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Family of Mixed-Valence Oxovanadium(IV/V) Dinuclear Entities Incorporating N_4O_3 -Coordinating Heptadentate Ligands: Synthesis, Structure, and EPR Spectra

Amrita Mondal,[†] Sumana Sarkar,[†] Deepak Chopra,[‡] T. N. Guru Row,[‡] Kausikisankar Pramanik,[†] and Kajal Krishna Rajak^{*†}

Inorganic Chemistry Section, Department of Chemistry, Jadavpur University, Kolkata 700 032, India, and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

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Dinuclear ($V^{IV}V^V$) oxophenoxovanadates of general formula $[V_2O_3L]$ have been synthesized in excellent yields by reacting bis(acetylacetonato)oxovanadium(IV) with H_3L in a 2:1 ratio in acetone under an N_2 atmosphere. Here L^{3-} is the deprotonated form of 2,6-bis[$\{(2\text{-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{amino}\}\text{methyl}\}$ -4-methylphenol (H_3L^1), 2,6-bis[$\{(5\text{-methyl-2-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{amino}\}\text{methyl}\}$ -4-methylphenol (H_3L^2), 2,6-bis[$\{(5\text{-}tert\text{-butyl-2-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{amino}\}\text{methyl}\}$ -4-methylphenol (H_3L^3), 2,6-bis[$\{(5\text{-chloro-2-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{amino}\}\text{methyl}\}$ -4-methylphenol (H_3L^4), 2,6-bis[$\{(5\text{-bromo-2-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{amino}\}\text{methyl}\}$ -4-methylphenol (H_3L^5), or 2,6-bis[$\{(5\text{-methoxy-2-hydroxybenzyl})(N',N'\text{-(dimethylamino)ethyl})\text{methyl}\}$ -4-methylphenol (H_3L^6). In $[V_2O_3L^1]$, both the metal atoms have distorted octahedral geometry. The relative disposition of two terminal $V=O$ groups in the complex is essentially cis. The $O=V\cdots V=O$ torsion angle is $24.6(2)^\circ$. The $V-O_{\text{oxo}}-V$ and $V-O_{\text{phenoxo}}-V$ angles are $117.5(4)$ and $93.4(3)^\circ$, respectively. The $V\cdots V$ bond distance is $3.173(5)$ Å. X-ray crystallography, IR, UV–vis, and 1H and ^{51}V NMR measurements show that the mixed-valence complexes contain two indistinguishable vanadium atoms (type III). The thermal ellipsoids of O2, O4, C10, C14, and C15 also suggests a type III complex in the solid state. EPR spectra of solid complexes at 77 K display a single line indicating the localization of the odd electron ($3d_{xy}^1$). Valence localization at 77 K is also consistent with the ^{51}V hyperfine structure of the axial EPR spectra ($3d_{xy}^1$ ground state) of the complexes in frozen (77 K) dichloromethane solution: $S = 1/2$, $g_{\parallel} \sim 1.94$, $g_{\perp} \sim 1.98$, $A_{\parallel} \sim 166 \times 10^{-4} \text{ cm}^{-1}$, and $A_{\perp} \sim 68 \times 10^{-4} \text{ cm}^{-1}$. In contrast isotropic room-temperature solution spectra of the family have 15 hyperfine lines ($g_{\text{iso}} \sim 1.974$ and $A_{\text{iso}} \sim 50 \times 10^{-4} \text{ cm}^{-1}$) revealing that the unpaired electron is delocalized between the metal centers. Crystal data for the $[V_2O_3L^1] \cdot CH_2Cl_2$ complex are as follows: chemical formula, $C_{32}H_{43}O_6N_4 \cdot Cl_2V_2$; crystal system, monoclinic; space group, $C2/c$; $a = 18.461(4)$, $b = 17.230(3)$, $c = 13.700(3)$ Å; $\beta = 117.88(3)^\circ$; $Z = 8$.

