Effect of ancillary ligand on electronic structure as probed by $^{51}$V solid-state NMR spectroscopy for vanadium–o-dioxolene complexes

Olga Goncharova-Zapata, Pabitra B. Chatterjee, Guangjin Hou, Laurence L. Quinn, Mingyue Li, Jenna Yehl, Debbie C. Crans and Tatyana Polenova

A series of vanadium(v) complexes with o-dioxolene (catecholato) ligands and an ancillary ligand, $\langle N$-(salicyldieneaminato)ethylenediamine $\rangle$ (hensal), were investigated using $^{51}$V solid-state magic angle spinning NMR spectroscopy ($^{51}$V MAS NMR) to assess the local environment of vanadium(v). The solid-state $^{51}$V NMR parameters of vanadium(v) complexes with a related potentially tetradentate ancillary ligand ($N$-salicylidene-$N'$-(2-hydroxyethyl)ethylenediamine) ($h_2$shed) were previously shown to be associated with the size of the HOMO–LUMO gap in the complex and, as such, provide insights on the interaction between metal ion and ligand (P. B. Chatterjee et al., Inorg. Chem., 2011, 50, 9794). Our results show that the modification of the ancillary ligand does not affect the observed trend between complexes ranging from catechols with electron-rich to electron-poor substituents. However, the ancillary ligand does affect the size of the HOMO–LUMO separation in the parent complex and thus the solid-state vanadium NMR chemical shift of the unsubstituted vanadium complex. For these complexes, significant changes observed in the isotropic shifts and more modest changes detected in the $C_Q$ reflect the electronic changes in the complex as the catechol is varied. However, no obvious trend was observed in the chemical shift anisotropies ($\delta_\sigma$ and $\eta_\sigma$) with the variation in the catechol. The electronic changes in the coordination environment of the vanadium can be determined using solid-state $^{51}$V NMR spectroscopy.

Introduction

Inorganic chemists rely on single crystal X-ray diffraction for compound characterization, but it is not uncommon that alternative characterization methods are needed because not all compounds crystallize. Alternative methods include powder diffraction, FTIR, and other solid-state techniques. We have used solid-state $^{51}$V NMR spectroscopy to characterize a series of vanadium(v) complexes and find that this method accurately describes the electronic properties of the systems under study. These properties are of particular interest due to the abundant applications of vanadium(v) complexes, including their use in bulk chemicals production,2–4 in model studies of enzymes,5–8 and as anti-diabetic agents.9–11

We and others demonstrated previously that $^{51}$V solid-state NMR spectroscopy as a sensitive tool for characterization of the electronic properties of vanadium(v) systems. Since vanadium complexes generally have $^{51}$V NMR chemical shifts in the range of $-300$ ppm to $-700$ ppm,33 in this work, we investigate a series of vanadium(v) complexes of o-dioxolenes (also called catecholates) with chemical shifts outside this range.

We and others demonstrated previously that $^{51}$V solid-state magic angle spinning NMR spectroscopy ($^{51}$V MAS NMR) can assess the local environment of the vanadium(v) and provide detailed insights into its interaction with ligands.1,15,33–39 A hybrid $^{51}$V SSNMR/Density Functional Theory (DFT) approach provides highly sensitive information regarding electronic structure and geometry not only in...
coordination complexes\cite{1,15,33–36,41–44} but also in large proteins, such as vanadium-containing haloperoxidases.\cite{37} This sensitivity arises from the fact that $^{51}$V is a half-integer quadrupolar nucleus ($I = 7/2$). Its electric field gradient (EFG) and the chemical shift anisotropy (CSA) tensors provide information on the local geometry and electronic structure of the metal site and extend solution-based $^{51}$V NMR isotropic chemical shift ($\delta$) information.\cite{1,15,33–39,41–45} For example, vanadium complexes with a range of different ligand donor groups have been investigated, and the nature of the charge distribution between vanadium and the ligand was described in detail.\cite{15,33–36} Most vanadium compounds investigated previously have chemical shifts from –300 to –700 ppm. In the case of two eight-coordinated nonoxovanadium(\textit{v}) compounds, the unusual chemical shifts found in solution (ca. –260 ppm) were the result of the unique electronic environment surrounding the vanadium, as demonstrated by the analysis of $^{51}$V EFG and CSA tensors.\cite{33} In addition, $^{51}$V SSNMR parameters were effectively used to describe the electronic properties of vanadium complexes containing the $\sigma$-dioxolene ligand and were reported to provide direct information regarding the changes in the HOMO-LUMO gap.\cite{33}

