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Effect of Ancillary Ligand on Electronic Structure as Probed by ^{51}V Solid-State NMR Spectroscopy for Vanadium-*o*-Dioxolene Complexes

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Abstract

A series of vanadium(V) complexes with *o*-dioxolene (catecholato) ligands and an ancillary ligand, (*N*-(salicylideneamino)ethylenediamine) (hensal), were investigated using ^{51}V solid-state magic angle spinning NMR spectroscopy (^{51}V MAS NMR) to assess the local environment of the 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*₂shed) 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* 50 (2011) 9794). Our results show that the modification of the ancillary ligand does not impact the observed trend between complexes ranging from catechols with electron rich to electron poor substituents. However, the ancillary ligand does impact 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 (δ_σ and η_σ) with the variation in the catechol. The electronic changes in the coordination environment of the vanadium can be described 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 characterizations 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

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electronic properties of the systems under study.¹ 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 such as catechol deoxygenases⁵ and haloperoxidases,^{6–11} and as antidiabetic agents.^{12–17} A number of vanadium(V) compounds have been used in oxidation reactions including asymmetric reactions.^{18–23} Catalysts can be a range of coordination complexes or simple vanadium oxides. Specific examples of vanadium-catalyzed reactions include aerobic cleavage of C-C and C-H bonds,^{24, 25} non-oxidative C-O bond breaking,²⁶ oxo-transfer reaction,^{27, 28} and selective epoxidation of olefins.^{20, 29} A recent interesting application of vanadium-based catalysts was reported with vanadium(V)-dipic for bio-fuels demonstrating the versatility of this metal in oxidation state five.^{27, 30} Information on the coordination chemistry and electronic structure can be used successfully to develop and fine tune the properties of vanadium based catalysts.^{31, 32} In this manuscript, we build on the body of previous work^{1, 15, 33–40} which established ⁵¹V solid-state NMR spectroscopy as a sensitive tool for characterization of the electronic properties of vanadium(V) systems. Since vanadium complexes generally have ⁵¹V NMR chemical shifts in the range of –300 ppm to –700 ppm³³ 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 ⁵¹V solid-state magic angle spinning NMR spectroscopy (⁵¹V MAS NMR) can assess the local environment of the vanadium(V) and provide detailed insights on its interaction with ligands.^{1, 15, 33–39} A hybrid ⁵¹V SSNMR / Density Functional Theory (DFT) approach provides highly sensitive information regarding electronic structure and geometry not only in coordination complexes^{1, 15, 33–36, 41–44} but also in large proteins, such-as vanadium-containing haloperoxidases.³⁷ This sensitivity arises from the fact that ⁵¹V is a half-integer quadrupolar nucleus ($I=7/2$). Its electric field gradient (EFG) and the chemical shift anisotropy (CSA) tensors inform on the local geometry and electronic structure of the metal site and extend solution-based ⁵¹V NMR isotropic chemical shift (δ) information.^{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 the vanadium and the ligand was described in detail.^{15, 33–36} Most vanadium compounds investigated previously have chemical shifts from –300 to –700 ppm. In the case of two eight-coordinated nonoxovanadium(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 ⁵¹V EFG and CSA tensors.³⁴ In addition, ⁵¹V SSNMR parameters were effectively used to describe the electronic properties of vanadium complexes containing *o*-dioxolene ligand and were reported to provide direct information regarding the changes in the HOMO-LUMO gap.³³

The *o*-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.⁴⁶ 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(III), Cu(II), and Mn(II), which are found in many proteins and inorganic catalysts, and which exhibit diverse functions.^{47–53}

For vanadium in oxidation state five, the common coordination geometries are six-coordinate (octahedral) and five-coordinate (distorted square pyramidal and trigonal bipyramidal).⁵⁴ The series of vanadium(V) compounds under investigation in this work, Figure 1, are related to the previously structurally characterized vanadium-*o*-dioxolene complex (Figure 2), where the vanadium is observed in a distorted octahedral geometry. This class of ternary complexes defined in Figure 1 and 2 consists of an oxovanadium(V), an *o*-dioxolene ligand, and a Schiff-base-type ancillary ligand abbreviated hshed. In these complexes, hshed uses three of the four coordinating moieties forming *o*-dioxolene complexes with vanadium, and readily undergoes ligand-to-metal charge transfer (LMCT).³³ Indeed, this is apparent by considering the solution ⁵¹V NMR chemical shifts of these compounds. Vanadium complexes generally have ⁵¹V 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 (δ_{iso}) and in solution (δ) suggesting the same structure of these complex in both phases and is important to the interpretation of the parameters shown here.³³

