Implications for the Spectroscopic Assignment of Vanadium Biomolecules: Structural and Spectroscopic Characterization of Monooxovanadium(V) Complexes Containing Catecholate and Hydroximate Based Noninnocent Ligands

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Abstract: Forty-one compounds of the general formula $\text{VO}^\text{II}L'$, where L is a tri dentate ligand ($\text{HSALIMH} = [4-(2-$

[Salicylidenemino)ethyl]imidazole; $\text{H}_{2}$SHED = $N$-(salicylidenemino)-$N'$-(2-hydroxyethyl)ethylenediamine; $\text{HENSAL} = $N$-(salicylidenemino)ethylenediamine and L' is a bidentate, noninnocent ligand (e.g., catechol (H$_2$CAT), pyrogallol (H$_2$PYR), or salicylhydroxamic acid (H$_2$SAL))) have been prepared and spectroscopically characterized. Three of these novel complexes have been structurally characterized by X-ray crystallography ($\text{VO(HSHED)}$($\text{CAT})$, $\text{I}$, $\text{VO(SALIMH)}$($\text{CAT}$), $\text{3}$, $\text{VO(HSHED)}$($\text{SHI)$, $35}$) which allows for a direct comparison of the coordination environments of $\text{(VO)2}$ and $\text{(VO)3}$ with nearly identical ligand sets. The complexes $\text{VO(SALIMH)L'}$ provide a direct test for a model for the enzyme vanadium bromoperoxidase that has coordinated imidazoles, a single, terminal oxo ligand and oxygen donors that may be part of a noninnocent ligand. Furthermore, one can directly ascertain the effects of substituting primary or secondary amines for imidazole in an isostructural environment by comparing the properties of $\text{VO(HSHED)L'}$ and $\text{VO(SALIMH)L'}$. Previously reported $\text{VO(O)}_{2}$N$_2$ complexes have shown chemical shifts in a narrow range between 300 and 600 ppm upfield of VOCI$_3$. In contrast, these $\text{VO}^\text{II}L'$ complexes cover nearly 1200 ppm and can have resonances as much as 600 ppm downfield of VOCI$_3$. This unprecedented shift range and location is a direct consequence of the coordinated noninnocent ligands. The observed chemical shifts linearly correlate with the inverse energies of the ligand-to-metal charge-transfer bands in the visible and near infrared spectrum, and, therefore, a modification of Ramsey theory has been applied to extract the absolute shielding of these compounds. By extension, the absolute shielding of vanadium in the bromoperoxidase and vanadium transferrin can be inferred. This shielding scale indicates that for vanadium bromoperoxidase the temperature independent shielding factor $\sigma$ is very small relative to most V(V) complexes implying that noninnocent ligands which have a large $\sigma$ are almost certainly not involved in the coordination sphere of the metal in this enzyme. Crystal data: 1, monoclinic, $P_2_1/n$, $a = 13.660$ (9); $b = 6.483$ (4); $c = 19.18$ (1); $\beta = 96.69$ (6); $V = 1681$ (2) $\text{Å}^3$; $Z = 4$. For 3527 data collected between $5 \leq 2\theta \leq 50^\circ$ and 2569 data $> 0.60\sigma(F)$ the structure refined to $R = 0.063$ $(R_1 = 0.059)$; 3, triclinic, $P_1$, $a = 6.773$ (1); $b = 10.717$ (2); $c = 12.150$ (4); $\alpha = 98.40$ (2); $\beta = 92.13$ (2); $\gamma = 94.05$ (2); $V = 862.8$ (4) $\text{Å}^3$; $Z = 2$. For 3427 data collected between $5 \leq 2\theta \leq 50^\circ$ and 2860 data $> 0.60\sigma(F)$ the structure refined to $R = 0.042$ $(R_1 = 0.057$; 35, monoclinic, $P_2_1/n$, $a = 10.569$ (3); $b = 11.698$ (4); $c = 15.498$ (4); $\beta = 98.85$ (2); $V = 1882.6$ (8) $\text{Å}^3$; $Z = 4$. For 3840 data collected between $5 \leq 2\theta \leq 50^\circ$ and 2764 data $> 0.60\sigma(F)$ the structure refined to $R = 0.068$ $(R_1 = 0.058$).  

Introduction

Despite the fact that mammalian vanadium concentrations are at the nano- to picomolar level, several lower organisms have a requirement for this element which is considerably more pronounced.1,2 Ascidians (sea squirts) accumulate vanadium at levels up to 10-fold over their marine environment,3 and the mushroom $\text{Amanita muscaria}$ accumulates vanadium to produce the natural product $\text{amavadin.4}$ Two enzymes have recently been isolated with a unique requirement for vanadium: (1) an alternative nitrogenase from several species of $\text{Azotobacter5}$ and (2) a haloperoxidase from many marine algae.6 The ligands pyrogallol (hydroxy catechol) and $N$-hydroxylamine-disopropionic acid are present in the tunicates and $\text{A. muscaria}$, respectively, and may be coordinated to the metal center in the native systems. Although the composition of the metal coordination sphere in the vanadium bromoperoxidases is unknown at present, the analogous $\text{V}^{3+}$ NMR chemical shift indicates a novel coordination environment. Since vanadium bromoperoxidase is a rare example of a non-heme haloperoxidase, the peroxidase mechanism, which is inherently dependent on the electronic structure of the active site, is of considerable interest.

