# Characterization of Non-Innocent Metal Complexes Using Solid-State NMR Spectroscopy: *o*-Dioxolene Vanadium Complexes

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## Abstract

[51]V solid-state NMR (SSNMR) studies of a series of non-innocent vanadium(V) catechol complexes have been conducted to evaluate the possibility that [51]V NMR observables, quadrupolar and chemical shift anisotropies, and electronic structures of such compounds can be used to characterize these compounds. The vanadium(V) catechol complexes described in these studies have relatively small quadrupolar coupling constants, which cover a surprisingly small range from 3.4 to 4.2 MHz. On the other hand, isotropic [51]V NMR chemical shifts cover a wide range from −200 ppm to 400 ppm in solution and from −219 to 530 ppm in the solid state. A linear correlation of [51]V NMR isotropic solution and solid-state chemical shifts of complexes containing non-innocent ligands is observed. These experimental results provide the information needed for the application of [51]V SSNMR spectroscopy in characterizing the electronic properties of a wide variety of vanadium-containing systems, and in particular those containing non-innocent ligands and that have chemical shifts outside the populated range of −300 ppm to −700 ppm. The studies presented in this report demonstrate that the small quadrupolar couplings covering a narrow range of values reflect the symmetric electronic charge distribution, which is also similar across these complexes. These quadrupolar interaction parameters alone are not sufficient to capture the rich electronic structure of these complexes. In contrast, the chemical shift anisotropy tensor elements accessible from [51]V SSNMR experiments are a highly sensitive probe of subtle differences in electronic distribution and orbital occupancy in these compounds. Quantum chemical (DFT) calculations of NMR parameters for [VO(hshed)(Cat)] yield [51]V CSA tensor in reasonable agreement with the experimental results, but surprisingly, the calculated quadrupolar coupling constant is significantly greater than the experimental value. The studies demonstrate that substitution of the catechol ligand with electron donating groups results in an increase in the HOMO-LUMO gap and can be directly followed by an upfield shift for the vanadium catechol complex. In contrast, substitution of the catechol ligand with electron withdrawing groups results in a decrease in the HOMO-LUMO gap and can directly be followed by a downfield shift for the complex. The vanadium catechol complexes were used in this work because the [51]V is a half-integer quadrupolar nucleus whose NMR observables are highly sensitive to the local

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environment. However, the results are general and could be extended to other redox active complexes that exhibit similar coordination chemistry as the vanadium catechol complexes.

## Introduction

The characterization of metal complexes containing redox active ligands also referred to as "non-innocent" can be particularly challenging because of the potential of ligand-to-metal charge transfer (LMCT) processes that can prevent unambiguous determination of the oxidation state of the coordinating metal ion.[1] Such redox active ligands are ubiquitous in biological chemistry where the ligand supporting a radical is abundant and plays a crucial role in the chemistry of metal complexes such as Fe-porphyrins,[2] Fe(III)-transferrin,[3] purple acid phosphatase,[4] Cu(II) in galactose oxidase[5] and Mn(II) in photosystem II.[6] A range of redox active ligands are $o$-quinone/semiquinone/catechol, dithiolene/ene-dithiolate, $O_2$(dioxygen)/$O_2^{\bullet-}$(superoxide)/$O_2^{2-}$ (peroxide), NO+(nitrosyl cation)/NO$^{\bullet}$ (nitric oxide radical)/NO$^-$ (nitroxide anion), and tyrosyl/tyrosilate.[1,7–11] The major method for characterization of metal complexes with redox active ligands in the solid state is X-ray crystallography.[9,10,12–15] Solution characterization is often done using electrochemistry, UV- vis spectroscopy and EPR spectroscopy.[8–10,15] Another characterization method used less frequently for such complexes in solution is multinuclear NMR spectroscopy.[16] Solid state methods commonly used include FTIR spectroscopy,[12,15,17] but a need exists for alternative characterization methods of these metal complexes with redox active ligands particularly in cases when the material is not crystalline. Solid-state NMR spectroscopy has been used for characterization of complexes containing any NMR active nucleus (e.g. [51]V) and is very informative with regard to the electronic properties of the complexes.[18–24]

Solid-state [51]V NMR spectroscopy (SSNMR) is a potent tool that provides important insights into the electronic structure of an active site(s) of vanadium-containing systems (i.e. proteins, bioinorganic solids, and inorganic catalysts).[25–46] [51]V is a half-integer quadrupolar nucleus (I=7/2). Its electric field gradient tensor (EFG) and the chemical shift anisotropy (CSA) tensor are much more sensitive reporters of the electronic structure of vanadium-containing materials than solution-based [51]V NMR isotropic chemical shifts.[26–38,47,48] The relationship between vanadium coordination environments and its [51]V SSNMR observables-quadrupolar and chemical shift anisotropy tensors– can be exploited to characterize the electronic properties of ternary vanadium complexes containing non-innocent ligands.[26,37,42,49–51]

One common class of non-innocent ligands is the $o$-dioxolene or also referred to as catechol ligand. Catechols coordinate as a neutral or anionic ligand with an (OO) motif and in a bidentate fashion, as catecholate dianion (electronic spin state $S$=0), as semiquinonato monoanions ($S$=1/2) or as a neutral $o$-benzoquinones ($S$=0).[9,13,15,52–59] Pierpont reported an equilibrium between $M^{n+1}(Cat^{2-})$ and $M^{n+}(SQ^-)$ where M is any 3d metal both in solution and in the solid state and these redox isomers are known as valence tautomers.[9] The electron transfer properties and valence tautomerism encouraged applications of these systems as data storage media and to sensor technology.[9,10] Low energy electronic transition have been reported from the excited state of $o$-dioxolene based chromophore to the semiconductor surfaces in numerous vital applications, including optoelectronics and solar cells.[60,61] Vanadium (oxidation state II to V) catechol complexes that have been reported thus far document the interesting and varied properties of these systems.[9,10,16,36,58]

A number of vanadium-catechol systems have been reported with interesting structural, electronic, reactivity, magnetic and spectroscopic properties.[13,15,62] [51]V NMR spectroscopy showed an unusual spread in the solution chemical shifts for a series of vanadium(V)-catechol complexes documenting that this method is sensitive to subtle changes in the

electronic structure of these complexes.[16] One vanadium-catechol compound, [(3,5-di-*tertiary*-butylcatecholato)-{*N*-(2-methylpyridine)-3-methoxysalicylideneaminato} oxovanadium(V)] (**SJZ00108**)[36] shown in Figure 1 has an unusual electronic environment which has been investigated by [51]V SSNMR spectroscopy. This complex has a [51]V isotropic chemical shift of 426 ppm and is outside of the chemical shift range generally observed for vanadium complexes (Figure 2). To build a general understanding of the NMR properties of catechol-based vanadium compounds and while basing these studies on the results of our earlier report, we have conducted [51]V SSNMR investigations of a series of known *o*-dioxolane-oxovanadium(V) complexes with (ONN & OO) ancillary ligand donor sets.

Normal and redox inactive (innocent) ligands are generally described as having a large energy gap between the HOMO and LUMO. Non-innocent ligands have a smaller energy gap as illustrated for comparison with the normal ligands in Figure 3. As shown recently for titanium (Ti) this energy gap for the non innocent ligands decrease upon complexation[61,63] and this is also illustrated in Figure 3. These considerations are not exclusive to simple solution Ti-complexes but extend to other metal-catechol complexes and surface systems. For example, changes in HOMO and LUMO energies were observed for catechol complexes formed on the interface of rutile $TiO_2(110)$; but in this case the shifts in orbital energies resulted in the orbitals are no longer at the HOMO-LUMO gap.[64] Changes in the electronic properties of these systems by substitution on the catechol moiety in catechol complexes with mononuclear Ti(IV) or $TiO_2$ nanoparticles were not found to be reflected in the reduction potential in these complexes.[65] V-catechol complexes in solution were, however, found to be sensitive to the subtle changes in electronic structure[16] and therefore excellent candidates to show the decrease previously reported in the HOMO-LUMO gap compared to the free catechol[66] also included in Figure 3. Substitution of the catechol-ligand with electron donating groups raises both the HOMO and LUMO compared to the free ligand. However, in the case of the t-Bu group the HOMO is raised more than the LUMO, and the HOMO-LUMO gap is decreased in the complex and this is illustrated in Figure 3. In contrast, substitution by bromo-substituents lowers the HOMO and the LUMO.[66] However, since the HOMO is lowered more than the LUMO the result is a net increase in the HOMO-LUMO gap[66] as shown in Figure 3. We propose that the electronic modifications that take place in the vanadium catechol complexes upon substitution can be observed directly in their [51]V NMR chemical shifts since the vanadium is sensitive to its electronic environment.

