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Solution Study of a Structurally Characterized Monoalkoxo-Bound Monooxo-Vanadium(V) Complex: Spontaneous Generation of the Corresponding Oxobridged Divanadium(V,V) Complex and its Electroreduction to a Mixed-Valence Species in Solution

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An interesting transformation of a structurally characterized monooxoalkoxovanadium(V) complex [VO(OEt)L] (LH_2 = a dibasic tridentate ONO donor ligand) in solution leading to the formation of the corresponding monooxobridged divanadium(V,V) complex $(VOL)_2O$ is reported. This binuclear species in solution is adequately characterized by elemental analysis, measurement of conductance (in solution), various spectroscopic (UV−vis, IR, NMR, and mass spectrometry) techiniques and by cyclic voltammetry. The corresponding mixed-valence vanadium(IV,V) species has been generated in CH_3CN solution by controlled potential electrolysis of $(VOL)_2O$. This mixed-valence species is identified and studied by EPR technique (at room temperature and at liquid nitrogen temperature) and also by UV−vis spectroscopy. This study may be regarded as a general method of obtaining monooxo-bridged binuclear vanadium(V,V) species from the corresponding mononuclear monooxoalkoxovanadium(V) complexes of some selected dibasic tridentate ONO chelating ligands, which can be utilized as the precursor of monooxobridged divanadium(IV,V) mixed-valence species in solution obtainable by controlled potential electrolysis.

Introduction

Vanadium is currently receiving considerable attention as a biologically important metal due to the existence of vanadoenzymes[1] and other vanadium containing biological molecules like amavadine.[2] Discovery of a vanadium-containing cofactor in bromoperoxidases[1a,3] and nitrogenases[4e] has evoked new interest in coordination chemistry of vanadium. Exploration of chemical and electrochemical reactivity of oxovanadium(V) complexes in general and vanadium(V) alkoxides[5] in particular are of current interest. Another important biological activity of vanadium is its

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insulin-mimetic characteristic, which can cause in vivo stimulation of the uptake and metabolism of glucose.[6] The minimal structural requirements of the vanadium active sites in haloperoxidases as delineated by EXAFS, and other spectroscopic investigations have shown a distinct preference of this metal center for N- and/or O-donor points provided by histidine- imidazole, tyrosine-phenolate, and carboxylate-oxygen of the protein residues.[5,7] All of these findings have drawn the attention of the inorganic chemists, bioinorganic chemists, and the pharmacologists to the coordination chemistry of vanadium involving N−O donor ligands. A good number of structural, spectroscopic and solution studies of such vanadium compounds in which the element is present in physiologically relevant oxidation states (+3 to +5) under assorted O/N donor environment[4,8] have been reported. Though the metal alkoxide−oxygen bond is somewhat stabilized in several mononuclear vanadium(V) complexes containing one coordinated alkoxide moiety,[5] it is also noted that occasionally [VOL(OR)]-type complexes undergo hydrolysis, leading to the formation of the corresponding monooxobridged binuclear species of the type $(VOL)_2O$ and liberation of the corresponding alcohol ROH.[10a] Such a process involving a mononuclear vanadium(V) complex in which the ligand H_2L is a tridentate ONO chelating donor can be utilized as a general method of generating monooxo-bridged binuclear vanadium(V,V) species of the type $(VOL)_2O$. It may also be noted that such binuclear complexes hold the possibility of acting as precursors of mixed-valence V(IV,V) species, which are of current interest.[9,10a,16]

We have been studying the chemistry of oxo-metal complexes including those of vanadium in O−N-containing donor environments[10a–e] along with electrogeneration of mixed-valence divanadium(IV,V) complexes.[10a] In this contribution, we report structural characterization and solution behavior of a mononuclear monoalkoxo-bound monooxo-vanadium(V) complex VOL(OEt) (**1**) mentioned in our earlier work,[13] which focused on the chemical reactivity of (**1**) and structural characterization of the reaction products. **1** is found (i) to undergo profound structural change when dissolved in chloroform (containing trace water) and lead to the isolation and characterization of a new binuclear vanadium(V,V) species $(VOL)_2O$ (**2**), the ONO donor ligand (H_2L), being *2*-hydroxybenzaldehydehydrazone of 2-hydroxybenzoylhydrazine. We also report here (ii) a new mixed-oxidation state species $[L(O)V^{IV}OV^{V}(O)L]^-$ (**3**) electrogenerated from the divanadium(V,V) species (**2**) in solution. This mixed-valence species is characterized by IR, EPR, and electronic spectroscopy.

Experimental Section

Materials. $[VO(acac)_2]$ was synthesized following a reported procedue.[11] Schiff base ligand *2*-hydroxybenzaldehydehydrazone of 2-hydroxybenzoylhydrazine (H_2L) and 5-bromo-2-hydroxybenzaldehydehydrazone of 2-hydroxybenzoylhydrazine (H_2L') were prepared by a standard procedure.[10a] Purification of dichloromethane and acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as reported in the literature.[12] All other chemicals and solvents were reagent grade commercial materials and were used as received.