The complexes shown in Figure 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(V) compounds containing substituted ancillary ligand, hshed, extended the linear relationships between isotropic chemical shifts in solution (δ) and in the solid state (δ_{iso}).³³ Interestingly, discrepancies between experimental and calculated solid-state NMR parameters were observed,³³ however most recent work by M. Bühl and colleagues demonstrated that excellent agreement between experiment and theory is achieved when adaptive quantum mechanics/molecular mechanics (QM/MM) treatment is used in order to accurately recapitulate long-range electrostatic effects.⁵⁵ In light of these recent theoretical developments enabling accurate computation of ⁵¹V 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 ⁵¹V NMR observables, which in turn will enable *de novo* 3D structure determination of noncrystalline vanadium(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 an oxovanadium(V), an *o*-dioxolene and ensal, and therefore are likely to be structurally similar to the corresponding series with h₂shed (*N*-salicylidene-*N'*-(2-hydroxyethyl)ethylenediamine). Considering that the ensal ligand contains a terminal amine group this series represent the base-structure for the hshed series previously reported.³³ The studies here thus represent ⁵¹V SSNMR data and analysis on a series of vanadium(V) complexes containing unsubstituted ancillary ligand 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,⁵⁶ (99.99 %), salicylaldehyde (98 %), ethylenediamine (99 %), catechol (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

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^{56, 57} by first preparing the VO₂ensal precursor. Samples purity has been checked by solution ¹H NMR spectroscopy and were in agreement with literature reports.

Solid-state NMR spectroscopy

All solid-state NMR spectra were acquired on a 9.4 T wide bore Tecmag Discovery spectrometer operating at Larmor frequencies of 400.2 (¹H) and 105.2 (⁵¹V) 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 Tecmag MAS controller. The temperature was set to +25 °C, and was controlled to ± 1 degrees by a Varian temperature controller.

The magic angle was set by maximizing the number of rotational echoes observed in the ²³Na NMR free-induction decay of solid NaNO₃. 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 8,192 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; 4) 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.¹ The solid-state NMR parameters, namely ⁵¹V quadrupolar coupling constant and quadrupolar anisotropy (*C_Q*, *η_Q*) as well as reduced chemical shift anisotropy and asymmetry parameter (*δ_σ*, *η_σ*) together with the relative quadrupolar and CSA tensor orientations described by the Euler angles (*α*, *β*, *γ*) were extracted by numerical simulations of the spinning sideband patterns using SIMPSON⁵⁸ 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,³⁷ where $|\delta_{xx} - \delta_{iso}|$, $|\delta_{yy} - \delta_{iso}|$, $|\delta_{zz} - \delta_{iso}|$ and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_{\sigma} = \delta_{zz} - \delta_{iso}$, $\eta_{\sigma} = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$. In this representation, δ_{ii} corresponds to the principal components of the chemical shift tensor. The EFG tensor parameters are $C_Q = eQV_{ZZ}/h$ and $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$ where $|V_{ZZ}|$, $|V_{YY}|$, $|V_{XX}|$, *e* is the electronic charge and *h* is the Planck's constant.

Results

⁵¹V Isotropic Chemical Shifts

Vanadium(V) complexes of different *o*-dioxolenes (**1–3**) with solution chemical shifts ranging from –171 to +350 ppm have been prepared, Figure 1. The solid-state ⁵¹V NMR spectra were recorded at different MAS frequencies and are shown in Figure 3. The spectra were simulated, and the data and simulations are compared in Figure 4. Compound **1**, containing a redox-active *o*-dioxolene ligand is coordinated to the oxovanadium(V) 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}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}V NMR chemical shifts are plotted as a function of the solid-state shifts, as shown in Figure 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 $\text{VO}(\text{ensal})\text{Cat}$ (**1**) in acetonitrile at the concentration in the range of 0.5 – 10 mM, while $\text{VO}(\text{ensal})\text{DTBCat}$ (**2**) formed one additional minor species above 10 mM, and $\text{VO}(\text{ensal})\text{TBCat}$ (**3**) showed two minor species at all concentrations studied. We note that considerable deviations between solution and solid-state NMR isotropic chemical shifts were previously detected for a number of vanadium (V) coordination compounds, and these differences were attributed to the changes in the ligand coordination sphere due to solvation.¹ While the differences observed in this work may, therefore, not be surprising *per se* (see below), it is the magnitude of these deviations that is somewhat puzzling. We speculate that this unusual behaviour is caused by the redox activity of the complexes under study.