The $\sigma$-dioxolene ligand is redox active and is referred to as “non-innocent” because upon complexation with some metal ions the resulting complex is redox active. These complexes can be difficult to prepare and keep pure because of their high redox activity. Characterization of metal complexes containing such “non-innocent” ligands is especially difficult because of the ligand-to-metal charge transfer (LMCT) that can prevent unambiguous determination of the oxidation state of the coordinating metal ion: it is challenging to define if the electrons are on the ligand or the metal.\cite{16} In these systems, strong deshielding at the vanadium nucleus is observed with the chemical shift range dramatically extended, which is a manifestation of the additional electron density placed on the vanadium center. Besides vanadium, redox-active ligands are ubiquitous in complexes of multiple other transition metals, notably, Fe(\textit{ii}), Cu(\textit{ii}), and Mn(\textit{ii}), which are found in many proteins and inorganic catalysts and which exhibit diverse functions.\cite{57–53}

For vanadium in oxidation state five, the common coordination geometries are six-coordinate (octahedral) and five-coordinate (distorted square pyramidal and trigonal bipyramidal).\cite{54} The series of vanadium(\textit{v}) compounds under investigation in this work, Fig. 1, are related to the previously structurally characterized vanadium–$\sigma$-dioxolene complex (Fig. 2), where the vanadium is observed in a distorted octahedral geometry. This class of ternary complexes defined in Fig. 1 and 2 consists of an oxovanadium(\textit{v}), an $\sigma$-dioxolene ligand, and a Schiff base-type ancillary ligand abbreviated hshed. In these complexes, hshed uses three of the four coordinating moieties, forming $\sigma$-dioxolene complexes with vanadium, and readily undergoes ligand-to-metal charge transfer (LMCT).\cite{33} Indeed, this is apparent by considering the solution $^{51}$V NMR chemical shifts of these compounds. Vanadium complexes generally have $^{51}$V NMR chemical shifts in the range of –300 ppm to –700 ppm, and linear correlation has been demonstrated between isotropic chemical shifts in the solid state ($\delta_{\text{iso}}$) and in solution ($\delta$), suggesting the same structure of these complexes in both phases, and is important to the interpretation of the parameters shown here.\cite{33}

The complexes shown in Fig. 1 all have solution chemical shifts outside the region common to most vanadium compounds (–300 to –700 ppm). Recent investigations showed that a series of related vanadium(\textit{v}) compounds containing substituted ancillary ligand, hshed, extended the linear relationships between isotropic chemical shifts in solution ($\delta$) and in the solid state ($\delta_{\text{iso}}$).\cite{33} Interestingly, discrepancies between experimental and calculated solid-state NMR parameters were observed;\cite{53} however, most recent work by Bühl and colleagues demonstrated that excellent agreement between experiment and theory is achieved when adaptive quantum mechanics/moloeclar mechanics (QM/MM) treatment is used in order to accurately recapitulate long-range electrostatic effects.\cite{55} In light of these recent theoretical developments enabling accurate computation of $^{51}$V solid-state NMR parameters, it becomes particularly important to garner more information on related systems. This information is necessary to establish general understanding of the structural features dictating the $^{51}$V NMR observables, which in turn will enable de novo 3D structure determination of noncrystalline vanadium(\textit{v}) complexes from solid-state NMR and quantum chemical calculations.