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Preparations of Complexes: VOL(OEt) (1). **1** was prepared by the method described in one of our recent publications.[13] Slow evaporation of the filtrate containing (**1**) in solution yielded dark-brown crystals. Yield: 70%. Anal. Calcd for $C_{16}H_{15}N_2O_5V$: C, 52.42; H, 4.12; N, 7.64; V, 13.93. Found: C, 52.50; H, 4.21; N, 7.63; V, 13.87.^{1}H NMR($CDCl_3$, δ): 10.18 (s, 1H, OH), 8.59 (s, 1H, −CH=N), 7.98−6.78 (m, 8H, C_6H_4), 5.5 (q, 2H, CH_2, J = 7.01 OEt,), 1.74(t, 3H, CH_3, J = 6.97, OEt).

$(VOL)_2O$ (2). To a chloroform (10 mL) solution of VOL(OEt) (0.37 g, 1.01 mmol), water (30 mL) was added and the mixture is vigorously stirred for 20 min when the chloroform layer became light brown. The mixture was heated on a water bath nearly to dryness. The process was repeated five times, and the solid mass was stirred with water, filtered, and dried over concentrated H_2SO_4. Yield: 80%. Anal. Calcd for $C_{28}H_{20}N_4O_9V_2$: C, 51.07; H, 3.04; N, 8.51; V, 15.50. Found: C, 50.88; H, 3.45; N, 8.28; V, 15.46. ^{1}H NMR: 7.79−6.15 (m,16H, aromatic), 8.52 (s, 1H, CH), 10.09 (OH). Mass Spectra: m/z: 658 [M^+]. **2** is soluble in acetonitrile and dichloromethane.

Electrosynthesis of $V_2O_3L_2^-$ (3). A solution of 10.4 mg (0.016-mmol) of $(VOL)_2O$ (**2**) in a 30 mL mixture of dichloromethane and acetonitrile (0.1 M TBAP) was reduced coulometrically at a constant potential of +0.3 V versus SCE under nitrogen atmosphere. Electrolysis was complete when 1.56 C had passed. The calculated one-electron coulomb count is 1.53. The reduced solution was used for spectral (UV−vis and EPR) studies.

$(VOL')_2O$ (4). It was prepared by a method similar to that of $(VOL)_2O$ (**2**) using VOL′(OEt) as the starting material. Yield: 76%. Anal. Calcd for $C_{28}H_{18}N_4O_9Br_2V_2$: C, 41.17; H, 2.20; N, 6.86; V, 12.5. Found: C, 41.21; H, 2.16; N, 6.81; V, 12.44. ^{1}H NMR: 7.84−6.26 (m,14H, aromatic), 8.47 (s, 1H, CH), 10.17 (OH).

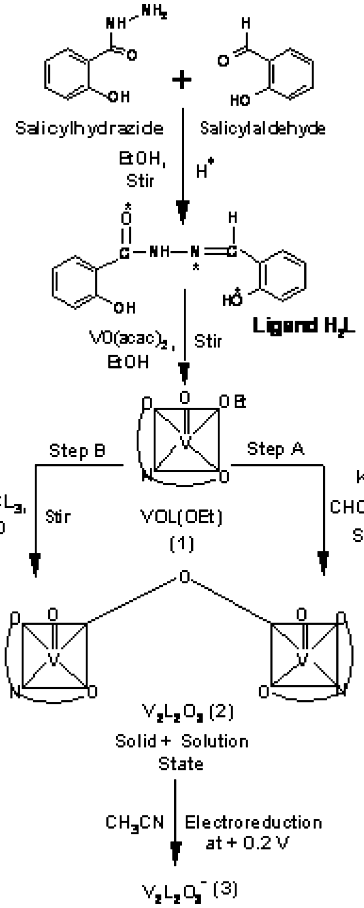
Physical Measurements. Elemental analyses were performed on a PerkinElmer 240 carbon, hydrogen, and nitrogen analyzer. Vanadium contents (%) of the complexes were determined gravimetrically[10c] as V_2O_5. IR spectra of solid compounds [VOL(OEt)] (**1**) and $(VOL)_2O$ (**2**) as KBr pellets and in $CHCl_3$ solution in NaCl cell] were recorded on a PerkinElmer 783 spectrometer. ^{1}H NMR spectra were recorded with a Bruker ADVANCE DPX 300 MHz spectrometer using $SiMe_4$ as an internal standard. Electronic spectra in the visible region 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. The spectrum at liquid nitrogen temperature was 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. Molar conductance values of the complexes in CH_3CN solution were measured with a Systronics 304 digital conductivity meter. Electrochemical measurements were made at 298 K under 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 and an SCE reference electrode and TBAP as the supporting electrolyte. The ferrocene/ferrocenium (Fe/Fe^+) couple was used as the internal standard. The mass spectrum was taken with a Micromass LCT electrospray mass spectrometer equipped with an electrospray ionization system.

