

Single Crystal-to-Single Crystal Irreversible Transformation from a Discrete Vanadium(V)–Alcoholate to an Aldehydic-Vanadium(IV) Oligomer

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Abstract: An unprecedented single crystal-to-single crystal transformation occurs when a binuclear oxovanadium(V) compound $[V^V_2O_2(L)_2]$ **1** involving 2,6-bis(hydroxymethyl)-*p*-cresol (H_3L) as a bridging ligand is exposed simultaneously to white light and aerial oxygen to generate an oligomeric compound $[V^{IV}_2O_2(L^*)_2]$ **2** (H_2L^* is 3-hydroxymethyl-5-methylsalicylaldehyde). Each vanadium(V) center in **1** is reduced to vanadium(IV) in **2** at the expense of a two-electron alcohol-to-aldehyde oxidation in the coordinated ligand. The additional electron being released is possibly consumed by molecular oxygen to generate hydrogen peroxide.

Single crystal-to-single crystal (SCSC) transformations involve coordinated movement of atoms in the solid matrices. Most of these transformations are reversible in nature and are triggered by light,¹ albeit a few thermally induced incidences are also known.² A good number of these studies have been reported for organic molecules,^{1a,c–f} while crystals of metallo–organic frameworks usually fail to retain their crystallinity after the generally robust rearrangements that occur in the solid phase. Nevertheless, quite a few SCSC transformations involving coordination compounds have been reported in recent years^{1b,2a,c,e,3} that are accompanied by many interesting changes in properties such as host–guest behavior,^{3a–c} magnetism,^{2e,3d} and photochemical reactivity.^{3e} Herein, we report a binuclear oxovanadium(V) compound $[V^V_2O_2(L)_2]$ **1** involving 2,6-bis(hydroxymethyl)-*p*-cresol (H_3L) as a bridging ligand, which on exposure to white light in air, undergoes an unprecedented coordination-driven oligomerization in the solid state to an infinite one-dimensional (1D) chain of oxovanadium(IV) entity $[V^{IV}_2O_2(L^*)_2]_\infty$ **2** in 100% yield through a SCSC transformation that ends up with a redox process leading to the reduction of the metal centers with concomitant oxidation of the organic component. We have investigated this transformation by X-ray diffraction, IR and UV–vis spectroscopy, magnetic susceptibility measurements, and EPR spectroscopy.

The interest in the coordination chemistry of H_3L as ligand has been invigorated in recent years because of the variable modes (μ_2 or μ_3) of coordination provided by this oxido-rich molecule, leading to the isolation of organic–inorganic hybrid architectures with multiple metal centers.⁴ In continuation of our long-standing interest in vanadium coordination chemistry,⁵ we sought to explore the chemistry of this alcohol-rich ligand with vanadium as the metal ion source. When $VO(acac)_2$ was reacted with H_3L in 1:1 molar ratio in dichloromethane, a dark-red crystalline compound **1** was obtained. X-ray diffraction analysis⁶ of **1** has revealed it to be a centrosymmetric molecule with two five-coordinated vanadium(V)

centers connected by a pair of bridging phenoxido oxygen atoms, each coming from a fully deprotonated ligand (L^{3-}) with three units of negative charge to meet the requirement of vanadium(V) (Figure 1a). The average C–O bond distances of the alkoxides (1.419 Å) and phenoxides (1.385 Å) are in the expected range, as are the average V–O (phenoxido) (2.017 Å) and V–O (alkoxido) (1.786 Å) distances.

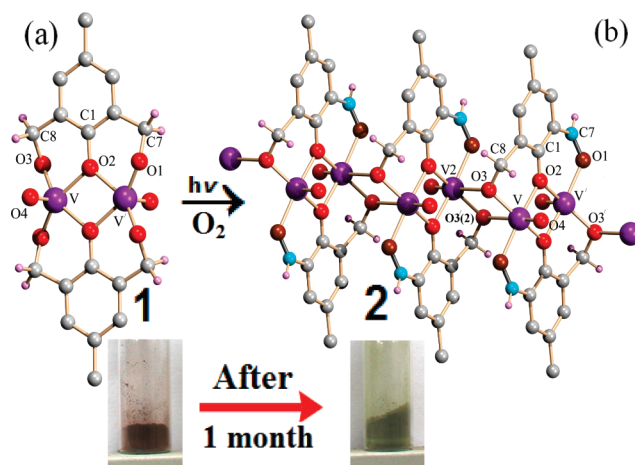


Figure 1. Perspective views of the binuclear vanadium(V)–alcoholate complex **1** (left, a) and the vanadium(IV)–aldehyde oligomer **2** (right, b).

Crystals of **1**, on being kept in the air at the ambient temperature for about a month or so, undergo an irreversible coordination-driven SCSC transformation to yield a greenish brown product **2** (the color change is shown in Figure 1 with powdered samples of **1** and **2**). Both compounds **1** and **2** are sparingly soluble in common organic solvents. Crystal structure determination for **2**⁶ has revealed that an internal redox process is involved to bring about this change. In the net process, one alcoholate functionality of the ligand in **1** is oxidized to an aldehyde moiety with simultaneous reduction of the oxovanadium(V) to oxovanadium(IV) center. A perspective view of **2** (Figure 1b) reveals that, unlike its precursor, the metal centers in it are all vanadium(IV) with distorted octahedral coordination environment. A change from five- to six coordination has its influence on the displacement of the vanadium center from the basal O_4 plane that changes substantially from 0.336 to 0.257 Å in going from **1** to **2**.

Perhaps the most interesting structural feature of **2** is the manifestation of an internal redox process that appears to be the driving force behind this unique transformation. One of the coordinated alkoxido group (C7–O1) of the completely deprotonated tridentate ligand $[L^{3-}]$ in **1** undergoes two-electron oxidation to an aldehydic C=O group, as reflected by the remarkable shortening of the bond length

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Table 1. Dynamics followed via Crystal Structure Monitoring

no. of day	C1–O2 / C7–O1(Å)	V–O4 / V'–O1(Å)	V–O3 / V2–O3(Å)	separation between monomer (Å)
1	1.385(3) / 1.401(4)	1.574(2) / 1.762(2)	1.8106(19) / 2.556(4)	3.368
8	1.384(4) / 1.381(5)	1.579(3) / 1.804(3)	1.829(2) / 2.492(8)	3.345
12	1.382(3) / 1.368(4)	1.584(2) / 1.819(2)	1.839(2) / 2.465(2)	3.333
14	1.348(14) / 1.305(15)	1.600(9) / 2.005(9)	1.923(8) / 2.292(9)	3.269
28	1.342(13) / 1.268(16)	1.615(9) / 2.064(9)	1.937(7) / 2.259(8)	3.256
35	1.347(14) / 1.244(18)	1.627(9) / 2.076(10)	1.936(8) / 2.250(10)	3.251

from 1.401(4) Å to 1.244(18) Å in going from **1** to **2** (Table 1). Thus, the anion of a new ligand, 3-hydroxymethyl-5-methylsalicylaldehyde (H_2L^*), is generated in **2** during this oxidation, having two types of C–O bonds (C7–O1 1.244(18) Å and C8–O3 1.417(15) Å) attached as the side arms to the aromatic ring. The binuclear entities of both **1** and **2** have closely similar compositions, viz. $[(\text{VO})_2\text{L}_2]$ and $[(\text{VO})_2\text{L}^*_2]$, respectively, with subtle differences in the oxidation states of vanadium, charges of the ligand anions $\text{L}(3-)$ and $\text{L}^*(2-)$, and reduction of formula weights by 2 mass units. The individual monomeric units in **2** are finally connected together by the alkoxido bridge via the O3 atom which binds the two adjacent vanadium centers (V and V2 as shown in Figure 1b) of two monomeric units, forming two V–O bonds of strikingly different lengths. The axial V–O3'(2) bond (2.25(10) Å) is much longer compared to the equatorial V–O3 distance (1.936(8) Å) due to the strong trans labilizing influence of the terminal oxido- group O4. The increased terminal V=O_t bond length in **2** (1.627(9) Å) compared to that in **1** (1.574(2) Å) also supports the lowering of the oxidation state of vanadium in **2** than that of **1**.⁷ The axial–equatorial mode of bridging by the alkoxido oxygens (O3 and O3') allows the individual monomeric units to stack one over the other, creating a staircase type of 1D chain structure in **2**. When viewed along the crystallographic *b*-axis, an overlaying type of structure is generated (Figure S1 in Supporting Information) where the centroids of the individual aromatic ring planes in the structure are separated by 3.251 Å, giving a clear indication of strong π – π interaction.

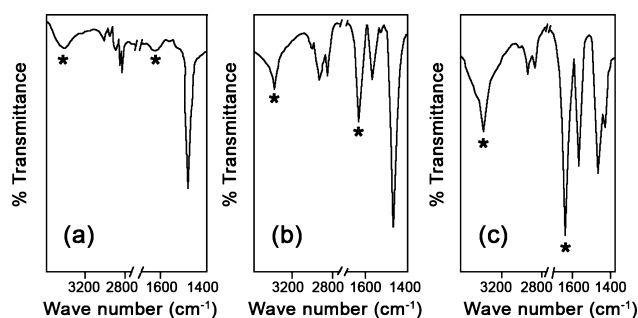
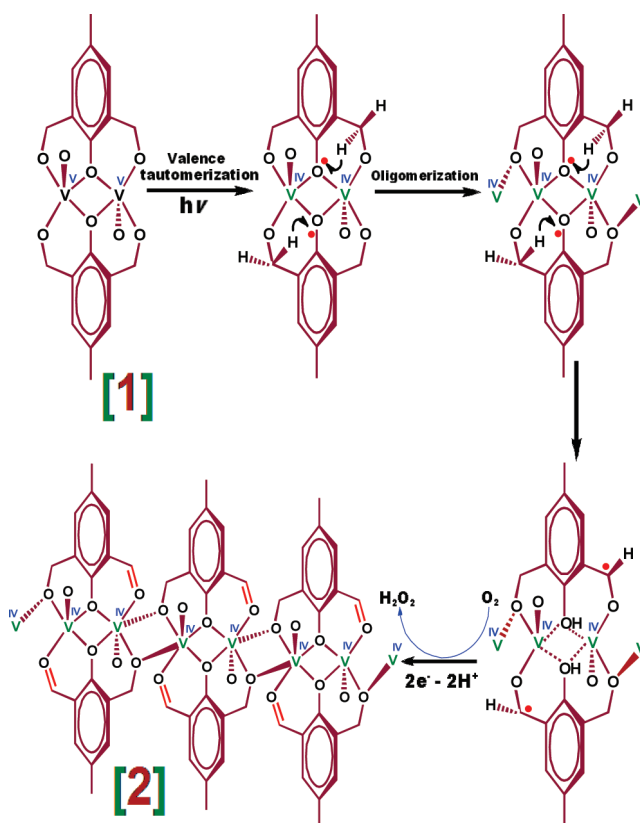


Figure 2. Time interval IR spectra of **1** recorded (a) immediately after isolation, (b) after 10 days of exposure, and (c) after 30 days of exposure to white light, showing gradual development of two new bands (marked with asterisks) at 1625 [$\nu(\text{C}=\text{O})$] and 3367 [$\nu(\text{aldehydic C–H})$] cm^{-1} .

It is important to note that throughout this SCSC transformation of **1** to **2**, the monoclinic space group $P2_1/c$ is retained, while the unit cell dimensions show only nominal changes (Table S1, Supporting Information). Clearly, this is a case of topotactic transformation where the crystallographic axes and the angles of the reactant (**1**) and product (**2**) molecules remain almost unchanged.⁸ Although SCSC reactions are usually homogeneous, the present transformation appears to be heterogeneous in nature proceeding inward from the surface of the crystal. The rate of the reaction is faster when the sample is in powdered form compared to that in the crystalline state.

The progress of the formation of **2** from **1** when followed by IR spectroscopy provides corroborative evidence in support of the involvement of an internal redox process. Thus, the formation of carbonyl functionality from alcohol is apparent from the growth of a sharp new band at 1625 cm^{-1} (Figure 2) when a freshly prepared sample of **1** is subjected to time interval IR scan. In addition, another new band at 3367 cm^{-1} is generated simultaneously, as could be expected for the aldehydic C–H stretch. Further, a sharp signature band at 978 cm^{-1} due to terminal V=O_t stretch in **1** is shifted to lower wavenumber at 960 cm^{-1} (not shown in Figure 2), providing evidence in support of a concomitant change in vanadium oxidation state and/or coordination geometry around the metal centers in **2**.

Scheme 1. Proposed Mechanistic Pathway for the Single Crystal-to-Single Crystal Transformation



When stored in dark or kept in an inert atmosphere of argon, **1** is stable for an indefinite period of time. Control experiments have also established that simultaneous exposures to white light and aerial oxygen are mandatory to initiate the above transformation. To understand the underlying mechanism, we followed the progress of this solid-state reaction through a day-to-day analysis of the change in crystallographic data of **1** during the course of its transformation to **2**. Figure S2 (Supporting Information) displays a collection of three such molecular views

obtained when the aerial exposure time is gradually increased, while Table 1 summarizes the changes in the relevant metrical parameters. A closer look at Table 1 reveals some interesting trends especially those occur during the first 14 days of exposure. These include, a perceptible decrease in the C1–O2 (phenoxido) bond length during this period with concomitant increase in the V–O4 terminal bond length (due to the formation of vanadium(IV) from vanadium(V)).⁷ This provides a hint to the generation of a phenoxyl radical,⁹ probably through a light-induced valence-tautomeric equilibrium process, which we believe, is initiating this transformation (Scheme 1). The resultant increase in vanadium ionic radius in going from vanadium(V) to vanadium(IV) makes the oligomerization credible through bridging via V2–O3 bond formation (see Table 1). The concluding step is the oxidation of an alcoholate group to an aldehyde (as revealed from the more pronounced decrease in C7–O1 bond length after the initial two weeks of exposure) by molecular oxygen, which in turn is converted to H₂O₂ through a mechanism as represented by eq 1 and elaborated in Scheme 1. Due to sluggish nature of this heterogeneous reaction, the detection of H₂O₂ remained elusive despite our best efforts.



The progress of this reaction has been followed also by EPR spectroscopic measurements (Figure 3), which provide support to the mechanism of this light-induced process. The EPR spectrum of **1** recorded after exposure to white light for a day shows a sixteen-line axial spectrum (Figure 3a) with $g_{\parallel} = 1.931$; $g_{\perp} = 1.977$; $A_{\parallel} = 170 \times 10^{-4} \text{ cm}^{-1}$; and $A_{\perp} = 60 \times 10^{-4} \text{ cm}^{-1}$, typical of a magnetically diluted solid vanadium(4+) species doped in a diamagnetic host lattice.¹⁰ The observed EPR spectrum supports the formation of vanadium(IV) in trace quantity through a process of valence tautomerism. As the reaction proceeds more toward the completion, incremental amounts of vanadium(IV) are generated in the solid sample to provide magnetically concentrated species,

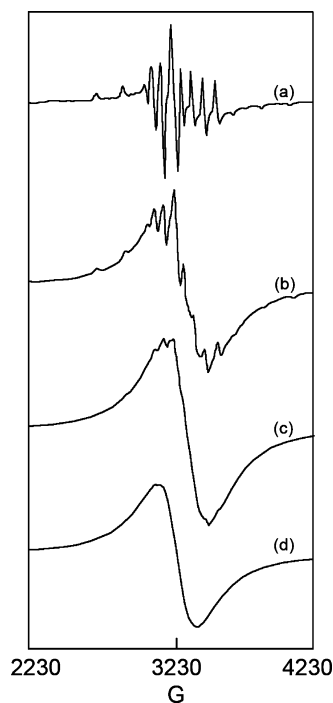


Figure 3. Changes in the EPR spectral pattern of **1** during its exposure to white light for (a) one day (amplitude 100), (b) 8 days (amplitude 25), (c) 14 days (amplitude 25), and (d) 35 days (amplitude 25).

that show gradual loss of spectral resolution due to the effect of dipolar broadening (Figures 3b and 3c).¹⁰ The final product **2** is an antiferromagnetically coupled solid with a subnormal magnetic moment of $1.81 \mu_B$ (per binuclear unit) at room temperature, while its EPR spectrum (Figure 3d) displays a broad isotropic feature with $\langle g \rangle = 1.967$. The observed spectral changes support the formation of vanadium(IV) initially on the surface of the crystal and subsequently moves inward at a rate controlled by the diffusion of molecular oxygen in to the bulk.

In summary, we have reported here an interesting example of a single crystal-to-single crystal transformation involving a binuclear alcoholato–vanadium(V) compound (**1**) to an oligomeric aldehyde-coordinated vanadium(IV) product (**2**). This irreversible topotactic transformation is apparently triggered by photoinduced generation of phenoxyl radical that initiates an internal redox process where vanadium(V) is reduced to vanadium(IV) at the expense of a two-electron ligand-based oxidation from an alcoholate to an aldehyde. The additional equivalent of an electron being released is scavenged by molecular oxygen, yielding hydrogen peroxide. Unfortunately, we are unable to detect the liberated hydrogen peroxide in spite of our best efforts due to the sluggish nature of this heterogeneous reaction. In this transformation, a reactant in the gaseous state (molecular oxygen) reacts with a crystalline solid to generate another crystalline compound along with a product (hydrogen peroxide) that is liberated to the atmosphere. This remarkable observation reported here is probably the first of its kind.

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Supporting Information Available: Synthesis, characterization details, tables of relevant crystallographic data, Figures S1 and S2, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Vanadium-Induced Nucleophilic IPSO Substitutions in a Coordinated Tetrachlorosemiquinone Ring: Formation of the Chloranilate Anion as a Bridging Ligand

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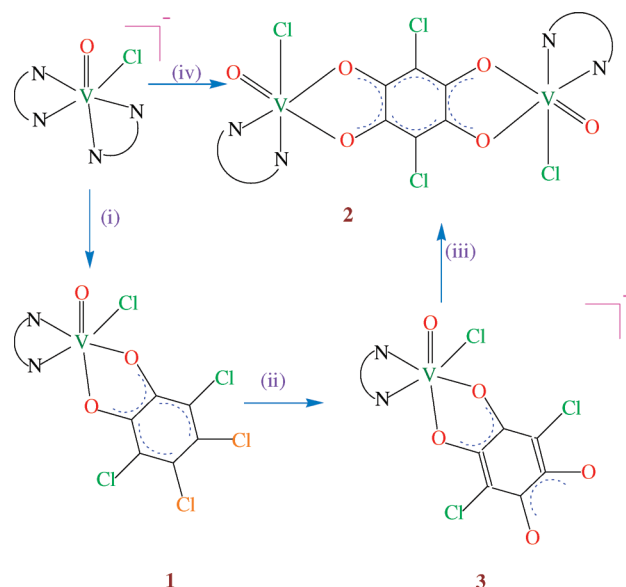
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In basic media, the coordinated semiquinone radical in the spin-coupled [(bipy)CIV^{IV}O(TCSQ)] **1** (HTCSQ = tetrachlorosemiquinone) undergoes nucleophilic ipso substitution (OH[−] for Cl[−]) to generate the chloranilate anion (CA^{2−}) that bridges the vanadium(IV) centers, forming a binuclear compound [(bipy)CIV^{IV}O(CA)OV^{IV}Cl(bipy)] **2**.

