Inorganic Chemistry

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 [LVO(*μ*-O)ReO$_3$]·H$_2$O [H$_2$L = *N*, *N'*-ethylene bis(salicylideneimine) (H$_2$salen) and its methoxy derivative] (**1**, **2**) are reported. The compounds have been prepared by a single-pot synthesis in which the precursor [V^{IV}OL] complexes are allowed to be oxidized aerially in the presence of added perrhenate. The oxidized [V^{V}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 [H$_2$en][(TBC)VO(*μ*-TBC)$_2$OV(TBC)]·5H$_2$O (**3**) when treated with tetrabromocatechol. Single crystal X-ray diffraction analysis and ^{1}H 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 [VO(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 (⟨*g*⟩ = 1.967; ⟨*A*⟩ = 87 × 10^{-4} cm^{-1}), characteristic of an unpaired electron being coupled to a vanadium nuclear spin (^{51}V, *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}Re) = 20.7 × 10^{-4} 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 [186]Re and [188]Re 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 ($RRe^{VII}O_3$) 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) [Mn$_2$-(saltmen)$_2$(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 [(Cu(pc))$_3$-(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 ^{1}H 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 H$_2$salen[17] and its methoxy derivative H$_2$metsalen, the precursor complexes [VO(salen)] and [VO(metsalen)]·H$_2$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. [(salen)VO(μ-O)ReO$_3$]·H$_2$O (1). To a stirred tetrahydrofuran solution (30 mL) of [VO(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$_4$O$_{10}$. Yield: 0.10 g (32%). Anal. Calcd for C$_{16}$H$_{16}$N$_2$O$_8$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$_3$CN) [λ_{max}, nm (ε, mol^{-1} cm^2)]: 596 (825); 400 (sh); 362 (2550); 288 (10400); 267 (14500); 228 (37800).

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

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

parameters	**2**	**3**
composition	$C_{18}H_{20}N_2O_{10}ReV$	$C_{26}H_{20}Br_{16}N_2O_{15}V_2$
formula wt.	661.50	1982.90
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.2522(7)	9.9723(13)
b, Å	9.1776(8)	11.1335(15)
c, 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)
V, 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
Z	2	1
μ mm^{-1}	9.905	16.629
$2\theta_{max}$ [deg]	66.28	62.20
reflections collected/unique	7434/4163	15416/6056
observed reflections ($I \geq 2\ \sigma(I)$)	3973	4285
R_{int}	0.0282	0.0438
data/restraints/parameters	4163/27/291	6056/0/276
$R1(F_0)$, $wR2(F_0)$ ($I \geq 2\ \sigma(I)$)	0.0431, 0.1099	0.0408, 0.1090
$R1(F_0^2)$, $wR2(F_0^2)$ (all data)	0.0446, 0.1112	0.0641, 0.1202
$F(000)$/GOF on F^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 (CH$_3$CN) [λ_{max}, nm (ε, mol^{-1} cm^2)]: 660 (1540); 416 (2650); 320 (10700); 267 (16700); 230 (35800).

[H$_2$en][(TBC)VO(μ-TBC)$_2$OV(TBC)]·5H$_2$O (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 × 10 mL) and finally dried in vacuo over P$_4$O$_{10}$. Yield: 0.04 g (22%). Anal. Calcd for C$_{26}$H$_{20}$Br$_{16}$N$_2$O$_{15}$V$_2$: 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 ^{1}H NMR (300 MHz) spectra were recorded on a Bruker model Avance DPX 300 spectrometer using SiMe$_4$ (δ_0) as internal reference.

Cyclic voltammetric measurements in CH$_2$Cl$_2$, 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 × 0.06 × 0.005 mm^3 (plate, green, **2**) and 0.15 × 0.08 × 0.03 mm^3 (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 methods[23] and the least-squares refinement [anisotropic displacement parameters, hydrogen atoms in the riding model approximation, and a weighing scheme of the form $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ for $P = (F_0^2 + 2F_c^2)/3]$ was on F^2.[23] Bruker SHELXTL[24] 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 ethylenedi-amine 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^{V}O(s-alen)]$^+$ in the presence of added anion, for example, ClO$_4^-$, BF$_4^-$, and PF$_6^-$, 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 ReO$_4^-$ as anion which has a tetrahedral geometry similar to ClO$_4^-$ and BF$_4^-$ but is