X-ray Structure Determination. Single crystals of **1** were obtained by slow evaporation of ethyl alcohol solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data on the crystal of **1** were collected on a Bruker Smart CCD area detector system using graphite-monochromatised Mo Kα radiation (λ = 0.71073 Å). The intensities were corrected for empirical absorption effects using *SADABS*.[14] 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.[15]

Table 1. Crystal Data and Details of Refinement for VOL(OEt) (**1**)

chem formula	$C_{16}H_{15}N_2O_5V$
fw	366.24
cryst syst	orthorhombic
space group	*Pbca*
a, Å	10.136 (3)
b, Å	8.868 (3)
c, Å	35.640 (10)
V, Å^3	*3203.7 (16)*
Z	8
T, K	293 (2)
λ, Å	0.71073
D_{calcd}, mg m^{-3}	1.519
μ (Mo Kα) mm^{-1}	0.648
F(000)	1504
R1, wR2 [$I > 2\sigma(I)$]	0.0391, 0.1141
GOF on F^2	1.038

Scheme 1. Reaction Diagram for the Isolation of Vanadium(V), Divanadium(V,V), and Mixed-Valence Vanadium(IV,V) Complexes



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Results and Discussion

As reported in our previous work,[13] the monoalkoxo-bound monooxo-vanadium(V) species VOL(OEt) **1** was obtained by stirring stoichiometric amounts (1:1 mol ratio) of VO(acac)$_2$ and the ligand H$_2$L in ethyl alcohol in open air. During this reaction, vanadium(IV) in VO(acac)$_2$ is oxidized by oxygen of air and the isolated vanadium(V) alkoxo complex highlights the ability of the alkoxo group to stabilize high oxidation states.[16]

The binuclear vanadium(V,V) species (VOL)$_2$O (**2**) was obtained by stirring a CHCl$_3$ solution of the monooxo vanadium(V) **1** with water under the conditions mentioned in the experimental section. The synthetic strategy is outlined in Scheme 1. Just like **1**, complex **2** is also diamagnetic and nonconducting in solution. IR data for **2** are similar to those of **1**, with the exception of the appearance of a new band at 863 cm^{-1} and the presence of two ν (V═O) bands at 996 and 957 cm^{-1} in the spectrum of **2**. The new band arround 860 cm^{-1} is assigned to asymmetric V−O−V bridge vibration[10a,17a] and is indicative of the monooxo-bridged binuclear nature of **2**. Spectroscopic data are summarized in Table 2.

Description of Structure. Though the preliminary characterization data (microanalytical and spectroscopic) of **1** gave some idea of its composition and about the donor points through which the ligand is attached to the oxovanadium(V) center, they could not definitely reveal the actual structure, which could only be provided by its structure determination by single-crystal X-ray diffraction technique. The molecular structure of **1** is shown in Figure 1, and some relevant bond parameters are listed in Table 3. The VO$_4$N coordination sphere around the mono alkoxo-bound monooxo-vanadium(V) is roughly square pyramidal. The basal plane is made up by the phenolic oxygen O(2), the enolic oxygen O(1), the imine nitrogen N(1) from the tridentate ligand, and O(4) from the deprotonated alkoxide oxygen. The Schiff base ligand *2*-hydroxybenzaldehydehydrazone of *2*-hydroxybenzoylhydrazine forms a six-membered and a five-membered chelate ring at the V(V) acceptor center. The apical position of square pyramid is occupied by the terminal oxo-group O(3). The short V(1)−O(3) distance of 1.581(16) Å indicates the presence of a vanadium−oxygen double-bond (V═O), which is commonly found in five- and six-coordinated octahedral complexes[4a–d,10a,b] of vanadium(IV) and vanadium(V). The central atom vanadium(1) is above the basal plane by 0.3808 Å and is directed toward the apical oxo ligand. This deviation is in between the corresponding values found for complexes[4a–d,10a,b] of vanadium(IV) and vanadium(V). The four V−O bond lengths are unequal; the V═O bond being the shortest and the V−O [enolate oxygen O(1)] being the longest. The V−O bond lengths follow the order V−O (oxo) < V−O (alkoxide) < V−O (phenoxide) < V−O (enolate). This data indicate stronger binding of the alkoxo group compared to those of phenoxo and enolate oxygen atoms. A notable feature of the crystal structure is that the phenolic hydrogen atom of the hydrazide part of the ligand participates in intramolecular hydrogen bond with the imine nitrogen atom N(2) to form a pseudo six-membered ring.