Introduction

The chemistry of mixed-valence vanadium incorporating nonporphyrinic O/N-coordinating ligands is of abiding interest.^{1,2} The coordination chemistry of the dinuclear mixed-

valence oxovanadium(IV/V) species offers easy access to the model systems $[3d^1, 3d^0]$ to understand the behavior of the unpaired electron and hence the oxidation state of metal both in solid and in solution. In addition, the mixed-valence vanadium compounds play an important role in different biological process.^{3–6} Although several dinuclear oxo-bridged

* To whom correspondence should be addressed. E-mail: kajalrajak@hotmail.com.

[†] Jadavpur University.

[‡] Indian Institute of Science.

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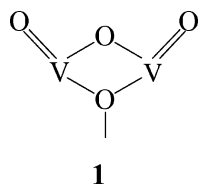
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oxovanadium(IV/V) complexes have been reported in this area,^{6–19} studies on mixed-bridged mixed-valence oxovanadium(IV/V) dimers have however been limited by the paucity of authentic complexes.^{20,21} Thus, there is an increasing demand for investigation of the underlying chemistry of the mixed-bridged type III mixed-valence oxovanadium(IV/V) species.

This work concerns the choice and design of trianionic symmetrical heptadentate ligands and the binding of these to vanadium. The chelation of conformationally labile trianionic symmetrical heptadentate ligands ensures the formation of a stable mixed-bridged mixed-valence vanadium(IV/V) dimer over an isovalent analogue. Thus, the introduction of such type of ligands may be a promising synthetic approach in the field of mixed-bridged type III mixed-valence dinuclear oxovanadium(IV/V) chemistry. Herein we explore the synthesis of a family of μ -oxo μ -phenoxo (motif **1**) dinuclear type III mixed-valence oxovanadium(IV/V) compounds with potentially bridging and chelating trianionic symmetrical ONN(O)NNO-coordinating heptadentate ligands. The crystal structure of one representative complex has been determined, which reveals the presence of a symmetrical $[\text{OV}(\mu\text{-O}_{\text{oxo}})(\mu\text{-O}_{\text{phenoxo}})\text{VO}]^{2+}$ core. The status of metal valence in the complexes is also examined with the help of FT-IR, UV-vis, EPR, and ^{51}V and ^1H NMR spectroscopic studies. Electrochemical properties of the complexes are reported.



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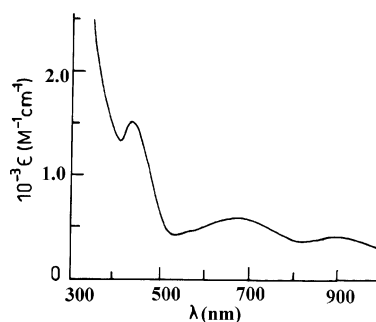
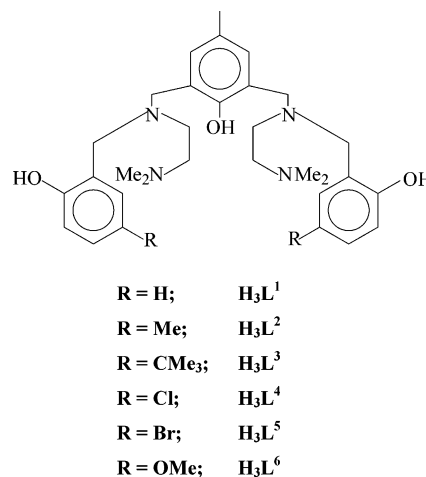


Figure 1. UV-vis spectrum of $[\text{V}_2\text{O}_3\text{L}^1]$ in dichloromethane solution.

Chart 1

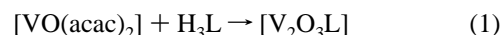


Results and Discussion

A. Synthesis. The six heptadentate H_3L^1 – H_3L^6 (general abbreviation, H_3L) ligands used in this work are given in Chart 1.

The ligands possess two sets of identical monoacidic ONN-chelating donor sites along with a central phenolate group (Chart 1). It is interesting to note that the choice of such ligands helps us to achieve our goal in the context of synthesis of mixed-bridged type III mixed-valence dinuclear oxovanadium(IV/V) complexes.

The reaction of $[\text{VO}(\text{acac})_2]$ with H_3L in a ratio of 2:1 in acetone under an inert atmosphere at ambient condition affords the green colored complexes of composition $[\text{V}_2\text{O}_3\text{L}]$ in excellent yields (eq 1).