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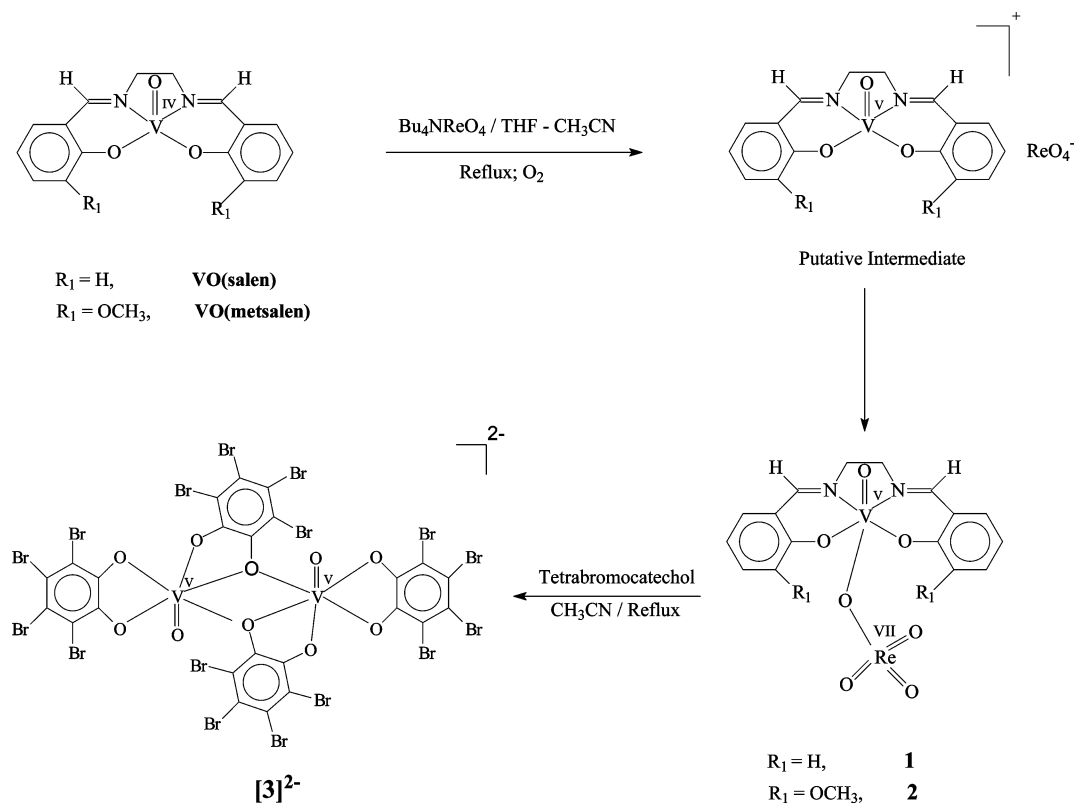
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Scheme 1. Synthesis of the Complexes **1**−**3**

$R_1 = H,$ **VO(salen)**
$R_1 = OCH_3,$ **VO(metsalen)**

Putative Intermediate

$[3]^{2-}$

Tetrabromocatechol
CH$_3$CN / Reflux

$R_1 = H,$ **1**
$R_1 = OCH_3,$ **2**

a better coordinating anion.[5−7,10,28] Thus [V^{IV}O(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$_4$NReO$_4$ 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 Ω^{-1} cm^2 mol^{-1} within about an hour, corresponding to a 1:1 electrolyte.[29]

Rhenium oxides such as Re$_2$O$_7$ 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 epoxi- dation catalysts with H$_2$O$_2$ 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$_2$TBC[17]