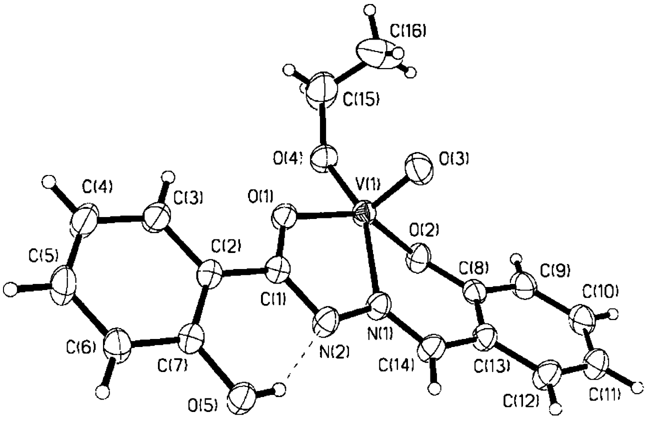

Figure 1. ORTEP plot of VOL(OEt) (**1**).

Table 3. Selected Bond Distances (Angstroms) and Bond Angles (Degrees) for **1**

	Distances		
V(1)−O(3)	1.581(16)	V(1)−O(1)	1.948(14)
V(1)−O(4)	1.743(15)	V(1)−N(1)	2.133(18)
V(1)−O(2)	1.855(15)	C(7)−O(5)	1.362(2)
	Angles		
O(3)−V(1)−O(4)	105.93(9)	O(3)−V(1)−N(1)	95.00(8)
O(3)−V(1)−O(2)	101.50(8)	O(4)−V(1)−N(1)	157.29(7)
O(4)−V(1)−O(2)	101.41(7)	O(2)−V(1)−N(1)	82.52(6)
O(3)−V(1)−O(1)	102.14(8)	O(1)−V(1)−N(1)	73.88(6)
O(4)−V(1)−O(1)	92.83(7)	O(2)−V(1)−O(1)	147.76(7)

Structural characterization of **2** by X-ray crystallography has not been possible, as good single crystals could not be grown. However, the composition of the binuclear species has been confirmed by its microanalytical, mass spectrometric, and spectroscopic data.

Solution Chemistry of 1. An interesting feature of the solution study of **1** was noted through recording of its NMR spectrum by the accidental use of a sample of CDCl$_3$ containing a little water. The ^{1}H NMR spectrum of the free ligand exhibits two close but separate OH (phenolic) resonances at 12.02 ppm and 11.76 ppm, signals for one CH proton at 8.68 ppm, and one NH proton at 11.18 ppm. Signals for aromatic protons are found in the 7.91−6.91 ppm range. The spectrum of **1** in CDCl$_3$ (which contained trace water) exhibits (part a of Figure 2) two sets of proton signals at an approximate ratio 2:1. The X-ray structure of **1** clearly shows that the ligand is coordinated in its enolate form with the

Table 2. IR, Electronic Spectral, and Cyclic Voltammetric Data of the Complexes

complex:	V−O Str, cm^{-1}	V−O−V Str, cm^{-1}	UV−vis[b] λ_{max}, nm (ε, M^{-1}cm^{-1})	E[c]$_{1/2}$(ΔE_p[d]), V (mv)
VOL(OEt) (**1**)	993[a]		391(13 275), 326(24 848) 267(34 218)	0.42(150)
V$_2$L$_2$O$_3$ (**2**)	996, 957[a]	863[a]	398(15 818), 328(28 998), 270(39 765)	0.45(80)
V$_2$L$_2$O$_3$- (**3**)	1005, 915[b]	869[b]	997(368), 649(754)	0.46(70)
V$_2$L'$_2$O$_3$ (**4**)	1000,920[a]	860[a]	399(16 641), 328(28 307), 268(41 226)	

[a] In KBr pellet. [b] In CHCl$_3$. [c] At a platinum electrode; supporting electrolyte, tetrabutylammonium perchlorate (TBAP; 0.1M); reference electrode, SCE; scan rate, 50 mVs^{-1}; $E_{1/>2}$ is calculated as the average of anodic (E_{pa}) and cathodic (E_{pc}) peak potentials. [d] $\Delta E_p = E_{pa} - E_{pc}$.

OH group of the hydrazide moiety remaining uncoordinated. Therefore, it is expected that in the NMR spectrum of **1**, only one OH proton signal (of the salicylhydrazide moiety) should be present along with a singlet CH proton signal. However, the spectrum exibits two close but separate sets of OH (phenolic) resonance (at 10.95 and 10.18 ppm), two close but separate sets of CH singlets (at 8.95 ppm and 8.59 ppm), and no signal for NH proton. The aromatic protons (a total of 16) appear in the range 7.98−6.24 ppm. In addition, it exhibits bands at 5.57 ($-CH_2$), 1.74 ($-CH_3$) ppm[4b,17a] due to the coordinated ethoxide moiety and bands due to free ethanol at 3.71($-CH_2$), 1.20 ($-CH_3$), and 5.20 ($-OH$) ppm.[4b,17a] These observations point to the presence of two different species (let the minor species be labeled as 2) in solution and demand proper explanation.