The work presented herein investigates the class of compounds with the tridentate ligand, hensal (N-(salicylideneaminato) ethylenediamine), using a series of three complexes (1–3) as representative molecules of the series. These complexes contain

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Molecular structures of the three vanadium(\textit{v}) compounds under study: VO(ensal)Cat (1), VO(ensal)DTBCat (2), and VO(ensal)TB-Cat (3).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Molecular structure of vanadium(\textit{v})–$\sigma$-dioxolene compound\textsuperscript{33} structurally related to the three vanadium compounds under study.}
\end{figure}
oxovanadium(V), o-dioxolene, and ensal and, therefore, are likely to be structurally similar to the corresponding series with $h_2$shed ($N$-salicylidene-$N'$-(2-hydroxyethyl)ethylenediamine). Considering that the ensal ligand contains a terminal amine group, this series represents the base structure for the shed series previously reported. The studies here thus represent $^{51}$V SSNMR data and analysis of a series of vanadium(V) complexes containing unsubstituted ancillary ligands and are important for gauging how ancillary ligand substitution modifies the electron density at the vanadium(V) center in redox non-innocent compounds.

**Experiments and methods**

**Materials**

Vanadyl triethoxide (99.99%), salicylaldehyde (98%), ethylenediamine (99%), catechol ($\geq$99%), 3,5-di-$tert$-butylcatechol (99%), and tetrabromocatechol (96%) were purchased from Sigma-Aldrich. All other reagents are commercially available and used as received. Solvents were ACS grade and used as received. Abbreviations

We used the following abbreviations: OEt = ethoxide; hensal = $N$-(salicylideneaminato)ethylenediamine; Cat = catechol; DTBCat = 3,5-di-$tert$-butylcatechol; and TBCat = tetrabromocatechol.

**Syntheses of compounds**

The compounds of the series 1–3 were prepared as described previously by first preparing the VO$_2$ ensal precursor. Sample purity has been checked by solution $^1$H NMR spectroscopy and was in agreement with literature reports.

**Solid-state NMR spectroscopy**

All solid-state NMR spectra were acquired on a 9.4 T wide bore Teagm Discovery spectrometer operating at Larmor frequencies of 400.2 ($^1$H) and 105.2 ($^{51}$V) MHz. All experiments were performed using a 3.2 mm Varian triple-resonance T3 probe. Spectra for each of the four compounds under investigation were acquired at the MAS frequency of 13, 17, and 20 kHz and controlled to ±5 Hz by a Teagm MAS controller. The temperature was set to +25 °C and was controlled to ±1° by a Varian temperature controller.

The magic angle was set by maximizing the number of rotational echoes observed in the $^{23}$Na NMR free induction decay of solid NaNO$_3$. All spectra were recorded using single pulse excitation; the non-selective excitation pulse width was 1.0 μs and the spectral width was 1.0 MHz. A recycle delay of 1 s was used for all measurements. The total number of scans acquired for each compound depended on the MAS frequency and the amount of sample packed in the rotor and ranged between 8192 and 110 000. The spectra were processed using MestReNova. The initial FIDs were (1) left shifted to the top of the first rotary echo, (2) apodized by 100–300 Hz exponential function, (3) Fourier transformed, (4) phase corrected, (5) baseline corrected. The isotropic chemical shifts were determined by the analyses of the spectra collected at the three different MAS frequencies and referenced with respect to a secondary reference, compound SJZ0032 whose isotropic chemical shift was reported by us previously.

The solid-state NMR parameters, namely $^{51}$V quadrupolar coupling constant and quadrupolar anisotropy ($Q_\sigma$, $\eta_\sigma$), as well as reduced chemical shift anisotropy and asymmetry parameter ($\delta_{i\sigma}$ $\eta_\sigma$) together with the relative quadrupolar and CSA tensor orientations described by the Euler angles ($\alpha$, $\beta$, $\gamma$) were extracted by numerical simulations of the spinning sideband patterns using the SIMPSON software package. The best-fit values are indicated in Table 1.

In this work, we define the chemical shift parameters according to the Haeberlen–Mehring–Spiess convention, where $|\delta_{xx} - \delta_{yy}| \leq |\delta_{zz} - \delta_{xx}| \leq |\delta_{yy} - \delta_{zz}|$ and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\eta_\sigma = (\delta_{yy} - \delta_{zz})/(\delta_{xx} - \delta_{yy} - \delta_{zz} - \delta_{iso})$. In this representation, $\delta_{i\sigma}$ corresponds to the principal components of the chemical shift tensor. The EFG tensor parameters are $Q_\sigma = eQVV/h$ and $\eta_\sigma = (VV_{xx} - V_{yy})/V_{zz}$, where $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$, $e$ is the electronic charge, and $h$ is the Planck’s constant.