^{51}V Quadrupolar and Chemical Shift Anisotropy Parameters

To define the components of the quadrupolar and chemical shift anisotropy tensors, we have collected ^{51}V MAS NMR spectra for the compounds (**1–3**) under study, at three MAS frequencies. The experimental spectra are shown in Figure 3. From these spectra, we have extracted the eight independent NMR observables characterizing each tensor (C_Q , η_Q , δ_σ , η_σ , δ_{iso}) and their relative orientations (α , β , γ), by numerical SIMPSON simulations. Figure 3 illustrates examples of the best-fit simulated spectra for each of the three complexes. As summarized in Table 1, the ^{51}V MAS NMR investigation reveals that vanadium(V)-*o*-dioxolene complexes (**1–3**) under study exhibit quadrupolar coupling constants in a tight range of 5.1 – 5.8 MHz, and the quadrupolar anisotropy parameters are close to 1.0. The reduced chemical shift anisotropies range from 323 to 485 ppm.

Both the quadrupolar coupling constants and the reduced chemical shift anisotropies are found to be considerably higher than in the series of hshed-containing complexes (parent structure shown in Figure 2) reported recently,³³ where we observed C_Q in the range of 3.4 – 4.2 MHz, and δ_σ in the range of 437 – −243 ppm. The isotropic chemical shifts vary dramatically and, notably, their magnitude and sign can be correlated empirically to the electron-withdrawing ability of the *o*-dioxolene ligand (see above). The variation in the reduced chemical shift anisotropy is much more modest, and there is no clear correlation of

its magnitude with the nature of the substituent on the catechol ring. The analysis of the principal components of the CSA tensor, δ_{11} , δ_{22} , and δ_{33} indicates that the individual components vary dramatically (resulting in the largely different isotropic chemical shifts), but reveals no immediately obvious trends that would enable simple empirical correlations to be established with respect to the nature of the substituent.

In summary, these results indicate that for the series of vanadium (V) *o*-dioxolene complexes (**1–3**) under investigation the isotropic chemical shifts correlate with the substituent changes on the catechol fragment. The chemical shifts are sensitive to the HOMO-LUMO gap size, and for this series of complexes the changes are observed as the substituents are added. Quantum chemical calculations could confirm these conclusions through a detailed analysis of individual orbital contributions; however, such analysis must await access to X-ray structures of the compounds under study.

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 report³³ 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.³³ 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.³³ In the absence of three-dimensional structure, we cannot conduct quantum chemical calculations of 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 compare to the hshed complexes. These findings are schematically illustrated in Figure 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 (δ_Q and η_Q) and the nature of the catecholate ligand, although dramatic variations were observed in the principal components of the corresponding CSA tensors (δ_{11} , δ_{22} , and δ_{33}). These observations indicate that these parameters are more sensitive to the electronic components contributed by the ancillary ligand, and as a result are not sensitive to changes in the *o*-dioxolene ligand. Alkylation of the coordinating NH_2 group in the ancillary ligand empowers 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 hshed 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 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 ensal. 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 ^{51}V 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 solutions,^{62, 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 previously been observed in several classes of vanadium alkoxides and hydroxylamido oxovanadium(V) dipicolinate complexes.^{1, 36, 75} Solution ^{51}V NMR spectroscopy documents structural changes that take place after dissolution of the solid matrix. The hydroxylamido complexes with the general formula $\text{VO}(\text{dipic})(\text{ONR}_1\text{R}_2)(\text{H}_2\text{O})$ 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 ^{51}V NMR could give us different results. In addition, it has been documented in the literature that the solid-state isotropic chemical shift for $\text{VO}(\text{OCH}_3)_3$ 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, $\text{VO}(\text{OCH}_3)_3$ is a dimeric unit in a polymeric network as documented in its crystal structure with a six coordinate vanadium atom. In solution, $\text{VO}(\text{OCH}_3)_3$ associates with coordinating solvents to form a five-coordinate adduct.⁷⁵ Similarly, for $\text{VO}(\text{OCH}_2\text{CH}_2\text{Cl})_3$, 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.⁷⁵ 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.¹