On addition of a drop of ethanol to the $CDCl_3$ solution of **1**, the minor set of bands disappeared and a cleared spectrum resulted (part b of Figure 2). This spectrum exhibits only one OH (phenolic) resonance at 10.99 ppm, one CH proton signal at 8.92 ppm, and signals for a total of eight aromatic protons in the 7.97−6.93 ppm region. In addition, the coordinated ethoxide bands present at 5.60 and 1.74 ppm are intensified, and the free ethanol bands at 3.72 and 1.22 ppm are also enhanced. We assigned this spectrum (part b of Figure 2) as a characteristic of the mononuclear species VOL(OEt) (1) which is isolated in the solid state and structurally characterized.

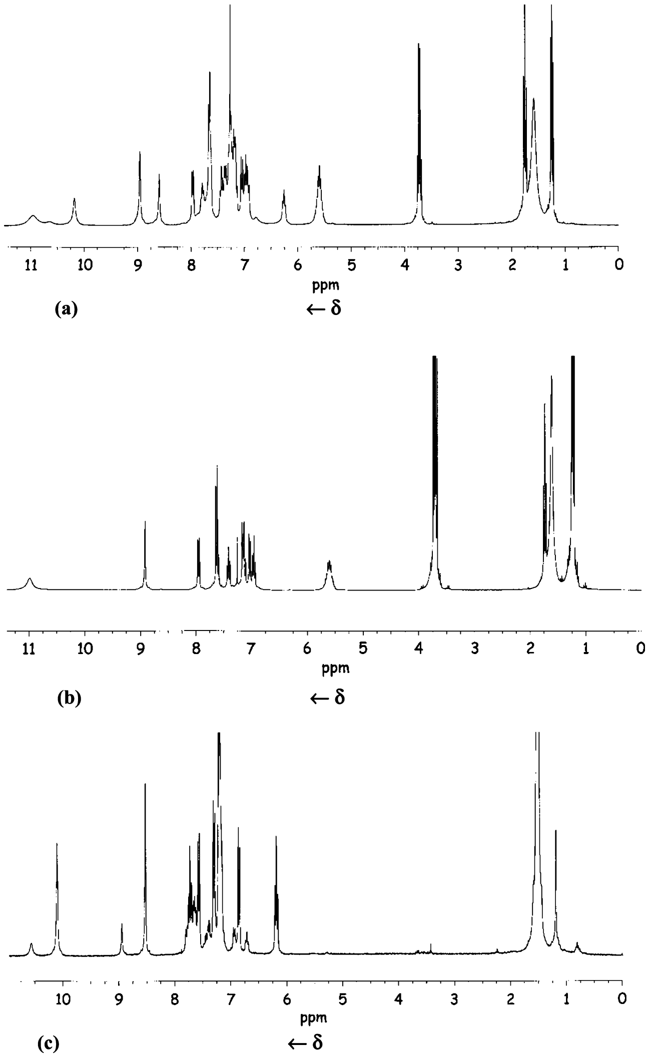

Figure 2. (a) NMR spectrum of VOL(OEt) (1) in $CDCl_3$ (b) NMR spectrum of VOL(OEt) (1) in $CDCl_3$ after addition of one drop of ethanol (c) NMR spectrum of $V_2O_3L_2$ (2) in CDCl.

These observations can be accounted for by proposing the following equilibrium (eq **1**) existing in $CDCl_3$ containing a little water, which also explains the simultaneous presence of the two species **1** (major species) and **2** (minor species) in solution.

$$2\,\mathrm{VOL(OEt)(1)} + \mathrm{H_2O} \rightleftharpoons \mathrm{(VOL)_2O(2)} + 2\,\mathrm{EtOH} \quad (1)$$

This equilibrium could be shifted more to the left by the addition of alcohol from outside, which is reflected in the change in NMR spectrum (part b of Figure 2) of **1** on addition of a little ethanol. Therefore, we can conclude that, in $CDCl_3$ solution in the presence of ethanol, **1** retains the structure in which it exists in the solid state and the other (minor, **2**) species, which was also present in solution, is reconverted into the mononuclear species (**1**). Conversion of **2** to **1** by the addition of ethanol has been conclusively proved by the isolation of **1** on refluxing **2** with dry ethanol. **2** exhibits all the characteristic signals of the μ-oxo binuclear species, which are similar to the corresponding signals of the μ-oxo binuclear complex reported in one of our earlier works.[10a] The spectrum of **2** in $CDCl_3$ (part c of Figure 2) exhibits only 1 OH (phenolic) resonance at 10.09 ppm (containing 2H), 1 singlet of CH proton at 8.52 ppm (containing 2H), and signals for a total of 16 aromatic protons in the 7.79−6.15 ppm region, but it does not exhibit any −NH− proton signal, signals of the coordinated ethoxide group, or of free ethanol.