Quantum chemical calculations have also been used to predict the [51]V NMR parameters and/or the electronic structure of a wide range of vanadium-containing bioinorganic compounds[26–29,33,34,36,66,67] and proteins,[37,68–70] including vanadium complexes containing non-innocent ligands.[66] DFT calculations generally predict the NMR parameters accurately. However, when a ligand is non-innocent with large [51]V isotropic chemical shifts, the experimentally observed de-shielding is less well described.[66]

Herein, we present [51]V SSNMR studies of a series of vanadium(V)-catechol complexes (Figure 4) to test the hypothesis that SSNMR observables (i.e. quadrupolar and chemical shift anisotropy tensors) can effectively describe the electronic properties of the complexes with redox non-innocent ligands. We also performed quantum chemical characterization of one of these complexes and found limited agreement between values calculated and experimentally measured. Our experimental results were used to provide information needed for application of [51]V SSNMR parameters in characterizing the electronic properties of systems containing non-innocent ligands. Our findings also demonstrate that the observed quadrupolar couplings are relatively small and cover a narrow range of values reflecting symmetric electronic charge distribution. Therefore, these quadrupolar interaction parameters alone are not sufficient to define the electronic structure of these complexes. On the contrary, the chemical shift anisotropy tensor elements accessible from [51]V SSNMR

measurements are a highly sensitive probe of the subtle differences in the electronic distribution and orbital occupancy in these compounds. The vanadium catechol complexes were used in this because the $^{51}$V is a half-integer quadrupolar nucleus whose NMR observables are highly sensitive to the local environment. However, similar experiments with other NMR active metal nuclei could be used for characterization of other redox active complexes.

## Experimental Section

### Materials

Vanadyl acetylacetonate, [VO(acac)$_2$] (99.99 %), vanadyl sulfate hydrate, [VO(SO$_4$).H$_2$O], salicyldehyde (98 %), *N*-(2-hydroxyethyl)ethylenediamine (99 %), catechol (   99 %), tetrabromocatechol (96 %), 3,5-di-*tert*-butylcatechol (99 %), tetrachloro-*o*-quinone (97 %) were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from Fisher Scientific. All reagents were commercially available and used as received. Solvents were ACS grade and used as received. Figure 4 shows the structures of the compounds selected for this study. Compounds **1a**-**1c** are from the V$^V$O-hshed series while compound **2** (acetylacetonatotetrachlorocatecholatooxovanadium(V)) represents a V$^V$O-acac compound. By going from the V$^V$O-hshed series to compound **2** we are changing the type and also the denticity of the ancillary ligand.

### Abbreviations

Acac = 2,4-pentanedionate; hshed = *N*-salicylidenyl-*N*′-(2-hydroxyethyl)ethylenediamine; Cat = catechol; DTBCat = 3,5-di-tert-butylcatechol; TBCat = tetrabromocatechol; and TCCat = tetrachlorocatechol.

### Syntheses of Compounds

The compounds of the V$^V$O-hshed series (**1a**-**1c**) were prepared as described previously[16] by first preparing the [VO$_2$(hshed)]$_2$ precursor. The pentacoordinate acetylacetonatotetrachlorocatecholatooxovanadium(V) compound (**2**) was prepared using the method described by Galeffi et al.[57] Sample purities were checked by solution $^1$H NMR spectroscopy and were in agreement with previous reports.[16,57]

### Solution $^{51}$V NMR Spectroscopy

The solution $^{51}$V NMR spectra were acquired on a Varian INOVA-300 spectrometer (7.0 T) at 78.9 MHz. The $^{51}$V NMR spectra were generally acquired using single pulse excitation with a pulse angle of 60°, a spectral width of 83.6 kHz, and an acquisition time of 0.096 s. The $^{51}$V chemical shifts were obtained using an external reference of VOCl$_3$ ($\delta_{iso}$ = 0.0 ppm).

### $^{51}$V SSNMR Spectroscopy

Solid-state $^{51}$V NMR spectra were recorded on a 9.4 T Tecmag Discovery spectrometer ($^{51}$V Larmor frequency of 105.23 MHz). A 3.2 mm Varian T3 MAS probe was employed for all solid-state NMR experiments. Neat VOCl$_3$ was used as an external reference ($\delta_{iso}$ = 0.0 ppm).[71] This sample was also used to determine the 90° pulse width which was set to 4.0 $\mu$s ($\gamma B_1/2\pi \approx$ 62 kHz). Between 8.0 and 16.0 mg of sample was packed into a 3.2 mm thick-wall rotor. For each compound, $^{51}$V MAS SSNMR spectra were acquired at $\omega_r$ = 13, 17, and 20 kHz. The MAS frequency was controlled to within ±5 Hz by a Tecmag MAS controller. The temperature was calibrated for this probe at different MAS frequencies using a PbNO$_3$ temperature sensor,[34] and the actual temperature at the sample was 25 °C

maintained to within ±1 °C throughout the experiments using the Tecmag 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 a single pulse excitation experiment with a pulse width of 1.0 $\mu$s and a spectral width of 1.0 MHz. A recycle delay of 1 s was used for all experiments. A total of 8192 scans were acquired for each compound. The spectra were processed by MestReNova NMR data processing software with a Gaussian line broadening function of 300 Hz and baseline correction. The isotropic chemical shifts were determined by the analyses of the spectra collected at the different MAS frequencies. $^{51}$V chemical shift anisotropy ($\delta_\sigma$, $\eta_\sigma$) and quadrupolar ($C_Q$, $\eta_Q$) parameters as well as the relative tensor orientations described by the Euler angles ($\alpha$, $\beta$, $\gamma$) were extracted by numerical simulations of the spinning sideband patterns using SIMPSON[72] software package. The best-fit values are shown in Table 1.

In this work, the chemical shift parameters are defined such that $|\delta_{xx} - \delta_{iso}|$ $|\delta_{yy} - \delta_{iso}|$ $|\delta_{zz} - \delta_{iso}|$ and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_\sigma = \delta_{zz} - \delta_{iso}$, $\eta_\sigma = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$ according to the Haeberlen-Mehring-Spiess convention.[37] $\delta_{ii}$ denotes the principal components of the chemical shift tensor. The EFG 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 electron charge and $h$ is Planck's constant.

### Density Functional Theory calculations

Quantum chemical calculations for the structurally characterized VO(hshed)(Cat) complex (compound **1a**) were performed with Density Functional Theory in Gaussian03.[73] The $^{51}$V magnetic shielding and EFG tensors were computed using B3LYP functional and several basis sets (6-311+G, 6-311++G, TZV, TZVP, Wachters+f). Calculations were carried out using either the non-optimized X-ray geometry or geometry optimized structures at the same level of theory as the NMR parameter calculations, as specified in Table 2. The $^{51}$V chemical shifts are referenced with respect to VOCl$_3$ (0 ppm) whose absolute magnetic shielding tensor was calculated at the same level of theory with prior geometry optimization.

## Results

### $^{51}$V Solution NMR Spectroscopy

A number of oxovanadium(V)catecholato complexes with chemical shifts ranging from −200 to +400 ppm have been prepared (**1a** – **1c**, **2**), Figure 4. Compound **1a** contains a redox-active catechol ligand in a bidentate dianionic mode to the oxovanadium(V) center resulting in a downfield chemical shift of 221 ppm for this non-innocent complex, Table 1. Upon introducing *tert*-butyl groups to the catechol ring (**1b**), further downfield chemical shift (at 382 ppm) is observed (Table 1). Introducing electron withdrawing bromo-substituents on the catechol moiety (**1c**) results in an upfield shift (−145 ppm). The pentacoordinate complex **2** has a chemical shift of −215 ppm. From Figure 2 it is evident that these four compounds represent a chemical shift region not observed previously for the majority of vanadium(V) compounds.