B. IR and UV-Vis Spectra. All the compounds display a strong $\text{V}=\text{O}$ stretch⁶ near 970 cm^{-1} , and this suggests that the two $\text{V}=\text{O}$ groups are indistinguishable.⁶ The $\text{V}-\text{O}-\text{V}$ vibration¹¹ occurs at a frequency of about 760 cm^{-1} . The electronic spectra of the complexes have similar features, and each displays several bands in dichloromethane solution. A representative spectrum is shown in Figure 1.

The observed absorption band near 900 nm is assigned to the intervalence charge-transfer transition observed in some known mixed-valence oxovanadium complexes.^{6–21} A relatively intense band near 700 nm corresponds to ligand field excitation. The remaining strong band at $\sim 410\text{ nm}$ is believed to be of $\text{O}(\text{phenoxide}) \rightarrow \text{V}$ LMCT origin. The intervalence

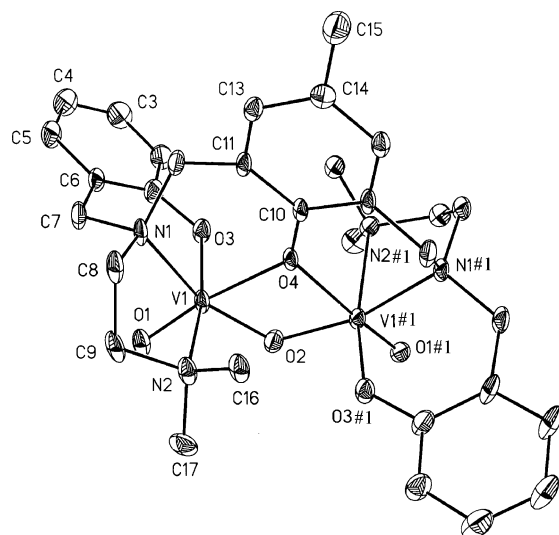


Figure 2. ORTEP plot and atom-labeling scheme for $[\text{V}_2\text{O}_3\text{L}^1]\cdot\text{CH}_2\text{Cl}_2$. All non-hydrogen atoms are represented by their 30% thermal probability ellipsoids.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [V₂O₃L¹] \cdot CH₂Cl₂

Distances			
V1-O1	1.631(5)	V1-O4	2.180(5)
V1-O2	1.856(4)	V1-N1	2.205(6)
V1-O3	1.931(4)	V1-N2	2.292(5)
V1...V1#1	3.173(5)		
Angles			
O1-V1-O2	102.6(3)	O3-V1-O4	91.4(2)
O1-V1-O3	97.7(2)	O3-V1-N1	84.9(2)
O1-V1-O4	170.7(2)	O3-V1-N2	164.0(3)
O1-V1-N1	97.5(3)	O4-V1-N1	85.4(2)
O1-V1-N2	86.0(2)	O4-V1-N2	85.8(2)
O2-V1-O3	94.1(2)	N1-V1-N2	79.2(2)
O2-V1-O4	74.5(2)	V1-O2-V1#1	117.5(4)
O2-V1-N1	159.8(3)	V1-O4-V1#1	93.4(3)
O2-V1-N2	100.3(2)		

charge-transfer transition band does not change upon variation of solvents having different polarity (DCM, CH₃CN, and DMF) suggesting that these complexes belong to type III²² in solution.¹⁰

C. Crystal Structure. The complex $[\text{V}_2\text{O}_3\text{L}^-]$ afforded single crystals as the solvate $[\text{V}_2\text{O}_3\text{L}^-]\cdot\text{CH}_2\text{Cl}_2$. A view of the dinuclear entity is shown in Figure 2. Selected bond lengths and angles are given in Table 1.

The dinuclear entity possesses a crystallographic mirror plane passing through the atoms O2, O4, C10, C14, and C15. The numbering scheme of the symmetry related atoms are *n* and *n*#1, e.g. V1–O1 and V1#1–O1#1. In the complex, the two vanadium centers are bridged by the oxo oxygen [V1–O2–V1#1 = 117.5(4)°] and the central phenolate oxygen (O4) of the ligand [V1–O4–V1#1 = 93.4(3)°], leading to a mixed-bridged dinuclear species with V1–V1#1 = 3.173(5) Å. The relative disposition of the two V=O groups in [V₂O₃L¹] is almost cis, the O1=V1...V1#1=O1#1 torsion angle being 24.6(2)°.