Finally, the existence of both the monoalkoxo-bound mononuclear **1** and the μ-oxo binuclear **2** without any coordinated alkoxo group has been proven by the isolation of the binuclear species in the solid state by repeatedly shaking a mixture of $CHCl_3$ solution of **1** to which water was added and evaporating it to dryness on water bath and finally dried over concentrated H_2SO_4. Thus, the most appropriate formulation for **2** present in $CDCl_3$ solution of **1** is a μ-oxo binuclear vanadium(V,V) complex, which is fully characterized by spectral (IR, NMR, UV−vis, mass) and electrochemical studies.

IR Study of 1: Detection of Simultaneous Presence of the Mononuclear 1 and the μ-Oxo Binuclear Species 2 in Solution. When the IR spectrum of **1** is recorded in a KBr disk, a single strong, sharp ν(V=O) band[8b,10a,13,18] at 993 cm^{-1} pointed to its mononuclear nature in the solid state, which is retained when the spectrum is recorded in dry $CHCl_3$ solution. However, when **1** is dissolved in $CHCl_3$ containing

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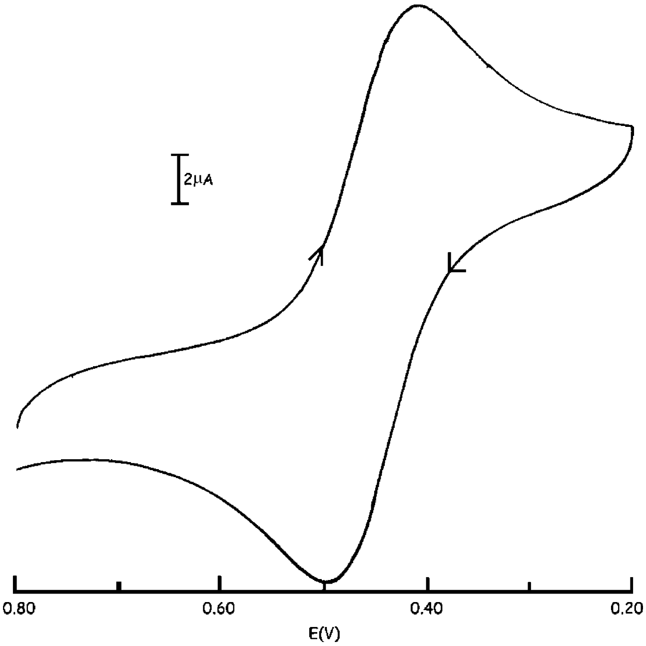

Figure 3

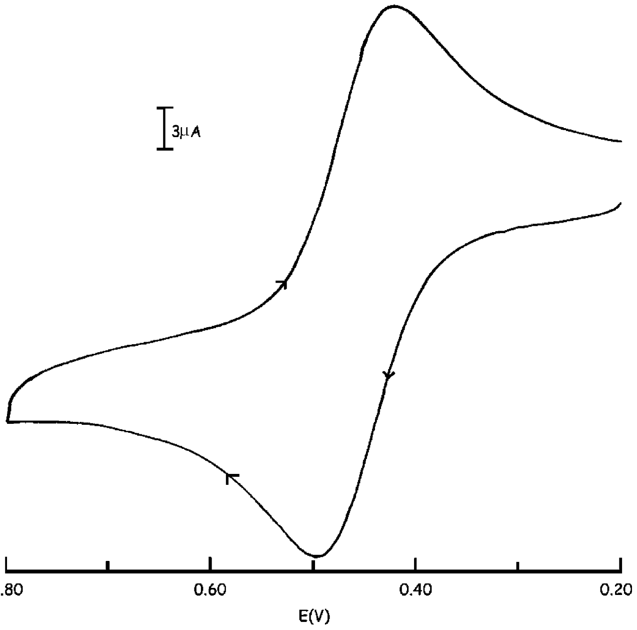

Figure 4

a drop of water two ν(V=O)[10,17a,19] bands appear at 996 cm^{-1} and 957 cm^{-1}, and another new band corresponding to the ν(V−O−V)[10a,17a,19] mode is observed arround 860 cm^{-1}. This last band was absent in the spectrum of **1** in the solid state as well as in dry $CHCl_3$ solution and is diagnostic of structurally characterized μ-oxo binuclear vanadium(V,V) complexes.[10a,17a,19] Presence of the same ν(V−O−V) band in the IR spectrum of **2** recorded as a KBr disk confirms its monooxobridged binuclear nature. Further confirmation of the ν(V−O−V) band is obtained in the following manner. A new ligand with 5-bromosalicylaldehyde ($L'H_2$) in place of salicylaldehyde has been synthesized, and the corresponding $(VOL')_2O$ has been prepared and characterized by elemental analysis and spectroscopic methods. Recording of the IR spectrum of $(VOL')_2O$ as a KBr disk exhibits a ν(V−O−V) mode in the same range (Table 2). Thus, IR spectrum of **1** in $CHCl_3$ containing a drop of water points to the simultaneous presence of both **1** and **2** in solution. This is corroborated by the results of NMR study.