### $^{51}$V Solid-State NMR (SSNMR) Spectroscopy

To further explore the electronic impact of these noninnocent ligands on the vanadium nucleus in compounds **1a**-**1c** and **2**, we performed $^{51}$V solid-state MAS NMR investigations. The $^{51}$V MAS NMR spectra of the four oxovanadium(V) -catecholato compounds (**1a**-**1c**, **2**) were acquired at 9.4 T using three spinning frequencies (13, 17, and 20 kHz). Figure 5 shows $^{51}$V NMR spectra of the four vanadium(V) catechol complexes (**1a**-**1c**, **2**) recorded at

the MAS frequency of 17 kHz. The chemical shift anisotropy and quadrupolar NMR parameters, as well as the relative orientation, were extracted by fitting the [51]V MAS spectra. The experimental and best-fit simulated spectra for compound **1a** acquired at MAS frequencies of 7, 13, 17, and 20 kHz are illustrated in Figure 6. The experimental and best-fit simulated spectra for compounds **1b**, **1c**, and **2** are presented in the Supporting Information. A summary of the SSNMR parameters obtained from these [51]V MAS NMR spectra is presented in Table 1.

Analysis of the results presented in Table 1 indicates that, quite surprisingly, the quadrupolar coupling constants for the four complexes are relatively small and cover a very narrow range of 3.4 – 4.2 MHz. On the other hand, a very wide [51]V isotropic chemical shift range is observed in these compounds and is similar to the solution NMR findings. Complex **1a** exhibits an isotropic chemical shift value at 58 ppm, complex **1b** at 531 ppm, **1c** at −1 ppm, and **2** at −219 ppm. These results show that the non-innocent characteristic of these complexes is reflected in their isotropic solid-state chemical shifts lying outside of the more common region of −300 to −700 ppm. Interestingly, the chemical shift anisotropy, $\delta_\sigma$, does not vary to as large extent as the isotropic shifts and is in the range of 243 to 437 ppm for these complexes. Analysis of the individual CSA tensor components, $\delta_{11}$, $\delta_{22}$, and $\delta_{33}$, indicates that all three tensor components vary dramatically with the series of complexes under investigation warranting further analysis of the individual orbital contributions to the corresponding magnetic shielding anisotropy tensors.

The isotropic chemical shifts for compounds **1a** - **1c**, **2** and other known vanadium(V) complexes were plotted as a function of solution chemical shifts (Figure 7).[26–38,49] The linear relationship shows that the expected correlation between solid state ($\delta_{iso}$) and solution isotropic chemical shifts ($\delta$) generally holds although significantly more scatter in the current data is observed for these non-innocent complexes.

## [51]V NMR Parameters of VO(hshed)(Cat) Complex (1a): Density Functional Theory

To understand the experimental [51]V solid-state NMR parameters we have conducted DFT calculations of the EFG and CSA tensors for the only structurally characterized compound from the current series under study, VO(hshed)(Cat) (compound **1a**). DFT calculations of the [51]V chemical shifts have already been reported for this compound.[66] However, the EFG tensor has not been computed and, furthermore, prior to our work only the isotropic solution chemical shift was determined. In Table 2 the results of the DFT calculations conducted at different levels of theory are summarized. Similar to the previous report,[66] the agreement between the experimental and calculated isotropic chemical shifts is rather poor for most of the methods used with the exception of the calculations performed with the Wachters+f basis set on vanadium atoms. In the latter case, the computed and experimental isotropic shifts agree remarkably well (within 3.7 ppm). Moreover, in this calculation, the principal components of the computed CSA tensor are also in reasonable agreement with the experiment ($\delta_\sigma$ agrees to within 90 ppm, and $\eta_\sigma$–to within 0.04) and the computed values are similar to the previously reported calculations conducted at a comparable level of theory.[66]

On the other hand, the calculated quadrupolar coupling constant deviates significantly from the experimental value of 4.0 MHz and for the different basis sets the $C_Q$ ranges between 7.0 and 10.7 MHz. When the Wachters+f basis set is used on vanadium atoms (this level of theory yields the best agreement between experiment and theory for the CSA tensor), $C_Q$ is 9.9 MHz. In our previous studies of multiple V(V) complexes with various mainly innocent ligands,[27–29,36,67] DFT calculations accurately predicted the experimentally observed quadrupolar coupling constants with the experimental/calculated $C_Q$ ratios (never exceeding

30% and typically within 5–15%). Therefore, the large discrepancies in $C_Q$ between the experiment and calculation observed in this study are surprising.

## Discussion

The potential of using magic angle spinning (MAS) [51]V SSNMR spectroscopy to evaluate the electronic structure of metal complexes with redox active ligands was investigated. Assessment of the interactions between vanadium(V) and a large number of ligands has been done using [51]V SSNMR spectroscopy.[27–29,36,37,67] [51]V SSNMR analysis has provided detailed electronic information regarding the active site of haloperoxidases and its catalytic mechanism.[37] Recently we found two nonoxovanadium(V) compounds with unusual solution chemical shifts (ca. −260 ppm) for which we gained additional insight from solid-state NMR analysis of [51]V EFG and CSA tensors.[67] Despite multiple reports, many important and ubiquitous classes of vanadium(V) compounds have not yet been examined by [51]V SSNMR spectroscopy. As demonstrated in this work, analysis of the [51]V SSNMR observables such as quadrupolar and chemical shift anisotropy provides fundamental information about the electronic structure of these systems as well as documenting a less traditional method for gaining information on these challenging systems.

The ternary vanadium(V) catechol complexes (**1a – 1c, 2**) examined in this work contain one coligand in addition to one catechol moiety and, as a result, have unusual electronic properties. Solution NMR spectroscopy of non-innocent vanadium complexes has been reported;[16] however, no generalized understanding on the relationships between different NMR parameters and the electronic structure in such compounds emerged to date. Bryliakov et al.[74] have shown how one can utilize [51]V NMR spectroscopy for characterizing the intermediates in vanadium-catalyzed oxidation reactions. Furthermore, a linear correlation has been demonstrated between isotropic chemical shifts in the solid state ($\delta_{iso}$) and in solution ($\delta$) of vanadium complexes formed from innocent ligands. The [51]V NMR chemical shifts for these complexes are in the range of −300 ppm to −700 ppm.[18,38,67] However, unusual electronic properties have been found in complexes formed from redox non-innocent ligands such as catechols[16,75] and hydroxylamines.[67] In these systems, strong de-shielding of the metal nucleus is observed with the chemical shift range dramatically extending outside the −300 ppm to −700 ppm region which is a manifestation of the significant changes in the electronic properties of these complexes.

According to the experimental results, the vanadium(V) catechol complexes (**1a – 1c, 2**) under investigation exhibit relatively small quadrupolar coupling constants in the range between 3.4 and 4.2 MHz. Similarly small quadrupolar coupling constants (ranging between 3.0 and 3.9 MHz) were observed in complexes of heptacoordinate geometry with dipicolinic acid ligands.[28] In comparison, hexacoordinate compounds typically show somewhat larger quadrupolar coupling constants, in the range of 3.0–6.3 MHz.[27,33,34,36,38] Pentacoordinate and octacoordinate complexes typically exhibit even greater quadrupolar coupling constants, 4.3–8.3 MHz.[27,33,34,36,38,67] In vanadium haloperoxidases, quadrupolar coupling constants of the vanadium site are even larger. In the resting state of vanadium chloroperoxidase (VCPO) at pH 8.0, $C_Q$ = 10.5 MHz[37] while $C_Q$ ranges between 13 and 17 MHz in the VCPO resting state at pH 6.3 and in its two mutants.(S. Bolte, K. Ooms, R. Renirie, R. Wever, and T. Polenova, unpublished results) Therefore, the experimental results documenting small similar quadrupolar coupling constants in catechol complexes are somewhat surprising in light of the fact that the coordination geometries between **1a-1c** and **2** differ; **1a-1c** are hexacoordinate while **2** is a pentacoordinate complex. We also note that, surprisingly, the DFT calculations predict the quadrupolar coupling constant for compound **1a** to be much greater than the experimental value and ranging between 7.0 and 10.7 MHz depending on the basis set employed (see the Results section). The current experimental

results in conjunction with the reports cited above indicate that in the oxovanadium(V)-catecholato complexes under investigation the electronic charge distribution is unexpectedly similar and relatively symmetric across the series. The electronic charge distribution in oxovanadium(V)hydroxylamido complexes examined previously were similar[28] where quadrupolar interaction parameters were small but measurable by changing functionality on the ligands. On the contrary, the chemical shift anisotropy tensor elements as well as the isotropic chemical shifts in solution and in the solid state span a very broad range between most systems investigated and compound **SJZ00108**[36] (Figure 1). The unusual electronic properties in the vanadium(V) catechol complexes are therefore appropriately reflected in the observed chemical shifts (Figure 7).