### Results

$^{51}$V isotropic chemical shifts

Vanadium(V) complexes of different o-dioxolene (1–3) with solution chemical shifts ranging from −171 to +350 ppm have been prepared (Fig. 1). The solid-state $^{51}$V NMR spectra were recorded at different MAS frequencies and are shown in Fig. 3. The spectra were simulated, and the data and simulations are compared in Fig. 4. Compound 1, containing a redox-active o-dioxolene ligand, is coordinated to the oxovanadium(V)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solid state</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(ensal)Cat (1)</td>
<td>$C_4 = 5.2 \pm 0.1$, $\eta_\sigma = 1.95$</td>
<td>$191 \pm 195$ (this work)</td>
</tr>
<tr>
<td>VO(ensal)DTBCat (2)</td>
<td>$C_4 = 5.1 \pm 0.2$, $\eta_\sigma = 1.95$</td>
<td>$345 \pm 350$ (this work)</td>
</tr>
<tr>
<td>VO(ensal)TBCat (3)</td>
<td>$C_4 = 5.8 \pm 0.1$, $\eta_\sigma = 1.95$</td>
<td>$-190 \pm 171$ (this work)</td>
</tr>
</tbody>
</table>
center in its bidentate dianionic mode of coordination, giving rise to a downfield chemical shift of 195 ppm (Table 1). Introduction of two \(t\)-butyl substituents to the catechol ring, compound 2, results in a further downfield chemical shift (350 ppm, Table 1). However, presence of electron-withdrawing bromo groups on the catechol ring gives rise to an upfield shift (~171 ppm, compound 3). The solid-state \(^{51}\text{V}\) isotropic chemical shifts along with other solid-state NMR parameters are listed in Table 1. Both solution and solid-state isotropic chemical shifts reveal the pronounced effects of the ancillary ligands on the electronic structure of the complexes under study as manifested by their magnetic shielding. We note that except for compound 3, the isotropic chemical shifts for these compounds fall outside of the range of shifts observed for the majority of vanadium(V) complexes, due to the non-innocent nature of the ligands.\(^{33,57}\)

Interestingly, the isotropic solution shifts differ significantly from the corresponding chemical shifts obtained from the solid-state measurements. This is particularly clearly illustrated when the solution \(^{51}\text{V}\) NMR chemical shifts are plotted as a function of the solid-state shifts, as shown in Fig. 5. The linear correlation between the shifts with a slope of 1.0 was previously reported for the hshed complexes, but for this ensal series a significant offset from other known compounds is observed.\(^{33}\) (We also note that there is a ~435 ppm difference between the observed chemical shift trend lines, which happens to be the chemical shift of the secondary reference SJZ0032 with respect to VOCl\(_3\);\(^1\) we have verified that this difference is coincidental and not a result of misreferencing.) In order to further explore this observation, we recorded solution NMR spectra of compounds 1–3 dissolved in several solvents including DMSO and acetonitrile, at different concentrations. Dissolution of complexes 1 and 2 in acetonitrile yielded spectra in accord with previous reports.\(^{57}\) A single species was detected for VO(ensal)Cat (1) in acetonitrile at the concentration range of 0.5–10 mM, while VO(ensal)DTBCat (2) formed one additional minor species above 10 mM, and VO(ensal)TBCat
Discussion

This work expands the range of vanadium(v) complexes whose electronic structure has been examined using $^{51}$V solid-state NMR spectroscopy. To date, solid-state NMR analyses of vanadium coordination compounds containing non-innocent ligands remain quite scarce, and together with our recent report, the current investigation adds to the body of knowledge of the NMR properties of such complexes. This set of six-coordinate complexes under investigation was found to have considerably greater quadrupolar coupling constants than the structurally related vanadium(v)-o-dioxolene complexes with hshed ligand. Furthermore, changes in the catecholate ligand give rise to variations in the isotropic chemical shifts, which as we showed recently is proportional to the changes in the complex’s HOMO–LUMO gap. In the absence of a three-dimensional structure, we cannot conduct quantum chemical calculations of the electronic structure for these compounds. However, on the basis of our previous work on compounds where structural information is available and we have pursued DFT-based calculations of NMR parameters and of electronic structure, the solid-state $^{51}$V NMR results for the ensal complexes under investigation here are consistent with (a) an increased HOMO–LUMO gap and (b) a decrease in the HOMO level compared to the hshed complexes. These findings are schematically illustrated in Fig. 6.