Redox Properties: Generation and Identification of the Electroreduced Mixed-Valence Product. The redox data (Table 2) for **2** have been examined in CH_3CN solution by cyclic voltammetry using a platinum working electrode, platinum counter electrode, and a SCE reference electrode. $(VOL)_2O$ (**2**) displayed a quasireversible cyclic voltammetric response (Figure 3) near 0.45 V. This response is due to the $(VOL)_2O/[(VOL)_2O]^-$ couple.[19] This is further supported by the successful generation of a new mixed-valence vanadium(IV,V) species by electroreduction of the corresponding divanadium(V,V) species[10a,19] containing the $V_2{}^VO_3{}^{4+}$core.

The mixed-valence vanadium(IV,V) species $V_2O_3L_2{}^-$ (**3**) is generated[7a,16] in acetonitrile solution using a constant potential electroreduction process at +0.3 V (vs SCE) from the $V_2O_3L_2$ species **2** (eq 2). The brown solution turned green at the end of electrolysis. The experimental coulomb count is 1.56, which is very close to the required coulomb count (1.53) for one-electron reduction.

$$(\mathrm{VOL})_2\mathrm{O} + \mathrm{e}^- \rightarrow \mathrm{V^VV^{IV}O_3L_2^-} \qquad (2)$$

Attempts to isolate the reduced complex, $V_2O_3L_2{}^-$ (**3**), in the form of a pure salt have not been successful. The initial anodic scan (Figure 4) of the above reduced species **3** (green solution) was a reversible one-electron ($V^{IV}V^V/V^VV^V$) oxidation at $E_{1/2} = 0.46$ V versus SCE. So, electrochemical results points to the presence of an oxidizable vanadium(IV) center in **3**, which is confirmed by EPR experiments. These results substantiate the conversion of the mononuclear **1** into the corresponding binuclear **2**, which is the divanadium(V,V) species that gets reduced to the mixed valence species **3**.

EPR: Valence Delocalization in $V_2O_3L_2{}^-$ (3). Despite our best effort, we are unable to isolate the green paramagnetic electroreduced product (**3**) in the solid state. In solution, however, **3**, unlike its precursor, is EPR active, providing a 15-line spectrum (part a of Figure 5) at room temperature with $\langle g \rangle = 1.99$ and the isotropic coupling constant $\langle A \rangle_{15} = 50$ G. This indicates generation of a species involving a coupled vanadium ($I = {}^7/_2$) center with an odd interacting electron.[9i,10a,17a] This 15-line room-temperature spectrum suggest that the $V_2O_3L_2{}^-$ species belongs to either class III (delocalized) or class II (hopping) according to Robin and Day.[10a,20] In contrast, the spectrum (part b of Figure 5) in the glassy state at 110 K has parallel and perpendicular lines characteristic of isolated axial $V^{IV}O$ centers[10a,17,19] with $g_{\mathrm{II}} < g\perp$ and $A_{\mathrm{II}} > A_{\perp}$. The relevant parameters are $g_{\mathrm{II}} = 1.97$, $g_{\perp} = 2.01$, $g_{\mathrm{av}} = 1.99$, $A_{\mathrm{II}} = 175$ G, $A_{\perp} = 50$ G, and $A_{\mathrm{av}} = 91.7$ G. These results imply that at 110 K the unpaired

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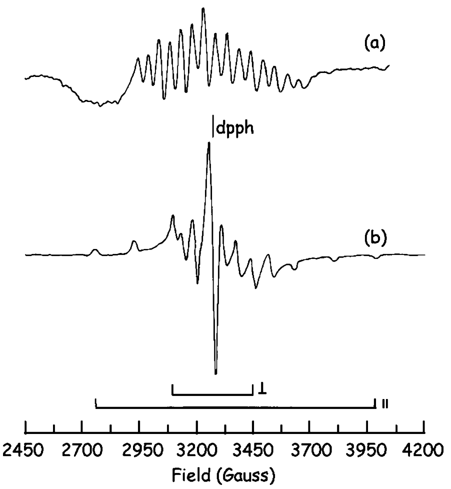

Figure 5. X-band EPR spectra of electrogenerated $[L(O)V^{IV}OV^{V}(O)L]^-$ (3) in CH_2Cl_2/tolune (1:3 v/v) solution: (a) at 300 K; (b) at 77 K. Instrument settings: power, 30 dB; modulation, 100 kHz; sweep center, 3200 G; sweep time, 240 s; sweep width, 2000 G.