The coordination chemistry of vanadium with dioxolene-type ligands is an area of contemporary research interest.^{1a–i} Much of these interests stem from the structural identification of a biological chromogen, called tunichrome.^{1j–m} The later species with several pyrogallol moieties in it is believed to play a pivotal role in the sequestration of vanadium from seawater in to the blood cell of *Ascidians*, a group of marine protochordates.^{1n,o} This proposal however has been contested recently by Michibata et al.^{1p}

As a part of our ongoing program on oxovanadium-(IV/V) chemistry,² we recently have synthesized (Scheme 1) a mixed-ligand compound [(bipy)CIV^{IV}O(TCSQ)] **1**,^{3a} isolated as a dark purple solid in moderate yield (57%) when the precursor compound *cis*-[VO(bipy)₂Cl]Cl·2H₂O^{3b} was allowed to react with H₂TCC^{3a} in a dichloromethane/acetonitrile (1:1 v/v) solvent combination. The IR spectrum of this compound contains a strong band at 1444 cm^{−1} corresponding to the C–O stretching mode of a semiquinone moiety.⁴ Thus, **1** has a rare distinction of being a vanadium(IV) compound bound to a semiquinone radical, also confirmed by single-crystal X-ray diffraction analysis.⁵

Scheme 1. Synthetic Protocol for the Preparation of the Complexes **1** and **2**^a



^a Conditions: (i) H₂TCC, DCM/CH₃CN; (ii) Bu₄NOH, O₂, CH₃CN, stirred; (iii) *cis*-[VO(bipy)₂Cl]Cl·2H₂O, CH₃CN, stirred; (iv) H₂TCC, CH₃CN, Bu₄NOH, O₂, stirred.

A molecular view of **1** is displayed in Figure 1. The coordination environment around vanadium is distorted octahedral in which the N(1), N(2), O(1), and Cl(1) atoms define the basal plane. The C–O bond lengths of the coordinated *o*-dioxolene often provide interesting clues as to the oxidation state of this redox-noninnocent ligand.^{1i,4,6} These ligands in the quinone or semiquinone state generally have shorter C–O distances (ca. 1.28 Å)^{4a,6,7} compared to the fully reduced catecholate ligand (ca. 1.34 Å).^{1g,h,5} In compound **1**, the average C–O distance is 1.285 Å, and the C(2)–C(3) (1.371(9) Å) and C(4)–C(5) (1.367(9) Å) distances are much shorter than the remaining C–C distances

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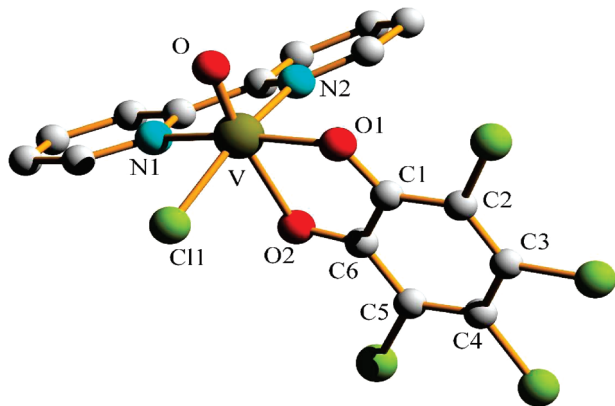


Figure 1. Perspective view and atom-numbering scheme for the neutral complex **1**. The hydrogen atoms have been omitted for clarity.

(1.432(8)–1.401(8) Å) of the *o*-dioxolene ring, indicating the semiquinone state of the ligand.^{4,6,7} The crystallographic data thus suggest compound **1** to be an oxovanadium(IV) compound connected to a semiquinone radical.

Magnetic susceptibility measurements for the polycrystalline sample of **1** reveal that the compound is diamagnetic in the temperature range 1.8–300 K. This diamagnetism is certainly due to a strong antiferromagnetic interaction between the two $S = 1/2$ spins, carried by the vanadium(IV) and a coordinated semiquinone radical.

When the reaction between *cis*-[VO(bipy)₂Cl]Cl·2H₂O and H₂TCC has been repeated in the presence of an added base (tetrabutylammonium hydroxide or Et₃N) with subsequent exposure to atmospheric oxygen (method A, Supporting Information), the product obtained is a binuclear compound [(bipy)CIV^{IV}O(CA)OV^{IV}Cl(bipy)] **2** in ca. 40% yield. Interestingly, this reaction involves an ipso replacement of two

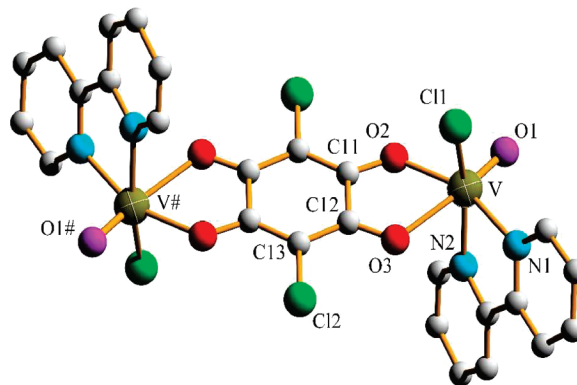


Figure 2. Ball-and-stick view of the centrosymmetric binuclear complex **2** showing the numbering scheme. The H atoms are omitted for clarity, and the symmetry-related atoms are shown with a # symbol.

chloro groups in the coordinated TCC²⁻ ligand by the incoming hydroxo groups from the added base to form the chloranilate anion [CA²⁻] as a bridge between the metal centers. The IR spectrum of **2** contains two strong bands at 1554 and 1377 cm⁻¹ which are diagnostic of the dianionic bis-bidentate bridging mode of the coordinated CA²⁻ ligand.⁸

The perspective view of the X-ray crystal structure of **2** is shown in Figure 2, confirming its proposed composition. The coordination geometry around each vanadium center is best described as a distorted octahedron with an equatorial plane, defined by the chlorido ligand Cl(1), two nitrogen atoms (N(1) and N(2)) from bipy, and the O(2) from the bridging dioxolene moiety, while the terminal oxido group O(1) and the second oxygen atom O(3) of the chloranilate dianion occupy the axial sites. The C(12)–C(11) and the

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average C–O chloranilate bond distances are 1.524(4) and 1.260(3) Å, respectively, and are characteristic of the CA^{2-} bridging moiety.⁸

Mechanistically, the synthesis of **2** from the reaction sequence followed in method A appears quite interesting and probably involves the formation of **1** as a precursor which subsequently is converted to the $[(\text{bipy})\text{ClV}^{\text{IV}}\text{O}(\text{CA})]^-$ anion, **3**, as an intermediate (Scheme 1). This necessitates the replacement of two chloro groups in the coordinated TCSQ^- ligand in **1** by the hydroxo groups from the added base. This is a metal-induced reaction, as revealed from control experiments. The attached $[(\text{bipy})\text{ClV}^{\text{IV}}\text{O}]$ moiety facilitates the drainage of electron density from the coordinated TCSQ ring that favors the aromatic nucleophilic ipso substitution of the chloro groups,⁹ leading to the formation of the chloranilate anion. In fact, the reaction of **1** with Bu_4NOH in acetonitrile did produce **3**, which unlike its diamagnetic precursor is expected to be EPR-active and shows an axial spectrum ($g_{\parallel} = 1.965$, $g_{\perp} = 1.988$, $A_{\parallel} = 163 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 48 \times 10^{-4} \text{ cm}^{-1}$) at 77 K with two sets of eight-line patterns (Figure S1, Supporting Information), typical of mononuclear vanadium(IV) (^{51}V , $I = 7/2$). The OH^- for Cl^- substitution in the TCSQ ring in **1**, followed by aerial oxidation generates the CA^{2-} anion that makes the vanadium(IV) unpaired electron in **3** available for the display of the characteristic EPR. The chloranilate dianion thus formed has an exceptional chelating ability⁸ that enables it to act as a bridge between the two adjacent vanadium centers, thus forming **2**. In fact, we have been successful in isolating **2** in moderate yield (25%) by combining **1** with *cis*- $[\text{VO}(\text{bipy})_2\text{Cl}]\text{Cl} \cdot 2\text{H}_2\text{O}$ in acetonitrile in the presence of an added base (method B, Supporting Information).

For complex **2**, the χT versus T and χ versus T plots are displayed in Figure 3. At 300 K, the χT value is $0.71 \text{ cm}^3 \text{ K mol}^{-1}$, which decreases monotonically with decreasing temperature to reach a value of $0.01 \text{ cm}^3 \text{ K mol}^{-1}$ below 5 K. This behavior is characteristic of antiferromagnetic coupling between the magnetic centers within this molecule. On the basis of its molecular structure, and the diamagnetic nature of the bridging chloranilate dianion, the complex can be viewed magnetically as a dinuclear complex composed of two octahedral vanadium(IV) centers ($S = 1/2$). Therefore, the magnetic properties have been analyzed using a Heisenberg $S = 1/2$ dimer model and the following Hamiltonian: $H = -2J(S_V \cdot S_{V\#})$, where S_V and $S_{V\#}$ are the spin operators for both V and V(#). The experimental data have been very well reproduced using the Bleaney–Bowers expression of the magnetic susceptibility deduced from the above Hamil-

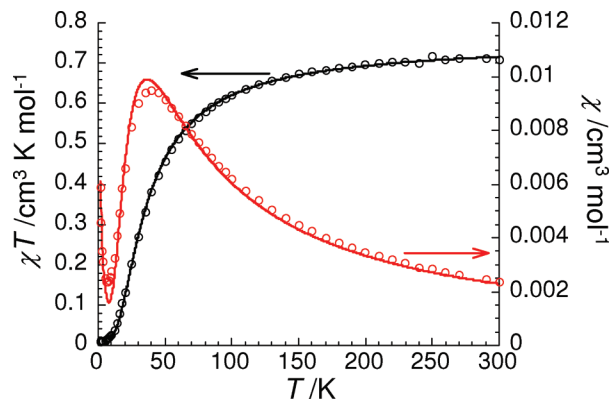


Figure 3. χT vs T (in black) and χ vs T (in red) plots for **2** (with $\chi = M/H$) under 1 kOe. The solid lines represent the best simulations obtained with the models described in the text.

tonian.¹⁰ The best set of parameters obtained using this model is $J/k_B = -31(1) \text{ K}$ ($-22(1) \text{ cm}^{-1}$) and $g = 1.97(2)$. It is worth mentioning that the CA^{2-} ligand is magnetically efficient enough to bridge antiferromagnetically two widely separated V(IV) centers ($\text{V} \cdots \text{V}\#$ separations, 8.153 Å). The sign of the magnetic interaction implies that these vanadium(IV) units possess an $S_T = 0$ spin ground state.

In summary, nucleophilic substitution in a coordinated tetrachlorosemiquinonato ring has been reported for the first time. Only the chloro groups which are in para positions with respect to the semiquinonato oxygen atoms in the TCSQ ring have been replaced. The electron-accepting vanadium(IV) center, attached to these donor oxygen atoms in **1**, takes out the excess electronic charge and activates the ring for such ipso substitution.⁹ Recently, Bruijninx et al.¹¹ have reported such unusual conversion of tetrachlorocatechol to chloranilic acid by a copper(II)-mediated oxidative double dehalogenation reaction.

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Supporting Information Available: X-ray crystallographic files in CIF format and detailed syntheses and characterization data for **1** and **2** and an EPR spectrum (77 K) of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Hetero-Bimetallic Complexes Involving Vanadium(V) and Rhenium(VII) Centers, Connected by Unsupported μ -Oxido Bridge: Synthesis, Characterization, and Redox Study

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Heterobimetallic complexes of a vanadium(V) and rhenium(VII) combination connected by a μ -oxido bridge [$\text{LVO}(\mu\text{-O})\text{ReO}_3$]· H_2O [$\text{H}_2\text{L} = \text{N}, \text{N}'$ -ethylene bis(salicylideneimine) (H_2salen) and its methoxy derivative] (**1**, **2**) are reported. The compounds have been prepared by a single-pot synthesis in which the precursor [$\text{V}^{\text{V}}\text{OL}$] complexes are allowed to be oxidized aeri ally in the presence of added perhenate. The oxidized [$\text{V}^{\text{V}}\text{OL}$]⁺ species accommodate the ReO_4^- anion in their vacant coordination site, trans to the terminal oxido group, providing the complexes **1** and **2**. The later generates a binuclear oxovanadium(V) compound [$\text{H}_2\text{en}[(\text{TBC})\text{VO}(\mu\text{-TBC})_2\text{OV}(\text{TBC})]\cdot 5\text{H}_2\text{O}$ (**3**) when treated with tetrabromocatechol. Single crystal X-ray diffraction analysis and ¹H NMR spectroscopy have been used to establish their identities. In compound **2**, the Re(1)–O(11)–V(1) bridge angle is barely linear [170.2(3)°] with a Re···V separation of 3.9647(9) Å. The redox behavior of **1** and **2** are quite interesting, each undergoing two reductions both in the positive potential range at $E_{1/2} = 0.59$ (process I) and $E_{1/2} = 0.16$ V (process II) versus Ag/AgCl reference (corresponding potentials are 0.59 and 0.18 V for **2**). Process I has a single-electron stoichiometry involving the [$\text{VO}(\text{salen})$] part of the complexes as established by combined coulometry-Electron Paramagnetic Resonance (EPR) experiments which provide an eight-line isotropic EPR pattern at room temperature ($\langle g \rangle = 1.967$; $\langle A \rangle = 87 \times 10^{-4} \text{ cm}^{-1}$), characteristic of an unpaired electron being coupled to a vanadium nuclear spin (⁵¹V, $I = 7/2$). The almost linear V–O–Re bridge in **1** and **2** allows this unpaired electron to interact effectively with the neighboring Re nuclear spin, leading to familiar “two-line pattern” superhyperfine coupling ($A(^{185,187}\text{Re}) = 20.7 \times 10^{-4} \text{ cm}^{-1}$). Process II, on the other hand, is based on a Re(VII/VI) electron transfer as confirmed by differential pulse and normal pulse voltammetric experiments.

Introduction

The chemistry of heterobimetallic systems involving M–O–M' frameworks has received increasing attention in recent years because of their interesting properties arising out of the cooperative influence of two dissimilar metal ions

held together in close proximity.^{1–10} Such asymmetry is often prevalent in many metalloenzymes that are known to

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catalyze some of the fundamental reactions of Biology.¹¹ These serve as an impetus for chemists to synthesize prototypes of catalysts involving two different metal centers, the idea being that such a system will be more efficient than the one involving the individual metal centers.¹²

Coordination chemistry of rhenium has experienced a strong upsurge in recent years.^{13a} The isotopes ¹⁸⁶Re and ¹⁸⁸Re being high energy β -emitters, many of their compounds have found therapeutic applications as nuclear medicines.^{13b} Herrmann et al.^{14,15} have extensively used various alkyl and aryl trioxorhenium ($\text{RRe}^{\text{VII}}\text{O}_3$) as epoxidation catalysts. Often perrhenate as ligand has a profound influence on the physical properties of the resulting compound. Thus, Miyasaka et al.⁶ have reported a single-molecule-magnet (SMM) $[\text{Mn}_2(\text{saltmen})_2(\text{ReO}_4)_2]$ in which ReO_4^- is coordinated axially to the metal centers. Ibers et al.⁵ on the other hand have

reported a copper phthalocyaninato compound $[(\text{Cu}(\text{pc}))_3(\text{ReO}_4)]$ which contrary to expected metallic conductivity, displayed a localized distribution of charge.

In our endeavor to synthesize unsupported μ -oxido binuclear complexes as a part of our ongoing program on oxometallate chemistry,¹⁶ herein we report the synthesis of two heterobimetallic compounds (**1** and **2**) with a hitherto unknown unsymmetrical combination involving a vanadium(V) and a rhenium(VII) center, connected together by a sole μ -oxido bridge. One of these compounds (**2**) has been structurally characterized by single crystal X-ray diffraction analysis. Confirmations in support of these unprecedented heterobimetallic structures have also come from the ¹H NMR and Electron Paramagnetic Resonance (EPR) spectroscopy. Their electrochemical behaviors have been explored in details. In this context, we have also studied the reactivity of **2** with tetrabromocatechol when a new binuclear oxovanadium(V) compound **3** is obtained.

Experimental Section

Materials. Tetradentate ligands $\text{H}_2\text{salen}^{17}$ and its methoxy derivative $\text{H}_2\text{metsalen}$, the precursor complexes $[\text{VO}(\text{salen})]$ and $[\text{VO}(\text{metsalen})]\cdot\text{H}_2\text{O}$ were prepared following literature methods.^{18,19} Tetrabutylammonium perrhenate, *o*-vanillin, and tetrabromocatechol were purchased from Aldrich. All other reagents are commercially available and used as received. Solvents were reagent grade, dried by standard methods,²⁰ and distilled under nitrogen prior to their use.

Syntheses. $[(\text{salen})\text{VO}(\mu\text{-O})\text{ReO}_3]\cdot\text{H}_2\text{O}$ (**1**). To a stirred tetrahydrofuran solution (30 mL) of $[\text{VO}(\text{salen})]$ (0.17 g, 0.5 mmol) was added an equimolar amount of tetrabutylammonium perrhenate (0.24 g), taken in acetonitrile (20 mL). The mixture was refluxed for about 3 h to get a green solution. It was then filtered, the filtrate volume was reduced to about 25 mL by rotary evaporation and allowed to stand in the air for 4–5 days. A green crystalline compound deposited at this stage was collected by filtration, washed with diethyl ether (3×10 mL), and dried in vacuo over P_4O_{10} . Yield: 0.10 g (32%). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_8\text{ReV}$: C, 31.95; H, 2.68; N, 4.66. Found: C, 31.72; H, 2.61; N, 4.69%. FT-IR bands (KBr pellet, cm^{-1}): 3429br, 1620vs, 1599s, 1543s, 1443s, 1391m, 1302s, 1273s, 1124s, 1080s, 987s, 910vs, 818m, 758s, 725s, 657m, 536s, 460m. UV–vis (CH_3CN) [λ_{max} , nm (ϵ , $\text{mol}^{-1} \text{cm}^2$): 596 (825); 400 (sh); 362 (2550); 288 (10400); 267 (14500); 228 (37800).