Isotropic $^{51}$V NMR chemical shifts for the selected compounds cover a very broad range from −200 to 400 ppm in solution and from −219 to 530 ppm in the solid state. These experimental results provide the information needed for the application of $^{51}$V SSNMR parameters in characterizing the electronic properties of systems containing non-innocent ligands and that have chemical shifts outside the range of −300 ppm to −700 ppm where no data were available before this work (Figure 2). Solution and solid-state isotropic chemical shifts exhibit linear correlation for the compounds under study thereby extending the known linear correlation for vanadium complexes (Figure 7) and thus documenting that the solution and solid-state structure are the same. On the other hand, there is no relationship between isotropic chemical shift (either solution or solid state) and the chemical shift anisotropy, which is due to the fact that the individual CSA tensor values ($\delta_{11}$, $\delta_{22}$, and $\delta_{33}$) vary widely within this series of complexes (see Table 1). All of the CSA tensors are rhombic and it is also noteworthy that Euler angles describing the relative orientations of the CSA tensors with respect to the EFG tensors also vary within the series (except in **1c** and **2**, where both tensors are collinear).

The above variations in the $^{51}$V CSA parameters are not surprising because there are significant differences in the electronic properties within the series of complexes under study. To understand the nature of the contributions of the individual MOs to the CSA tensor and to the electronic charge distribution that defines the EFG tensor in these compounds, quantum chemical calculations of the NMR parameters were done of the structurally characterized complex is VO(hshed)(Cat) (compound **1a**). Our results discussed above and summarized in Table 2 indicate that while the experimental and calculated isotropic chemical shifts are in excellent agreement, the reduced anisotropy $\delta_{\sigma}$ is only predicted to within 90 ppm using Wachters+f basis set on vanadium. These findings are in line with the previous report where DFT calculations evaluated the chemical shifts of this and other vanadium catechol complexes.[66] This limited agreement between the experimental and theoretical chemical shifts in $^{51}$V(V) complexes with non-innocent ligands has been attributed to several possible factors:[66] i) that the paramagnetic contributions in the closed-shell wavefunctions are severely underestimated; ii) that a temperature-dependent paramagnetic term arises from non-zero spin density at the metal due to the mixing of V(IV)-semiquinone configurations into the electronic ground state. In addition, the contributions of the frontier molecular orbitals (HOMO and LUMO) in VO(hshed)(Cat) to the $^{51}$V magnetic shieldings were analyzed and it was demonstrated, that the "non-innocent" ligand character resulting in strong deshielding is due not only to the bidentate catechol ligand but also to the coligand tridentate salicylideneaminato Schiff base,[66] which is consistent with an earlier work by Pecoraro.[16] The X-ray crystal structures for the other compounds are needed before detailed quantum chemical analyses of compounds **1b**, **1c**, and **2** other complexes based on their NMR parameters can be carried out.

Substitution of the catechol moiety induces small electronic changes in the complex and for vanadium catechol complexes should result in measurable differences in the HOMO-LUMO

gap as illustrated in Figure 3. How the electronic properties of the complexes are represented in their NMR spectra can be understood in a qualitative manner by an empirical analysis of the orbital contributions to chemical shifts. According to Ramsey's equation,[76] the shielding, $\sigma$, at the NMR active nucleus is defined as the sum of the generally positive diamagnetic ($\sigma_{dia}$) component and a paramagnetic ($\sigma_{para}$) component (Equation 1):

$$\sigma = \sigma_{dia} + \sigma_{para} \qquad (1)$$

For the majority of metal-containing complexes, the $\sigma_{dia}$ term is controlled by the core electrons and thus constant for a given metal nucleus.[16,28] The donor atoms of the ligand(s) and the valence molecular orbital(s) of the metal therefore do not contribute significantly to $\sigma_{dia}$, but instead tune the $\sigma_{para}$ term and thus the shielding.[77–80] The $\sigma_{para}$ term is dependent on the average mixing between the symmetry matched excited and ground states of the molecule in the presence of an applied magnetic field,[16,28] which in turn is determined by the relative energy separation ($\Delta E$) between the HOMO and the LUMO in these complexes. In fact, $\sigma_{para}$ varies inversely with $\Delta E$ and it also contains a $<r^{-3}>$ term indicating that only the orbitals near the metal center need to be considered.[16,28] The overlap of the ligand's valence $\pi$-orbitals and the metal's d-orbitals controls the degree of mixing between them, which eventually directs the electronic delocalization.[79–80] Indeed, the extent of ligand-to-metal charge transfer (LMCT) controls the electron density redistribution surrounding the central nucleus[16] and is readily modified using substitutions on the catechol.[66] The oxovanadium(V)catecholato complexes **1a – 1c** and **2** under study possess variable electronic properties of the nucleus, which can be probed by changes in Equation (1)'s $\sigma_{para}$ term.

The small energy gap between the HOMO and the LUMO in vanadium catechol complexes makes these systems ideally suited for the analysis of electronic effects using [51]V SSNMR spectroscopy. Electronic excitation in free catechol is attributed to the transition from $\pi$ HOMO to $\pi^*$ LUMO[61,66] but this is not observed in its vanadium complexes (Figure 3). In complexes, the predominantly vanadium-based LUMO is lower in energy than the ligand-based LUMO for **1a**-**1c**. The non-innocent nature of these ligands results in little separation between the HOMO and the LUMO in these complexes as well as in a few vanadium(V)-sulfur complexes.[26] This is in contrast to other vanadium(V) compounds without any redox-active ligand(s) which exhibit high excitation energy (Figure 3). Empirical molecular orbital methods were used for several heavy metals e.g. [51]V, [95]Mo and [183]W to examine the experimental observations made in solution state.[16,81] These calculations revealed that the small HOMO-LUMO gap and the effect on $\sigma_{para}$ could explain the downfield chemical shifts.[16,81] Complexes investigated previously have upfield chemical shifts (from –300 to –700 ppm) with the exception of **SJZ00108**[36] (Figure 1). Since insufficient information is available for compounds with chemical shifts outside the range –300 to –700 ppm and since the coordination of catechol gives rise to the [51]V NMR isotropic chemical shifts in the range between –145 and +382 ppm, we took the opportunity to explore the moderate-to-large deshielding at the vanadium center in the $o$-dioxolene complexes (**1a**–**1c**).