in dry acetonitrile. The only product isolated is a divanadi- um(V) compound [H$_2$en][(TBC)VO(μ-TBC)$_2$-VO(TBC)]· 5H$_2$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 ν(C=N) and ν(C−O/phenolate) stretching modes of the coordinated Schiff base moieties, respec- tively.[16,30] In addition, a sharp strong band is observed due to the terminal V=O$_t$ stretching at 987 cm^{-1}. The appearance of prominent bands in the 910−917 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 ν(O−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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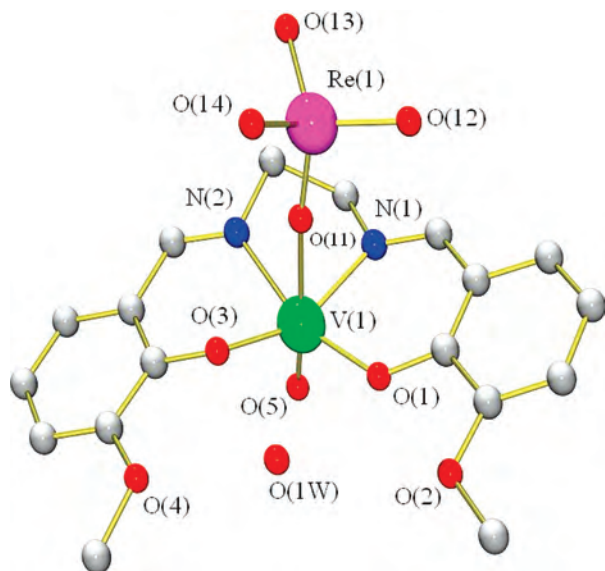
Figure 1. Molecular structure and crystallographic numbering scheme for the neutral complex [(metsalen)VO(μ-O)ReO$_3$]·H$_2$O **2**. The hydrogen atoms have been omitted for clarity.

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
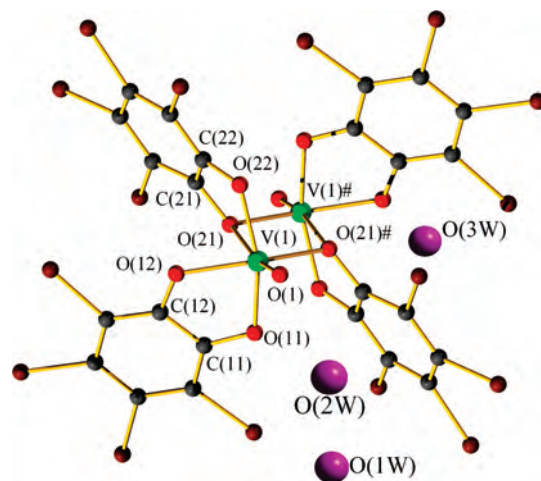

Figure 2. Perspective view of the of the centrosymmetric binuclear complex anion in [H$_2$en][(TBC)VO-(μ-TBC)$_2$-OV(TBC)]·5H$_2$O **3** showing the crystallographic numbering scheme. The cation [H$_2$en]$^{2+}$ has been omitted for clarity. The atoms with "#" symbol are symmetry related.

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 N$_2$O$_2$ donor set of the tetradentate ligand, together with the O(5) and O(11) atoms, contributed by the terminal oxido and ReO$_4^-$ 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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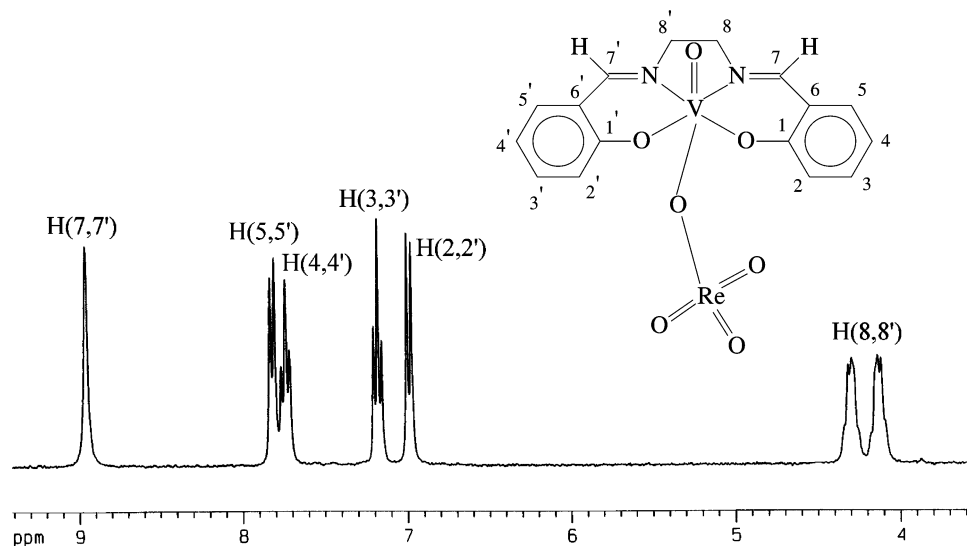
Figure 3. ^{1}H NMR spectrum of [(salen)VO(μ-O)ReO$_3$]·H$_2$O **1** in acetonitrile-d_3 at 263 K.
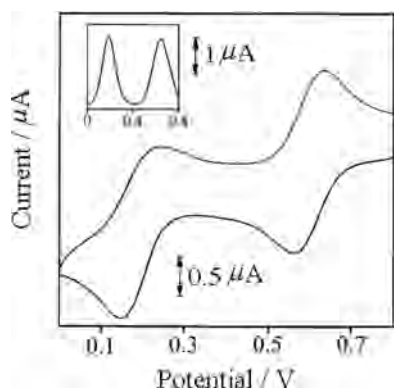