In the current series of compounds, the $C_Q$ variations are very modest despite the profound differences in the nature of the o-dioxolene ligand. These differences in the nature of the ligand result in dramatic variation in the isotropic chemical shifts across the current series of compounds. No immediately obvious trends emerged that would relate the chemical shift anisotropy parameters ($\delta_\alpha$ and $\eta_\sigma$) and the nature of the catecholate ligand, although dramatic variations were observed in the principal components of the corresponding CSA tensors ($\delta_{11}$, $\delta_{22}$, and $\delta_{33}$). These observations indicate that these parameters are more sensitive to the electronic components contributed by the ancillary ligand and, as a

![Fig. 6 Schematic representation of proposed energy differences in HOMO and LUMO for redox-active “non-innocent” vanadium(v) compounds containing ensal or hshed co-ligands. As reference, vanadium(v) complex with the HOMO–LUMO gap for redox-inactive “innocent” ligand is shown.](image)
result, are not sensitive to changes in the o-dioxolene ligand. Alkylation of the coordinating NH₂ group in the ancillary ligand endows this moiety with significantly more electron density and could be the dominant factor determining the variations in the CSA parameters.

We do not currently understand the origins of the differences between the isotropic solution and solid-state chemical shifts. In the past, our studies have always yielded an agreement between the solution and solid-state shifts of the compounds of different classes.1,15,33–36 Specifically, the series of compounds with lashed as ancillary ligand yielded results in which the solution and solid state were in reasonable agreement.33 Accordingly, it was not expected that the removal of an alkyl group on the coordinating amine group would have such dramatic effects on the series of chemical shifts. Although some minor changes and fluctuations in the shifts could be expected, the dramatic deviation of the chemical shifts upon complexation with electron-rich and electron-poor o-dioxolene derivatives is surprising and contrary to the behavior observed in compounds formed by the ancillary ligand enol. Information on other series of these non-innocent complexes is important to begin to understand the determinants of the electronic properties in these molecules.

The difference between the solid-state ⁵¹V NMR chemical shift of the solid-state material and the solution shift of the dissolved compound may be observed because of the interactions in solution. Few detailed studies in aqueous solution of these types of compounds exist.6,59–64 Part of the problem is the limited solubility of vanadium(v)-o-dioxolene complexes in water because of their hydrophobic ligands.65–69 Many vanadium complexes are known to hydrolyze or to undergo redox reactions in aqueous solutions62,70,71 or to undergo intramolecular ligand exchange processes.59,61,72 Other systems have also been documented where decomposition of the complexes results in new vanadium(v) species.71,73,74 These literature precedents support the possibility that the observed deviations between the solid-state and the solution chemical shifts can arise because of reactions taking place in solution.

A large difference in the chemical shifts both in solution and in the solid state has been previously observed in several classes of vanadium alkoxides and hydroxylamido oxovanadium(v) dipicolinate complexes.1,36,75 Solution ⁵¹V NMR spectroscopy documents structural changes that take place after dissolution of the solid matrix. The hydroxylamido complexes with the general formula VO(dipic)(ONR₁R₂)(H₂O) show a chemical shift change up to ~80 ppm upon substitution of the protons on the parent hydroxylamine by alkyl groups.36 In such systems, solid-state ⁵¹V NMR could give us different results. In addition, it has been documented in the literature that the solid-state isotropic chemical shift for VO(OCH₃)₃ is about 150 ppm off from its solution value.75 This difference is readily explained by the different structures in both states. In the solid state, VO(OCH₃)₃ is a dimeric unit in a polymeric network as documented in its crystal structure with a six-coordinate vanadium atom. In solution, VO(OCH₃)₃ associates with coordinating solvents to form a five-coordinate adduct.75 Similarly, for VO(OCH₃CH₂Cl)₃, the crystal structure reported by Rehder et al.63 shows the dinuclear pentacoordinate oxovanadium(v) complex. In solution, the dinuclear complex dissociates to form a five-coordinate adduct with a chemical shift 105 ppm further downfield with respect to the solid-state shift.73 Recently, we have reported more modest discrepancies between solution and solid-state chemical shifts attributed to solvent molecules such as DMSO and THF interacting with the vanadium atom in solution.5