$[(\text{metsalen})\text{VO}(\mu\text{-O})\text{ReO}_3]\cdot\text{H}_2\text{O}$ (**2**). This compound was prepared as a greenish brown crystalline solid following essentially the same procedure as described for **1** using $[\text{VO}(\text{metsalen})]\cdot\text{H}_2\text{O}$ as a replacement for $[\text{VO}(\text{salen})]$. Yield: 36%. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_{10}\text{ReV}$: C, 32.68; H, 3.05; N, 4.23. Found: C, 32.80; H,

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- (17) Abbreviations used: H_2salen , *N,N'*-ethylene bis(salicylideneimine); $\text{H}_2\text{metsalen}$, *N,N'*-ethylene bis(3-methoxysalicylideneimine); H_2TBC , tetrabromocatechol; en, ethylenediamine).
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Table 1. Summary of the Crystallographic Data for the Complexes **2** and **3**

parameters	2	3
composition	C ₁₈ H ₂₀ N ₂ O ₁₀ ReV	C ₂₆ H ₂₀ Br ₁₆ N ₂ O ₁₅ V ₂
formula wt.	661.50	1982.90
crystal system	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> , Å	8.2522(7)	9.9723(13)
<i>b</i> , Å	9.1776(8)	11.1335(15)
<i>c</i> , Å	15.1526(13)	12.3743(16)
α , deg	89.625(2)	73.630(2)
β , deg	85.627(2)	80.697(2)
γ , deg	64.734(2)	68.817(2)
<i>V</i> , Å ³	1034.35(15)	1226.4(3)
ρ_{calc} , Mg m ⁻³	2.124	2.682
temp, K	150(2)	193(2)
λ , Å	0.8460	0.77490
<i>Z</i>	2	1
μ mm ⁻¹	9.905	16.629
2 θ_{max} [deg]	66.28	62.20
reflections collected/unique	7434/4163	15416/6056
observed reflections (<i>I</i> \geq 2 σ (<i>I</i>))	3973	4285
<i>R</i> _{int}	0.0282	0.0438
data/restraints/parameters	4163/27/291	6056/0/276
<i>R</i> 1(<i>F</i> _o), <i>wR</i> 2(<i>F</i> _o) (<i>I</i> \geq 2 σ (<i>I</i>))	0.0431, 0.1099	0.0408, 0.1090
<i>R</i> 1(<i>F</i> _o ²), <i>wR</i> 2(<i>F</i> _o ²) (all data)	0.0446, 0.1112	0.0641, 0.1202
<i>F</i> (000)/GOF on <i>F</i> ²	640/1.071	918/1.030

3.09; N, 4.18%. FT-IR bands (KBr pellet, cm⁻¹): 3416br, 2930m, 1620vs, 1554m, 1444vs, 1294s, 1250vs, 1222s, 1085s, 987s, 917vs, 860m, 739vs, 651m, 536s, 458m. UV-vis (CH₃CN) [λ_{max} , nm (ϵ , mol⁻¹ cm²): 660 (1540); 416 (2650); 320 (10700); 267 (16700); 230 (35800).

[H₂en][(TBC)VO(μ -TBC)₂OV(TBC)]·5H₂O (3**).** To a stirred acetonitrile solution (40 mL) of **2** (0.13 g, 0.2 mmol) was added, in portions, tetrabromocatechol (0.32 g, 0.8 mmol) in solids. The resulting mixture was refluxed for about 4 h, when a green solution was obtained. It was then cooled, filtered, and the filtrate volume was reduced to about 25 mL by rotary evaporation and finally stored in a refrigerator at 4 °C for about 5–6 days. A brown crystalline compound deposited at this stage was collected by filtration, washed with acetonitrile (3 \times 10 mL) and finally dried in vacuo over P₄O₁₀. Yield: 0.04 g (22%). Anal. Calcd for C₂₆H₂₀Br₁₆N₂O₁₅V₂: C, 15.77; H, 1.02; N, 1.41. Found: C, 15.92; H, 0.98; N, 1.42%. FT-IR bands (KBr pellet, cm⁻¹): 3437br, 3020m, 2926m, 1578m, 1549m, 1410s, 1341vs, 1252vs, 1194s, 978s, 937s, 864m, 750s, 648m, 554m.

Physical Measurements. Elemental (C, H, and N) analyses were performed on a Perkin-Elmer model 2400 Series II CHNS Analyzer. UV-visible spectral measurements in solution were recorded on a Perkin-Elmer Lambda 950 UV-vis/NIR spectrophotometer, while for IR spectra, a Shimadzu model 8400S FT-IR spectrometer with samples prepared as KBr pellets was employed. Solution electrical conductivities were measured with a Systronics Model 304 bridge. The ¹H NMR (300 MHz) spectra were recorded on a Bruker model Avance DPX 300 spectrometer using SiMe₄ (δ_0) as internal reference.

Cyclic voltammetric measurements in CH₂Cl₂, methanol, and dimethylsulfoxide (DMSO) were recorded on a BAS model 100 B/W electrochemical workstation using a platinum disk (i.d. = 1.6 mm) working and a platinum wire counter electrode. Ag/AgCl electrode was used for reference and Fc/Fc⁺ couple as the internal standard.²¹ Solutions were ~1.0 mM in samples and contained 0.1 M TBAP as supporting electrolyte. Bulk electrolyses were carried out using a platinum-gauze working electrode at 298 K.

EPR spectra of the catholyte solutions in dichloromethane/toluene (1:10 v/v) were recorded on a JEOL Model JES-FA 300 X-band spectrometer equipped with a standard low temperature apparatus (at 77 K) and data processing system ESPRIT 330.

X-ray Crystallography. Crystals of dimensions 0.20 \times 0.06 \times 0.005 mm³ (plate, green, **2**) and 0.15 \times 0.08 \times 0.03 mm³ (block, brown, **3**) were mounted on glass fibers aligned on a Bruker AXS APEX II CCD diffractometer in case of **2** while a Bruker AXS Platinum 200 CCD diffractometer was employed for **3**. Intensities were collected with silicon 111 monochromatized synchrotron radiation at 150(2) and 193(2) K, using the ω -rotation scan techniques with wide and narrow frames for **2** and **3**, respectively. There was no deterioration of the crystals during the data collections. Accurate cell dimensions were refined from setting angles of 5570 and 4919 reflections for **2** and **3**, respectively, in the ranges of θ , 4.18–33.13° (**2**) and 2.39–33.29° (**3**). In all cases, absorption corrections based on multiscan using SADABS (Sheldrick, 1996)²² were applied.

The structures were solved by direct methods²³ and the least-squares refinement [anisotropic displacement parameters, hydrogen atoms in the riding model approximation, and a weighing scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ for $P = (F_o^2 + 2F_c^2)/3$] was on *F*².²³ Bruker SHELXTL²⁴ was used both for structure solutions and refinements for both **2** and **3**. Crystallographic parameters and the final residuals are given in Table 1. In the refinements of both **2** and **3**, the presence of residual electron density peaks is consistent with the solvent of crystallization. These were modeled anisotropically with 100% site occupancy factors each, except the O3W atom in **3**, which was disordered over two positions of identical occupancy. The water-bound hydrogen atoms could be neither placed nor found and were therefore omitted for the refinements. On the other hand, the hydrogens on the ethylenediamine moiety were found in the Fourier difference map and constrained using a riding model. Data reductions were accomplished with Bruker SAINT, and “Bruker SAINT V7.23a” software packages. Crystallographic diagrams were drawn with the DIAMOND program.²⁵

Results and Discussion

Syntheses. Compounds reported in this work (**1–3**) have been synthesized following procedures as outlined in Scheme 1. As described in our previous communications,^{16c,d} [V^{IV}O(salen)] and its derivatives in solution are prone to aerial oxidation to generate the product, namely, [V^{VO}(s-alen)]⁺ in the presence of added anion, for example, ClO₄⁻, BF₄⁻, and PF₆⁻, and so forth.^{26,27} In most of the cases, the products obtained have the added anion, included in the vacant coordination site of vanadium(V), trans to the terminal oxido group.²⁶ As a sequel to these investigations, it has been our objective to examine the effect of ReO₄⁻ as anion which has a tetrahedral geometry similar to ClO₄⁻ and BF₄⁻ but is

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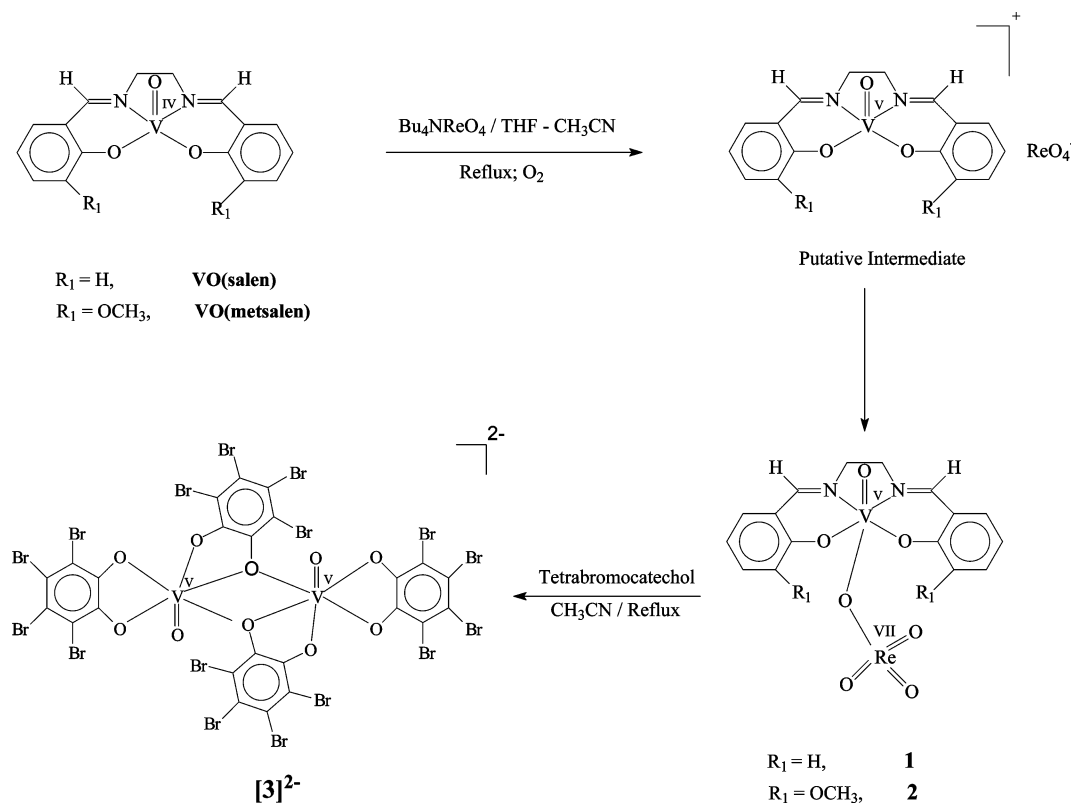
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Scheme 1. Synthesis of the Complexes 1–3



a better coordinating anion.^{5–7,10,28} Thus $[\text{V}^{\text{VO}}(\text{salen})]$ and its analogues have been allowed to oxidize aerially in a THF/acetonitrile solvent combination (3:2 v/v) in the presence of Bu_4NReO_4 to produce brownish-green crystalline products (**1** and **2**) in moderate yields. The compounds are electrically nonconducting in acetonitrile solution. In DMSO, however, their molar conductivities (Λ_{M}) increase with time to attain a value of about $50 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ within about an hour, corresponding to a 1:1 electrolyte.²⁹

Rhenium oxides such as Re_2O_7 or ReO_3 have long been known to exhibit modest catalytic activities.¹⁵ However, interest in the efficiency of rhenium oxidation catalysts has taken a new turn when Herrmann et al.^{14a} discovered catalytic activity in methyl trioxorhenium (MTO). They found that MTO and its derivatives are powerful oxidation and epoxidation catalysts with H_2O_2 as the reagent. Because **1** and **2** have an attached ReO_3 fragment as in MTO, we thought it would be prudent to check the oxidizing ability of these compounds. For this, **2** was allowed to react with H_2TBC ¹⁷

in dry acetonitrile. The only product isolated is a divanadium(V) compound $[\text{H}_2\text{en}][(\text{TBC})\text{VO}(\mu\text{-TBC})_2\text{-VO}(\text{TBC})] \cdot 5\text{H}_2\text{O}$ (**3**) with oxovanadium(V) centers connected by a pair of bridging catecholate ligands. Unfortunately, all our efforts to isolate any oxidation product of tetrabromocatechol have been unsuccessful. Compound **3** is insoluble in common organic solvents. It contains as counterion the protonated form of ethylenediamine which is generated from the salen part of the precursor compound.

Selected IR data for the complexes (**1**–**3**) are summarized in the Experimental Section. In the case of **1** and **2**, the data include a couple of strong bands at 1620 and 1294 cm^{-1} regions due to the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O}/\text{phenolate})$ stretching modes of the coordinated Schiff base moieties, respectively.^{16,30} In addition, a sharp strong band is observed due to the terminal $\text{V}=\text{O}_t$ stretching at 987 cm^{-1} . The appearance of prominent bands in the $910\text{--}917 \text{ cm}^{-1}$ region also confirms the presence of the ReO_4^- anion in the unidentate mode of coordination.^{6b,10a,d,28f,31} A broad but moderately intense peak is observed at approximately 3425 cm^{-1} due to the $\nu(\text{O}-\text{H})$ vibration in the structure, as expected for the presence of water of crystallization in the molecule. The spectrum of **3** displays a strong band at 978 cm^{-1} due to the

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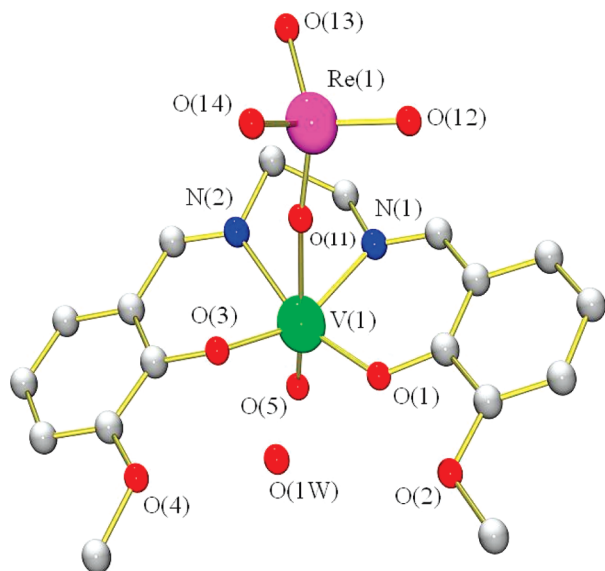


Figure 1. Molecular structure and crystallographic numbering scheme for the neutral complex [(metsalen)VO(μ -O)ReO₃] \cdot H₂O **2**. The hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **2**

Bond Distances (Å)			
V(1)–O(5)	1.593(4)	Re(1)–O(11)	1.736(4)
V(1)–O(3)	1.831(4)	Re(1)–O(12)	1.733(4)
V(1)–O(1)	1.816(4)	Re(1)–O(13)	1.703(5)
V(1)–O(11)	2.243(4)	Re(1)–O(14)	1.720(4)
V(1)–N(1)	2.087(5)	V(1)···Re(1)	3.9647(9)
V(1)–N(2)	2.079(5)		
Angles (deg)			
O(5)–V(1)–O(1)	101.75(19)	O(3)–V(1)–O(1)	106.21(18)
O(5)–V(1)–O(3)	99.07(19)	O(1)–V(1)–N(2)	160.44(19)
O(5)–V(1)–N(1)	98.6(2)	O(3)–V(1)–N(1)	155.77(19)
O(5)–V(1)–N(2)	90.89(19)	O(5)–V(1)–O(11)	173.81(19)
O(11)–V(1)–O(1)	83.90(17)	V(1)–O(11)–Re(1)	170.2(3)
O(11)–V(1)–O(3)	81.57(17)	O(11)–Re(1)–O(12)	110.0(2)
O(11)–V(1)–N(1)	79.14(17)	O(11)–Re(1)–O(13)	109.6(2)
O(11)–V(1)–N(2)	83.00(18)	O(11)–Re(1)–O(14)	110.1(2)
O(1)–V(1)–N(1)	86.20(18)	O(12)–Re(1)–O(13)	108.5(2)
N(1)–V(1)–N(2)	77.11(19)	O(12)–Re(1)–O(14)	109.3(2)
N(2)–V(1)–O(3)	86.15(19)	O(13)–Re(1)–O(14)	109.2(2)

terminal V=O_t stretching. In addition, the presence of a sharp band at 1252 cm^{−1} confirms the binding in it of TBC^{2−} ligands in catecholate mode.³²

The UV–vis absorption spectra of the complexes **1** and **2** in dichloromethane have been also summarized in the Experimental Section, showing two intense absorption bands, one in the visible region at 596–660 nm and the other in the 400–416 nm region in the form of a shoulder. We interpret these bands as arising from ligand-to-metal charge-transfer (LMCT, PhO[−]→V(V)) considering their positions being sensitive to the substituents present in the phenyl ring. All the remaining bands appearing in the UV regions are due to the ligand internal transitions.

Description of Crystal Structures. The perspective view of the heterodinuclear compound **2** is displayed in Figure 1. Relevant interatomic parameters are listed in Table 2. The complex crystallizes in a triclinic space group *P* $\bar{1}$ with two molecular mass units per cell. The asymmetric unit comprises one neutral binuclear species and an independent water molecule of crystallization. The molecule contains a bridging

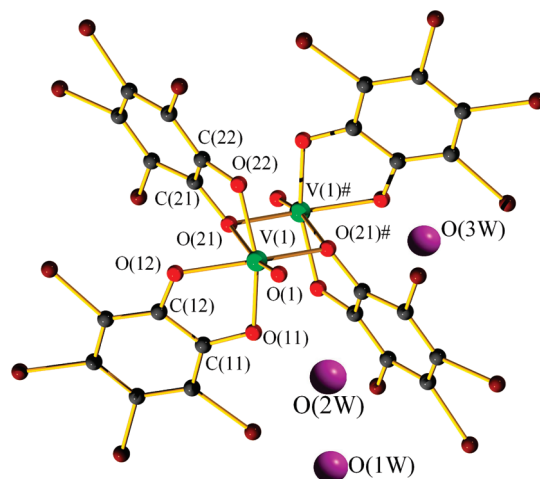


Figure 2. Perspective view of the centrosymmetric binuclear complex anion in [H₂en][(TBC)VO(μ -TBC)₂OV(TBC)] \cdot 5H₂O **3** showing the crystallographic numbering scheme. The cation [H₂en]²⁺ has been omitted for clarity. The atoms with “#” symbol are symmetry related.