Figure 4. Cyclic voltammogram of **1** in dichloromethane solution; potentials vs Ag/AgCl, 0.1 M TBAP at a platinum electrode, scan rate 100 mV s^{-1}. The inset shows the differential pulse voltammogram establishing the involvement of identical number of electron(s) for both processes I and II.
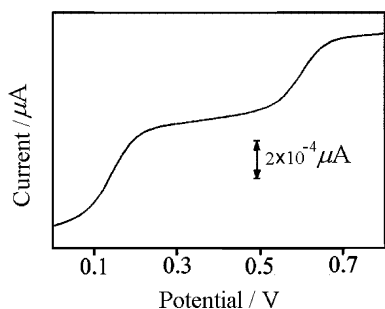

Figure 5. Normal pulse voltammogram of **1** in dichloromethane (0.1 M TBAP), confirming the involvement of identical numbers of electrons for both processes I and II (at a platinum electrode; scan rate 100 mV s^{-1}).

(155.77(19)°) are short of linearity, forcing the vanadium center to move out of the least-squares meridian plane by 0.2831 Å 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) Å, respectively, comparable with those previously reported in compounds containing the [VO(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$_2$O$_2$ plane which is decreased approximately from 0.5 to 0.25 Å.[33a]

The Re–O distances (1.703(5)–1.736(4) Å) and the O–Re–O bond angles (108.5(2)–110.1(2)°) indicate almost ideal tetrahedral geometry around the metal center.[5,6,10a] The V⋯Re separation is 3.9647(9) Å. The V(1)–O(11)–Re(1) angle is 170.2(3)° and the V(1)–O(11) bond length (2.243(4) Å) 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) Å) 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 [metsalen]$^{2-}$, so that O(2)⋯O(1W) and O(4)⋯O(1W) distances are 3.014(7) and 2.996(7) Å, 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 countercation. 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 [(TBC)VO(μ-TBC)$_2$-VO(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)° and O(12)–V(1)–O(21)# 152.92(15)° 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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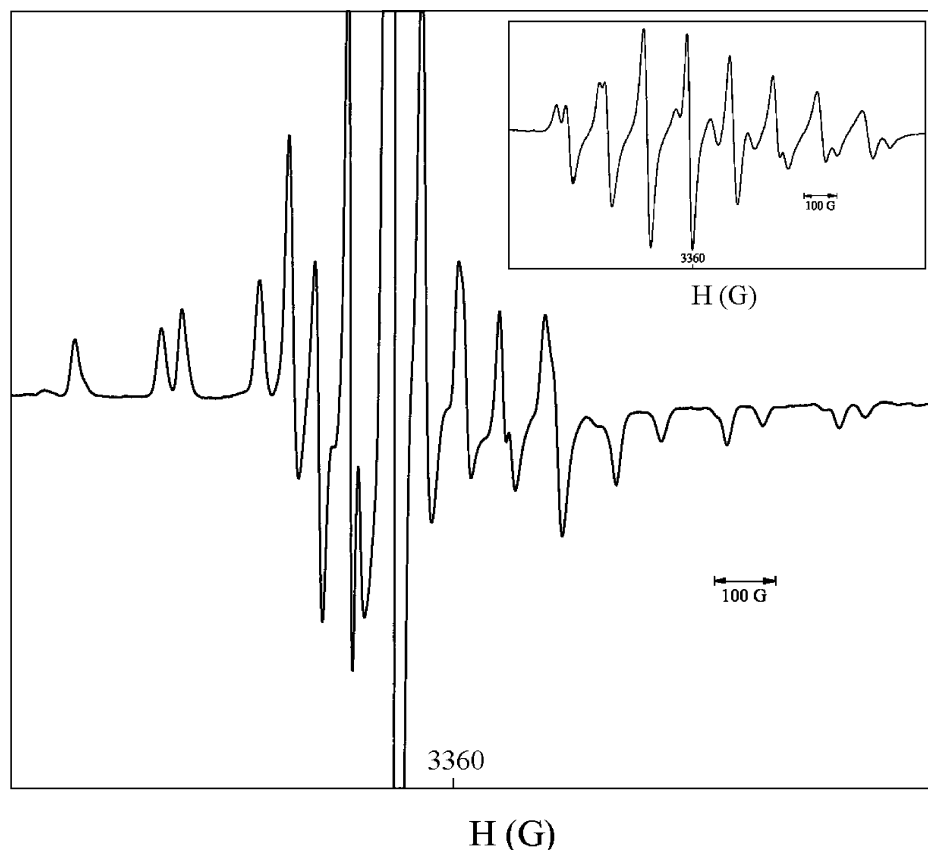
Figure 6. EPR spectrum at 77 K of the catholyte solution (in dichloromethane/toluene, 1:10 v/v) generated after coulometric reduction of **1** (E_w set at 0.4 V vs Ag/AgCl). The inset shows an eight-line isotropic pattern of the same solution at room temperature.