To date, no X-ray crystal structures have been presented for vanadium complexes isolated from natural sources. Vanadium bromoperoxidases have been studied by X-ray absorption,7 electron paramagnetic resonance,8 electronic9 and $\text{V}^{3+}$ NMR spectroscopies.10 These have been used to probe the structure of the metal site in these metallobiomolecules. Further, both EPR for vanadium($IV$) and NMR for vanadium($V$) have been utilized to study metal binding sites in vanadium substituted proteins such as bovine serum albumin and transferrin.10,11 These studies have been especially useful in differentiating multiple binding sites in proteins such as the N and C terminal iron binding sites in transferrin. Specific assignment of the ligands which are coordinated to the metal center is a more difficult task. For this, one must understand


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how each ligand modifies the magnetic field at the observed nucleus and how these modifications affect the experimentally observable parameters such as chemical shift and g value. Accumulation of data for a large number of compounds has led to the development of empirical relationships between spectroscopic observables and the local metal environment. Chasteen has shown a correlation between ligand (O or N donor) type and number and the g and A values for vanadium(IV) complexes.10 Rehder has proposed a relationship between the vanadium-51 NMR chemical shift and the sum of the ligand electronegativities for a large, yet incomplete, set of coordination complexes.12

Empirical and semiquantitative relationships between the NMR chemical shift and electronic properties of the metal complexes, such as the energy of electronic transitions, have been advanced for most NMR observable nuclei.11 These correlations are based on the theoretical treatment of the chemical shift presented by Ramsey in the early 1950s for molecules without intrinsic spin or orbital angular momentum.14 According to this treatment, the total chemical shielding, σ, is a combination of diamagnetic and temperature independent paramagnetic contributions as shown in eq 1. Since σd is essentially constant for each nuclide, the

\[ \sigma = \sigma_d + \sigma_p \]  

chemical shift observed by the NMR technique is dependent on changes in the paramagnetic shielding term, \( \sigma_p \), which are associated with changes in the electronic structure of the different molecules being examined. Based on this electronic dependence, one might expect complexes of common amino acid donor ligands such as imidazole, phenolate, or alkoxide to have significantly different chemical shifts compared to the more novel donors such as catechol derivatives, found in ascidians, or hydroxylamine.

Table I. Summary of Crystallographic Data for Compounds 1, 3, and 35

<table>
<thead>
<tr>
<th>compound</th>
<th>1</th>
<th>3</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>mw</td>
<td>382.29</td>
<td>389.29</td>
<td>425.31</td>
</tr>
<tr>
<td>space</td>
<td>( P1 )</td>
<td>( P2_1/n )</td>
<td>( P2_1/n )</td>
</tr>
<tr>
<td>( a ) (Å)</td>
<td>6.773 (1)</td>
<td>13.660 (9)</td>
<td>10.569 (3)</td>
</tr>
<tr>
<td>( b ) (Å)</td>
<td>10.717 (2)</td>
<td>6.483 (4)</td>
<td>11.698 (4)</td>
</tr>
<tr>
<td>( c ) (Å)</td>
<td>12.150 (4)</td>
<td>19.18 (1)</td>
<td>15.498 (4)</td>
</tr>
<tr>
<td>( \sigma ) (deg)</td>
<td>98.40 (2)</td>
<td>96.69 (6)</td>
<td>98.85 (2)</td>
</tr>
<tr>
<td>( \beta ) (deg)</td>
<td>92.13 (2)</td>
<td>96.69 (6)</td>
<td>98.85 (2)</td>
</tr>
<tr>
<td>( \gamma ) (deg)</td>
<td>94.05 (2)</td>
<td>96.69 (6)</td>
<td>98.85 (2)</td>
</tr>
<tr>
<td>( V ) (Å³)</td>
<td>862.8 (4)</td>
<td>1681 (2)</td>
<td>1882.6 (8)</td>
</tr>
<tr>
<td>( Z )</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>( \mu ) (cm⁻¹)</td>
<td>5.84</td>
<td>5.98</td>
<td>5.44</td>
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<tr>
<td>( \rho_{m} ) (g/cm³)</td>
<td>1.471</td>
<td>1.537</td>
<td>1.500</td>
</tr>
<tr>
<td>( \rho_{o} ) (g/cm³)</td>
<td>1.46 (1)</td>
<td>1.50 (2)</td>
<td>1.49 (1)</td>
</tr>
<tr>
<td>crystal size (mm)</td>
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<td>0.20 × 0.24 × 0.26</td>
<td>0.32 × 0.16 × 0.04</td>
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<td>data range (2θ, deg)</td>
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<td>5–50</td>
<td>5–50</td>
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<tr>
<td>no. of data</td>
<td>3427</td>
<td>3527</td>
<td>3840</td>
</tr>
<tr>
<td>data points</td>
<td>2860</td>
<td>2569</td>
<td>2764</td>
</tr>
<tr>
<td>( F \geq 0.6 \sigma(F) )</td>
<td>0.4922</td>
<td>0.0630</td>
<td>0.0680</td>
</tr>
<tr>
<td>( R_l )</td>
<td>0.0568</td>
<td>0.0586</td>
<td>0.0579</td>
</tr>
<tr>
<td>res density (g/cm³)</td>
<td>0.39/0.30</td>
<td>0.61/0.42</td>
<td>0.04/0.33</td>
</tr>
</tbody>
</table>

Table II. Comparison of Important Bond Lengths and Angles (Å) for 1, 3, and 35

<table>
<thead>
<tr>
<th>VO-(SALIMH)²⁺ (Ca²⁺)</th>
<th>VO-(SHEDH)²⁺ (cat)²⁺</th>
<th>VO-(SHEDH)²⁺ (HSHI)²⁺</th>
<th>VO-(SALIMH)²⁺ IMH (ACAC)²⁺</th>
<th>VO-(SALIMH)²⁺ IMH (ACAC)²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-O₁, 1.59</td>
<td>V-O₁, 1.60</td>
<td>V-O₂, 1.92</td>
<td>V-O₁, 1.92</td>
<td>V-O₁, 1.60</td>
</tr>
<tr>
<td>V-O₂, 1.92</td>
<td>V-O₁, 1.60</td>
<td>V-O₂, 1.90</td>
<td>V-O₁, 1.92</td>
<td>V-O₁, 1.60</td>
</tr>
<tr>
<td>V-O₂, 1.92</td>
<td>V-O₂, 1.90</td>
<td>V-O₂, 1.92</td>
<td>V-O₂, 1.92</td>
<td>V-O₂, 1.92</td>
</tr>
<tr>
<td>V-O₁, 1.88</td>
<td>V-O₁, 1.90</td>
<td>V-O₁, 1.90</td>
<td>V-O₁, 1.97</td>
<td>V-O₁, 1.99</td>
</tr>
<tr>
<td>V-O₄, 2.20</td>
<td>V-O₁, 1.64</td>
<td>V-O₄, 2.15</td>
<td>V-O₂, 2.12</td>
<td>V-O₂, 2.20</td>
</tr>
<tr>
<td>V-N₁, 2.15</td>
<td>V-N₁, 2.11</td>
<td>V-N₁, 2.09</td>
<td>V-N₁, 2.05</td>
<td>V-N₁, 2.09</td>
</tr>
<tr>
<td>V-N₂, 2.11</td>
<td>V-N₂, 2.20</td>
<td>V-N₂, 2.17</td>
<td>V-N₂, 2.10</td>
<td>V-N₂, 2.19</td>
</tr>
</tbody>
</table>

\( ^{a} \) Numbering changed to reflect that of VO(SALIMH)²⁺(CAT).