[51]V NMR isotropic chemical shifts as well as the principal components of the CSA tensor in compounds **1a**–**1c** changed drastically upon modification of the $o$-dioxolene ligand indicating considerable change of the HOMO-LUMO energy gap. Compound **1a**, $\delta$(solution) = 221 ppm/$\delta_{iso}$(solid) = 58 ppm, is halfway between that in the V(V) complexes examined previously and complex **SJZ00108**[36] (Figure 1). Introduction of tertiary butyl groups to the catechol ring (**1b**) results in electron redistribution within the complex increasing the energies of both HOMO and LUMO in **1b**. Since the HOMO increases more in energy than the LUMO, the HOMO-LUMO gap is decreased (Figure 3) which is directly

observed as a downfield shift for **1b** ($\delta$(solution) = 382 ppm/$\delta_{iso}$(solid) = 531 ppm). In contrast, as illustrated in Figure 3, bromo substitution on the catechol ring increases the HOMO-LUMO gap leading to an upfield shift in **1c** ($\delta$(solution) = −145 ppm/$\delta_{iso}$(solid) = −1 ppm). These three compounds are the first example of complexes with $^{51}$V chemical shifts in this range. Furthermore, the dramatic variation in chemical shifts with subtle substitutions on the ligand can be rationalized as the tuning of the HOMO-LUMO gap. In contrast, for other series of known V(V) complexes, little change in isotropic chemical shifts both in solution and in the solid state was observed upon substitution on the ligand.[27,28] In those cases local electronic environments surrounding the vanadium site are similar.

An alternative approach to obtain compounds with similar electronic properties is to combine a non-innocent ligand with another redox-inactive oxygen-rich co-ligand. By changing the supporting ligand donor sites from tridentate (ONN) (as in **1a-1c**) to a bidentate (OO) acetylacetonate (**2**), we are introducing an additional oxygen donor to the vanadium metal center. Changing the nitrogen atom from the ternary ligand (as in **1a**–**1c**) by a harder donor atom, oxygen, stabilizes the energy level of HOMO. This results in a larger HOMO and LUMO gap in compound (**2**), which is reflected in the observed upfield chemical shift (−215 ppm in solution and −219 ppm in the solid state, respectively). In contrast, replacing bromo- substituents by chloro- on catechol moiety has very little influence on $^{51}$V NMR chemical shifts as documented earlier by Pecoraro et al.[16] and consistent with minor changes in the HOMO-LUMO gap.

## Conclusions

We have examined a series of four vanadium(V) catechol complexes by $^{51}$V solid-state NMR spectroscopy. The objective with this work was to address whether SSNMR observables, quadrupolar and chemical shift anisotropy tensors, can effectively describe the electronic properties of the metal complexes containing redox non-innocent ligands and those isotropic chemical shifts are in the ranges not explored previously. Because $^{51}$V is a sensitive NMR-active nucleus, we used vanadium(V)-catechol complexes for these studies. In addition to the SSNMR studies, one complex that was characterized structurally by X-ray crystallography was also examined used DFT calculations of the NMR parameters.

We discovered that the $^{51}$V quadrupolar coupling constants are surprisingly small and similar, indicating a relatively symmetric electronic charge distribution across the series. To the contrary, the isotropic chemical shifts and the chemical shift anisotropy parameters cover a broad range and extend the scale of chemical shifts beyond the commonly observed values for vanadium complexes with normal ligands. The observed effects can be attributed to changes in the HOMO-LUMO energy gaps, which are tuned by the nature of the substituent on the catechol ligand. After complexation, the HOMO-LUMO gap of the ligand decreases. When the catechol is substituted with electron-donating groups, the HOMO-LUMO gap decreases, and the corresponding chemical shift for the complex is downfield from the vanadium-catechol complex. When the catechol is substituted with an electron-withdrawing group, the HOMO –LUMO gap increases, which is reflected in an upfield shift. These findings contribute to the generalized understanding of the relationships between the NMR parameters and the electronic structure in metal complexes.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

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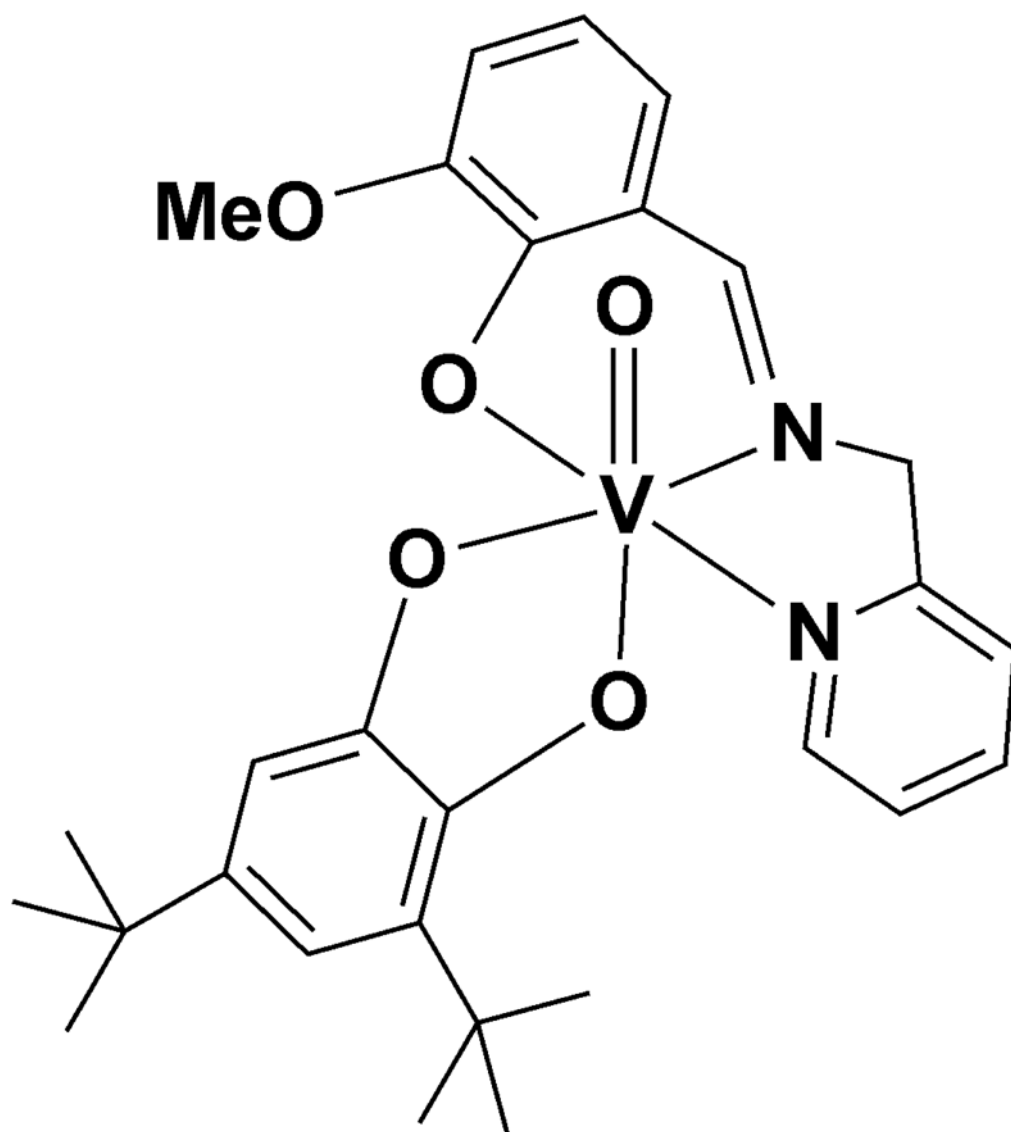
SJZ00108

