K					
g	A/G	$g_{\parallel}$	$g_{\perp}$	g_{av}[a]	$A_{\parallel}$/G	$A_{\perp}$/G	A_{av}[b]/G
1.994	29.8	1.976	2.016	2.002	104.2	32.8	56.6

[a] $g_{av} = {}^1/_3(2g_{\perp} + g_{\parallel})$. [b] $A_{av} = {}^1/_3(2A_{\perp} + A_{\parallel})$.

respectively.[33] On coordination, the signal for the OH proton disappears, indicating deprotonation of the phenolic OH in the complex $V_2O_3L_2$. The presence of methyl protons of $V_2O_3L_2$ in the form of two close but separated singlets (at 2.50 and 2.46 ppm) and spreading out of the aromatic protons in the region 8.0−6.38 ppm indicate that the ligand environment surrounding the individual vanadium centers is not magnetically exactly equivalent.

EPR Spectroscopy. EPR spectra of the electroreduced species $V_2O_3L_2^-$ are measured in liquid as well as in frozen CH_2Cl_2 and are shown in Figure 2, and the spectral parameters are presented in Table 2. At room temperature (300 K), the EPR spectrum exhibits a 15 line profile that is characteristic of the mixed-valence divanadium (IV, V) complexes[21,28−30] (51 V, $I = {}^7/_2$) and is indicative of the odd electron being coupled to both the participating vanadium centers. In a few cases,[32,34] an eight line spectrum is also observed at room temperature. In those cases, the unpaired electron is localized on one of the vanadium centers. In a frozen solution (77 K), it exhibits the spectrum of a localized vanadium (IV) species[21,30,35] with axial features, which indicates that the species is valence-trapped at this temperature. The room-temperature spectrum (15 line) suggests that, according to Robin and Day,[36] the $V_2O_3L_2^-$ species belongs to either class III (delocalized) or class II (hopping) on the EPR time scale ($\sim 10^{-9}$ s).[37,38]

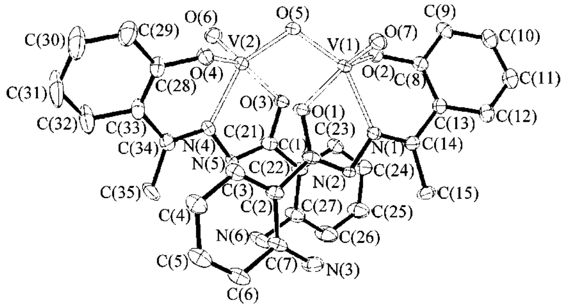

Figure 3. ORTEP plot of $V_2O_3L_2$ with atom labeling scheme.

Table 3. Crystal Data and Details of Refinement for the Complex $V_2O_3L_2$

formula	$C_{30}H_{26}N_6O_7V_2$
fw	684.45
cryst syst	monoclinic
space group	$P2_1/c$
a, Å	7.9240(18)
b, Å	16.211(4)
c, Å	23.381(5)
β, deg	96.145(5)
V, Å^3	2986.1(12)
Z	4
T, K	293(2)
λ, Å	0.71073
D_c, Mg m^{-3}	1.522
μ(Mo Kα) mm^{-1}	0.684
F(000)	1400
R1, wR2 [$I > 2\sigma(I)$]	0.0694, 0.1536
GOF on F^2	1.027

Crystal Structure of $V_2O_3L_2$. The bridging O atom does not lie on a 2-fold axis, and the two halves of the molecule are not crystallographically equivalent, although they have closely matching dimensions. The molecular structure and the atomic labeling scheme are illustrated in Figure 3. Experimental details are given in Table 3, and bond parameters are included in Table 4.

The terminal oxygen atom, ONO of H_2L, and the oxygen atom binding two vanadium centers complete the distorted square-pyramidal geometry around the metal center in a VO_2L unit. Least-squares calculation shows the vanadium atoms V(1) and V(2) to be 0.474(6) and 0.471(6) Å above the basal planes defined by (O1, O2, O5, N1) and (O3, O4, O5, N4), respectively. The dihedral angle between the pyramid bases corresponding to V(1) and V(2) is 58.53(17)°. The V═O distances 1.576(3) and 1.578(3) Å are typical of a vanadium−oxygen double bond.[17−21] The V−N distances [2.075(3)−2.084(3) Å] are very similar to the reported analogous complexes.[18,20] The vanadium to bridging oxygen distance [1.800(2)−1.803(2) Å] is unexceptional.[18] In the

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(33) We are unable to detect the NH protons in the spectrum because of the presence of a broad solvent peak in the 3−4 ppm region.