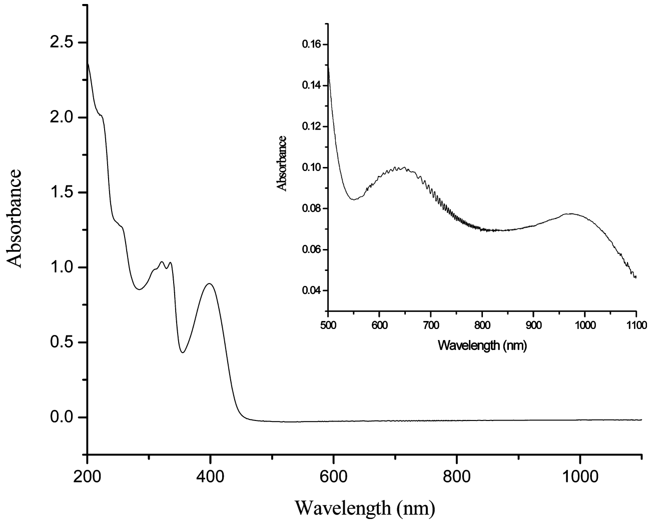

Figure 6. Electronic absorption spectra (near IR) of electrogenerated $[L(O)V^{IV}OV^{V}(O)L]^-$ solution in $CHCl_3$.

electron is localized on a single ^{51}V nucleus[10a,17,19] without interacting with the other ^{51}V nucleus of the binuclear species. The above values of the hyperfine splitting parameter (A) and the g factor are almost same as that of a localized and delocalized spectrum reported earlier[10a] for a μ-oxo divanadium(IV,V) compound electrogenerated from its structurally characterized divanadium(V,V) precursor of a related type of ligand. This observation again corroborates the generation of a bis μ-oxo binuclear species in solution, which can act as the precursor of a binuclear species with mutually interacting vanadium(IV,V) centers after electroreduction. During electroreduction process of the divanadium(V,V) complex, trace of the mononuclear vanadium(V) complex (precursor of the divanadium(V,V) complex) present as an impurity gets reduced to the corresponding vanadium(IV) species as both the binuclear and the mononuclear complexes are found to undergo reduction at almost the same potential (Table 2). EPR being a very sensitive technique could sense the presence of this vanadium(IV) species. This may be a plausible reason for increased intensities of the EPR lines.

Electronic Spectra. Electronic spectral data of **1**, **2**, and **3** are summarized in Table 2. Spectra of the vanadium(V) **1** and **2** exhibit several absorption bands in the 300−500 nm region (Figure 7 in the Supporting Information). Characteristic feature of these spectra are very similar to each other and therefore could not be utilized to follow the mononuclear-binuclear equilibrium. The band near 400 nm is assigned to ligand (L^{2-}) to metal (V^{V}) charge transfer transition, whereas the other higher energy bands are due to intraligand transitions.[10a,13] Specrtum of the mixed-valence divanadium(IV,V) complex $[V_2O_3L_2]^-$ (Figure 6) obtained by electroreduction of (**2**) $[V_2O_3L_2]$ display a band of moderate intensity near 1000 nm along with a low intensity band near 650 nm. The band around 1000 nm is assigned to intervalence transfar (IT) transition characteristic of the $[V_2O_3]^{3+}$ core[9d–k,10a,f,17,19] present in **3**. The 650 nm band is due to ligand field transition.[10a,17,19]

Conclusions

We have prepared and structurally characterized a monomeric monoalkoxo vanadium(V) complex, [VOL(OEt)], which is found to undergo hydrolysis in presence of water to yield the corresponding monooxobridged divanadium(V,V) species, $(VOL)_2O$ [H_2L = diacidic tridentate ONO chelating ligand]. The whole process may be regarded as a general route for the synthesis of monooxobridged divanadium(V,V) complexes of the type $[L(O)V^{V}(\mu\text{-}O)\ V^{V}(O)L]$ involving some selected H_2L type of tridentate ONO donor ligands. Successful generation of a mixed-oxidation divanadium(IV,V) complex, $[L(O)V^{IV}OV^{V}(O)L]^-$ (**3**) in solution by constant potential electroreduction of the corresponding μ-oxo divanadium(V,V) $[OV^{V}(\mu\text{-}O)\ V^{V}O]^{4+}$ core (**2**) has been achieved. Observed similarities of the properties with those of the authentic monooxo bridged mixed-oxidation state vanadium(IV,V) species points to the conclusion that **2**, the precursor of the present mixed-oxidation state **3**, must be a μ-oxodivanadium(V,V) complex similar to the μ-oxodivanadium(V,V) precursor of the previously reported and structurally characterized complex $V_2O_3L_2$ (ref 10a). So, this work also opens up a general route for the generation of mixed oxidation state divanadium(IV,V) species of the type $[L(O)V^{IV}OV^{V}(O)L]^-$.

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Supporting Information Available: IR spectra of **1**, **2**, and **4**, and crystallographic data for the structural analysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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