**Figure 1.**
Redox non-innocent vanadium(V)-catechol complex (3,5-di-*tertiary*butylcatecholato- -{*N*-(2-methylpyridine)-3-methoxysalicylideneaminato} oxovanadium(V) (**SJZ00108**).[36]
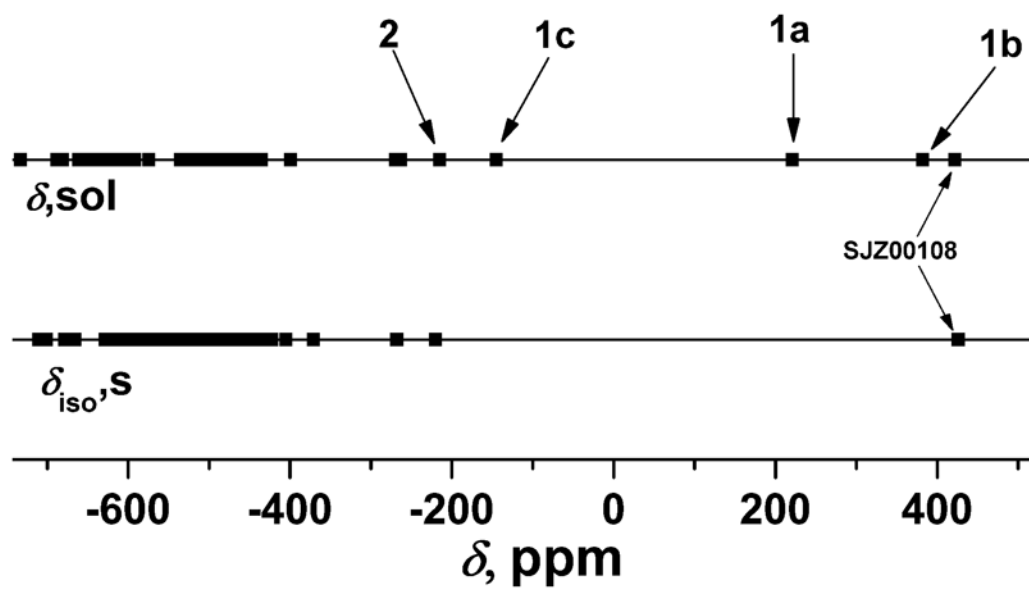
**Figure 2.**
Comparison between $^{51}V$ isotropic chemical shifts obtained from solid-state and solution NMR for all the compounds reported thus far in the literature demonstrating a missing domain in the solid-state NMR investigation.
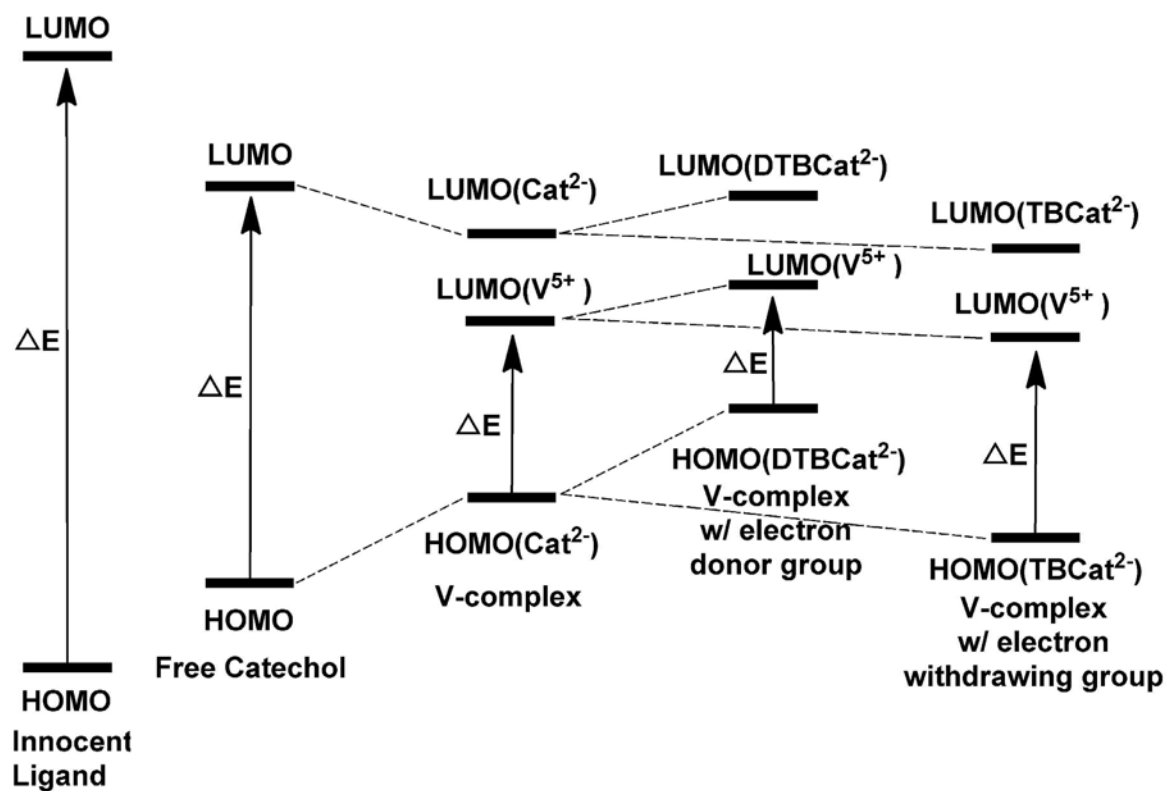
**Figure 3.**
Qualitative presentation of molecular orbital energies and electronic excitation in free and vanadium-coordinated *o*-dioxolenes. For comparison separation between HOMO-LUMO for redox innocent ligands is also shown (left). The solid arrows correspond to the lowest energy excitation in each system.
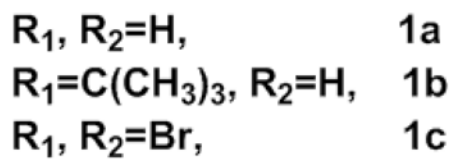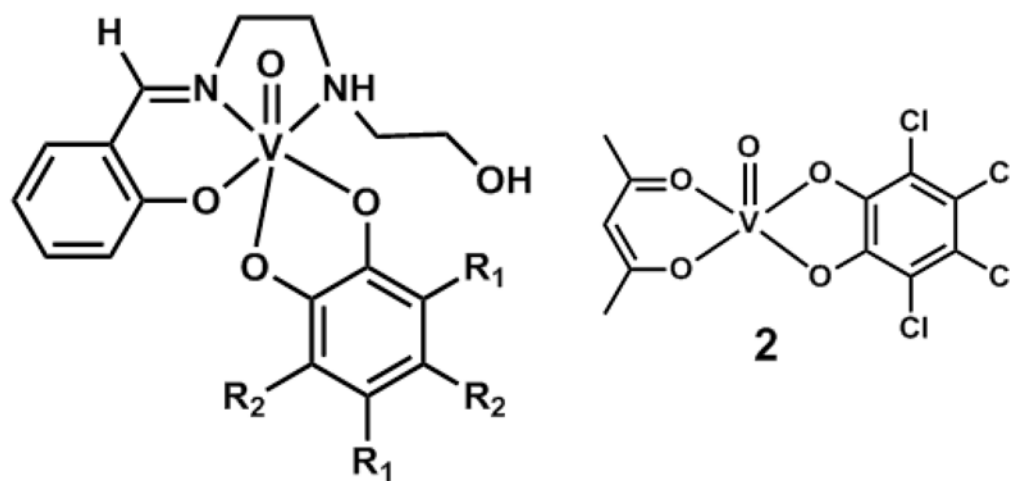
**Figure 4.**
Molecular structures of the four vanadium(V)-*o*-dioxolene compounds under investigation. [VO(hshed)(Cat)] (**1a**), [VO(hshed)(DTBCat)] (**1b**), [VO(hshed)(TBCat)] (**1c**), and [VO(acac)(TCCat)] (**2**).
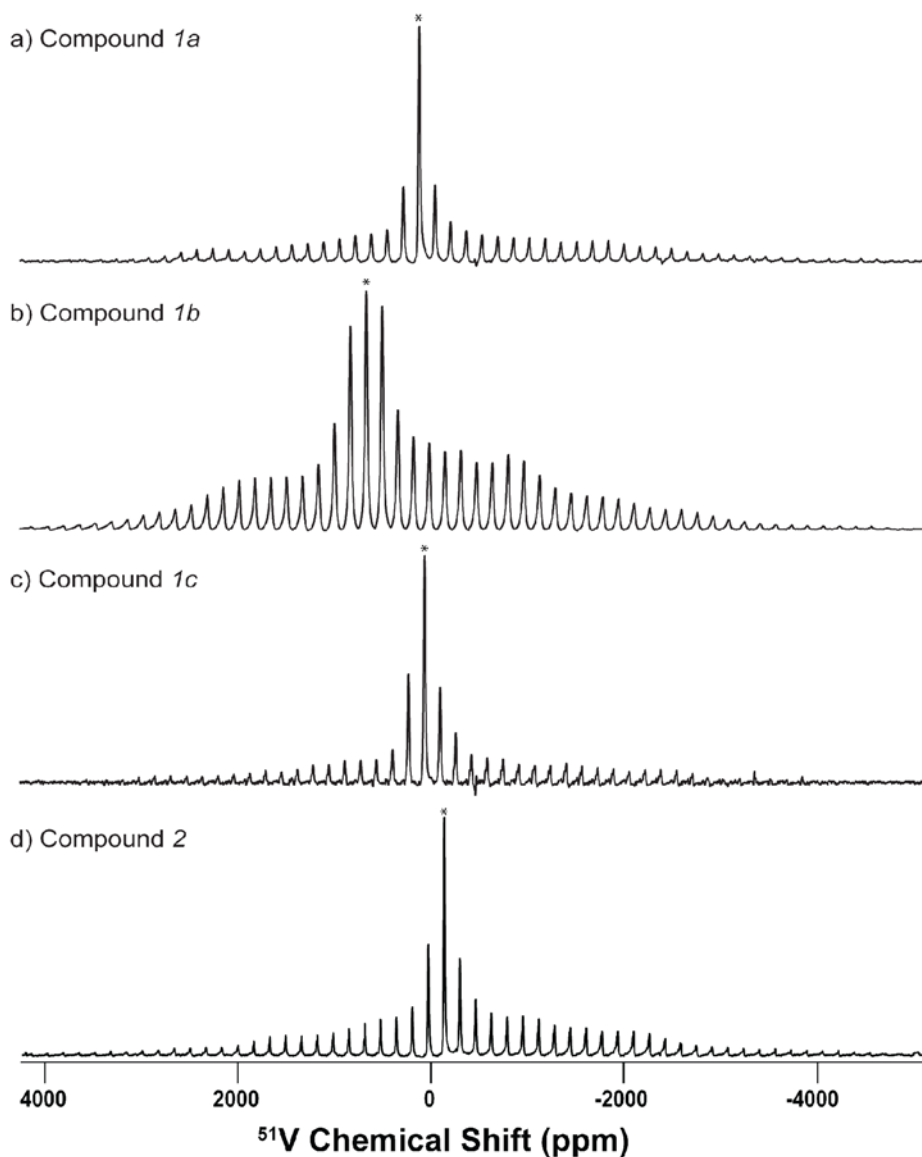