The vanadium atoms have a distorted octahedral geometry, and this is characterized by the O1–V1–O4 bond angle of

~170°, which significantly deviated from the ideal value of 180°. In the distorted VO₄N₂ coordination sphere the metal atom is shifted toward the oxo oxygen atom O1 by ~0.21 Å from the equatorial plane (md ~ 0.13 Å) defined by N1, N2, O2, and O3. The mixed bridging leads to noncoplanarity of the basal planes (N1 N2 O2 O3 and N1#1 N2#1 O2 O3#1), realized by a folding angle of ~84°.

The short V1–O1 bond distance [1.631(5) Å] is comparable with other structurally characterized oxovanadium complexes,²³ and this bond length is consistent with a typical multiple (V=O) bond. The N1 and N2 nitrogen atoms are coordinated trans to the bridging and the phenolate oxygen atoms, respectively. The V1–N2 [2.292(5) Å] bond is significantly longer than that of the V1–N1 [2.205(6) Å] bond revealing the weaker binding of the side arm nitrogen atom. The V1–O2 bond distance [1.856(4) Å] is slightly larger than usual.⁶ The relatively longer V1–O4 length [2.180(5) Å] can be attributed to the strong trans influence of the oxo oxygen atom.²³

In summary, X-ray crystallographic studies reveal the presence of indistinguishable vanadium atoms in the complex suggesting a type III or a disordered type I (or II) compound, but the thermal ellipsoids of O2, O4, C10, C14, and C15 are fairly good; hence, these studies render support to a type III compound.

D. Magnetism and EPR Spectra. All the compounds are paramagnetic, and the magnetic moment value/molecule at 300 K is $\mu \sim 1.78 \mu_B$, which corresponds to one electron paramagnetism.

EPR spectroscopy proved to be an important tool for the diagnosis of the distribution of the odd electron in the complex. It is well documented that the 15-line isotropic profile^{11,13,15} (^{51}V , $I = 7/2$) arises from the delocalization of the odd electron between the two vanadium centers, whereas an 8-line pattern^{9,11,13} shows a valence-trapped situation for the odd electron on the EPR spectroscopy time scale. The $[\text{V}_2\text{O}_3\text{L}]$ complexes are EPR active in the solid at 77 K as well as in dichloromethane solution (300, 77 K). Resonance parameters are listed in Table 2, and representative spectra are shown in Figure 3.

At room temperature, the EPR spectra of the pure solid were not resolved. However, at 77 K the solid complexes display an ill-resolved broad single line resonance at $g \sim 1.986$ (Figure 3a). These spectral features signify the localization of an odd 3d electron on one vanadium center^{7,24} at 77 K on the X-band EPR time scale. The complexes exhibit a 15-line isotropic hyperfine structure (Figure 3b) in dichloromethane solution at room temperature. From the spectra it is clear that there is a systematic increase of successive hyperfine lines as the central line is approached from either side. This observation corroborates with complete

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Table 2. X-Band EPR Data

complex	matrix	g_{iso}	$10^4 A_{\text{iso}}/\text{cm}^{-1}$	g_{\parallel}	g_{\perp}	g_{av}^a	$10^4 A_{\parallel}/\text{cm}^{-1}$	$10^4 A_{\perp}/\text{cm}^{-1}$	$10^4 A_{\text{av}}^b/\text{cm}^{-1}$
[V ₂ O ₃ L ¹]	CH ₂ Cl ₂ , 300 K	1.968	50						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.985 1.979		1.934	1.979	1.964	165.2	69.3	101.2
[V ₂ O ₃ L ²]	CH ₂ Cl ₂ , 300 K	1.985	48						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.979 1.984		1.948	1.999	1.981	168.6	64	97.33
[V ₂ O ₃ L ³]	CH ₂ Cl ₂ , 300 K	1.968	51						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.987 1.974		1.947	1.975	1.965	166.2	65.4	99
[V ₂ O ₃ L ⁴]	CH ₂ Cl ₂ , 300 K	1.983	51						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.971 1.986		1.942	1.985	1.971	168.4	68.25	101.6
[V ₂ O ₃ L ⁵]	CH ₂ Cl ₂ , 300 K	1.983	50						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.971 1.983		1.945	1.987	1.973	167	66.5	100
[V ₂ O ₃ L ⁶]	CH ₂ Cl ₂ , 300 K	1.983	50						
	CH ₂ Cl ₂ /toluene, 77 K solid, 77 K	1.988 1.988		1.946	1.997	1.980	164	68.75	100.5