The question of how much a compound changes from solid state to solution could be investigated using a combined experimental-theoretical approach encompassing theoretical quantum chemical analysis of the chemical shifts. However, such studies generally require that the materials have been characterized by single crystal X-ray diffraction. To date, most of these compounds under study are powders that resist crystallization and thus preclude detailed structural analysis. Therefore, in the absence of the X-ray structural details, access to the solid-state ⁵¹V NMR chemical shifts is important and provides insight into the electronic properties of these complexes, not otherwise accessible. The upfield shift for the solution ⁵¹V NMR signals or, conversely, the downfield shift for the solid-state ⁵¹V NMR indicates either a dramatic solvent effect or a significant change in the electronic structure at the vanadium center.

The studies presented here demonstrate the sensitivity of the anisotropic NMR parameters to both the variations in the ancillary ligand and the catecholate environment and thus the electronic structure in the vicinity of the metal. Importantly, the results for the series of complexes investigated provide us with the observations that both the chemical shift anisotropies and isotropic shifts reflect the electronic structure of the complex. The current work inspires further solid-state NMR investigations of catecholate complexes with a broader range of ancillary ligands to establish general principles affecting the electronic properties and determining the ⁵¹V NMR chemical shifts in this class of redox-active compounds.

Conclusions and future outlook

Our study demonstrates that for the vanadium(v) complexes containing N-(salicyldiene)aminato)ethylenediamine ligand, enol, ⁵¹V chemical shift anisotropy tensor parameters are very sensitive to the nature of the ancillary o-dioxolene ligand and provide information on the variations in the electronic structure in the vicinity of the metal site. These findings expand our prior observations concerning the relationships between the electronic structure and ⁵¹V NMR observables for structurally related sets of lashed-substituted compounds with non-innocent ligands33 as well as for a wide range of other vanadium compounds.1,15,43–49,41–44 Furthermore, the current investigations report on the changes in the chemistry of the compounds because these systems contain the parameters for the unsubstituted ancillary ligand. As a result, one would expect that in these systems the distribution of the electron density between vanadium and the ancillary ligand...
systematically changes with the ligand substitution. It is interesting that these differences in the ligand substitution give rise to pronounced changes in electronic properties of the complexes, which in turn affect the chemistry and render these compounds much more difficult to synthesize and characterize. On the basis of our previous work with related compounds, we posit that changes in the chemical shifts provide information on the changes in the HOMO–LUMO gap in the current series of compounds as well.

The geometric and electronic structure of vanadium(v) coordination complexes can be effectively inferred from experimental $^{51}$V solid-state NMR measurements, which are particularly informative when coupled with quantum chemical analysis of the NMR observables. Even though quantum chemical calculations for redox-active vanadium(v) complexes remain challenging and are beyond the scope of the current manuscript, the recent work by Buhl and colleagues established the methodology needed for accurate calculation of $^{51}$V solid-state NMR parameters. Therefore, continued developments of experimental and computational methodologies for vanadium systems containing diverse types of ligands will provide an alternative method for the description of the electronic structure of these complexes, particularly in the absence of X-ray crystal structures.

Acknowledgements

This work was supported by the National Science Foundation (CHE-0750079 to T.P. and D.C.C. and CHE-0628260 to D.C.C.). T.P. acknowledges partial support of this work by the National Institutes of Health (grant 8P30GM103519-03 from NIGMS and 5P30RR031160-03 from NCRR).

Notes and references