\( ^{b} \) There is a hydrogen bond between O5 (uncoordinated hydroxyl oxygen) and O3.

at the metal nucleus and are thus described hereafter as noninnocent ligands. Molybdenum complexes of noninnocent ligands have novel spectroscopic properties which are directly related to the coordination of the noninnocent ligand as shown by Schultz and co-workers.15 To the best of our knowledge, the metal centers in vanadium(V) complexes of these ligand types have not been examined by nuclear magnetic resonance spectroscopy except as a fingerprint technique. To increase our understanding of the relationship between the chemical shift of the metal nucleus and the structural/electronic properties of the metal complex, we have undertaken the synthesis and characterization of a series of vanadium complexes that contain both innocent and noninnocent ligands. This series of six-coordinate monooxovanadium(V) complexes contain meridional tridentate ligands, shown in Figure 1, which maintain phenolate and imino coordination and vary the third donor using primary and secondary amines or imidazole nitrogen atoms. The remaining two coordination positions are satisfied using a noninnocent, bidentate ligand derived from catechol or hydroxamic acids. These complexes exhibit low-energy ligand-to-metal charge-transfer transitions that significantly affect the spectroscopy observed for the complexes.


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Experimental Section

Catechol, 3,5-di(tert-butyl)catechol, tetrachlorocatechol, 4-nitrocatechol, pyrogallol, salicylaldehyde, acetohydroxamic acid, acetonitrile, or methylene chloride. Powders could be obtained either by slow evaporation of the reaction mixture by addition of a nonpolar cosolvent, usually either methanol or hexane. Hydroxamic acid complexes were prepared in a similar manner.

**VO(SALIMH)(CAT), 3.** In a typical preparation, VO(SALIMH)ACACMeOH (0.51 g, 2.0 mmol) was dissolved in acetonitrile (50–100 mL). Catechol (0.15 g, 1.4 mmol) was added as a solid, and the solution was stirred overnight. Slow evaporation of the reaction mixture provided a purple powder (0.19 g). Yield: 39%. Average yield for 3 was 278 g (0.82 mmol, 82%).

**VO(Br-SALIMH).** In parentheses provided in Table III.

**Preparation of Complexes.** Two general procedures were employed to prepare and isolate the V(II) complexes described in this study. The first was direct displacement of a terminal oxo ligand from a VOX complex by addition of a bidentate ligand such as catechol. The second was through addition of a bidentate ligand (e.g., catechol) to a vanadium(V) precursor such as VO(SALIMH)ACAC followed by air oxidation to the V(V) oxidation level.

**Reaction of H_{2}L' with VO_{L}.** These reactions involved adding a stoichiometric amount of ligand H_{2}L' to the vanadium(V) starting material. VO(ENSAL)CAT. 5. Catechol (recrystallized from benzene, 0.121 g, 1.10 mmol) and solid VO(ENSAL)CAT (0.246 g, 1.0 mmol) were weighed into a 250-mL Erlenmeyer flask. Absolute ethanol was then added to bring the solution volume to 50 mL. The conversion of the yellow VO(ENSAL) to the purple/blue VO(ENSAL)(CAT), 5, was rapid. The mixture was stirred for 2 days after which time the purple reaction mixture was filtered, leaving a blue black solid on the filter. The solid was washed twice with cold (0 °C) absolute ethanol and then air-dried. A second crop of material (VIVO(SALIMH)ACAC in most cases) with atmospheric oxidation to the V(V) oxidation level.

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The microcrystalline product was collected on a glass frit and dried under N2 (0.64 g, 83%). FAB (+) 355 [M + 1]++, 281 [VO(SALIMH)]++, FAB (--) 354 [M]-. Anal. Calcd for C19H18N3O13V: C, 47.47; H, 4.27; N, 15.82. Found: C, 47.12; H, 4.42; N, 15.89. The balance of the vanadium(V) complexes were prepared in situ and not isolated. In the in situ preparations, equal volumes of 5 mM solutions of VVO(SALIMH)ACAC, VO2(ENSAL), VO2(HSHED), and the appropriate salicylidenamine ring-substituted derivatives were reacted with the desired ligand L', and the solutions were stirred for approximately 3 h. We were collecting the UV-visible-NIR and 51V NMR spectra. Spectroscopic results for the fully characterized complexes were identical to those obtained for the same complexes prepared by the in situ method.

Collection and Reduction of X-ray Data. Suitable crystals of 1, 3, and 35 were obtained as described above. These crystals were mounted in glass capillaries. Intensity data were collected at room temperature on a Siemens R3 diffractometer using Mo Kα1 radiation (0.7107 Å). Three standard reflections were measured every 97 reflections. Modified crystal and data parameters are given in Table I. Intensity data were collected using 2θ/2θ scans. The data were reduced, the structures solved, and the model refined using the Siemens SHELXL PLUS program package.18 Computations were carried out on a VAX Station 3100. In the subsequent refinement, the function $\sum (F_{o} - F_{c})^2$ was minimized where $F_{o}$ and $F_{c}$ are the observed and calculated structure factor amplitudes. The agreement indices $R_{1} = \sum (F_{o} - F_{c}) / \sum (F_{o})$ and $R_{2} = \sum (wF_{o} - F_{c})^2 / \sum (wF_{o})^2$ were used to evaluate the results. Atomic scattering factors are from The International Tables for X-ray Crystallography.19 All hydrogen atoms, except the hydrogen attached to O6 of complex 35, were located on a difference Fourier map and allowed to refine isotropically. The hydrogen on O6 was placed in a calculated position with $d_{O-H} = 0.85$ Å and $U(H) = 1.2(eq)$ for O6. Unique data and final $R$ indices are reported in Table I. Fractional atomic coordinates for 1, 3, and 35 are also provided in supplementary Tables S5, S11, and S17, respectively. Selected bond distances and angles for these compounds are provided in Table II.