Table 3. Relevant Bond Distances (Å) and Angles (deg) for **3**

Bond Distances (Å)			
V(1)–O(1)	1.602(4)	C(11)–O(11)	1.333(6)
V(1)–O(11)	1.893(4)	C(12)–O(12)	1.338(6)
V(1)–O(12)	1.969(4)	C(21)–O(21)	1.344(6)
V(1)–O(22)	1.897(4)	C(22)–O(22)	1.325(6)
V(1)–O(21)	2.349(3)	V(1)···V(1)#	3.3985(18)
V(1)#–O(21)	1.959(3)		
Angles (deg)			
O(1)–V(1)–O(11)	104.33(18)	O(21)–V(1)–O(21)#	76.23(13)
O(1)–V(1)–O(12)	105.45(18)	O(11)–V(1)–O(12)	80.65(15)
O(1)–V(1)–O(21)#	101.03(17)	O(12)–V(1)–O(22)	85.03(15)
O(1)–V(1)–O(22)	95.57(17)	O(22)–V(1)–O(21)#	98.04(15)
O(1)–V(1)–O(21)	169.42(18)	O(11)–V(1)–O(21)#	85.87(14)
O(21)–V(1)–O(11)	87.51(15)	O(11)–V(1)–O(22)	157.92(15)
O(21)–V(1)–O(12)	78.68(14)	O(12)–V(1)–O(21)#	152.92(15)
O(21)–V(1)–O(22)	74.90(13)	V(1)–O(21)–V(1)#	103.77(13)

Hydrogen Bonding Parameters (Å, deg)^a

D–H···A	d(D–H)	d(H···A)	d(D–A)	<DHA
N(31)–H(31A)···O(2W) ^{#1}	0.91	1.95	2.859(9)	178.5(5)
N(31)–H(31B)···O(1W) ^{#1}	0.91	2.02	2.869(6)	153.7(4)
N(31)–H(31C)···O(12C) ^{#2}	0.91	1.94	2.820(6)	162.9(3)

^a Symmetry transformations used to generate equivalent atoms: (#1) *x*, *y*, *z*; (#2) *x*, *y* − 1, *z*.

oxygen atom O(11) that links the vanadium(V) and rhenium(VII) centers and provides a heretofore unknown example of a single μ -oxido bridged vanadium(V)–rhenium(VII) compound. The coordination environment around the vanadium center is distorted octahedral, completed by the N₂O₂ donor set of the tetradentate ligand, together with the O(5) and O(11) atoms, contributed by the terminal oxido and ReO₄[−] groups, respectively. The phenoxo oxygen atoms O(1) and O(3) along with the imino nitrogen atoms N(1) and N(2) form the equatorial plane, while the apical positions are taken up by the oxygen atoms O(5) and O(11). The trans angles O(1)–V(1)–N(2) (160.44(19)°) and O(3)–V(1)–N(1)

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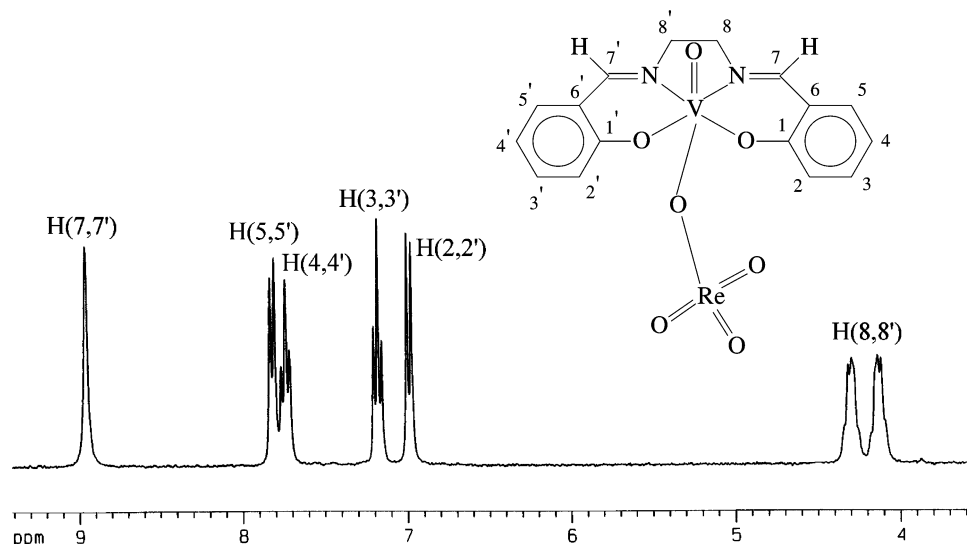


Figure 3. ^1H NMR spectrum of $[(\text{salen})\text{VO}(\mu\text{-O})\text{ReO}_3] \cdot \text{H}_2\text{O}$ **1** in acetonitrile- d_3 at 263 K.

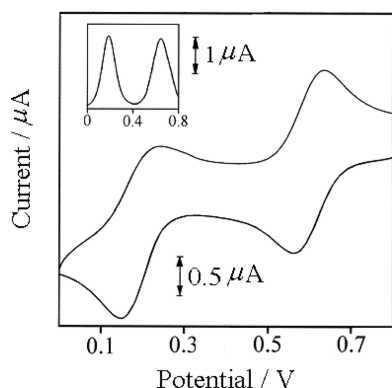


Figure 4. Cyclic voltammogram of **1** in dichloromethane solution; potentials vs Ag/AgCl, 0.1 M TBAP at a platinum electrode, scan rate 100 mV s^{-1} . The inset shows the differential pulse voltammogram establishing the involvement of identical number of electron(s) for both processes I and II.

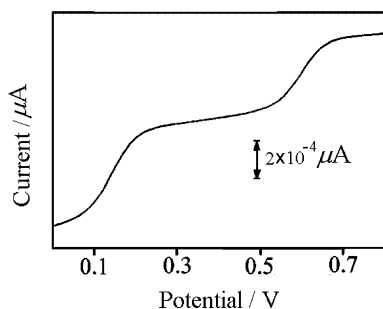


Figure 5. Normal pulse voltammogram of **1** in dichloromethane (0.1 M TBAP), confirming the involvement of identical numbers of electrons for both processes I and II (at a platinum electrode; scan rate 100 mV s^{-1}).

($155.77(19)^\circ$) are short of linearity, forcing the vanadium center to move out of the least-squares meridian plane by 0.2831 \AA toward the apical oxo-atom O(5). In the basal plane, the average V–O(phenoxo) and V–N(imino) bond lengths are $1.824(6)$ and $2.086(7) \text{ \AA}$, respectively, comparable with those previously reported in compounds containing the $[\text{VO}(\text{salen})]^+$ motif.^{16c,26,30,32} A change from five to six coordination around vanadium is normally reflected in the distance of the metal center from the basal N_2O_2 plane which is decreased approximately from 0.5 to 0.25 \AA .^{33a}

The Re–O distances ($1.703(5)$ – $1.736(4) \text{ \AA}$) and the O–Re–O bond angles ($108.5(2)$ – $110.1(2)^\circ$) indicate almost ideal tetrahedral geometry around the metal center.^{5,6,10a} The V...Re separation is $3.9647(9) \text{ \AA}$. The V(1)–O(11)–Re(1) angle is $170.2(3)^\circ$ and the V(1)–O(11) bond length ($2.243(4) \text{ \AA}$) shows distinct elongation compared to the relevant distances in the basal plane owing to the trans labilizing influence of the terminal oxido group.^{16c,30,33} The terminal V=O(5) distance ($1.593(4) \text{ \AA}$) is in the expected range.^{16c}

The solvated water molecule O(1W) sits in a position almost equidistant from the two methoxy oxygen atoms of the deprotonated ligand $[\text{metsalen}]^{2-}$, so that O(2)...O(1W) and O(4)...O(1W) distances are $3.014(7)$ and $2.996(7) \text{ \AA}$, respectively (Figure 1). Thus, the water molecule (O(1W)) functions as a hydrogen bonding donator and occupies the coordination pocket created by the acceptor combination of O(4), O(3), O(1), and O(2) atoms.

The molecular structure and atomic labeling scheme for **3** is shown in Figure 2, and its selected interatomic parameters are given in Table 3. The asymmetric unit of **3** comprises half of the complex anion and ethylenediammonium counteranion. In addition, two and a half-independent water molecules occupy the void volume. The compound crystallizes in a triclinic space group $P\bar{1}$ with one molecular mass unit accommodated in the unit cell. The complex anion has a centrosymmetric dinuclear $[(\text{TBC})\text{VO}(\mu\text{-TBC})_2\text{-VO}(\text{TBC})]^{2-}$ structure in which each vanadium center exhibits a distorted octahedral geometry. The basal positions in this octahedron are occupied by the oxygen atoms contributed by the *o*-dioxolene ligands. The apical positions are taken up by the terminal oxo-group O(1) and the oxygen atom O(21) from the bridging *o*-dioxolene moiety. The trans angles in the equatorial plane O(11)–V(1)–O(22) $157.92(15)^\circ$ and O(12)–V(1)–O(21) $152.92(15)^\circ$ are somewhat compressed and force the V(1) atom out of the least-squares basal plane toward the apical oxygen atom O(1). The terminal

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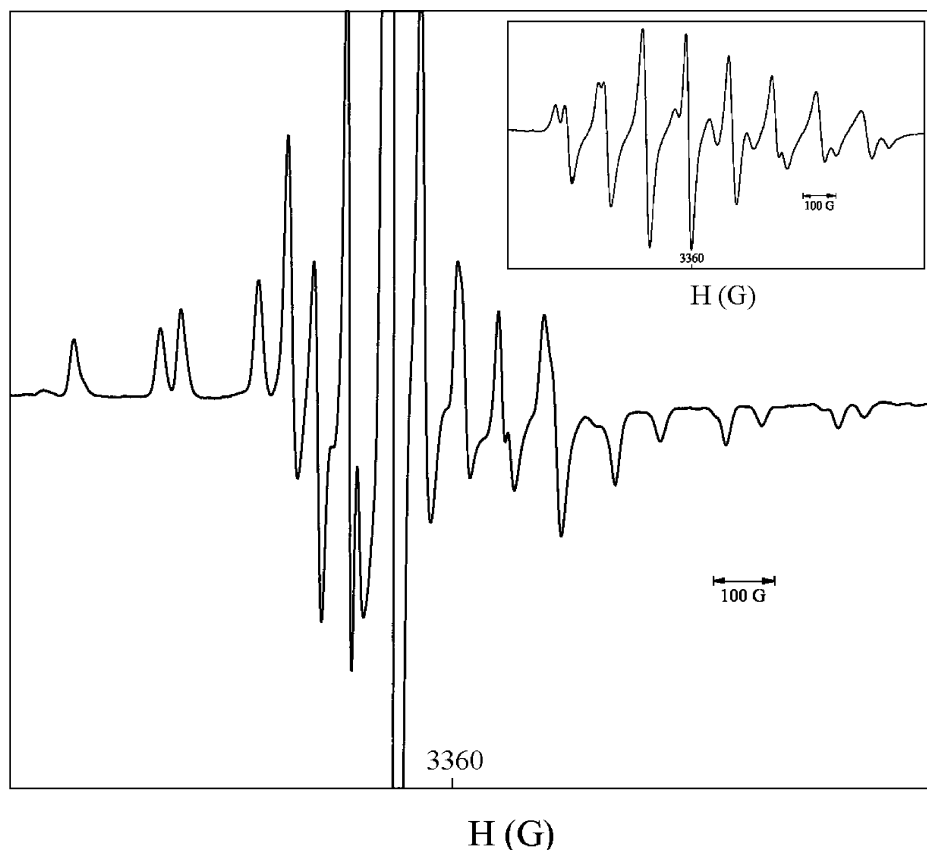


Figure 6. EPR spectrum at 77 K of the catholyte solution (in dichloromethane/toluene, 1:10 v/v) generated after coulometric reduction of **1** (E_w set at 0.4 V vs Ag/AgCl). The inset shows an eight-line isotropic pattern of the same solution at room temperature.

V=O(1) distance (1.602(4) Å) is in the expected range.³⁴ The adjacent vanadium centers in this structure are connected by the oxygen atoms O(21) and O(21)#, each contributed by a bridging *o*-dioxolene ligand. The remaining oxygen atom O(22) of that bridging moiety on the other hand is coordinated to a single vanadium center. Between the two bridging distances V(1)–O(21) and V(1)#–O(21), the former, 2.349(3) Å, is much elongated because of the trans labilizing influence of the terminal oxido ligand O(1). The remaining V–O distances are in the expected range of 1.893(4)–1.969(4) Å. The C–O distances in the ligand moiety are in the range 1.325(6)–1.344(6) Å, while the C–C distances in the *o*-dioxolene rings vary between 1.368(8) and 1.411(7) Å, all indicating a fully reduced catecholato mode of coordination from the *o*-dioxolene ligands.^{32,35} The V(1)···V(1)# separation is 3.3985(18) Å. The bite angle O(21)–V(1)–O(22) 74.90(13)° and the bridge angles O(21)–V(1)–O(21)# 76.23(13)° and V(1)–O(21)–V(1)# 103.77(13)° are very similar to those found in the related

catecholato-bridged divanadium(V) complexes.^{34,35c,36} Also the basal planes around V(1) and V(1)# are exactly parallel as judged by the zero dihedral angle between them.

The ethylenediammonium (H₂en)²⁺ cation in this molecule is well connected through hydrogen bonding (Table 3). For example, hydrogen atoms attached to N(31) are connected to the phenolic oxygen O(12C), as well as to the neighboring solvent water molecules O(1W) and O(2W), such that the distances N(31)···O(12C), N(31)···O(1W), and N(31)···O(2W) are 2.820(6), 2.869(6), and 2.859(9) Å, respectively. Corresponding angles N(31)–H(31C)···O(12C) (162.9(3)°), N(31)–H(31B)···O(1W) (153.7(4)°), and N(31)–H(31A)···O(2W) (178.5(5)°) are close to linearity, indicating strong hydrogen bonds.

¹H NMR Spectroscopy. ¹H NMR spectra of the complexes (**1** and **2**) have been recorded in acetonitrile-*d*₃. The complexes, as expected, do not display any low field resonance beyond 9.21 ppm, thus indicating the absence of phenolic-OH protons of the free tetradentate ligands H₂salen and H₂metsalen. The spectral profiles of **1** at 263 K and that of **2** at room temperature are displayed in Figures 3 and S1 (in the Supporting Information), respectively. The former involves a singlet at 8.96 ppm (9.02 in **2**) due to the azomethyne protons. All the aromatic protons in **1** appear in the 7.83–6.97 ppm region (7.43–7.18 ppm in **2**) with the expected integration and splitting patterns. The ethylenic

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protons H(8) and H(8') (Figure 3) are diastereotopic in these complexes because of the anisochronous nature of the bridge-head protons in the coordinated salen moiety and appear as an AA'BB' spin system involving two multiplets centered at 4.30 and 4.12 ppm (4.42 and 4.20 ppm in **2**). A sharp singlet at 3.96 ppm is characteristic of the OCH₃ protons in **2**. Of particular interest here is the position of the azomethyne protons. Because of the coordination of the ReO₄[−] moiety to the oxovanadium(V) center, the position of this singlet is shifted upfield to 8.96 ppm compared to what have been observed (9.35–9.39 ppm) for the [L¹OV(μ-O)VO(salen)] complexes in which [VO₂L¹][−] (H₂L¹ = tridentate dithiocarbamate- and amino acid-based Schiff base ligands) is coordinated to the oxovanadium(V) center.^{16c,d} The results are in conformity with the indication that the heterodinuclear structures of **1** and **2** remain intact in acetonitrile solution.

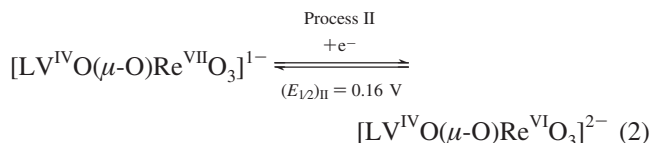
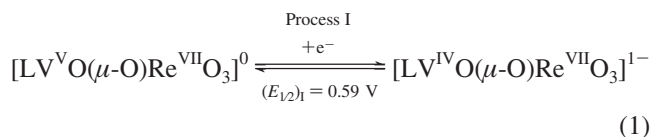
Electrochemistry. The redox properties of **1** and **2** have been examined by cyclic voltammetry (CV) at a platinum working electrode under an envelope of purified dinitrogen in dichloromethane solution (0.1 M TBAP) at 25 °C in the potential range of −2.0 to +1.0 V versus Ag/AgCl reference. The ligands are electrode inactive in this potential window. Voltammetric features are nearly identical for these compounds. Both CV and differential pulse voltammogram (DPV) of **1** are displayed in Figure 4 as a representative example, showing two electrochemical responses at (E_{1/2})_I = 0.59 V (process I) and (E_{1/2})_{II} = 0.16 V (process II) involving identical numbers of electrons. On the basis of comparison with the ferrocenium/ferrocene couple (ΔE_p, 70 mV; i_{pc}/i_{pa} = 1 at 100 mV s^{−1})²¹ as well as using the criteria of scan rate (50–500 mV s^{−1}) dependence of peak current and width and equivalence of the cathodic and anodic peak heights,³⁷ processes I and II, in the case of **1** (ΔE_p, 72 and 79 mV at 100 mV s^{−1} for processes I and II, respectively), may be appropriately described as reversible, while for **2** process II appears to be quasireversible (ΔE_p, 112 mV). Both these processes are cathodic as indicated by steady-state voltammetry (using an ultramicro platinum electrode, 10 μM diameter).

Redox properties of [V^{IV}O(salen)] are well investigated.³⁸ These involve a reversible V(IV)/V(V) couple appearing at 0.6 V versus Ag/AgCl in dichloromethane.^{38c} Taking a cue from these studies, process I may be regarded as arising from a vanadium-based electron-transfer involving a V(V)–Re(VII)/V(IV)–Re(VII) couple. Process II on the other hand is presumed to be a rhenium-based one. In fact, the latter process fails to appear in the voltammogram of [V^{VO}(salen)Cl],³⁹ recorded in methanol under identical experimental conditions (Figure S2a, Supporting Information). Also the voltammogram of **1** in DMSO displayed a single reduction

couple at E_{1/2} = 0.45 V (Figure S2b, Supporting Information) corresponding to a V(V/IV) electron transfer and confirms the dissociation of the ReO₄[−] moiety from the vanadium coordination sphere in **1**, an observation that already has a backing from the electrical conductivity measurements (vide supra). All these observations seem to support that process II is a rhenium-centered electron-transfer.