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 ^{51}V NMR chemical shifts is important, and provides insight into the electronic properties of these complexes, not otherwise accessible. The upfield shift for the solution ^{51}V NMR signals or conversely the downfield shift for the solid-state ^{51}V 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 broader range of ancillary ligands, to establish general principles affecting the electronic properties and determining the ^{51}V 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*-(salicylideneaminato)ethylenediamine ligand, *ensal*, ^{51}V chemical shift anisotropy tensor parameters are very sensitive to the nature of the ancillary *o*-dioxolene ligand, and report 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 ^{51}V NMR observables for structurally related sets of hshed-substituted compounds with non-innocent ligands³³ as well as for a wide range of other vanadium compounds.^{1, 15, 34–39, 41–44} Furthermore, the current investigations report on the changes in the chemistry of the compounds because these systems contain the parameters for 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 impact the chemistry and render these compounds much more difficult to synthesize and characterize. On the basis of our previous work with related compounds,⁴⁰ we posit that changes in the chemical shifts report 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 Bühl and colleagues established the methodology needed for accurate calculation of ^{51}V solid-state NMR parameters.⁵⁵ 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.

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$R_1, R_2 = H,$	1
$R_1 = C(CH_3)_3, R_2 = H$	2
$R_1, R_2 = Br$	3

Figure 1.
Molecular structures of the three vanadium (V) compounds under study: VO(ensal)Cat (**1**), VO(ensal)DTBCat (**2**), and VO(ensal)TBCat (**3**).

Figure 2. Molecular structure of vanadium(V)-*o*-dioxolene compound ³³ structurally related to the three vanadium compounds under study.

Figure 3. ^{51}V MAS NMR spectra of the three compounds under investigation: A) VO(enSAL)Cat (**1**); B) VO(enSAL)DTBCat (**2**); and C) VO(enSAL)TBCat (**3**). The spectra were acquired at the MAS frequency of 13 kHz (top), 17 kHz (middle), and 20 kHz (bottom).

Figure 4.

Experimental (top) and simulated (bottom) ^{51}V MAS NMR spectra of the three compounds under investigation: A) VO(enSAL)Cat (**1**) at $\omega_r = 13$ kHz; B) VO(enSAL)DTBCat (**2**) at $\omega_r = 17$ kHz; and C) VO(enSAL)TBCat (**3**) at $\omega_r = 17$ kHz. The best-fit parameters are indicated in Table 1.

Figure 5.

A plot of the solid state ^{51}V NMR isotropic chemical shifts versus solution ^{51}V NMR chemical shifts for vanadium(V) compounds reported (red line). Blue line represents the corresponding relationship for compounds (1–3). The corresponding vanadium(V) compounds with hshed co-ligand are indicated by green squares.

Figure 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.

Table 1
Experimental ^{51}V NMR parameters for six-coordinate vanadium(V)-*o*-dioxolene compounds (**1** – **3**).

Compound	Solid state										Solution	
	C_Q MHz	η_Q ± 0.05	δ_{iso} ppm ± 0.5	δ_f ppm ± 5	η_σ ± 0.1	$\delta_{11'}$ ppm ± 5	$\delta_{22'}$ ppm ± 5	$\delta_{33'}$ ppm ± 5	$\alpha/$ degree ± 10	$\beta/$ degree ± 15	$\gamma/$ degree ± 30	δ_{iso} ppm
VO(ensal)Cat (1)	5.2 ± 0.1	0.87	-120.5	323	0.68	202.5	-172.2	-391.8	22	0	0	191^{57} 195 (this work)
VO(ensal)DTBCat (2)	5.1 ± 0.2	1.0	-16.3	425	0.75	408.7	-69.4	-388.2	0	0	0	345^{57} 350 (this work)
VO(ensal)TBCat (3)	5.8 ± 0.1	0.95	-558.3	485	0.25	-73.3	-740.2	-861.4	0	0	0	-190^{57} -171 (this work)