Spectroscopic and Magnetic Measurements. Infrared spectra were obtained on a Nicolet 60-SX FT-IR as KBr pellets. Electronic spectra were recorded on a Perkin-Elmer Lambda 9 UV-visible-NIR spectropho-
tometer equipped with a Perkin-Elmer 3600 3600 data station.

Fast atom bombardment (FAB) mass spectra were recorded on a VG 70-250-S mass spectrometer (VG Instruments, Manchester, UK). It was equipped with the standard VG FAB ion source and an Ion Tech Saddle-field ion gun. Xenon was used for the bombarding atom beam, with the atom gun controller set to 1 mC and 8 kV. 3-Nitrobenzyl alcohol was used as the FAB matrix.

The 51V NMR spectra were collected using a Bruker AM200 instrument operating at 52.62 MHz and utilizing 8k or 16k data points over a 125 000 Hz spectral window. The data were collected on acetonitrile solutions (≥10 mM). Chemical shifts are reported in ppm versus VCl3. (0 ppm) as an external standard and the error on the chemical shift is estimated to be ±1 ppm for resonances with a line width ≥1000 and ±3 ppm for resonances with line widths >1000 Hz. Typically, 10 to 10000 transients were acquired using a 90° pulse (14 μs) and no prepulse delay. The signal-to-noise ratio was improved via exponential multiplication of the FID which induced 10-100 Hz of line broadening.

Results and Discussion

Description of Structures. Other than simple VO3+ halides and esters (e.g., VOCl or VO(OCH3)3), monooxo-oxovanadium(V) complexes are rare and few have been structurally characterized.20 In particular, other than VO2(SALEN) and VO2(SALEN)*, there are no examples of VO3+ and VO4+ complexes with complete ligand sets common to both oxidation states. We were particularly interested in comparing the changes in the vanadium coordination sphere upon oxidation of the vanadium(IV) compounds containing imidazole since this represents a direct analogy to structural changes that may occur upon reduction of the active V(IV) enzyme to the inactive V(IV) protein in vanadium bromoperoxidase. We have previously reported the molecular structures of VVO(SALIMH), where L = ACAC, salicylaldehyde amion, or SALIMH, and also the secondary amine containing VVO(O-

(18) SHEXLTL PLUS; Copyright 1988, Siemens Analytical Instruments, Inc. Madison, WI.


Figure 2. ORTEP diagram of (bottom) VO2(HSHED)(SHI), 1, and (top) VO2(SALIMH)(CAT), 3, showing 50% probability ellipsoids for all non-hydrogen atoms.

Figure 3. ORTEP diagram of VO2(HSHED)(SHI), 35 showing 50% probability ellipsoids for all non-hydrogen atoms.

(HSHED)ACAC.17b In this contribution we can compare these vanadium(IV) materials with VO2(HSHED)(CAT), 1, VO2(SALIMH)(CAT), 3, and VO2(HSHED)(SHI), 35. Important bond lengths for 1, 3, 35, VO2(HSHED)ACAC, and VO2(SALIMH)ACAC are reported in Table II. ORTEP diagrams of compounds 1, 3, and 35 are presented as Figures 2 and 3, respectively.

There is surprisingly little variability in the vanadium-to-oxygen bond distances across the five compounds. The terminal oxo-to-vanadium distance range is 1.59-1.64 Å; however, there is no significant oxygen state dependence. The only obvious trend is that the phenolate oxygen atoms (O2) and the in-plane oxygen atom (O3) of the bidentate ligand are significantly shorter in the vanadium(V) compounds. The latter effect may be due to the fact that these oxygen atoms are further away from the nitrogen ligands which carry an extra negative charge. The vanadium–imidazole nitrogen atom (N1) distances are slightly longer in the vanadium(IV) complexes reflecting the preference of the more highly oxidized centers for oxygen rather than nitrogen ligation. Most interestingly, there is essentially no difference in the vanadium–imidazole nitrogen (N2) bond distance between VVO(SALIMH)ACAC and VO2(SALIMH)(CAT). The vanadium–imidazole N(2) distance in both the vanadium(IV) and vanadium(V) complexes is 2.1 Å.
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which is equivalent to the V-N distance (EXAFS data) reported for the native (vanadium(V)) and reduced (vanadium(IV)) forms of vanadium bromoperoxidase. Although the vanadium-to-imidazole distance is essentially invariant on oxidation-state change, there is a marked elongation in V-N2 when a secondary amine replaces the imidazole. In both the V(IV) and V(V) oxidation levels, the V-N(imidazole) distance is 0.06-0.09 Å shorter than that of the corresponding V-N(secondary amine).

Thus, it would appear that imidazole is a better ligand to V(IV) and V(V) than secondary amines.

As with other metal complexes of catechol type ligands which have readily accessible semiquinone and quinone oxidation states, it is important to assign the relative oxidation states of the metal and ligand. Several vanadium complexes of catechols and semiquinones are reported in the literature. The important distances to be considered in these complexes are the vanadium-oxygen distance and the carbon-oxygen and carbon-carbon distances of the ligand. The vanadium-oxygen distance is indicative of the metal oxidation state (vide supra) and the carbon-oxygen and carbon-carbon distances are indicative of ligand oxidation levels. To the best of our knowledge, 13 the vanadium-semiquinone complexes have readily accessible semiquinone and quinone oxidation states, and a comparison of the "bare" vanadium(V) complexes of catechol in the literature should not be overinterpreted. However, if one considers the equatorial V-O_CAT distance of 1.91 and 1.88 Å in 1 and 3, respectively, it is found that these complexes favorably with the average V-O_CAT distances in the "bare" vanadium(V) complexes of Woolins and co-workers (1.91 and 1.93 Å)23 and Peirpont and co-workers (1.91 Å).24 The 1.90 Å average distance for 1 and 3 can be contrasted to the corresponding monooxovanadium(IV)-O_CAT distance of 1.96 Å for k3[VO(CAT)3] reported by Cooper, Koh, and Raymond.21 The range of C-O distances reported for vanadium-catecholate complexes is 1.32-1.35 Å. The average C-O distances in 1 and 3 are 1.31 and 1.33 Å, respectively. The average C-C distances for the catechol rings in 1 and 3 are 1.39 Å which is consistent with an aromatic ring. Crystallographically characterized vanadium-semiquinone complexes have not been excepted, but for the relatively short C-O distance in 1, all the structural information suggests that 1 and 3 are best formulated as vanadium(V)-catecholate complexes in the solid state. The short C-O distance in 1 may indicate a slight contribution of a semiquinone resonance form in this species. The discussion of catecholate versus semiquinone structural contributions will be continued below with respect to the NMR spectroscopy of these complexes.