The electron stoichiometry for process I has been further examined by constant-potential bulk-electrolysis, carried out at a working potential of 0.4 V. The catholyte gradually changed color from green to a lighter shade during the progress of the electrolysis. The results show the consumption of 1 mol of electrons per mole of compound **1**. Similar experiments with process II (E_w = −0.1 V vs Ag/AgCl) did not, however, yield any meaningful result because of unidentified electrode reaction(s). However, differential and normal pulse voltammetric (NPV) experiments done under the identical experimental conditions in CH₂Cl₂ have displayed identical peak (Figure 4, inset) and current heights (Figure 5), respectively, for both the processes I and II.

The electrochemical results for **1** and **2**, based on CV, DPV, NPV, and constant potential coulometric experiments, are thus consistent with two successive one-electron steps as shown by eqs 1 and 2.



EPR Spectroscopy. The solution from the bulk electrolysis of **1** (process I) has been further characterized by EPR spectroscopy (Figure 6). The one-electron reduced species [LV^{IV}O(μ-O)Re^{VII}O₃]^{1−} in dichloromethane/toluene solution (1:10 v/v) at room temperature shows (Figure 6, inset) an eight-line isotropic pattern (⟨g⟩ = 1.977; ⟨A⟩ = 87 × 10^{−4} cm^{−1}) characteristic of an unpaired electron being coupled to the vanadium nuclear spin (⁵¹V, I = 7/2). Interestingly, each of these spectral lines again is split into a doublet because of the familiar “two-line pattern” superhyperfine coupling (A (^{185,187}Re) = 20.7 × 10^{−4} cm^{−1}) from the attached rhenium center (¹⁸⁵Re, ¹⁸⁷Re, I = 5/2).⁴⁰ In the frozen solution, however, the spectrum displayed a well-resolved axial anisotropy with two sets of eight-line patterns. Some of these lines are distinctly split into doublets due to ¹⁸⁵Re and ¹⁸⁷Re superhyperfine coupling. The corresponding spin-Hamiltonian parameters are g_{||} = 1.948, A_{||} = 153 × 10^{−4} cm^{−1}, g_⊥ = 1.988, and A_⊥ = 53 × 10^{−4} cm^{−1}.

Concluding Remarks. Perrhenate coordinated vanadium(V) compounds (**1** and **2**) containing an almost linear Re(VII)–O–V(V) bridge (V(1)–O(11)–Re(1) is 170.2(3)° in **2**) have been

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reported here. These heterobimetallic compounds remain almost intact in acetonitrile and dichloromethane solutions but undergo dissociation in DMSO. In dichloromethane, both **1** and **2** undergo two one-electron reductions at $E_{1/2} = 0.59$ and 0.16 V versus Ag/AgCl reference. In the first process, the reducing electron enters the vanadium(V) center and remains partially delocalized between the metal centers as evident from the EPR spectrum of $[\mathbf{1}]^-$, involving $^{185}, ^{187}\text{Re}$ superhyperfine coupling ($A(^{185,187}\text{Re}) = 20.7 \times 10^{-4} \text{ cm}^{-1}$). When allowed to react with H_2TBC , **2** generates a binuclear vanadium(V) compound **3** that contains both bridging and nonbridging catecholate moieties. Thus, the work described here gives an opportunity to solubilize a perrhenate anion in organic solvents for its potential use as catalyst for various oxidation reactions on organic substrates.^{15,41}

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Supporting Information Available: ^1H NMR spectrum of **2** (Figure S1), cyclic voltammograms of $[\text{V}^{\text{VO}}(\text{salen})\text{Cl}]$ in methanol and **1** in DMSO (Figure S2) and the X-ray crystallographic files in CIF format for the compounds **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Reporting a New Class of Divanadium(V) Compounds Connected by an Unsupported Hydroxo Bridge

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Dinuclear oxovanadium(V) compounds $[LV^VO(\mu-OH)OV^VL](PF_6)$ [$H_2L = N,N'$ -tert-ethylene bis(salicylideneimine) (H_2Salen) and its derivatives] (**1–3**) have been obtained by aerial oxidation of $V^{IV}OL$ precursors in THF in the presence of added NH_4PF_6 . The oxidized vanadium(V) probably extracts an OH^- ligand from the residual moisture in the solvent and is retained as an unsupported hydroxo-bridge between the metal centers of these compounds as confirmed by single-crystal X-ray diffraction analyses. The molecules of **1–3** have centrosymmetric structures with each vanadium center having a distorted octahedral geometry. The bridging OH^- group is located *trans* to the terminal $V=O_t$ bond. The latter exerts strong *trans* labilizing influence to set the participating vanadium centers apart by about 4.1 Å. These separations are by far the largest (e.g., $V \cdots V\#$, 4.131 Å in **1**) among all binuclear compounds containing an unsupported hydroxo bridge reported to date. The complexes retain their identity also in solution as established by 1H NMR spectroscopy. Electrochemically, the behaviors of **1–3** are quite interesting as studied by cyclic voltammetry in acetonitrile, each undergoing three (except **3**) nearly reversible metal-based reductions, all in the positive potential range (e.g., at $E_{1/2} = 0.57, 0.39$, and 0.04 V versus $Ag/AgCl$ reference for **1**) as indicated by steady state voltammetry. The electrode process at 0.39 V appears to involve a single-step two-electron transfer as revealed from the normal and differential pulse voltammetric data and probably includes a combination of $V^V-V^{IV} \leftrightarrow V^{III}-V^{IV}$ mixed oxidation states. Compounds **1–3** thus provide a unique example of divanadium compounds in which the metal centers are linked by an unsupported hydroxo-bridge.

Introduction

Dinuclear metal complexes connected by a sole μ -oxo bridge continue to attract increasing attention in contemporary coordination chemistry. Such species, often supported by ancillary bridging ligand(s) (viz. carboxylates, etc.) are known to play pivotal roles in biology during dioxygen activation by a host of metalloenzymes, namely, methane monooxygenase, Δ^9 -desaturase, ribonucleotide reductase, cytochrome *c* oxidase, and so forth.^{1–3} These enzymes containing homo- ($Fe^{II/IV}$, $Fe^{II/IV}$) and heterobinuclear (Fe^{II} , Cu^{II}) active sites are known to activate dioxygen molecule

by a variety of complex mechanisms which frequently involve a putative μ -hydroxo species as a key intermediate, responsible for the oxidation of organic substrates.⁴ Efficient use of μ -oxo species as catalysts by mother nature in the biological domain is a source of motivation for chemists to replicate the use of such species as efficient catalysts.⁵

Unlike the single μ -oxo bridged binuclear complexes, the chemistry of “unsupported” μ -hydroxo bridged analogues is less explored because of the lack of any straightforward

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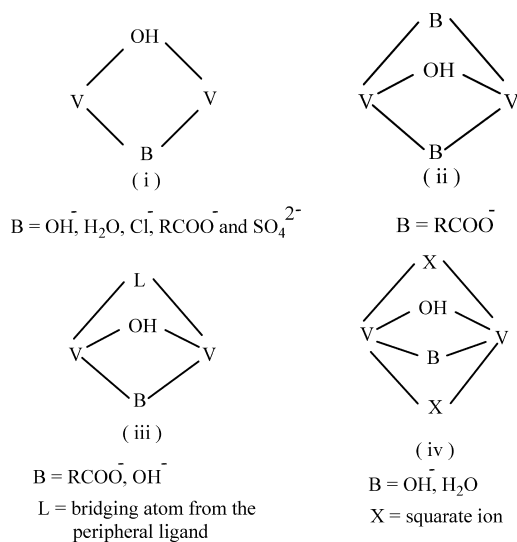
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method for their synthesis. However, the relevance of such species as a model for many oxidase biosites has prompted several studies with the objective to synthesize “unsupported” μ -hydroxo binuclear compounds involving both homo and heterometal centers that helped in unfolding the chemistry associated with such complex biomolecules.^{6–12}

In vanadium chemistry, the ubiquity of oxovanadium species in higher oxidation states (4+ and 5+) is well established. A large number of unsupported μ -oxo divanadium compounds containing $[\text{V}_2\text{O}_3]^{n+}$ ($n = 2, 3$, and 4) cores have been already reported and discussed briefly in our previous communications.¹³ Far less numerous are the hydroxo-bridged divanadium compounds. Surprisingly, to our knowledge, all the μ -hydroxo divanadium compounds reported thus far^{14–17} have one or more supporting bridging group(s) [B and X] that can be classified under the following four categories (Chart 1) depending upon the type and the number of supporting bridges. The results seem to suggest that a sole μ -OH bridge by itself is not capable of holding the vanadium centers together!

Chart 1. Classification of the Hydroxo-Bridged Divanadium Compounds Containing One or More Supporting Bridge(s) Found in μ -Hydroxo Divanadium Compounds



Herein, we report a new class of divanadium(V) compounds (**1–3**) containing a hitherto unknown $[\text{V}_2\text{O}_2(\text{OH})]^{5+}$ core. Oxovanadium(V) centers in these compounds are connected by a single μ -OH group with no further ancillary

bridging moiety. Results of single-crystal X-ray diffraction analysis, NMR spectroscopy (including ^1H , ^{19}F , and ^{51}V), and electrospray ionization mass spectra (ESI-MS) studies have confirmed such unprecedented bridging mode in **1–3** both in the solid state as well as in solution. Complete details on the preparation and structural and physicochemical properties of all the compounds (**1–3**) have been discussed.

Experimental Section

Materials. Unless stated otherwise, all reactions were carried out under an atmosphere of purified dinitrogen. Precursor complexes $[\text{VO}(\text{Salen})]$ and its analogues were prepared following the literature methods.¹⁸ All other reagents are commercially available and used as received. Solvents were reagent grade, dried by standard methods,¹⁹ and distilled under nitrogen prior to their use.

Preparation of Complexes. $[(\text{L}^1)\text{OV}(\mu\text{-OH})\text{VO}(\text{L}^1)]\text{PF}_6 \cdot 2\text{THF}$ (**1**).²⁰ To a stirred solution of $[\text{VO}(\text{Salen})]$ (0.17 g, 0.5 mmol) in tetrahydrofuran (THF, 25 mL) was added solid ammonium

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hexafluorophosphate (0.16 g, 1.0 mmol) in portions. The resulting mixture was refluxed for about 3 h, when a green solution was obtained. It was then cooled and filtered. The filtrate volume was reduced to about 15 mL by rotary evaporation, allowed to stand in the air for about 24 h, and became gradually blue in color. The solution was finally cooled at 4 °C in a refrigerator for an overnight period. A brown crystalline compound deposited at this stage was collected by filtration, washed with diethyl ether (3 × 10 mL), and finally dried in vacuo over P₄O₁₀. Yield: 0.14 g (57%). Anal. Calcd for C₄₀H₄₅N₄O₉V₂PF₆: C, 49.35; H, 4.63; N, 5.76. Found: C, 48.96; H, 4.57; N, 5.69%. FT-IR bands (KBr pellet, cm⁻¹): 3438br, 1625s, 1598s, 1554s, 1446m, 1275s, 951s, 843vs, 816m, 760s, 658s, 557s, 462s. UV-vis (CH₃CN) [λ_{\max} , nm (ϵ , mol⁻¹ cm²): 572 (2100); 325 (17200); 285 (sh); 249 (51650); 223 (65800)]. ⁵¹V NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -584 (s) [$\Delta\nu_{1/2}$, 2500 Hz]. ¹⁹F NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -72.27 (d, J_{P-F} = 751 Hz, PF₆). Λ_M (CH₃CN/ Ω^{-1} cm² mol⁻¹): 131. ESI-MS (positive) in CH₃CN: m/z , 684.14 [M-PF₆-2THF]⁺.

[(L²)OV(μ -OH)VO(L²)PF₆] (2). This compound was prepared as a brown crystalline solid following essentially the same procedure as described for 1 using [VO(L²)] as the precursor complex. Yield: 0.13 g (61%). Anal. Calcd for C₃₄H₃₃N₄O₇V₂PF₆: C, 47.64; H, 3.85; N, 6.54. Found: C, 47.25; H, 3.76; N, 6.44%. FT-IR bands (KBr pellet, cm⁻¹): 3443br, 2926m, 1626s, 1599s, 1554m, 1446m, 1277s, 956s, 843vs, 816m, 750s, 656s, 559s, 459s. UV-vis (CH₃CN) [λ_{\max} , nm (ϵ , mol⁻¹ cm²): 571 (2400); 332 (17500); 290 (sh); 252 (89000); 223 (116500)]. ⁵¹V NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -580 (s) [$\Delta\nu_{1/2}$, 3600 Hz]. ¹⁹F NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -72.27 (d, J_{P-F} = 750.5 Hz, PF₆). Λ_M (CH₃CN/ Ω^{-1} cm² mol⁻¹): 134. ESI-MS (positive) in CH₃CN: m/z , 711.70 [M-PF₆]⁺.

[(L³)OV(μ -OH)VO(L³)PF₆] (3). An identical procedure as mentioned above (for 1) yielded the product 3 in 37% yield when [VOL³] was employed as a replacement for [VO(Salen)]. Anal. Calcd for C₃₆H₃₇N₄O₁₁V₂PF₆: C, 45.50; H, 3.90; N, 5.90. Found: C, 45.17; H, 3.85; N, 5.81%. FT-IR bands (KBr pellet, cm⁻¹): 3428br, 2929m, 1628s, 1597m, 1563m, 1445s, 1269s, 1084s, 947s, 843vs, 815m, 737s, 652s, 559s, 462m. UV-vis (CH₃CN) [λ_{\max} , nm (ϵ , mol⁻¹ cm²): 644 (2200); 352 (17100); 255 (60500)]. ⁵¹V NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -564 (s) [$\Delta\nu_{1/2}$, 3600 Hz]. ¹⁹F NMR (500 MHz, acetonitrile-d₃, 299 K, δ /ppm): -72.30 (d, J_{P-F} = 750.5 Hz, PF₆). Λ_M (CH₃CN/ Ω^{-1} cm² mol⁻¹): 143. ESI-MS (positive) in CH₃CN: m/z , 803.89 [M-PF₆]⁺.

Physical Measurements. Microanalyses (for C, H, and N) were performed at IACS on a Perkin-Elmer model 2400 Series II elemental analyzer. UV-visible spectral measurements in solution were recorded on a Perkin-Elmer model Lambda 950 UV-vis-NIR spectrophotometer, while for IR spectra, a Shimadzu model 8400S FT-IR spectrometer with samples prepared as KBr pellets was employed. ¹H NMR (300 MHz) spectra were recorded on a Bruker model Avance DPX 300 spectrometer using SiMe₄ (δ_0) as internal reference. ⁵¹V and ¹⁹F NMR spectra were obtained on a JEOL Lambda 500 spectrometer (500 MHz) with data analysis system (ALICE) operating at ambient temperature (299 K). Chemical shifts were referenced to external neat VOCl₃ and CF₃COOH, respectively. The ESI-MS in positive ion mode were measured on a Micromass Qtof YA 263 mass spectrometer. Molar conductivities (Λ_M) for a 1 mM solution of the complexes 1–3 in acetonitrile were measured at 298 K with a Systronics model 306 bridge.

Cyclic voltammetry in acetonitrile was recorded on a BAS model 100 B/W electrochemical workstation using a platinum disk (i.d. = 1.6 mm) working electrode and a platinum wire counter electrodes. Ag/AgCl was used for reference and Fc/Fc⁺ couple as the internal standard. Solutions were ~1.0 mM in the samples and contain 0.1 M TBAP as supporting electrolyte.

X-ray Crystallography. Crystals suitable for X-ray diffraction analyses were grown by slow evaporation from solutions in THF at 4 °C. Single crystals of 1 (plate, black crystals, 0.302 × 0.295 × 0.106 mm³), 2 (block, black crystals, 0.186 × 0.100 × 0.071 mm³), and 3 (rod like, black crystals, 0.177 × 0.089 × 0.082 mm³) were mounted on glass fibers without protection. Cell dimensions were determined at 293 K from the setting angles of a Bruker SMART 1000 CCD diffractometer using a graphite monochromated Mo K α (λ = 0.71073 Å) radiation source. Data collections were completed using the $\omega/2\theta$ scan techniques. There was no deterioration of the crystals during the data collections. Accurate cell dimensions were refined from setting angles of 5158, 2220, and 3629 reflections for 1, 2, and 3, respectively, in the ranges of θ , 2.3005–26.5575° (1), 2.218–20.507° (2), and 2.219–23.4635° (3). Pertinent cell parameters, data collection conditions, and refinement details are provided in Table 1. The structures were solved by direct methods,²¹ developed by successive difference Fourier synthesis and refined on F^2 by a full-matrix least-squares procedure using the SHELXL-97 program.²² The positions of all nonhydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms except on the central bridging moiety (i.e., hydroxo-bridge) were geometrically calculated and isotropically fixed at positions recalculated after each cycle of refinement [$d(C-H)$ = 0.95 Å, with the isotropic thermal parameter of $U_{iso}(H)$ = 1.2 $U_{iso}(C)$]. In all the cases, absorption corrections based on multiscan using SADABS (Sheldrick, 1996) software²³ were applied. The P atom of the hexafluorophosphate anion in 1 also lies on a crystallographic mirror plane. Data reduction was accomplished using the SAINT plus software,²⁴ and crystallographic diagrams were drawn using the (Oak Ridge thermal ellipsoid plot) ORTEP-3 at the 30% probability level.²⁵

Results and Discussion

Syntheses. Unsupported hydroxo-bridged divanadium(V) compounds 1–3 have been prepared for the first time through a single-pot synthesis as outlined in Scheme 1. Quite a few vanadium compounds with a hydroxo group as ligand have been synthesized. Some of these compounds contain an OH group as a terminal ligand^{14d,26} showing interesting relevance to metallobiosites.²⁶ In the majority of these compounds, however, it is attached in the μ -OH mode along with one or

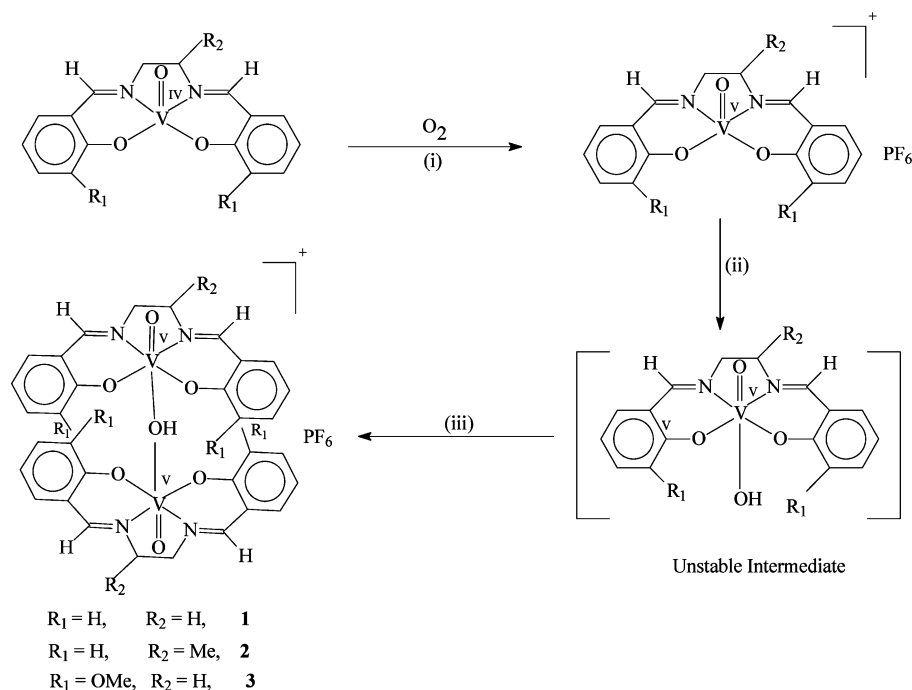
(20) Abbreviations used: H₂L¹, *N,N'*-bis(salicylidene)-1,2-diaminoethane; H₂L², *N,N'*-bis(salicylidene)-1,2-diaminopropane; H₂L³, *N,N'*-bis(3-methoxysalicylidene)-1,2-diaminoethane; TBAP, tetrabutylammonium perchlorate.