**Figure 5.**
$^{51}$V solid-state NMR spectra of the four vanadium(V)-*o*-dioxolene compounds of the series V$^V$O-hshed (**1a** – **1c**) (a–c) and [VO(acac)(TCCat)] (**2**) (d) obtained at a magnetic field of 9.4 T with MAS frequency of 17 kHz. 8192 scans were accumulated for each spectrum, and the pulse delay was 1.0 s. Experimental spectra are shown in black and best-fit simulated spectra are shown in red. The simulated spectra were obtained from SIMPSON using the NMR parameters listed in Table 1.
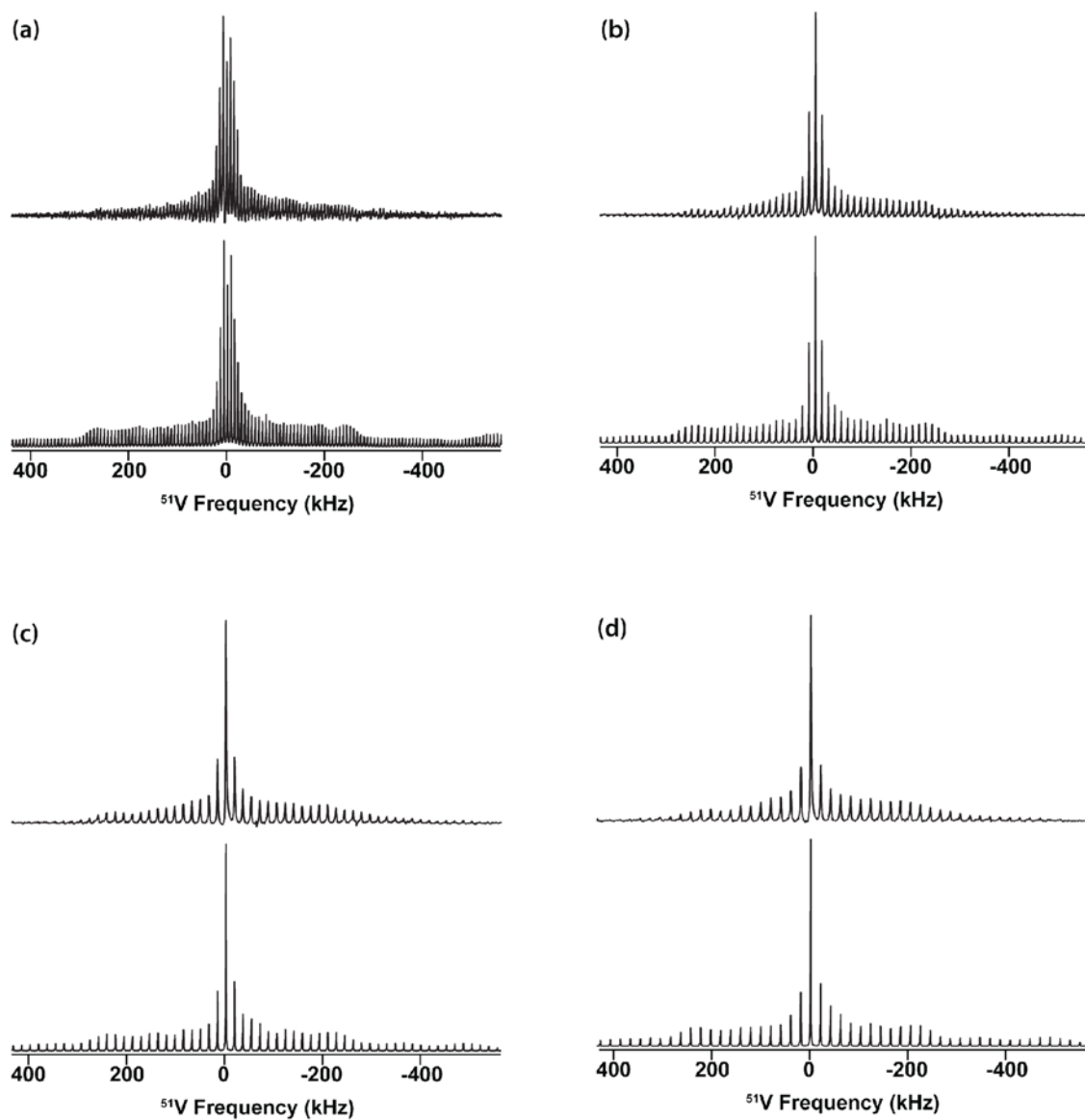
**Figure 6.**
Experimental (top) and simulated (bottom) $^{51}V$ solid-state NMR spectra of [VO(hshed)(Cat)] acquired at the MAS frequencies of (a) 7 kHz, (b) 13 kHz, (c) 17 kHz and (d) 20 kHz. The spectra were simulated with the following parameters: $C_Q = 4.0 \pm 0.1$ MHz; $\delta_\sigma = -243 \pm 30$ ppm; $\eta_Q = 1.0 \pm 0.05$; $\eta_\sigma = 0.93 \pm 0.05$; $\alpha = 81 \pm 10$; $\beta = 70 \pm 15$; $\gamma = 87 \pm 15$.
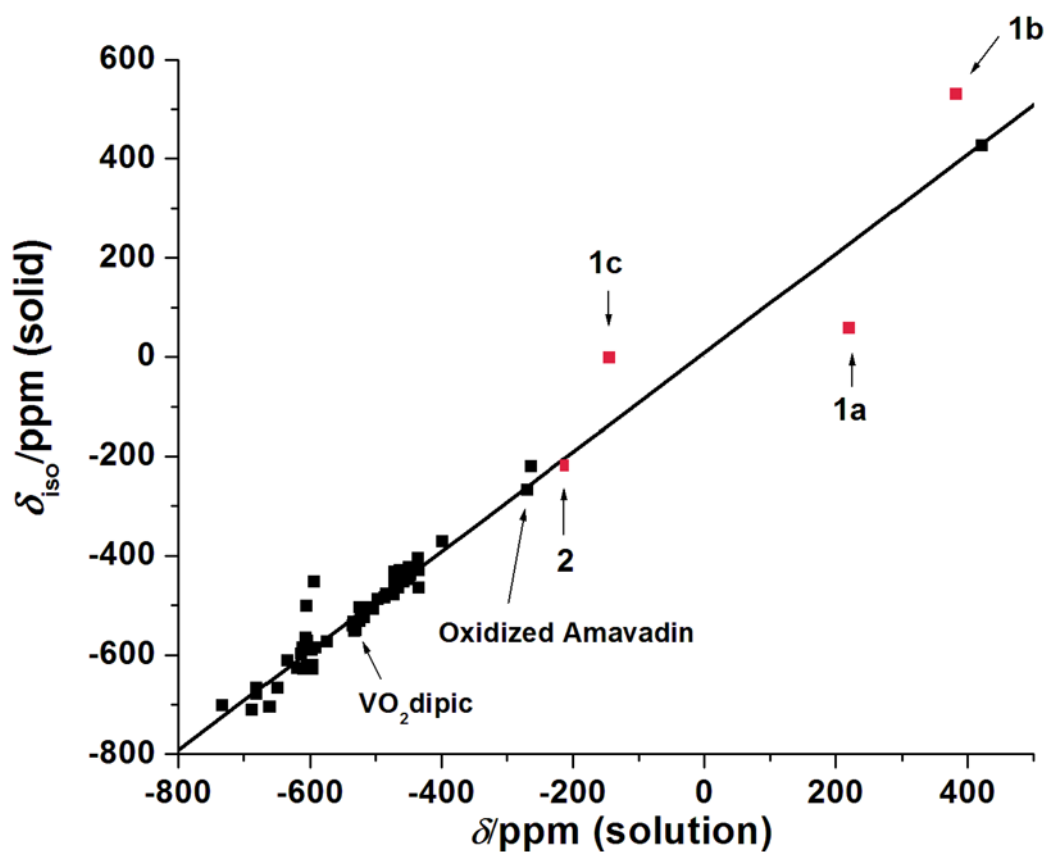
**Figure 7.**
Plot of the solution $^{51}$V NMR isotropic chemical shifts *vs.* experimentally obtained solid-state NMR chemical shifts for all the compounds reported hitherto in the literature along with the results reported in this study establishing a linear correlation between the different methods of investigations; solid state versus solution.