One final structural comment is warranted on the V^2O-(HSHED)(SHI). We have previously shown that the trianion of the salicylhydroxamic acid molecule can form ring structures called metallocrown when SHI acts as a dinucleating unit with metals bound both to the hydroxyl amine (ν1-bonding mode) to an equatorial site and by the carbonyl to the trans-axial coordination site in an analogous manner to 35. The vanadium-oxo-equatorial bond distance is very comparable across the series of three compounds (1.85-1.88 Å). In contrast, the vanadium-oxo-equatorial distance is 2.12 Å in 35 and 2.19 Å in the two Raymond complexes. This probably is a result of the change in charge between the hydroximate and hydroxamate ligands and indicates that the end form of the hydroximate ligand has a stronger interaction with the monooxovanadium(V) center.

Electronic Spectroscopy of the Complexes. Dioxovanadium(V) complexes [e.g., VO2(HSHED)] have strong UV transitions that lead to pale yellow solutions, while the vanadium(IV) complexes of the type V(OH)2(μ-OH)(μ-SALIMH)2 or VO(SALIMH)2ACAC are pale red with weak d-d transitions in the visible spectrum. In contrast, all of the VO^2+ complexes reported herein exhibit strong absorption bands, designated herein as E1, in the visible spectral region. As shown in Figure 4, the complexes containing catechol (or derivatives) show an additional band, designated as E2, in the near IR. Spectral parameters for these complexes are provided in Table III. Based on the intensity of the absorption, we assign these transitions as ligand-to-metal charge-transfer (LMCT) excitations.

Without the aid of resonance Raman spectroscopy, it is difficult to establish definitively whether the LMCT bands are phenolate-to-metal or catecholate-to-metal in origin in molecules such as VO(SALIMH)(CAT). Ideally, substitutions of either electron donating or withdrawing substituents on the catecholate or phenolate would produce corresponding changes (increasing or decreasing, respectively) in the charge-transfer energy of each band, E1 and E2, such that a definitive assignment can be made. If this were the case, one would assume that the donor was based on the substituted ligand. Unfortunately, the trends in energy upon substitution of these compounds are not this simple. In lieu of a definitive description of the orbitals involved in the charge-transfer transitions, the general trends observed for each substitution will be outlined below.

The visible band for the SHI complexes is always lower in energy than the corresponding transition for the AHI complexes. For the catechol complexes the LMCT donor set is predominantly localized on the catechol, while the acceptor orbitals are metal centered (d_π*, d_π', or d_π ). An alternative and essentially indistinguishable formulation is to localize the proton on the hydroximate to form a hydroxamate and refer to the pendant group as a phenolate moiety. Based on the strength of the interaction of SHI with vanadium we prefer the first description; however, a combination of both models must be occurring. Raymond and co-workers have prepared and structurally characterized two vanadium complexes of alkyl hydroxamates in which the ligand is a monoanion. It should be noted that in these complexes, the second acidic proton has been replaced by the alkyl group. These structures contain two hydroxamate ligands, one of which is coordinated via the hydroxyl amine (ν1-bonding mode) to an equatorial site and by the carboxyl to the trans-axial coordination site in an analogous manner to 35. The vanadium-oxo-equatorial bond distance is very comparable across the series of three compounds (1.85-1.88 Å). In contrast, the vanadium-oxo-equatorial distance is 2.12 Å in 35 and 2.19 Å in the two Raymond complexes. This probably is a result of the change in charge between the hydroximate and hydroxamate ligands and indicates that the end form of the hydroximate ligand has a stronger interaction with the monooxovanadium(V) center.
In the course of these studies, we observed an interesting trend related to imidazole ligation. The energy of the near IR band, E2, is dominated by the presence of the SALIMH ligand such that the nine lowest energy transitions correspond to VO(SALIMH) and VO(BrSALIMH) complexes with an energy order: TCC < TBC < CAT < DBC < PYR. The reasons for this order, which is opposite of that predicted from Scheme I, are complex and remain at this time; however, the observations are consistent with a model in which the acceptor orbital (influenced by the coordinated imidazole) and catechol substitution is lowered in energy to a greater extent than the corresponding donor orbital (influenced predominantly by catechol ring substitution).

In summary, the donor orbitals for the LMCT bands have significant contributions from the bidentate ligand as is observed for many transition-metal–catechol complexes. These conclusions are consistent with findings for the homoleptic complexes [V(\text{CAT})\text{\textsubscript{2}}]^+ and [V(\text{DBC})\text{\textsubscript{2}}]^+ in which both a low- and high-energy LMCT band are reported.\(^{23}\) The vanadium(V) phenolate complexes reported to date which do not contain coordinated noninnocent ligands have electronic transitions at energies higher than the E2 bands reported for these catecholate complexes.\(^{25}\)

**Vanadium-51 NMR Spectroscopy.** Vanadium-51 NMR has been increasingly utilized to probe the electronic environment of biologically relevant V(\text{V}) compounds. The majority of complexes with exclusively oxygen and nitrogen ligation fall far upfield of the standard VOCl\textsubscript{3} in the general region of -400 to -700 ppm. Exceptions include bare V(\text{V}) compounds such as V(\text{N(S\textsubscript{2}})\text{\textsubscript{2}})(\text{DBC})(\text{phenanthrolone}) at +780 ppm.\(^{26}\) The remaining complexes with downfield chemical shifts are halide or sulfur containing species.\(^{16}\) Rehder has presented a referencing scale based on a correlation of \(^{51}\text{V}\) NMR shifts with \(\Sigma\chi\) the sum of the coordinated heteroatom electronegativities (using the Zhang formalism\(^{26}\)), for a wide variety of V(\text{V}) complexes with coordination numbers 4–6.\(^{12}\) A carboxylate rich, six- or seven-coordinate structure for the active site of vanadium bromoperoxidase has been proposed based on this correlation in which the carboxylate ligands are probably bound in an \(\eta^2\) manner.