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Table 1. Summary of the Crystallographic Data for the Complexes **1**, **2**, and **3**

parameter	1	2	3
composition	C ₄₀ H ₄₅ N ₄ O ₉ V ₂ PF ₆	C ₃₄ H ₃₃ N ₄ O ₇ V ₂ PF ₆	C ₃₆ H ₃₇ N ₄ O ₁₁ V ₂ PF ₆
fw	972.65	856.49	948.55
crystal system	monoclinic	triclinic	tetragonal
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>I</i> 4 ₁ / <i>acd</i>
<i>a</i> , Å	13.3764(8)	9.8688(9)	24.9901(10)
<i>b</i> , Å	12.4181(8)	11.7361(10)	24.9901(10)
<i>c</i> , Å	12.6910(8)	17.0989(15)	27.0502(11)
α , deg	90.00	84.526(2)	90.00
β , deg	96.0200(10)	77.938(2)	90.00
γ , deg	90.00	75.156(2)	90.00
<i>V</i> , Å ³	2096.5(2)	1870.2(3)	16893.0(10)
ρ_{calc} , Mg m ⁻³	1.541	1.521	1.492
temp, K	293(2)	293(2)	293(2)
λ (Mo K α), Å	0.71073	0.71073	0.71073
<i>Z</i>	2	2	16
<i>F</i> (000), μ mm ⁻¹	1000/0.570	872/0.624	7744/0.568
$2\theta_{\text{max}}$ [°]	56.70	56.66	56.58
reflections collected/unique	21182/5238	19233/9150	59632/5256
<i>R</i> _{int} , GOF on <i>F</i> ²	0.0343/1.051	0.0622/0.980	0.1011/1.013
no. of parameters	293	506	278
<i>R</i> 1 ^a (<i>F</i> _o), <i>wR</i> 2 ^b (<i>F</i> _o) (<i>I</i> \geq 2 σ (<i>I</i>))	0.0464, 0.1165	0.0753, 0.2055	0.0622, 0.1720
CCDC No.	616937	616938	616939

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

Scheme 1. Synthetic Strategy for the Preparation of the Unsupported Hydroxo-Bridged Complexes **1–3**^a

^a Conditions: (i) NH₄PF₆, THF, reflux, anion-assisted aerial oxidation; (ii) OH⁻ (presumably from residual moisture in the solvent); (iii) [VOL¹⁻³]⁺PF₆ (present in the reaction mixture).

more ancillary bridging ligands, connecting a pair or more of the vanadium centers together.^{14a-c,e-h,15-17} Excepting a few,^{14f,h} all these compounds have been prepared at controlled pH by the addition of acid or base that helped in the generation of the hydroxo group as ligand. The protocol used for the synthesis of **1–3**, on the other hand, does not include any deliberate attempt to introduce an OH⁻ ligand in the reaction medium. [V^{IV}O(Salen)] is known, as discussed in our earlier communication,^{13a} to undergo aerial oxidation in solution in the presence of an added anion which is accommodated in the vacant coordination site of vanadi-

um(V), *trans* to the terminal oxo-ligand.²⁷ This binding is more of an ionic nature as confirmed in solution by NMR study.^{27b} We followed the same reaction of [V^{IV}O(Salen)] in the presence of bulky PF₆⁻ anion. The oxidized [V^VO(Salen)]⁺ cation fails to accommodate PF₆⁻ in its vacant coordination site, possibly because of the large size and low surface charge density of the anion. This in turn forces the vanadium(V) center in [V^VO(Salen)]⁺ to accept a hydroxo

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group as ligand from the residual moisture present in the solution^{14f,h} and to get stabilized through the formation of an unsupported μ -OH bridge between a pair of participating vanadium(V) centers. Of particular interest in the structures of **1–3** is the *trans* location of μ -OH group relative to the terminal oxo- ligand (*vide infra*). All the structurally characterized oxovanadium compounds with bridging or terminal hydroxo ligand(s) on the contrary have a terminal oxo-group, *cis* to the coordinating OH^- ligand.^{14–17,26}

Magnetic susceptibility values indicate that all the complexes (**1–3**) are diamagnetic in nature. The molar conductivities of these compounds in acetonitrile are in the range 131–143 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ as expected for 1:1 electrolytic behavior.²⁸

IR spectra of the complexes are summarized in the Experimental Section, containing all the characteristic bands of the coordinated N_2O_2 ligands. These include prominent bands at about 1626 and 1275 cm^{-1} attributable to the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O}/\text{phenolate})$ stretching modes of the ligands. In addition, a sharp strong band is observed attributable to the terminal $\text{V}=\text{O}_t$ stretching at about 951 cm^{-1} , which is significantly lower in wavenumber than what previously has been reported for the mononuclear $[\text{V}^{\text{VO}}(\text{S-alen})]^+$ entity (981 cm^{-1}).^{27a} The results confirm the presence of a bridging moiety *trans* to the terminal oxo-groups in **1–3**. Of particular interest here is the appearance of a new signal at about 658 cm^{-1} , considered to be a signature for the antisymmetric $\nu(\text{V}-\text{OH})$ stretching mode.^{26c} Also, the μ -hydroxo-bridge that connects the vanadium centers together provides a moderately strong antisymmetric bridge vibration at about 815 cm^{-1} along with a broadband in the 3422–3446 cm^{-1} region. The strong vibrations observed at about 843 cm^{-1} are characteristic of the PF_6^- counteranion in these compounds.²⁹

The cationic complexes in **1–3** thus appear to be dinuclear with a 2-fold axis of symmetry and bridged by a uninegative atom or a group of atoms, namely, F^- or OH^- . Leigh et al.³⁰ have recently reported a single fluoride bridged compound $[(\text{Salen})\text{VO}(\mu\text{-F})\text{OV}(\text{Salen})]\text{BF}_4$ obtained by a closely comparable reaction which involves interaction of $[\text{V}^{\text{VO}}(\text{Salen})]$ with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in acetonitrile. The presence of an F^- ion in the bridging portion has been conclusively established by a ^{19}F NMR study. For compounds **1–3**, ^{19}F NMR spectra are all identical (Supporting Information Figure S1) involving a single strong feature in the form of a doublet at -72.2 ppm ($J_{\text{P-F}} = 751$ Hz) due to ^{31}P ($I = 1/2$) coupling, corresponding to the PF_6^- anion.³¹ The lack of a characteristic signal due to the bridging F^- ion (at ca. -136 ppm)³⁰ in **1–3**

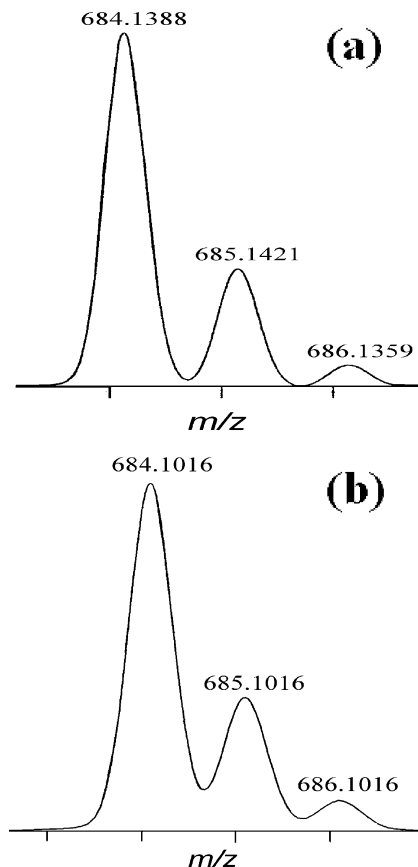


Figure 1. Molecular ion peak in the ESI mass spectrum (positive) for complex **1** in acetonitrile with observed (top, **a**) and simulated (bottom, **b**) isotopic distributions.

therefore leaves the OH^- ion as the only viable alternative for the bridging moiety in these compounds.

^{51}V NMR spectra in acetonitrile- d_3 of **1–3** display a single broad signal in the -584 to -564 ppm region (spectral width at half-height, $\Delta\nu_{1/2}$ varies between 3600 and 2500 Hz) thus fulfilling the symmetry requirement for these molecules.

Mass Spectroscopy. ESI-MS spectral data (in the positive ion mode) for the complexes **1–3** are listed in the Experimental Section. All these complexes display their respective molecular ion peak due to the $[\text{M-PF}_6]^+$ ionic species ($[\text{M-PF}_6 \cdot 2\text{THF}]^+$ in case of **1**). The isotope distribution pattern for the molecular ion peak of **1** is displayed in Figure 1a together with its simulation pattern (Figure 1b). Results confirm the identities of these compounds as containing two identical vanadium(V) centers connected by an unsupported hydroxo-bridge.

Description of Crystal Structures. Perspective views of the molecular structures of **1–3** are shown in Figures 2, 3, and Supporting Information Figure S2, respectively. Selected bond distances and angles are summarized in Table 2. The results provide confirmatory evidence in support of their proposed binuclear compositions. Complex **1** crystallizes in the monoclinic space group $P2_1/c$ while **2** crystallizes in the triclinic space group $P\bar{1}$, both having two molecular weight units accommodated in the unit cell. **3** on the other hand, has a tetragonal space group $I4_1/acd$ with sixteen molecular weight units in the unit cell. In **1** are also present two independent THF molecules as solvent of crystallization,

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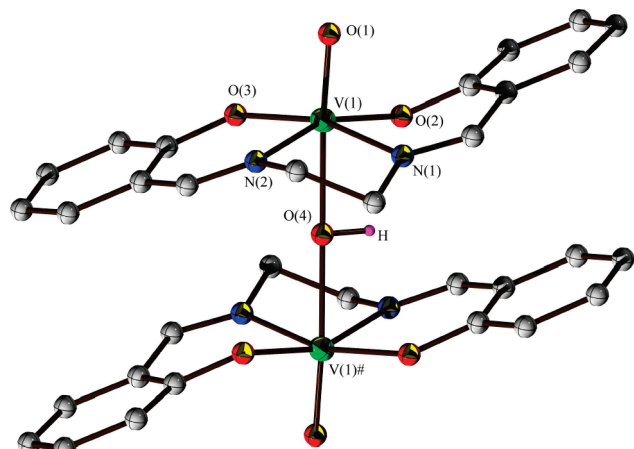


Figure 2. Molecular structure and atom-numbering scheme for **1** with thermal ellipsoids drawn at the 30% probability level. The refined hydrogen atom position of the bridging hydroxide ligand is shown. The V—O(H)—V bridge is in the plane of the paper.

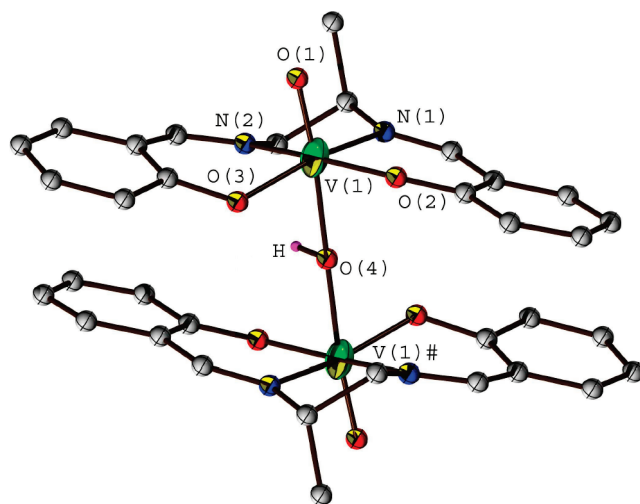


Figure 3. ORTEP view of the hydroxo-bridged cation in **2**, showing the atomic numbering scheme with thermal ellipsoids drawn at the 30% probability level. The H atoms of the two $(L)^{2-}$ ligands are omitted for clarity, while that bound to oxygen atom of hydroxo-bridge is depicted as its refined position.

occupying the void volumes. The asymmetric unit of **2** contains two independent molecules (**2A** and **2B**) with only minor conformational differences between these as summarized in Supporting Information Table S1. For the sake of brevity, in the remaining part of this discussion, only the salient features of **2A** will be discussed along with **1** and **3**.

All the reported compounds have the PF_6^- as counterion. The cationic parts are all centrosymmetric involving two $[V^VO]^{+}$ units ($H_2L = H_2L^1-H_2L^3$)²⁰ connected together by an oxygen atom O(4) from the bridging hydroxo moiety, thus forming a hitherto unknown linear V(V)—(μ -OH)—V(V) core.

Each vanadium(V) center in these molecules has a distorted octahedral geometry. The basal positions are occupied by the donor atoms O(2), O(3), N(1), and N(2), all contributed by the tetradentate ligand $(L)^{2-}$ (Salen and its derivatives). The apical positions are taken up by the terminal oxygen atom O(1), together with the bridging oxygen atom O(4). In **1**, the *trans* angles in the basal plane

Table 2. Selected Bond Distances (Å) and Angles (deg) for the Complexes **1**, **2**, and **3**

	1	2A	3
Bond Distances (Å)			
V(1)—O(1)	1.609(2)	1.570(5)	1.598(2)
V(1)—O(2)	1.833(2)	1.812(4)	1.834(2)
V(1)—O(3)	1.8233(18)	1.842(5)	1.836(2)
V(1)—O(4)	2.0655(2)	2.0552(12)	2.0533(6)
V(1)—N(1)	2.061(2)	2.101(5)	2.098(3)
V(1)—N(2)	2.085(2)	2.074(5)	2.071(3)
O(4)—H	0.884(10)	0.901(12)	0.888(10)
V(1)···V(1)#	4.131	4.110	4.107
Bond Angles (deg)			
O(1)—V(1)—O(2)	97.44(10)	100.6(3)	100.41(12)
O(1)—V(1)—O(3)	100.70(10)	97.3(3)	97.43(11)
O(1)—V(1)—O(4)	172.28(7)	172.37(19)	172.82(10)
O(1)—V(1)—N(1)	91.10(9)	98.7(3)	96.91(12)
O(1)—V(1)—N(2)	96.85(10)	90.4(2)	89.85(13)
O(4)—V(1)—N(1)	81.48(6)	79.37(17)	80.50(8)
O(4)—V(1)—N(2)	79.51(7)	81.97(16)	83.04(8)
O(4)—V(1)—O(2)	84.31(6)	86.69(17)	86.13(8)
O(4)—V(1)—O(3)	85.95(7)	82.39(15)	83.13(7)
O(2)—V(1)—O(3)	106.20(9)	108.11(19)	108.81(10)
O(2)—V(1)—N(1)	86.78(9)	86.4(2)	85.67(11)
O(2)—V(1)—N(2)	158.63(9)	160.2(2)	160.58(11)
O(3)—V(1)—N(2)	86.60(9)	86.4(2)	85.88(11)
O(3)—V(1)—N(1)	160.97(9)	155.9(2)	157.33(11)
N(1)—V(1)—N(2)	77.13(9)	75.6(2)	76.69(12)
V(1)—O(4)—H	90.01(4)	90.4(6)	90.5(6)
V(1)—O(4)—V(1)#	180.00(2)	180.00(8)	180.00(4)

Table 3. Bond Valence Sum^a for the Oxygen Atom O(4) of the Bridging Hydroxo Group in **1–3**

compound ^b	bond description	r_{ij} , Å	s_{ij}	$V_{ij} = \sum_j s_{ij}$
1	O(4)—V(1)	2.0655	0.492	0.984
	O(4)—V(1)#	2.0655	0.492	
2	O(4)—V(1)	2.0552	0.506	1.012
	O(4)—V(1)#	2.0552	0.506	
3	O(4)—V(1)	2.0533	0.508	1.016
	O(4)—V(1)#	2.0533	0.508	

^a $r_0 = 1.803$ Å; $B = 0.37$. ^b The independent molecule **2A** has been taken from the asymmetric unit of **2**.

O(2)—V(1)—N(2) 158.63(9)° (corresponding angles in **2A** and **3** are 160.2(2)° and 160.58(11)°, respectively) and O(3)—V(1)—N(1) 160.97(9)° (155.9(2)° and 157.33(11)°) are somewhat compressed and force the V(1) atom by 0.2309 Å (0.2401 and 0.2235 Å) out of the least-squares basal plane toward the more tightly held apical oxo- atom O(1). The distances and angles made by the donor atoms in the equatorial plane at V(1) (Table 2) are in the expected range as previously reported for compounds containing the $[V^VO(Salen)]^{+}$ moiety.^{27,30} These basal planes surrounding the two vanadium(V) centers are almost parallel with a staggered conformation as judged by the near zero value of the dihedral angle between them.

In the linear V(V)—(μ -OH)—V(V) core of **1–3**, the oxygen atom O(4) is situated at the center of inversion. Of particular interest here is the *trans* location of the bridging hydroxo moiety relative to the terminal oxygen atom O(1), such that the angle O(1)—V(1)—O(4) 172.28(7)° (172.37(19)° and 172.82(10)°) is close to linearity, as expected for a nearly ideal octahedral geometry. This leads to a significant increase in the V(1)—O(4) distance, 2.0655(2) Å (2.0552(12) and 2.0533(6) Å) attributable to the *trans* labilizing influence of the terminal oxo- atom O(1). In consequence, the enlarged

V(1)⋯V(1)# separation 4.131 Å (4.110 and 4.107 Å) is by far the largest in these compounds compared with the other divanadium(V, IV, and III) compounds containing one or more hydroxo group(s) as bridging ligands.^{14–17} The terminal V(1)—O(1) distance 1.609(2) Å (1.570(5) and 1.598(2) Å) is a little longer compared with those (1.576 Å)²⁷ in [V^{VO}(Salen)ClO₄] and [V^{VO}(Salen)BF₄], indicating stronger interactions from the OH[−] ligand compared to those from its ClO₄[−] and BF₄[−] analogues.