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 catecholate 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 ($H_2en)^{2+}$ 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 OCH$_3$ protons in **2**. Of particular interest here is the position of the azomethyne protons. Because of the coordination of the ReO$_4^-$ 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 [L^{1}OV(μ-O)VO(salen)] complexes in which [VO$_2$L^1]$^-$ (H$_2$L^1 = tridentate dithiocarbazate- 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.
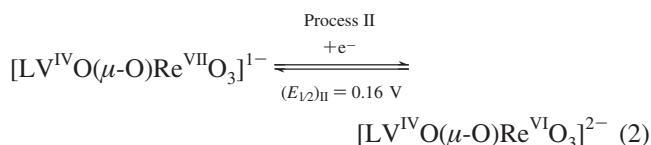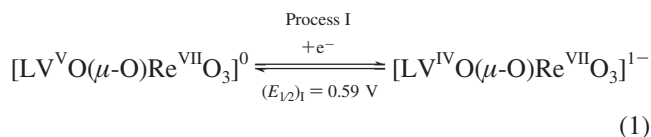
Electrochemistry. The redox properties of **1** and **2** have been examined by cyclic voltammetry (CV) at a platinum working electrode under an envelope of purified dinitrogen in dichloromethane solution (0.1 M TBAP) at 25 °C in the potential range of −2.0 to +1.0 V versus Ag/AgCl reference. The ligands 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/ferrocine 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.[38e] 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^{V}O(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 ReO$_4^-$ 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 CH$_2$Cl$_2$ 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.

Process I

$$[LV^VO(\mu\text{-}O)Re^{VII}O_3]^0 \underset{(E_{1/2})_I = 0.59 \text{ V}}{\overset{+e^-}{\rightleftarrows}} [LV^{IV}O(\mu\text{-}O)Re^{VII}O_3]^{1-}$$

(1)

Process II

$$[LV^{IV}O(\mu\text{-}O)Re^{VII}O_3]^{1-} \underset{(E_{1/2})_{II} = 0.16 \text{ V}}{\overset{+e^-}{\rightleftarrows}}$$

$$[LV^{IV}O(\mu\text{-}O)Re^{VI}O_3]^{2-} \quad (2)$$

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}O$_3$]$^{1-}$ in dichloromethane/toluene solution (1:10 v/v) at room temperature shows (Figure 6, inset) an eight-line isotropic pattern ($\langle g \rangle = 1.977$; $\langle A \rangle = 87 \times 10^{-4}$ cm^{-1}) characteristic of an unpaired electron being coupled to the vanadium nuclear spin (^{51}V, $I = 7/2$). 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 (^{185}Re, ^{187}Re, $I = 5/2$).[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 ^{185}Re and ^{187}Re superhyperfine coupling. The corresponding spin-Hamiltonian parameters are $g_{\parallel} = 1.948$, $A_{\parallel} = 153 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 1.988$, and $A_{\perp} = 53 \times 10^{-4}$ 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 $^{185,\ 187}$Re superhyperfine coupling (A (^{185,187}Re) $= 20.7 \times 10^{-4}$ cm^{-1}). When allowed to react with H$_2$TBC, **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: ^{1}H NMR spectrum of **2** (Figure S1), cyclic voltammograms of [V^{V}O(salen)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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