While this correlation effectively predicts the chemical shift range for most complexes of VO\textsuperscript{2+} and VO\textsuperscript{3+}, it is less effective in describing materials that have coordinated noninnocent ligands. Based on the heteroatom electronegativities tabulated by Zhang, one would calculate \(\Sigma\chi = 20.69\) for 1 and \(\Sigma\chi = 17.05\) for 3. Applying these values to the Rehder referencing scale would predict \(\delta\) values in the upfield region between -480 and -600 ppm. In contrast, the chemical shift range for the complexes of VO\textsubscript{2}(L)\textsubscript{\textsuperscript{\textsubscript{2}}}(\text{DBC}) (where L = SALMHI, HSHED, ENSAL, and their phenolate ring substituted derivatives and L' = catecholate and derivatives, salicylhydroxamic and acetohydroxamic acids or a terminal oxo moiety) extend over a remarkable 1130 ppm including downfield shifts to +604 ppm. Apparently a new correlation is required to describe chemical shifts of complexes with noninnocent type ligands. It will be shown below that these marked deviations from the predictions based on electronegativity values are a direct consequence of the coordination of noninnocent ligands to the VO\textsuperscript{3+} unit and that the magnitude of the downfield shift correlates with the LMCT energies in complexes with electronically similar noninnocent ligands. Chemical shifts for complexes 1–41 are provided in Table III.

The progressive downfield shift of the \(^{51}\text{V}\) NMR resonances is illustrated by the spectra of VO\textsubscript{2}(ENSA\textsubscript{L}), 44 VO(EN\textsubscript{SAL})(\text{CAT}), 5, and VO(ENSAL)(\text{DBC}), 13, which are presented in Figure 5 from top to bottom, respectively. The VO\textsubscript{2}\textsuperscript{+} complex, 44, has a single resonance at -555 ppm. This shift is typical for dioxovanadium(V) complexes which are bound in an approximation in eq 2b is valid. The general theoretical description of the shielding constant, \(\sigma\), through eq 2a where \(\delta\) is the chemical shift of the nucleus of interest, \(\sigma_{\text{ref}}\) and \(\sigma_\text{ref}\) are the shielding constants for a reference compound (VOCl\textsubscript{3} for vanadium) and the compound of interest, respectively. If one assumes \(\sigma_{\text{ref}} \ll 1\), then the approximation in eq 2b is valid. The general theoretical description of the shielding constant, \(\sigma\), as presented by Rausch for nuclei without unpaired spin, indicates that \(\sigma\) equals the sum of a diamagnetic and paramagnetic term, \(\sigma^\text{d}\) and \(\sigma^\text{p}\), as shown in eq 1 (\(\sigma = \sigma^\text{d} + \sigma^\text{p}\)).\(^{14}\) In the presence of nuclei with unpaired spin, the equation for total shielding would require a third term to account for the local field at the observed nucleus which is induced by the unpaired spin.\(^{27}\)

Since the primary contribution to \(\sigma^\text{p}\) is from core electrons of the nucleus being observed, and, to a much lesser extent, the...
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Electrons of neighboring atoms, the diamagnetic component of the total shielding is essentially constant for any one nucleus, and for vanadium it is approximately equal to the free atom value of 1710 ppm.28 The paramagnetic term describes the mixing of excited states, \([n]\), into the ground state, \((0)\), of the molecule in the presence of a magnetic field as shown in eq 3 where \(r_{kn}\) is the position vector for the \(k\)th electron with respect to the nucleus being observed, \(I_k\) is the \(k\)th component of the angular momentum operator with respect to the observed nucleus, \(I_0\) is the angular momentum operator with respect to the chosen origin, and the other terms have their usual meanings.13 It should be noted that this is a general equation that takes the sum over all molecular states which transform via the angular momentum operator. While eq 3 may be useful for small systems such as dihydrogen, the lack of accurate wave functions for larger molecules decreases the utility of this equation for calculating reasonable shielding factors.

Since the paramagnetic shielding is affected predominantly by the electronic structure of the nucleus being observed \(\left(r^3\right)\) dependence, Saika and Slichter have approximated the total shielding to be the sum of the local diamagnetic and paramagnetic contributions and a nonlocal term as shown in eq 4 where \(\sigma_{\text{local}}\) represents the "diamagnetic correction for the atom in question," \(\sigma_{\text{local}}\) represents "the contribution from magnetic fields set up by the orbital motion of the valence orbitals" for the atom in question, and \(\sigma_{\text{non-local}}\) represents the contribution from closed shell and valence orbitals of other atoms.29 For most coordination complexes, \(\sigma_{\text{non-local}}\) is relatively small and therefore need not be evaluated. Since this diamagnetic contribution is essentially constant, the major contributor to chemical shift is \(\sigma_{\text{local}}\).