**Table 1**

Experimental $^{51}$V NMR parameters for six and five coordinated vanadium(V)-$o$-dioxolene compounds (**1a** - **2**)[a,b]

| Compound | C$_Q$/MHz ± 0.1 | $\eta_Q$ ± 0.05 | $\delta_{iso}$/ppm ± 5 | $\delta_\sigma$/ppm ± 30 | $\eta_\sigma$ ± 0.05 | Solid state | | | | | | Solution |
| | | | | | | $\delta_{11}$/ppm ± 30 | $\delta_{22}$/ppm ± 30 | $\delta_{33}$/ppm ± 30 | $\alpha$/degree ± 10 | $\beta$/degree ±15 | $\gamma$/degree ±30 | $\delta_{iso}$/ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **1a** | 4.0 | 1.00 | 58 | –243 | 0.93 | –185 | 66 | 292 | 81 | 70 | 87 | 221[16] |
| **1b** | 3.4 | 0.60 | 531 | 437 | 0.90 | 968 | 509 | 116 | 10 | 40 | 120 | 382[16] |
| **1c** | 4.2 | 1.0 | 31 | –314 | 0.65 | –314 | 54 | 258 | 45 | 45 | 90 | –145[16] |
| **2** | 4.1 | 0.77 | 3219 | –302 | 0.70 | –521 | –145 | 9 | 40 | 40 | 75 | 215 (This work) |
| **SJZ00108**[16] | 6.0±0.4 | 0.7±0.05 | 426.3± 3 | 570±19 | 0.6±0.1 | - | - | - | 0±60 | 0±10 | 30±30 | 422 & 375[16] |

[a]The chemical shift parameters are defined such that $|\delta_{XX} - \delta_{ISO}| \leq |\delta_{YY} - \delta_{ISO}| \leq |\delta_{ZZ} - \delta_{ISO}|$ and $\delta_{ISO} = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3$, $\delta_\sigma = \delta_{ZZ} - \delta_{ISO}$, $\eta_\sigma = (\delta_{YY} - \delta_{XX})/(\delta_{ZZ} - \delta_{ISO})$ according to the Haeberlen-Mehring-Spiess convention.[16] Here $\delta_{ii}$ denotes the principal components of the chemical shift tensor.

[b]The EFG parameters are $C_Q = eQV_{ZZ}/h$ and $\eta_Q = (V_{XX} - V_{YY})/V_{ZZ}$ where $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, $e$ is the electron charge, and $h$ is Planck's constant.

**Table 2**

Experimental and Computed $^{51}$V NMR parameters for VO(hshed)(Cat) (**1a**)$^{a,b}$

| Method | Solid state | | | | | | | | | | | Solution |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | $C_Q$/MHz | $\eta_Q$ | $\delta_{iso}$/ppm | $\delta_\sigma$/ppm | $\eta_\sigma$ | $\delta_{11}$/ppm | $\delta_{22}$/ppm | $\delta_{33}$/ppm | $\alpha$/degree | $\beta$/degree | $\gamma$/degree | $\delta_{iso}$/ppm |
| **Experiment** | 4.0 ±0.1 | 1.00 ±0.05 | 58 ±5 | −243 ±30 | 0.93 ±0.05 | 291 ±30 | 68 ±30 | −185 ±30 | 81 ±10 | 70 ±15 | 87 ± 30 | 221[16] |
| **b3lyp/6-311+G (non-optimized)** | 7.76 | 0.38 | −16.3 | −472.0 | 0.82 | 413.2 | 26.2 | −488.3 | 89 | 109 | 69 | |
| **b3lyp/TZV (non-optimized)** | 7.00 | 0.39 | −51.4 | −477.3 | 0.84 | 387.7 | −13.2 | −528.7 | 87 | 115 | 71 | |
| **b3lyp/6-311++G (proton geometries optimized)** | 7.97 | 0.32 | −32.0 | −461.8 | 0.77 | 376.7 | 21.1 | −493.8 | 149 | 21 | 16 | |
| **b3lyp/TZVP (proton geometries optimized)** | 7.79 | 0.32 | 30.1 | −434.0 | 0.92 | 446.7 | 47.5 | −403.9 | 150 | 24 | 23 | |
| **b3lyp/6-311++G (all atom geometries optimized)** | 10.66 | 0.45 | −233.3 | −484.3 | 0.62 | 159.0 | −141.3 | −717.6 | 92 | 4 | 148 | |
| **b3lyp/Wachters+f on V, 6-31*G on other atoms** | 9.92 | 0.50 | 61.7 | −333.9 | 0.89 | 377.2 | 80.1 | −272.2 | 82 | 107 | 64 | |

$^a$The chemical shift parameters are defined such that $|\delta_{XX} - \delta_{ISO}|$ $|\delta_{YY} - \delta_{ISO}|$ $|\delta_{ZZ} - \delta_{ISO}|$ and $\delta_{ISO} = (\delta_{XX} + \delta_{YY} + \delta_{ZZ})/3$, $\delta\sigma = \delta_{ZZ} - \delta_{ISO}$. $\eta\sigma = (\delta_{YY} - \delta_{XX})/(\delta_{ZZ} - \delta_{ISO})$ according to the Haeberlen-Mehring-Spiess convention.16 Here $\delta_{ii}$ denotes the principal components of the chemical shift tensor.

$^b$The EFG parameters are $CQ = eQV_{ZZ}/h$ and $\eta Q = (V_{XX} - V_{YY})/V_{ZZ}$ where $|V_{ZZ}|$ $|V_{YY}|$ $|V_{XX}|$, $e$ is the electron charge, and $h$ is Planck's constant.