$$^a g_{\text{av}} = 1/3[2g_{\perp} + g_{\parallel}]. \quad ^b A_{\text{av}} = 1/3[2A_{\perp} + A_{\parallel}].$$

delocalization of the odd electron between the two vanadium nuclei (⁵¹V, $I = 7/2$) in fluid solution at 300 K (type III).^{22,25}

All the compounds show well-resolved 8-line spectra in 2:1 dichloromethane/toluene solution at 77 K. The hyperfine structure can be attributed to the coupling of unpaired electron to a single ⁵¹V ($I = 7/2$) center. The order and ($g_{\parallel} < g_{\perp}$ and $A_{\parallel} \gg A_{\perp}$) magnitude of resonance parameters are consistent with the oxovanadium(IV) site of compressed d_{xy}¹ configuration.^{26–28}

The results demonstrate that metal valences are localized^{11,13} on a particular vanadium atom (type I)²² at 77 K on the X-band EPR time scale. The frozen solution (77 K) and the fluid solution (300 K) spectral parameters are related by eqs 2a and 2b, and these relations²⁵ is in good agreement with the type III nature of the mixed-valence species at room temperature.¹⁰

$$g_{\text{av}} \sim g_{\text{iso}} \quad (2a)$$

$$A_{\text{av}} \sim 2A_{\text{iso}} \quad (2b)$$

E. NMR and Electrochemical Studies. ⁵¹V and ¹H NMR of complexes were measured to understand more about the solution behavior of such complexes. The complexes are NMR (¹H and ⁵¹V) silent in CDCl₃ solution indicating that the unpaired electron and hence the metal valence is delocalized over both metal atoms in solution.

The redox properties of the mixed-oxidation dimer have been examined by cyclic voltametry using platinum as working and SCE as reference electrodes. The cyclic voltammogram were recorded with scan rate of 50 mV/s. All the compounds exhibit two irreversible one-electron waves in acetonitrile/dichloromethane (5:1) solution. The

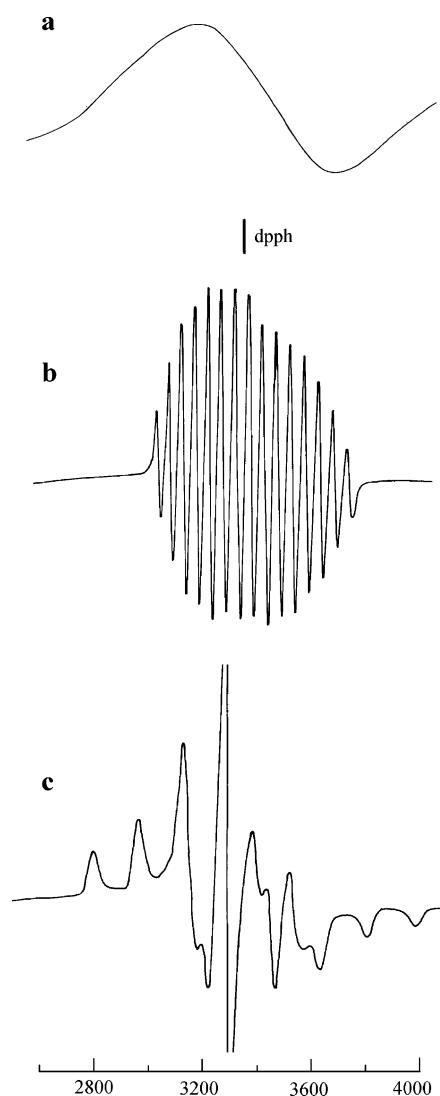
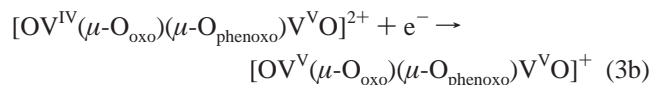
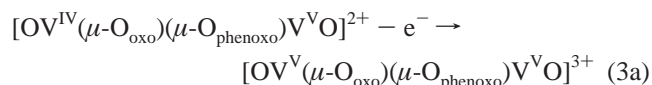