The torsion angle O(1)—V(1)⋯V(1)#—O(1)# is exactly 180° in **1–3**, making the [V₂O₂(OH)]⁵⁺ core perfectly linear in these compounds. To our knowledge, such linearity is an unprecedented structural feature in divanadium compounds.

Bond Valence Sum (BVS) Approach. The bond length (r_{ij}) between the two participating atoms (i, j) is related to the bond valence (s_{ij}) by eq 1 where r_0 and B are

$$s_{ij} = \exp[(r_0 - r)/B] \quad (1)$$

two empirically determined parameters, the former being the characteristic of a bond in question.³² For a multiatomic system containing a central atom, the bond valence s_{ij} may be regarded as the amount of electrons by which the central atom (i) is enriched (or depleted) in forming a bond with a neighboring atom (j). Accordingly, the BVS (V_i) of an atom in question is a measure of the total number of electrons it uses to form the compound (i.e., oxidation state) and is calculated by eq 2. As long as the bond

$$V_i = \sum s_{ij} \quad (2)$$

lengths are all controlled by electronic factors in a particular compound, BVS provides an excellent fit to the observed oxidation state. However, in molecules having steric encumbrances where nonelectronic factors (steric, etc.) have dominant role(s) to play in controlling bond lengths, the BVS value cannot be used as a measure of the formal oxidation state unless the steric feature is constant.³³ Brown and Altermatt³⁴ have calculated the r_0 value for the V⁵⁺—O^{2−} bond to be 1.803 Å, with the empirical parameter B being set to 0.37. Substituting these numbers in eqs 1 and 2, the bond valence contributions of the attached vanadium center to the bridging oxygen atom O(4) have been calculated for **1–3**. As summarized in Table 3, the data indicate one unit of V_i being contributed to the bridging oxygen atom O(4) by the attached vanadium centers V(1) and V(1)#. The results thus provide a strong evidence in favor of O(4) being a part of a bridging hydroxo moiety. The hydrogen atom of that moiety consumes the remaining unit of V_i with the central oxygen atom.

¹H NMR Spectroscopy. ¹H NMR spectra of **1–3** have been recorded at room temperature in acetonitrile-*d*₃, and the data are summarized in Table 4. The complexes, as expected, do not display any low field resonance beyond 8.40 ppm, thus indicating the absence of phenolic-OH protons of the free tetradentate ligands, H₂L¹—H₂L³. The spectra of **1**,

Table 4. ¹H NMR Data (δ , ppm)^a for the Complexes **1–3** in Acetonitrile-*d*₃

1		2		3		assignments
8.26 s	4H	8.42–8.06 s	4H	8.26 s	4H	H(7), H(7')
7.23 (7.28) d	4H	7.80–6.68 m	16H	7.13 (6.56) d	4H	H(5), H(5')
7.60 (7.13) t	4H			6.97–6.89 m	8H	H(4), H(4')
6.92 (8.23) t	4H					H(3), H(3')
6.78 (8.05) d	4H					H(2) ^b , H(2') ^b
4.06, 3.90 (5.03) q	8H	4.19–3.80 m	6H	4.07, 3.80 brd	8H	H(8), H(8')
		1.29 (5.83) d	6H			H(9) ^c
				3.88 s	12H	H(10) ^d , H(10') ^d

^a Chemical shifts (δ) relative to internal TMS at room temperature. Protons labels are as in the insets in Figures 4 and 5 and Supporting Information Figure S3. s, singlet; d, doublet; t, triplet; brd, broad doublet; q, AB quartet. Values in parentheses represent coupling constants (J in Hz). ^b H(2) protons are absent in **3**. ^c H(9) protons are present only in **2**. ^d H(10) protons are present only in **3**.

2, and **3** are displayed in Figures 4, and 5, and Supporting Information Figure S3, respectively, along with their possible interpretations.

For compounds **1** and **3**, their spectral features have very much in common, both involving a singlet (appearing at 8.26 ppm) corresponding to the presence of the azomethine moiety and a broad doublet due to the bridge-head ethylene protons. The latter protons H(8) and H(8') are diastereotopic in these complexes because of the rigidity of the metal-bound bridge-head moiety in the coordinated ligands and appear as an AB spin system with $\delta_A = 4.06$ and $\delta_B = 3.90$ ppm in **1**. A sharp singlet at 3.88 ppm is characteristic of the OMe protons in **3**. All the aromatic protons in **1** appear in the 7.62–6.76 ppm region with the expected splitting and integration patterns.

Because of the presence of two chiral centers in **2**, the spectral features of this compound (Figure 5) is a bit more complicated but at the same time quite interesting. Thus, the azomethine protons H(7), which appear as a singlet in **1**, are split into four lines of equal intensity in the 8.4–8.0 ppm region. With a couple of methyl groups attached to the anisochronous bridge-head carbon atoms C(8) and C(8)#, two diastereomeric pairs of enantiomers (RR/SS and RS/SR) are possible for this compound, and for each pair, two azomethine signals are expected because of the inequivalence of the H(7) and H(7') protons. The appearance of four signals of equal intensities (shown in the inset) thus indicates the presence of both the diastereomeric pairs to form a racemic mixture. Interestingly, these singlets gradually lose their integrity with the rise in temperature and eventually coalesce partially into a pair of broad signals at 70 °C (Figure 6). This change, as expected, is reversible and points to an equilibrium between these two diastereomeric pairs. The aromatic protons in **2**, all appear in the form of complex multiplets in the 7.80–6.68 ppm range as against a couple of doublets and triplets observed for **1**. The bridge-head aliphatic protons H(8) and H(8') appear as a cluster of three signals in the 4.19–3.80 ppm region. The methyl protons H(9), which emerge as a twin signal at 1.29 ppm near room temperature, show up as a pseudo triplet (consisting of two overlapping doublets) at 0 °C, as expected for the diastereomeric forms. Unfortunately, we are unable to detect any signal corresponding

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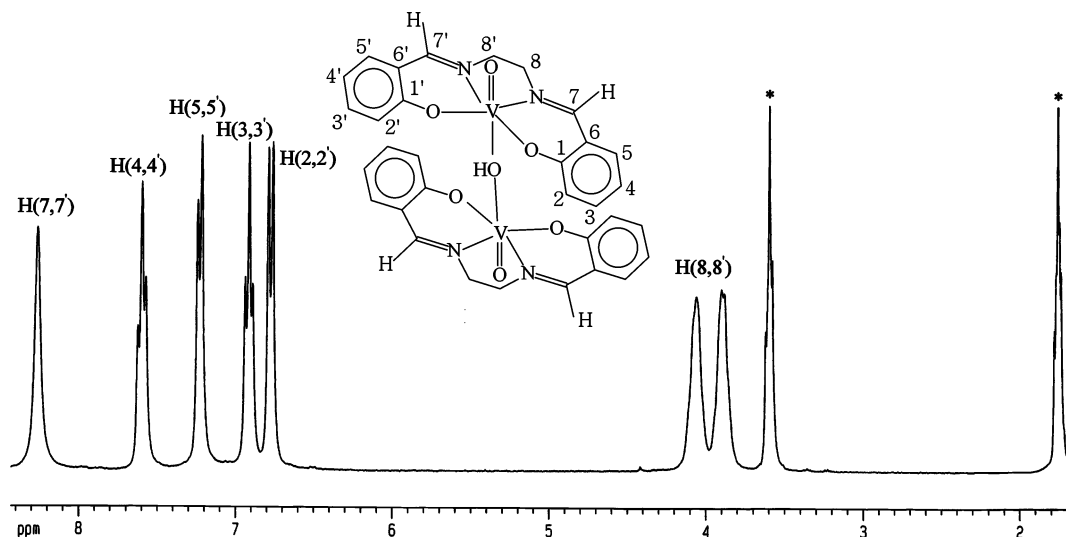


Figure 4. 300 MHz ^1H NMR spectrum of compound **1** in acetonitrile- d_3 at 293 K. The peaks marked with asterisk denote solvent impurities.

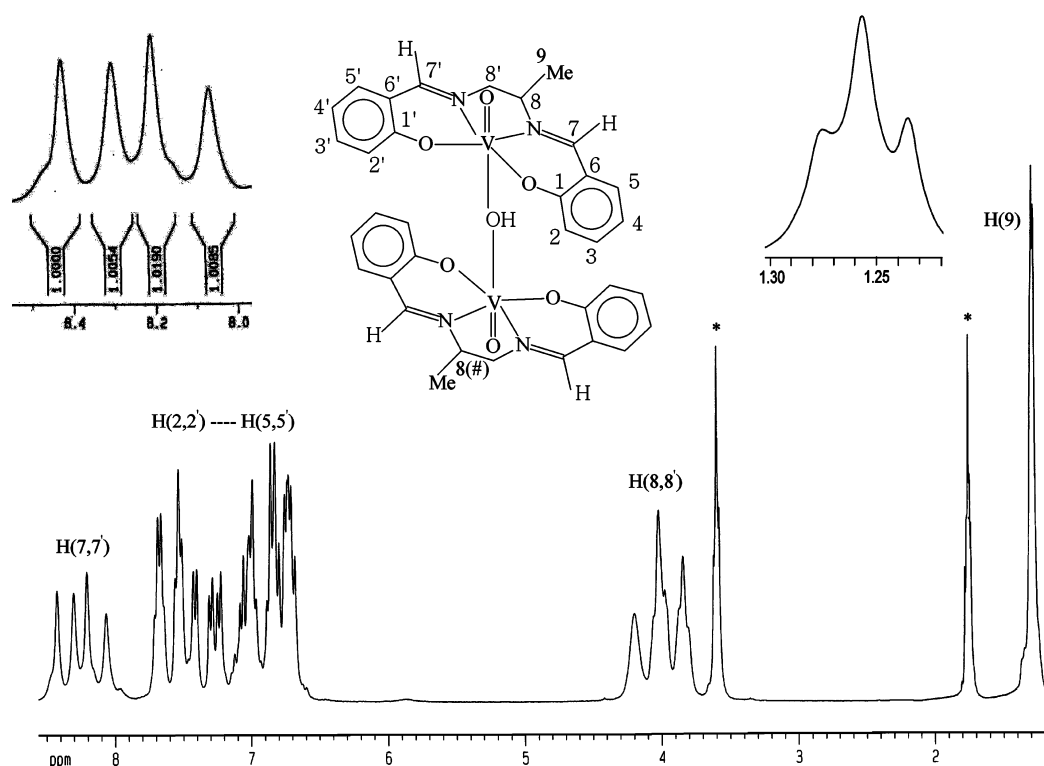


Figure 5. ^1H NMR spectrum of compound **2** in acetonitrile- d_3 at room temperature. The insets show azomethine and methyl signals in magnified forms. The peaks marked with an asterisk denote solvent impurities.

to the bridging hydroxo moiety in these compounds. The results, however, have conclusively established the retention of the dimeric structures in solution for **1–3**.

Electronic Spectroscopy. Electronic absorption spectra of the complexes **1–3** have been recorded in acetonitrile, and the relevant data are summarized in the Experimental Section. A representative spectrum of **3** is displayed in the Supporting Information Figure S4. All these complexes display two prominent absorptions, one in the visible region (575–640 nm) in the form of a medium intensity (ϵ , 2100–2400 $\text{mol}^{-1} \text{cm}^2$) band whose position appears to be sensitive to the substituent present in the phenyl ring. We interpret this band as arising from a ligand-to-metal charge-transfer (LMCT,

$\text{PhO}^- \rightarrow \text{V} (d\pi)$). The second one in the near-UV region (320–355 nm), appearing as a shoulder with much stronger intensity (ϵ , ca. 17 000 $\text{mol}^{-1} \text{cm}^2$), also has a charge-transfer ($\text{OH}^- \rightarrow \text{V}$) origin.^{7d,35} The remaining band maxima in the UV region are attributable to ligand internal transitions.

Electrochemistry. The electrochemical behavior of **1–3** has been examined by cyclic voltammetry (CV) in acetonitrile (0.1 M TBAP) using a platinum working electrode. A potential window of -2.0 to $+2.0$ V versus Ag/AgCl reference has been chosen in which the ligands are electrode inactive. The voltammetric features are roughly identical for

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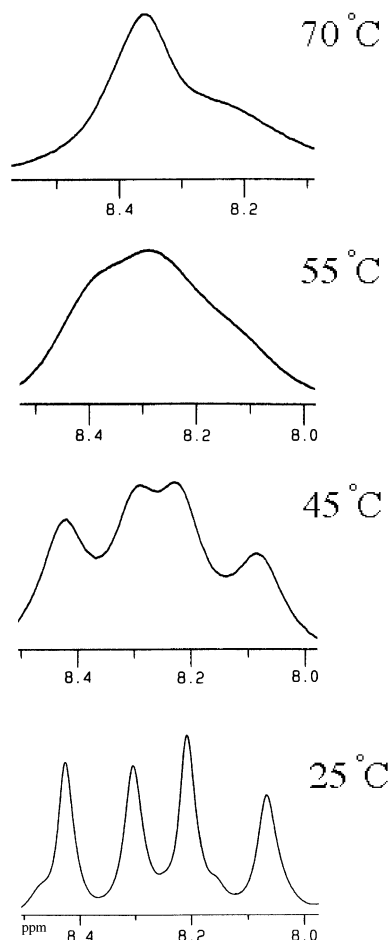


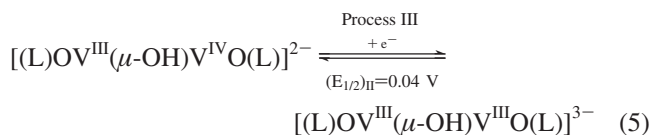
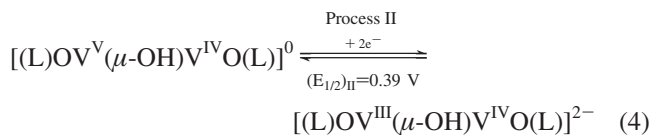
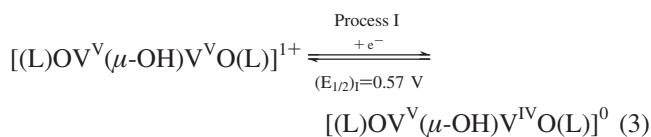
Figure 6. Variable temperature ^1H NMR spectra of **2** in acetonitrile- d_3 solution, showing a gradual coalescence of the signals due to azomethine protons with the rise in temperature.

these compounds as summarized in Table 5. Both CV and normal pulse voltammogram (NPV) of **1** in the potential range from -0.4 to $+0.8$ V are displayed in Figure 7 as a representative example. The voltammograms include three electrochemical responses at $(E_{1/2})_{\text{I}} = 0.57$ V (process I), $(E_{1/2})_{\text{II}} = 0.39$ V (process II), and $(E_{1/2})_{\text{III}} = 0.04$ V (process III). On the basis of a comparison with the ferrocenium/ferrocene couple (ΔE_p , 70 mV at 100 mVs^{-1}), processes I and III may be appropriately described as reversible,³⁶ both involving a single electron (ΔE_p , 60 and 74 mV at 100 mVs^{-1} for processes I and III, respectively).

All the three processes are cathodic as judged by the steady state voltammetry (using an ultramicro platinum electrode, $10 \mu\text{M}$ diameter). Electron stoichiometry determination for these processes by constant potential coulometry, unfortunately, proved unsuccessful because of the continuous coulomb accumulation due to unidentified electrode reaction(s) in the larger time-scale of the experiment. However, a comparison of the wave heights in the adjoining NPV (Figure 7) indicates that processes I and III have identical electron stoichiometry while process II involves twice as many numbers of electrons.

The electrochemical behavior of $[\text{VO}(\text{Salen})]$ is well documented.^{27,37} It undergoes a reversible one electron oxidation at 0.54 V attributable to $\text{V(IV)}/\text{V(V)}$ electron-transfer. Taking a cue from these studies, one can describe process I as arising from a $\text{V(V)}-\text{V(V)}/\text{V(V)}-\text{V(IV)}$ electron-transfer, generating a V(V/IV) mixed-oxidation product. Process II on the other hand appears to be a single-step two-electron process as indicated by both NPV and differential pulse voltammetric (DPV) experiments (shown in Figure 7, inset), comprising a $\text{V(V)}-\text{V(IV)}/\text{V(III)}-\text{V(IV)}$ redox couple. Finally, for process III, an isovalent divanadium(III) species is conjectured to be the product of the electrode reaction through a $\text{V(III)}-\text{V(IV)}/\text{V(III)}-\text{V(III)}$ electron-transfer.^{26c,38} Interestingly, process III fails to appear in the voltammogram of **3**. We believe that the electron donating OCH_3 groups in the ligand aromatic rings of **3** make the coordinated vanadium center richer in electron density, and that probably resists the incoming electron needed for this reduction process.

In summary, the electrochemical results (combined with NPV and DPV) thus indicate the possible involvements of four binuclear vanadium species with oxidation state combinations shown by eqs 3–5.



In the cathodic range, **1–3** also display an irreversible process at about -1.6 V (process IV). A similar irreversible electrode process is known to appear in the voltammogram of $[\text{VO}(\text{Salen})]$ ³⁷ and is tentatively explained as attributable to the elimination of a terminal oxygen from the vanadium center. Further discussion on this process is beyond the scope of this investigation.

Concluding Remarks

A series of divanadium(V) compounds (**1–3**) bridged by an unsupported hydroxo-group has been reported for the first time. The bridging group is situated *trans* to the terminal oxo-group. In consequence, the separations between the two participating vanadium centers $\text{V(1)} \cdots \text{V(1)}\#$ in these com-

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Table 5. Summary of Electrochemical Data^a

compound	process I		process II		process III		process IV
	$(E_{1/2})_I$, V	ΔE_p^c , mV	$(E_{1/2})_{II}$, V	ΔE_p^c , mV	$(E_{1/2})_{III}$, V	ΔE_p^c , mV	E_{pc} , V
1	0.57	60	0.39	65	0.04	74	-1.55
2	0.55	48	0.36	80	0.04	60	-1.60
3	0.53	41	0.34	71			-1.57

^a Solvent, acetonitrile; supporting electrolyte, TBAP (0.1 M); solute concentration, about 10^{-3} M; working electrode, platinum; temperature, 25 °C. All potentials are vs Ag/AgCl reference, estimated by cyclic voltammetry at a scan rate of 100 mV s⁻¹. ^b $E_{1/2} = 0.5(E_{pc} + E_{pa})$. ^c $\Delta E_p = E_{pc} - E_{pa}$.