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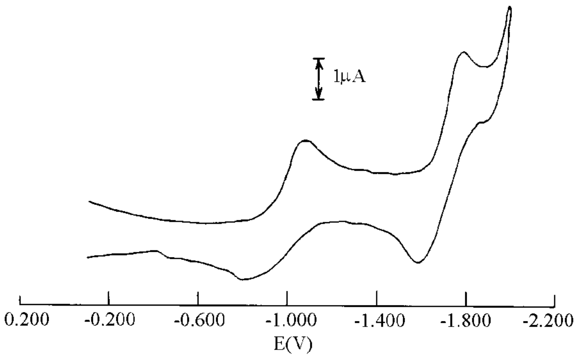

Figure 4. Cyclic voltammogram of $V_2O_3L_2$ in CH_2Cl_2 (0.1 M TBAP) at a platinum electrode; scan rate = 50 mV/s, and potentials recorded vs SCE.

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) for $V_2O_3L_2$

V(1)−O(7)	1.576(3)	V(2)−O(6)	1.578(3)
V(1)−O(2)	1.814(3)	V(2)−O(4)	1.814(3)
V(1)−N(1)	2.075(3)	V(2)−N(4)	2.084(3)
V(1)−O(5)	1.800(2)	V(2)−O(5)	1.803(2)
V(1)−O(1)	1.949(2)	V(2)−O(3)	1.931(2)
V(1)−V(2)	2.987(10)		
O(7)−V(1)−O(5)	108.13(13)	O(6)−V(2)−O(4)	104.42(15)
O(5)−V(1)−O(2)	101.14(11)	O(6)−V(2)−O(3)	104.05(14)
O(5)−V(1)−O(1)	86.39(10)	O(4)−V(2)−O(3)	146.87(12)
O(7)−V(1)−N(1)	102.16(13)	O(5)−V(2)−N(4)	149.45(12)
O(2)−V(1)−N(1)	83.31(11)	O(3)−V(2)−N(4)	74.83(11)
O(7)−V(1)−O(2)	103.91(14)	O(6)−V(2)−O(5)	107.78(13)
O(7)−V(1)−O(1)	102.82(12)	O(5)−V(2)−O(4)	100.09(12)
O(2)−V(1)−O(1)	148.27(11)	O(5)−V(2)−O(3)	86.96(11)
O(5)−V(1)−N(1)	147.14(11)	O(6)−V(2)−N(4)	100.43(13)
O(1)−V(1)−N(1)	74.58(11)	O(4)−V(2)−N(4)	83.67(12)
V(1)−O(5)−V(2)	112.06(12)		

present complex, $V_2L_2O_3$, the V—O—V angle is 112.06(12)°, one of the smallest values among the $V_2VO_3^{4+}$ complexes reported to date. The V—V distance [2.9875(10) Å] is also very similar to those of other reported complexes. Two other complexes of $V_2O_3^{3+}$ are known,[21,30] where mixed-valence V(IV, V) species are electrogenerated from divanadium (V) analogues.

Redox Properties: Mixed-Valence $V_2O_3\ L_2^-$. Figure 4 depicts a representative voltammogram of $V_2O_3L_2$ (**1**) in dichloromethane solution which is found to undergo two successive one electron reductions at $E_{1/2} = -0.96$ ($\Delta E_P = 230$ mV) and $E_{1/2} = -1.68$ ($\Delta E_P = 200$ mV) (Table 1), which are assigned to $V^VV^V/V^{IV}V^V$ and $V^{IV}V^V/V^{IV}V^{IV}$ couples. Our result is thus somewhat different from that of Chakravorty et al.[21] where both the V^V centers were reduced at the same potential. An interpretation of our results may be offered in the following way. First, it is well-known that in a binuclear complex if communications between the two metal centers are good, then they tend to undergo oxidation/reduction at the same potential, whereas, if the metal centers are not communicating with each other effectively, they undergo redox activity at different potentials. In our complex, the V−O−V angle is 112.06°, while it is 160.8° in the complex reported by Chakravorty et al.[21] In the oxo-bridged metal complexes, the communication between the metals is known to increase as the M−O−M angle approaches 180°. Second, as the two halves of the molecule are not crystallographically equivalent, the electronic environment around each VOL unit is somewhat different (also evidenced by the NMR spectrum) which may cause them to get reduced at different potentials.

Constant potential coulometry at −1.3 V in a dichloromethane−acetonitrile mixture leads to the generation of the mixed-valence species $V^{IV}V^V$ in solution which was characterized by EPR, IR, and electronic spectra, but unfortunately, it could not be isolated in the solid state.

Conclusion

The synthesis of new (μ-oxo) divanadium (V) complex $V_2O_3L_2$, **1**, has been achieved in excellent yield and is characterized by X-ray crystallography, various spectroscopic techniques, and electrochemistry. As the V−O−V angle is very low, 112.06°, the effective communication between the two metal centers is rather weak, and hence, they undergo redox activity at different potentials. The mixed-valence vanadium $V^{IV}V^V$ complex $V_2O_3L_2^-$, generated by constant potential (−1.3 V) electroreduction of the corresponding $V_2O_3^{4+}$ core, has been characterized in solution with the help of IR, EPR, and electronic spectroscopy. The unpaired electron is interacting with both 51 V ($I = {}^7/_2$) nuclei in fluid solution at 300 K, and in a frozen glass (77 K), parallel and perpendicular components characteristic[35] of a localized $V^{IV}O$ center are observed. Such delocalization appears to be a common feature of most $V_2O_3^{3+}$ complexes so far examined in solution.