Figure 3. X-band EPR spectra for [V₂O₃L¹] in (a) the solid state at 77 K, (b) DCM at 300 K, and (c) DCM/toluene at 77 K. Instrument settings: microwave frequency, 9.1 GHz; microwave power, 30 dB; modulation frequency, 100 kHz; modulation amplitude, 12.5 G; sweep center, 3200 G.

irreversible peak (anodic peak) near +0.4 V corresponds to [OV^{IV}(μ-O_{oxo})(μ-O_{phenoxo})V^{VO}O]²⁺ to [OV^V(μ-O_{oxo})(μ-O_{phenoxo})-

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V^VO^{3+} oxidation (eq 3a). The second irreversible peak (cathodic peak) near -0.94 V is due to $[OV^{IV}(\mu-O_{oxo})(\mu-O_{phenoxo})V^VO]^{2+}$ to $[OV^{IV}(\mu-O_{oxo})(\mu-O_{phenoxo})V^VO]^{+}$ reduction (eq 3b). The irreversibility of both peaks signifies that isovalent dimers formed from the respective compounds are unstable in solution. Thus, the electrochemical studies show the superior specificity of the ligands toward the formation of a stable mixed-bridged type III mixed-valence dimer over an isovalent analogue.



F. Type of Mixed Valence. The experimental results employed in this work demonstrate that the metal valences are practically identical. The X-ray studies reveal that the metal atoms are indistinguishable. In addition, the thermal ellipsoids of atoms that lie on the C_2 axis strongly support in favor of type III compounds. The NMR (1H and ^{51}V), UV-vis, and IR spectroscopic results also attest to the interpretation of the presence of a delocalized electron. The complete delocalization of the unpaired electron and hence the metal valence over both the metal centers is reflected from the 15-line X-band EPR spectra^{22,25} in dichloromethane solution at room temperature (300 K) (Figure 3b). Interestingly, the broad single-line resonance^{4,24} of the polycrystalline solid (Figure 3a) at 77 K and the axial spectra^{26–28} (Figure 3c) in frozen solution (77 K) of the whole family revealed a complete localization of unpaired electron on one metal center (type I)²² at least on the X-band EPR scale. However, the relation between frozen solution (77 K) and room-temperature (330 K) solution spectral parameters,²⁵ vide supra (eqs 2a,b, Magnetism and EPR Spectra section), indicates the type III nature of the complexes. Thus, all the above observations collectively suggest that the oxo-phenoxo-bridged dinuclear mixed-valence oxovanadium(IV/V) species isolated in this report is more suitably described as a type III compound.

Conclusion

The main findings of this work can now be summarized. Six potentially bridging and chelating N_4O_3 -coordinating triacidic heptadentate ligands have been successfully utilized to generate air-stable oxo-phenoxo-bridged dinuclear mixed-valence oxovanadium(IV/V) complexes in excellent yields. X-ray crystallography, IR, UV-vis, and NMR (^{51}V and 1H) spectroscopic measurements reveal that the metal valences are indistinguishable. Cyclic voltammetric studies reflect the stability of the mixed-valence dimer over the isovalent analogue.

The 15-line isotropic hyperfine EPR signal in solution at room temperature is consistent with the complete delocalization of the odd electron ($3d^1$). On the other hand at 77 K the unpaired electron is localized on a vanadium center.

However, the relation ($g_{av} \sim g_{iso}$ and $A_{av} \sim 2A_{iso}$) between the frozen and fluid solution spectral parameters agrees with the type III nature of the compounds.