Griffith and Orgel have evaluated the local paramagnetic shielding for low-spin octahedral cobalt(III) complexes in terms of crystal field theory in the strong field limit. The most recent revision of the crystal field treatment of \(\sigma_{\text{total}}\) has been presented by Bramley and co-workers for molecules of high symmetry \((O_h, C_{2v}, D_{4h})\) using an intermediate field approach and is shown in eq 5 where \(A_{1g}\) and \(T_{1g}\) are the ground and excited states mixed by the angular momentum operator \(I_0\) and \(\epsilon_{\text{LMCT}}\) represents the contribution from magnetic fields set up by the orbital motion of the valence orbitals for the atom in question, and \(\sigma_{\text{local}}\) represents the contribution from closed shell and valence orbitals of other atoms.29

\[
\sigma^\text{eq} = -\left(\frac{\mu e^2}{2m^2}\right) \left(\sum_{i=m}^n E_i - E_0\right)^{-1} \left(\sum_{n=1}^N \left| I_0 \right| + \sum_{n=1}^N \left| I_0 \right| \right)
\]

\[
\sigma^\text{eq} = \left(\sum_{i=m}^n \left(\sum_{k=m}^n \left| I_0 \right| \right) \right)
\]

The complexes reported herein are high valent \((d^3)\) and of low symmetry \((C_s)\), and the electronic transitions are dominated by LMCT transitions. Since vanadium \((V)\) has no valence electrons, the local contribution to the paramagnetic shielding, as defined by Saika and Slichter, is zero. Therefore, the large chemical shift range for these vanadium complexes of noninnocent ligands must be due to the nonlocal term of eq 4. In the general context of the Ramsey equation, this point is one of semantics since all transitions are considered; however, the effect of LMCT transitions on the paramagnetic term of eq 1 are rarely considered explicitly since they are of high energy and thus would have a small effect relative to d-d transitions. Schultz and co-workers have described this relationship for \(^{95}\text{Mo}\) chemical shifts and the energy of LMCT transitions in molybdenum–catechol complexes.

We have evaluated the nonlocal term for the vanadium complexes by analogy to the treatment of Bramley for the local paramagnetic shielding as discussed above. Given the low symmetry of these complexes, all transitions will transform as the angular momentum operator, and therefore the LMCT transitions should produce a sizeable shielding of the vanadium nucleus.

Figure 6. Correlation between \(^{51}\text{V}\) NMR chemical shift and 1/\(E\) for \(\text{VO}_{\text{LL}}\) complexes according to bidentate ligand, \(L\). Plots A, B, and C are for catechols with electron donating substituents and catechols with electron withdrawing substituents and hydroximates, respectively. Note that the axes are different for each plot. The symbols denote the following bidentate ligand series: CAT, DBC, PYR, TCC, 4-NC, TBC, SHI, AHI.

Since \(\sigma^p\) is not an observable parameter, we have combined eqs 1, 2b, and 6 to obtain the relationship between the chemical shift and the shielding factor as shown in eq 7. From eq 7 it follows that a plot of \(\delta\) versus \(1/\Delta E\) should yield a line with a positive slope of magnitude \(B\) and an intercept (at \(1/\Delta E = 0\)) which is the paramagnetic shielding of the reference. If \(\sigma_{\text{ref}}^p\) and \(\delta\) are known, the total shielding for the vanadium nucleus can be calculated from eq 2b, and thus an absolute shielding scale may be formulated.

\[
\sigma^p = -B/\Delta E
\]

\[
\delta = \sigma^p_{\text{ref}} + B/\Delta E
\]
Plotting $\delta$ versus $1/\Delta E$ for the monooxo vanadium(V) complexes according to the derivatives of the tridentate ligands ENSAL, HSHED, and SALIMH yields three nonlinear groups of data which correspond to complexes of hydroximates, catecholates with electron donating substituents, or catecholates with electron withdrawing substituents. This result indicates that the assumptions of eq 6 are not valid when the complexes are grouped according to tridentate ligand type. However, reploting the data according to bidentate ligand type as suggested by the above analysis, one obtains the linear relationships shown in Figures 6A–C for complexes of electron donating catecholates, electron withdrawing catecholates, and hydroximates, respectively. While it is clear that the energy of the LMCT correlates with the downfield chemical shift, the different slopes for the three families of lines indicate that the factor $B$ of eq 6 also contributes to the shielding of the vanadium nucleus. The $B$ dependence of the chemical shift is evidenced when one compares the chemical shifts for the hydroximate complexes to the chemical shifts obtained for the complexes of electron withdrawing catecholates. As seen in Figure 6 (parts B and C), the chemical shift for these two series are quite similar even though the charge-transfer energy is very different. According to Ramsey theory, one would predict very different chemical shifts for these compounds if $B$ were indeed comparable for the two series. As this is not the case, it is concluded that $B$ for the hydroximate complexes is smaller than the $B$ for the catecholate complexes with electron withdrawing substituents.

**Absolute Shielding Scale.** From eq 2b the total shielding of a nucleus can be obtained if one knows the chemical shift and the total shielding of the reference. The reference shielding term can be obtained from eq 1 ($\sigma_{ref} = \sigma^0_{ref} + \sigma^D_{ref}$) where $\sigma^0_{ref}$ is extrapolated from plots of eq 6 and $\sigma^D_{ref} = 1710$ ppm. Since $\sigma^D$ is expected to be negative we can set an upper limit for $\sigma^0_{ref}$ of $\sigma^0_{ref} \leq -1963$ ppm. Figure 7 presents plots of $\delta$ vs $2/(E_1 + E_2)$. The average energy approximation has been used for these plots since all low-energy transitions involving metal orbitals should be utilized according to Ramsey theory in which the sum of all appropriate transitions is utilized. In this case, since values for $B$ are not known, we have taken the average energy. Extrapolating the plots to $2/(E_1 + E_2) = 0$, it is apparent that the intercept is not constant, as predicted by eq 6. The intercepts for the complexes of CAT, DBC, and PYR are spread over $\approx 3000$ ppm ($-6000$ to $-9000$ ppm). Other studies have been presented in which the extrapolated intercept is not constant. Verkade and Weiss have reported different lines (with disparate intercepts) for cobalt complexes with ligands from different rows of the periodic table.

**Figure 7.** Correlation between $^{51}$V NMR chemical shift and the inverse of the average energies of $E_1$ and $E_2$ for complexes which have both visible and near-IR transitions.

**Figure 8.** Absolute shielding scale for vanadium indicating the absolute shielding of the LMCT complexes reported in this paper as well as the absolute shielding for the vanadium substituted proteins RNase T1 ($\delta = -516$ ppm), phosphoglycerate mutase ($\delta = -560$ ppm), and transferrin ($\delta = -530$ ppm for both signals); four, six- and seven-coordinate complexes of O and N donors (as compiled by Rehder); and low valent vanadium$^{(1-)}$ and vanadium$^{(1+)}$ complexes.