Experimental Section

Materials. $[VO(acac)_2]$ was prepared as described in the literature.[39] Reagent grade solvents were dried and distilled prior to use. All other chemicals were reagent grade, available commercially, and used as received.

Instrumentation. Elemental analyses were performed on a Perkin-Elmer 240 C, H, N analyzer. IR spectra of solid compound ($V_2O_3L_2$ as KBr pellets) and in solution state ($V_2O_3L_2^-$ in NaCl cell) were recorded on a Perkin-Elmer 783 spectrometer. ^{1}H NMR spectra were recorded with a Bruker AVANCE DPX 300 MHz spectrometer using $SiMe_4$ as an internal standard. Electronic spectra were recorded on a Shimadzu UV−vis recording spectrophotometer, and electronic spectra in the near-IR region were recorded on a Hitachi U-3400 UV/vis/near-IR spectrophotometer. EPR spectra were obtained at X-band frequencies on a Varian E-109C spectrometer equipped with a gas-flow temperature controller for variable- temperature studies. Spectra at 77 K were collected using a quartz dewar. The calibrant was DPPH ($g = 2.0037$). Magnetic susceptibility was measured with a PAR model 155 vibrating sample magnetometer with $Hg[Co(SCN)_4]$ as calibrant. Electrochemical measurements were made at 298 K under a dry nitrogen atmosphere using a PC-controlled EG&G/PAR-273A potentiostat. A conventional three electrode configuration was used, consisting of platinum wire working and auxiliary electrodes, an SCE reference, and TEAP as supporting electrolyte. The ferrocene/ferrocenium (Fe/Fe^+) couple was used as the internal standard.

Crystallography. A deep brown prismatic crystal of **1** (0.93 × 0.68 × 0.11 mm^3) was chosen for X-ray diffraction study. The compound crystallized in the monoclinic space group $P2_1/c$. Intensity data were collected at 293 K on a Bruker Smart CCD area detector system using graphite-monochromatized Mo Kα

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radiation ($\lambda = 0.71073$ Å). The intensities were corrected for empirical absorption effects using SADABS.[40] The structure was solved by direct method. All non-hydrogen atoms were refined anisotropically by full-matrix least squares, with a riding model for the hydrogen atoms, using the SHELXTL package.[41]

Synthesis of Ligand (H_2L). Schiff base ligand, 2-aminobenzoylhydrazone of 2-hydroxy acetophenone, was prepared by reacting anthranilhydrazide (7.6-g/50.33-mmol) and 2-hydroxy acetophenone (6.8-g/50.00-mmol) in stirring ethanol (25 mL) for 2 h. The resulting yellowish-white compound was filtered, washed three times with ethanol, and dried over fused $CaCl_2$. Mp 170 °C. Yield 70%. Anal. Calcd for $C_{15}H_{15}N_3O_2$: C, 66.91; H, 5.58; N, 15.61. Found: C, 66.73; H, 5.53; N, 15.67. ^{1}H NMR (DMSO-d_6, δ): 7.64−6.57 (m, 8H, C_6H_4), 2.46 (s, 3H, CH_3), 13.4 (s, OH).

Synthesis of $V_2O_3L_2$. A 0.28-g (1.04-mmol) sample of ligand **H_2L** was dissolved in 30 mL of ethanol. When a 0.27-g (1.02-mmol) sample of vanadium (IV) acetylacetonate was added to the solution, the solution changed color to dark brown. After 3 h of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 5 days produced dark brown crystals. Yield ~ 80%. Anal. Calcd for $C_{30}H_{26}N_6O_7V_2$: C, 52.59; H, 3.79; N, 12.27. Found: C, 52.39; H, 3.32; N, 12.18. ^{1}H NMR (DMSO-d_6, δ): 8.0−6.38 (m, 16H, C_6H_4), 2.50 (s, 3H, CH_3), 2.46 (s, 3H, CH_3).

Electrosynthesis of $V_2O_3L_2^-$. A solution of 20 mg (0.03-mmol) of $V_2O_3L_2$ in 30 mL of a mixture of dichloromethane and acetonitrile (0.1 M TBAP) was reduced coulometrically at a constant potential of −1.3 V versus SCE in nitrogen atmosphere. Electrolysis was complete when 2.84 C had passed. The calculated one-electron coulomb count is 2.82. The reduced solution was used for spectral studies.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, atomic and hydrogen coordinates, equivalent displacement parameters, and anisotropic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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