The studies presented herein provide valuable insights into the synthetic strategy in the field of mixed-valence chemistry of vanadium. In addition, these results proved to be helpful in the identification of the behavior of type III species having a symmetrical $[OV(\mu-O_{oxo})(\mu-O_{phenoxo})VO]^{2+}$ core in the solid and in solution. Further research aimed at the synthesis of polynuclear oxo-alkoxo/phenoxovanadates and studying their behavior in solid and solution using different polydentate ligands is currently in progress.

Experimental Section

Materials. Bis(acetylacetonato)oxovanadium(IV)²⁹ and the ligands³⁰ were prepared as reported in the literature. All the starting chemicals were analytically pure and used without further purification, and the solvents were purified by standard procedure.³¹ All reactions were carried out under an inert dry dinitrogen atmosphere.

Physical Measurements. UV-vis spectra were recorded on a Perkin-Elmer Lambda EZ-301 spectrophotometer, and IR spectra were measured with Perkin-Elmer L-0100 spectrometer. Electron paramagnetic resonance experiments were performed on a Varian E-109C (X-band, 9.1 GHz) spectrometer at a microwave power of 30 dB and modulation amplitude of 12.5 G. Spectra at 77 K were collected using a quartz dewar. Diphenylpicrylhydrazyl (dpph, $g = 2.0037$) was used to calibrate the spectra. Electrochemical measurements were performed (acetonitrile solution) on a CH 620A electrochemical analyzer using a platinum electrode. Tetraethylammonium perchlorate (TEAP)³² was used as a supporting electrolyte, and the potentials are referenced to the standard calomel electrode (SCE) without junction correction. The cyclic voltammogram were recorded with a scan rate of 50 mV/s with iR compensation in all cases. 1H NMR spectral measurement were carried out on a Bruker FT 300 MHz spectrometer with TMS as an internal reference, and ^{51}V NMR spectra at 298 K were recorded on a Bruker AMX 400 instrument with spectral width of 100 kHz, externally referenced to $VOCl_3$. Magnetic susceptibilities were measured on a PAR-155 vibrating-sample magnetometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 Series II elemental analyzer.

Synthesis of Complexes. The complexes were prepared by the same general methods. Details are given here for a representative case.

[V₂O₃L¹]. To a stirred solution of $[VO(acac)_2]$ (0.10 g, 0.37 mmol) in 20 mL of acetone was added H_3L^1 ligand (98 g, 0.19 mmol). The reaction mixture was then stirred for 2 h at ambient temperature, and in this time a green precipitate separates from the solution. This solution was filtered, washed with acetone, and dried in vacuo over fused calcium chloride. Yield: 119 mg (95%). Anal. Calcd for $C_{31}H_{41}O_6N_4V_2$: C, 55.77; H, 6.15; N, 8.39. Found: C, 55.61; H, 6.21; N, 8.21. UV-vis (λ_{max}/nm ($\epsilon/M^{-1} cm^{-1}$)): CH_2Cl_2 : 425 (1505); 675 (530); 903 (400). IR (KBr, cm^{-1}): $\nu(V=$

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O) 965; $\nu(\text{V}-\text{O}-\text{V})$ 760. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.42 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.94 V (irr). μ_{eff} : 1.78 μ_{B} .

[V₂O₃L²]. Yield: 120 mg (92%). Anal. Calcd for C₃₃H₄₅O₆N₄V₂: C, 56.98; H, 6.47; N, 8.05. Found: C, 56.88; H, 6.55; N, 7.91. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$); CH₂Cl₂): 440 (2710); 700 (1100); 906 (860). IR (KBr, cm⁻¹): $\nu(\text{V}=\text{O})$ 970; $\nu(\text{V}-\text{O}-\text{V})$ 770. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.55 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.97 V (irr). μ_{eff} : 1.75 μ_{B} .

[V₂O₃L³]. Yield: 123 mg (90%). Anal. Calcd for C₃₉H₅₇O₆N₄V₂: C, 60.08; H, 7.32; N, 7.08. Found: C, 59.92; H, 7.49; N, 7.08. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$); CH₂Cl₂): 430 (2110); 693 (710); 910 (650). IR (KBr, cm⁻¹): $\nu(\text{V}=\text{O})$ 971; $\nu(\text{V}-\text{O}-\text{V})$ 775. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.43 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.85 V (irr). μ_{eff} : 1.76 μ_{B} .