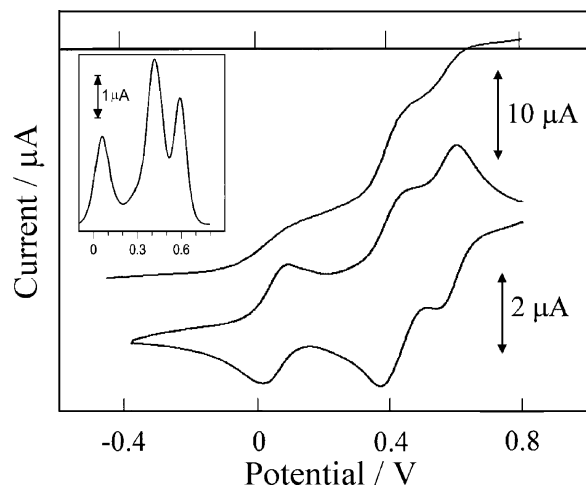


Figure 7. Cyclic and normal pulse voltammograms of **1** in acetonitrile solution; potentials vs Ag/AgCl, 0.1 M TBAP at a platinum electrode, scan rate 100 mVs⁻¹. The inset shows the differential pulse voltammogram establishing the single-step two-electron involvement in process II.

pounds are by far the largest (ca. 4.131 Å) compared with any other divanadium(V, IV, and III) compounds containing one or more hydroxo group(s) as bridging ligands.^{14–17} These

compounds also retain their identity in solution (in dry organic solvents) as confirmed by ¹H NMR spectroscopy. Electrochemically also, **1–3** are quite interesting, undergoing three (two for **3**) nearly reversible metal-centered electron transfers, all in the positive potential range (vs Ag/AgCl). One of these is a single-step two-electron transfer as indicated by normal and differential pulse voltammetries.

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Supporting Information Available: ¹⁹F NMR spectra of **1** and **2**, ORTEP diagram, ¹H NMR and electronic absorption spectrum of **3** (Figures S1–S4), selected bond distances and bond angles for the independent molecule **2B** (Table S1, PDF), and X-ray crystallographic files in CIF format for the compounds **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>. IC702286H

Targeted Synthesis of μ -Oxo Divanadium(V) Compounds with Asymmetry in Coordination Environments†Pabitra Baran Chatterjee,[‡] Nabanita Kundu,[‡] Subhojit Bhattacharya,[‡] Ki-Young Choi,[§] Akira Endo,[‡] and Muktimoy Chaudhury^{*,‡}*Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India, Department of Chemistry Education, Kongju National University, Kongju 314-701, South Korea, and Department of Chemistry, Faculty of Science and Technology, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan*

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Isovalent μ -oxo divanadium(V) compounds [$L^1VO(\mu-O)VO(salen)$] (**1**) and its bromo derivative [$L^2VO(\mu-O)VO(salen)]\cdot CH_3CN$ (**2**) (both H_2L^1 and H_2L^2 are tridentate dithiocarbazate-based ONS ligands) with ligands providing donor set and coordination number asymmetry in tandem have been synthesized for the first time; confirmations in favor of these unsymmetrical molecular structures have come from single-crystal X-ray diffraction analysis, as well as from NMR (both 1H and ^{51}V) spectroscopy.

To our knowledge, all the μ -oxo divanadium compounds containing a $V_2O_3^{n+}$ core ($n = 4, 3$, and 2) reported thus far have symmetrical structures involving identical ligand molecule(s) attached to both the metal centers.^{1–6} When the vanadium centers have octahedral geometry,^{1–3} the majority of these compounds^{2,3} have a linear V–O–V bridge with the terminal oxo- groups in mutually trans positions (anti-

linear structure).^{4b} On the other hand, when the vanadium centers have square pyramidal geometry,^{4–6} the bridging and terminal oxygen atoms have diverse range of arrangements, from anti-linear^{5k,5l} to syn-angular^{4,5a,b} through anti-angular^{5c–j} and twist-angular⁶ structures. Herein, we sought to explore further the electronic and molecular structures of μ -oxo divanadium(V) compounds with a heretofore unknown unsymmetrical combination involving an octahedral and a square pyramidal vanadium(V) center coupled together by a μ -oxo bridge. For this to happen, we have chosen [$VO(salen)$] as the precursor compound to generate the octahedral vanadium site. This compound in solution is known to get aerially oxidized to [$V^VO(salen)$]⁺ in the presence of added anions, viz. ClO_4^- , BF_4^- , etc.⁷ The vanadium centers in these oxidized compounds have octahedral geometry with the incoming anions being accommodated in to the vacant coordination site of the metal ion, trans to the terminal oxo-group. In order to generate the square pyramidal vanadium(V) center, we have chosen the tridentate biprotic ligands, *S*-methyl-3-(2-hydroxyphenyl)methylenedithiocarbazate (H_2L^1)

† Dedicated to Professor K. Nag on the occasion of his 65th birthday.

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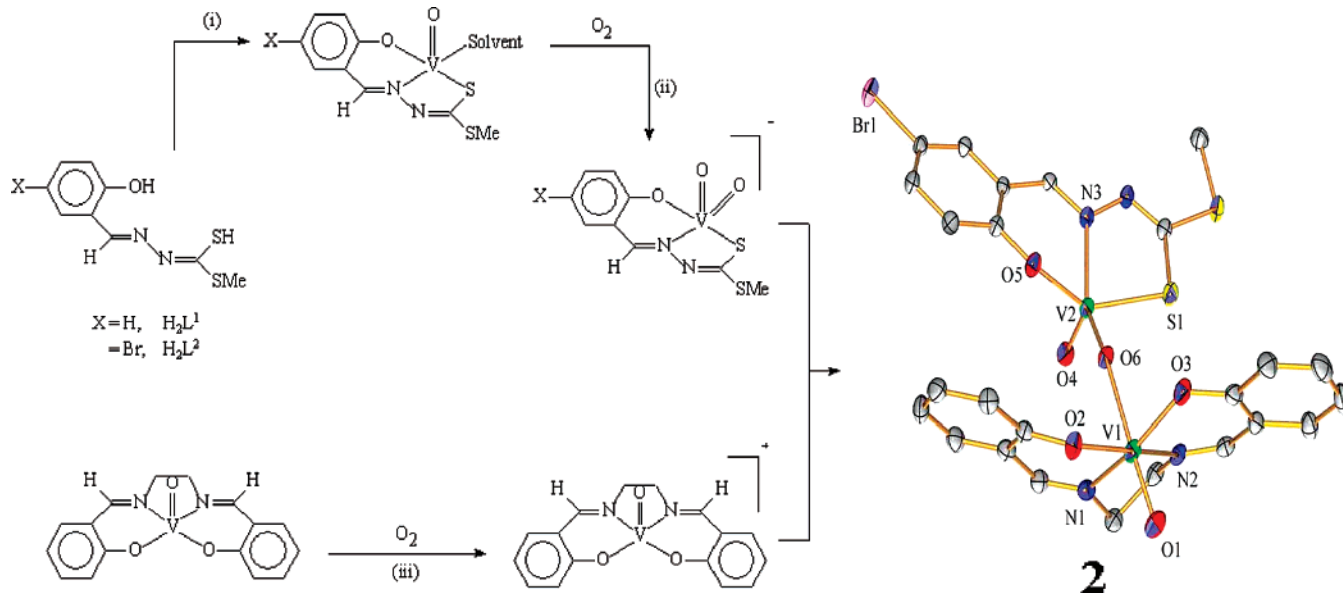
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Scheme 1. Synthetic Strategy for the Preparation of the Unsymmetrical Complexes and an ORTEP View of **2** (Acetonitrile Molecule and the Hydrogen Atoms have been Omitted for Clarity).^a



^a Conditions: (i) $\text{VO}(\text{acac})_2$, CH_3CN , reflux; (ii) cation-assisted aerial oxidation; (iii) anion-assisted aerial oxidation in CH_3CN . Selected interatomic distances (Å) and angles (deg) in **2**: $\text{V}(1)-\text{O}(1)$ 1.587(3), $\text{V}(1)-\text{O}(2)$ 1.816(3), $\text{V}(1)-\text{O}(3)$ 1.855(3), $\text{V}(1)-\text{N}(1)$ 2.081(3), $\text{V}(1)-\text{N}(2)$ 2.081(3), $\text{V}(1)-\text{O}(6)$ 2.140(3), $\text{V}(2)-\text{O}(4)$ 1.596(3), $\text{V}(2)-\text{O}(5)$ 1.881(3), $\text{V}(2)-\text{N}(3)$ 2.178(3), $\text{V}(2)-\text{S}(1)$ 2.3694(13), $\text{V}(2)-\text{O}(6)$ 1.669(3), $\text{V}(1)-\text{O}(6)-\text{V}(2)$ 157.79(16), $\text{O}(1)-\text{V}(1)-\text{O}(6)$ 173.25(13), $\text{O}(4)-\text{V}(2)-\text{O}(6)$ 108.11(18).

and its bromo derivative (H_2L^2). These ligands can generate square pyramidal cis-dioxo anionic species $[\text{LV}^{\text{VO}}\text{O}_2]^-$ when H_2L ($\text{L} = \text{L}^1$ and L^2) is refluxed with $[\text{VO}(\text{acac})_2]$ in acetonitrile in the presence of an added cation.⁸ In the synthetic strategy outlined in Scheme 1, stoichiometric amounts of $[\text{V}^{\text{IV}}\text{O}(\text{acac})_2]$, H_2L , and $[\text{V}^{\text{IV}}\text{O}(\text{salen})]$ (1:1:1 mol ratio) were refluxed in acetonitrile and subsequently exposed to atmospheric oxygen to get both $[\text{V}^{\text{VO}}(\text{salen})]^+$ and $[\text{LV}^{\text{VO}}\text{O}_2]^-$ species together, thus allowing the anionic species to be accommodated in to the vacant coordination site of $[\text{VO}(\text{salen})]^+$, leading to the desired products **1** and **2** as brown crystalline solids. The formation of $[\text{V}^{\text{VO}}(\text{salen})]^+$, we believe, is favored by the anion ($[\text{LV}^{\text{VO}}\text{O}_2]^-$)-assisted oxidation of $[\text{V}^{\text{IV}}\text{O}(\text{salen})]$,⁷ while that of $[\text{LV}^{\text{VO}}\text{O}_2]^-$ is facilitated by the cation ($[\text{V}^{\text{VO}}(\text{salen})]^+$)-assisted oxidation of the putative species $[\text{LV}^{\text{IV}}\text{O}(\text{solvent})]$.⁸ The infrared spectrum of **1** displays two strong bands at 953 and 917 cm^{-1} (964 and 911 cm^{-1} for **2**) due to terminal $\text{V}=\text{O}$ stretchings, corresponding to the individual vanadium centers.

An unambiguous description of the coordination geometry around the vanadium centers in these compounds has been obtained through single-crystal X-ray diffraction analysis.⁹ An ORTEP view of **2** is displayed in Scheme 1 as a representative example. The two halves of the molecule, bridged by an oxygen atom, O6, have different geometry. The coordination environment around V1 is octahedral, while that about V2 is square pyramidal. The angles at the vanadium centers made by the bridging and terminal oxo atoms, viz. $\text{O}1-\text{V}1-\text{O}6$ 173.25(13)° (the corresponding angle in **1** is 171.89(8)°) and $\text{O}4-\text{V}2-\text{O}6$ 108.11(18)° (108.54(9)°) are as expected for a nearly ideal octahedral and square pyramidal geometry, respectively. The $\text{V}1-\text{O}6-\text{V}2$ bridge angle of 157.79(16)° (166.20(9)°) is in between the values expected for symmetric divanadium compounds with octahedral (ca. 180°)² and square pyramidal (ca. 145°)^{4,5a,b} metal centers. The V_2O_3 core in these compounds has a rare twist-angular structure,⁶ somewhat intermediate between the regular anti-linear and syn-angular modes. Of particular interest here is the trans location of the bridging oxygen atom O6 relative to the terminal oxo-atom O1 attached to the octahedral V1. Such a trans arrangement is unique in divanadium compounds containing $\text{V}_2\text{O}_3^{n+}$ core.¹⁻⁶ Consequently, the $\text{V}1-\text{O}6$ distance 2.140(3) Å (2.1416(16) Å) is significantly enlarged due to trans-labilizing influence of the terminal oxo-atom O1, compared to the other bridging distance $\text{V}2-\text{O}6$ 1.669(3) Å (1.6733(16) Å). In effect, the enlarged $\text{V}1\cdots\text{V}2$ separation in **2**, 3.739 Å (3.792 Å), is by far the largest among its peers (divanadium compounds containing the V_2O_3 core) reported thus far in the literature.¹⁻⁶

To understand more about the electronic and molecular structures of these compounds in solution, both ^1H and ^{51}V NMR spectra have been measured in $\text{DMSO}-d_6$ solution at

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(9) Crystal data for **1**: $\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_6\text{S}_2\text{V}_2$, $M = 640.47$, triclinic, space group $P\bar{1}$, $a = 9.9337(8)$ Å, $b = 10.6502(9)$ Å, $c = 13.4951(11)$ Å, $\alpha = 107.3840(10)^\circ$, $\beta = 101.890(2)^\circ$, $\gamma = 97.5190(10)^\circ$, $V = 1304.67(19)$ Å³, $Z = 2$, $D_c = 1.630$ g cm⁻³, $F(000) = 652$, $\mu(\text{Mo K}\alpha) = 0.926$ mm⁻¹, $T = 293(2)$ K, 6457 unique reflections [$R(\text{int}) = 0.0290$], R (on F) = 0.0607, R_w (on F^2) = 0.0983 (based on all data). Crystal data for **2**· CH_3CN : $\text{C}_{27}\text{H}_{24}\text{BrN}_5\text{O}_6\text{S}_2\text{V}_2$, $M = 760.42$, triclinic, space group $P\bar{1}$, $a = 11.1599(6)$ Å, $b = 11.5448(7)$ Å, $c = 14.1841(8)$ Å, $\alpha = 81.3900(10)^\circ$, $\beta = 67.0010(10)^\circ$, $\gamma = 63.1810(10)^\circ$, $V = 1500.47(15)$ Å³, $Z = 2$, $D_c = 1.683$ g cm⁻³, $F(000) = 764$, $\mu(\text{Mo K}\alpha) = 2.144$ mm⁻¹, $T = 293(2)$ K, 7426 unique reflections [$R(\text{int}) = 0.05$], R (on F) = 0.1104, R_w (on F^2) = 0.1315 (based on all data).

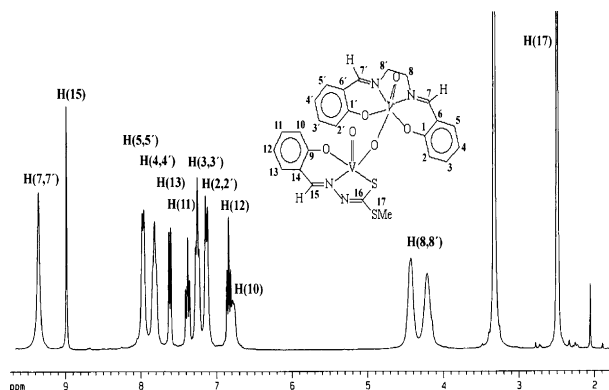


Figure 1. ^1H NMR spectrum of compound **1** in $\text{DMSO}-d_6$ solution at 293 K.

room temperature. The ^1H NMR spectrum of **1** (data summarized in the Supporting Information) is shown in Figure 1, which displays a pair of singlets at 9.35 and 8.98 ppm (2:1 intensity ratio) corresponding to the presence of two different kinds of azomethine moiety in this molecule. Also deserving of mention is the triplet at 7.38 ppm due to the H11 proton. Substitution of bromine at C12 in compound **2** makes the same proton (H11) to appear as a pair of doublets (Figure S1) centered at ca. 7.48 ppm ($J = 2.5$ Hz) due to ortho–meta couplings. All these and the remaining signals along with their corresponding splitting patterns are in conformity with the presence of unsymmetrical coordination environments in these molecules as exist solution.

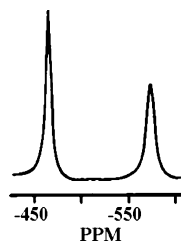


Figure 2. ^{51}V NMR spectrum of compound **1** in $\text{DMSO}-d_6$ solution at room temperature.

In the ^{51}V NMR spectrum, two signals have been observed as displayed in Figure 2 for compound **1**. One of these appearing at -467 ppm (relative to VOCl_3 as standard) is due to the vanadium center included in the V^{VOL} part,^{4b} while the other at -575 ppm is arising from the $\text{V}^{\text{VO}}(\text{salen})$ moiety.¹⁰ Corresponding signals in the spectrum of **2** appear at -466 and -575 ppm, respectively, and are in compliance with the unsymmetrical vanadium coordination environ-

ments. The ESI mass spectrum (Figure S2) of compound **1** in CH_3CN shows the molecular ion peak at $m/z = 641$ [$\text{M} + \text{H}]^+$ (100% relative abundance) with the expected isotope distribution.

The cyclic voltammogram (Figure S3) of **2** in DMSO shows a cathodic reversible process at $E_{1/2} = 0.45$ V vs Ag/AgCl reference (25 °C, Pt working electrode, 100 mV s^{-1} scan rate), as confirmed by steady-state voltammetry. Results of constant potential coulometry ($E_w = 0.2$ V) indicate single-electron stoichiometry for this process, thus confirming the generation of a mixed-oxidation divanadium(IV/V) product [**2** $^-$] during the course of electrolysis. The EPR spectrum at room temperature (Figure S4) of the electrolyzed solution displayed an eight-line (^{51}V , $I = 7/2$) hyperfine pattern ($\langle g \rangle = 1.990$, $\langle A \rangle = 88 \times 10^{-4} \text{ cm}^{-1}$) indicating a trapped-valence nature of the reduced product in the EPR time scale.^{1c} Electronic spectrum of the catholyte solution failed to show any characteristic band in the NIR region, expected for a possible intervalence charge-transfer, lending support to the results of EPR spectroscopy in confirming the trapped-valence nature of the reduced mixed-oxidation species. The valence-trapped situation probably is arising here from the bent V–O–V bridge, preventing the symmetry-constrained vanadium d_{xy} orbitals, containing the odd unpaired electron, to overlap effectively via the $p\pi$ orbital of the bridging oxygen atom.¹¹

In summary, a novel synthetic route has been developed for the synthesis of μ -oxo divanadium(V) compounds containing a hitherto unknown V_2O_3 core involving vanadium centers with separate donor atoms set. The identities of the compounds have been conclusively established both in solution, as well as in the solid state. The V...V separations in these compounds are by far the largest, 3.792 Å (3.739 Å for **2**), among their peers due to the trans-labilizing influence of a terminal oxo-group. The V_2O_3 core in these compounds has a twist-angular structure⁶ somewhat intermediate between the anti-linear and syn-angular modes, often encountered in symmetrical divanadium compounds.^{4b}

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Supporting Information Available: Full synthetic details, ^1H NMR data, and CIF files for **1** and **2**, ESI mass spectrum of **1**, cyclic voltammogram followed by EPR spectrum of the catholyte solution of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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