Bonded distances do not change substantially upon changing the tridentate ligand (see Table II). Second, some of these complexes, in particular the complexes of CAT, PYR, and DBC, may have a small but significant vanadium$^{IV}$–semiquinone contribution to the ground state. If this is the case, the shielding may have a temperature dependent paramagnetic term, $\sigma^{TP}$, which would need to be included in the total shielding. Therefore, the intercept for these compounds would equal $\sigma^0_{ref} + \sigma^{TP}$, not just $\sigma^0_{ref}$. This explanation is qualitatively appealing since metal reduction is the extreme limit of ligand to metal charge transfer. The broad resonances observed for $V^0$(SALIMH)CAT and $V^0$(SALIMH)DBC ($2000$–$4000$ Hz) indicate that relaxation of the vanadium nuclear spin is more rapid in these complexes than observed in the complexes of hydroximates or electron withdrawing catecholates. This enhanced relaxation of the nuclear spin may be a result of interactions between the nuclear spin and the unpaired electron spin in the vanadium$^{IV}$–semiquinone ground state.

Based on $\sigma^0_{ref} = -2130$ ppm, we propose the shielding scale shown in Figure 8. Importantly, all reported chemical shifts for vanadium complexes are downfield (deshielded) relative to $\sigma^0 = 1710$ ppm (the right hand border of the plot). Also, the calculated $\sigma^0$ values for $V$(CO)$^6$ and $CrV$(CO)$^4$THF are $-165$ and $-2023$ ppm, respectively, values which compare favorably with those reported by Jameson, Rehder, and Hoch ($-500$ and $-2500$ ppm) based on the relationship between the chemical shift, $\delta$, and the absolute shielding scale for vanadium indicating the absolute shielding of the LMCT complexes reported in this paper as well as the absolute shielding for the vanadium substituted proteins RNase T1 ($\delta = -516$ ppm), phosphoglycerate mutase ($\delta = -560$ ppm), and transferrin ($\delta = -530$ ppm for both signals); four, six- and seven-coordinate complexes of O and N donors (as compiled by Rehder); and low valent vanadium$^{(1-)}$ and vanadium$^{(1+)}$ complexes.

*Figure 8.* Absolute shielding scale for vanadium indicating the absolute shielding of the LMCT complexes reported in this paper as well as the absolute shielding for the vanadium substituted proteins RNase T1 ($\delta = -516$ ppm), phosphoglycerate mutase ($\delta = -560$ ppm), and transferrin ($\delta = -530$ ppm for both signals); four, six- and seven-coordinate complexes of O and N donors (as compiled by Rehder); and low valent vanadium$^{(1-)}$ and vanadium$^{(1+)}$ complexes.

**Table II.** Chemical shifts for vanadium indicating the absolute shielding of the LMCT complexes reported in this paper as well as the absolute shielding for the vanadium substituted proteins RNase T1 ($\delta = -516$ ppm), phosphoglycerate mutase ($\delta = -560$ ppm), and transferrin ($\delta = -530$ ppm for both signals); four, six- and seven-coordinate complexes of O and N donors (as compiled by Rehder); and low valent vanadium$^{(1-)}$ and vanadium$^{(1+)}$ complexes.
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The order of the chemical shifts for \( V^{\text{O}}(\text{ENSAL}) \text{CAT}, V^{\text{O}}(\text{BrENSAL}) \text{CAT}, \) and \( V^{\text{O}}(\text{ClENSAL}) \text{CAT} \) in trace B of Figure 9 provides some insight into the bonding in these complexes. If the equatorial phenolate contributes to the energy of the donor orbital, then one would expect the dichloro substituted complex, \( V^{\text{O}}(\text{ClENSAL}) \text{CAT} \), to have the largest \( \Delta \delta \) and the highest field (less positive chemical shift). In contrast, the unsubstituted complex, \( V^{\text{O}}(\text{ENSAL}) \text{CAT} \), should have the lowest field (most positive chemical shift) since \( \Delta \delta \) should be smaller in the absence of electron withdrawing substituents. In fact, the opposite order is observed. This suggests that the phenolato ligand must contribute predominantly to the acceptor orbital, and the donor orbital must be predominantly of catecholate or hydroximate character. This is also consistent with the trends found upon catechol substitution.

Conclusion

In this paper we have shown that vanadium complexes of nitrogen and oxygen ligands can have \( V^{15} \text{NMR} \) chemical shifts which are significantly downfield of the "normal" shift range for these compounds based on empirical relationships. The dominant factor in the deshielding of these compounds is the low-energy ligand-to-metal charge-transfer transitions which are directly associated with the presence of noninnocent ligands such as catecholate or hydroximate. The magnitude of the deshielding is inversely proportional to the energy of the LMCT. Anomalous intercepts for plots of \( \delta \) versus \( 1/\Delta \delta \) for the complexes of ligands with high energy occupied molecular orbitals may indicate a temperature dependent contribution to the chemical shielding.

An absolute shielding scale which is consistent with all reported chemical shifts has been proposed. From this scale it is clear that the vanadium bromoperoxidases have a smaller temperature independent paramagnetic shielding (\( \sigma = -100 \)) than most complexes of vanadium(\( V \)) and that noninnocent ligands of the type examined here are almost certainly not involved in the metal coordination sphere in this enzyme. We have shown that imidazole ligation deshields the vanadium nucleus in vanadium complexes of catechols and hydroxamic acids. This may not be true for other ligand sets. The novel spectroscopy of these complexes may be relevant to the solution characterization of vanado-biomolecules such as complexes of ion sequestering agents based on hydroxylamines, catechols, or pyrogallol moieties.

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Supplementary Material Available: Tables of fractional atomic coordinates, anisotropic thermal parameters of all non-hydrogen atoms, fractional atomic positions for hydrogen atoms, a complete set of bond distances, and a complete set of bond angles for 1, 3, and 35, respectively, and Figures 10–12 of complete numbering schemes for all atoms in 1, 3, and 35 (18 pages); list of observed and calculated structure factors (34 pages). Ordering information is given on any current masthead page.