[V₂O₃L⁴]. Yield: 130 mg (94%). Anal. Calcd for C₃₁H₃₉O₆N₄ClV₂: C, 50.54; H, 5.30; N, 7.60. Found: C, 50.41; H, 5.44; N, 7.51. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$); CH₂Cl₂): 425 (2245); 690 (800); 899 (670). IR (KBr, cm⁻¹): $\nu(\text{V}=\text{O})$ 978; $\nu(\text{V}-\text{O}-\text{V})$ 769. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.56 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.92 V (irr). μ_{eff} : 1.79 μ_{B} .

[V₂O₃L⁵]. Yield: 140 mg (91%). Anal. Calcd for C₃₁H₃₉O₆N₄BrV₂: C, 45.09; H, 4.73; N, 6.62. Found: C, 44.98; H, 4.87; N, 6.62. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$); CH₂Cl₂): 420 (1970); 699 (905); 901 (700). IR (KBr, cm⁻¹): $\nu(\text{V}=\text{O})$ 963; $\nu(\text{V}-\text{O}-\text{V})$ 771. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.50 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.98 V (irr). μ_{eff} : 1.81 μ_{B} .

[V₂O₃L⁶]. Yield: 135 mg (92%). Anal. Calcd for C₃₃H₄₅O₈N₄V₂: C, 54.47; H, 6.18; N, 7.70. Found: C, 54.33; H, 6.25; N, 7.59. UV-vis ($\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$); CH₂Cl₂): 424 (1920); 696 (620); 912 (520). IR (KBr, cm⁻¹): $\nu(\text{V}=\text{O})$ 975; $\nu(\text{V}-\text{O}-\text{V})$ 760. E_{pa} ($[\text{OV}^{\text{V}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{3+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}$): +0.49 V (irr). E_{pc} ($[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{VO}}]^{2+}/[\text{OV}^{\text{IV}}(\mu-\text{O}_{\text{oxo}})(\mu-\text{O}_{\text{phenoxo}})\text{V}^{\text{IV}}\text{O}]^{+}$): -0.88 V (irr). μ_{eff} : 1.75 μ_{B} .

Crystallographic Studies. Single crystals of suitable quality for single-crystal X-ray diffraction studies on the complex [V₂O₃L¹]-CH₂Cl₂ were grown by slow diffusion of hexane into dichloromethane solution. The crystal loses solvent in air, and hence, the data were collected in the presence of mother liquor taken in a capillary. The X-ray intensity data were measured at 293 K on Bruker AXS SMART APEX CCD diffractometer (Mo K α , λ = 0.710 73 Å). The detector was placed at a distance 6.03 cm from the crystal. A total of 606 frames were collected with a scan width of 0.3° in

Table 3. Crystal Data and Structure Refinement Parameters for [V₂O₃L¹]-CH₂Cl₂

formula	C ₃₂ H ₄₃ O ₆ N ₄ Cl ₂ V ₂
fw	752.48
cryst system	monoclinic
space group	C2/c
<i>a</i> (Å)	18.461(4)
<i>b</i> (Å)	17.230(3)
<i>c</i> (Å)	13.700(3)
β (deg)	117.88(3)
<i>V</i> (Å ³)	3852.0(13)
<i>Z</i>	8
<i>D</i> _{calcd} (mg m ⁻³)	1.566
μ (mm ⁻¹)	0.820
θ (deg)	2.50–25.35
<i>T</i> (K)	293(2)
R1, ^a wR2 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.1020, 0.2568
GOF on <i>F</i> ²	0.958

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|. \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

different settings of φ . The data were reduced in SAINTPLUS,³³ and an empirical absorption correction was applied using the SADABS package.³³ Metal atoms were located by direct methods, and the rest of the non-hydrogen atoms emerged from successive Fourier synthesis. The structure were refined by full-matrix least-squares procedures on *F*². All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included in calculated positions. Calculations were performed using the SHELXTL V5.03³⁴ program package. Molecular structure plots were drawn using ORTEP.³⁵ Relevant crystal data are given in Table 3.

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Supporting Information Available: X-ray crystallographic file in CIF format for the [V₂O₃L¹]-CH₂Cl₂. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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