Inorganic Chemistry

FORUM ARTICLE

pubs.acs.org/IC

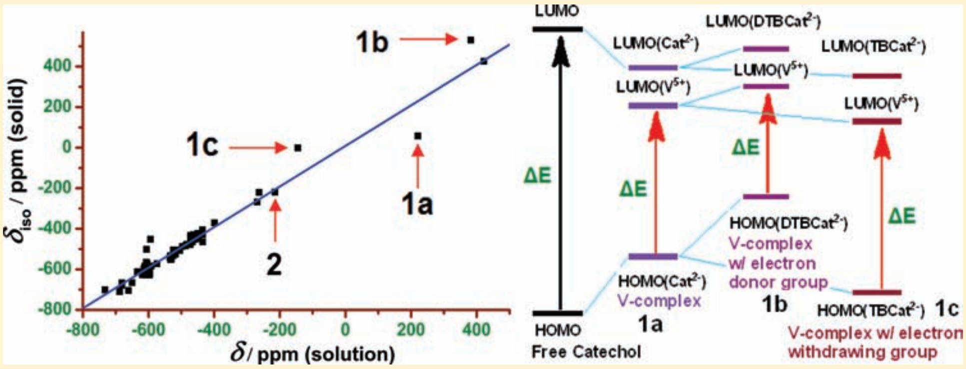
Characterization of Noninnocent Metal Complexes Using Solid-State NMR Spectroscopy: *o*-Dioxolene Vanadium Complexes

Pabitra B. Chatterjee,[†] Olga Goncharov-Zapata,[‡] Laurence L. Quinn,[†] Guangjin Hou,[‡] Hiyam Hamaed,[§] Robert W. Schurko,[§] Tatyana Polenova,[*,‡] and Debbie C. Crans[*,†]

[†]Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872, United States
[‡]Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States
[§]Department of Chemistry, University of Windsor, Windsor, Ontario, Canada N9B 3P4

S *Supporting Information*

ABSTRACT:



^{51}V solid-state NMR (SSNMR) studies of a series of noninnocent 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 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 noninnocent 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 noninnocent ligands and that have chemical shifts outside the populated range of −300 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 (density functional theory) calculations of NMR parameters for [VO(hshed)(Cat)] yield a ^{51}V chemical shift anisotropy 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 ^{51}V is a half-integer quadrupolar nucleus whose NMR observables are highly sensitive to the local environment. However, the results are general and could be extended to other redox-active complexes that exhibit coordination chemistry similar to that of the vanadium catechol complexes.

INTRODUCTION

Characterization of metal complexes containing redox-active ligands, also referred to as "noninnocent", 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

Received: January 7, 2011
Published: August 15, 2011

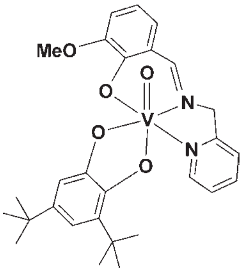
© 2011 American Chemical Society

ligand supporting a radical is abundant and plays a crucial role in the chemistry of metal complexes such as iron porphyrins,[2] iron(III) transferrin,[3] purple acid phosphatase,[4] copper(II) in galactose oxidase,[5] and manganese(II) in photosystem II.[6] A range of redox-active ligands are *o*-quinone/semiquinone/catechol, dithiolene/enedithiolate, 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 electron paramagnetic resonance (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 Fourier transform infrared (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 (SSNMR) has been used for the 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 is a potent tool that provides important insights into the electronic structure of the 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 (EFG) and chemical shift anisotropy (CSA) tensors 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 CSA tensors—can be exploited to characterize the electronic properties of ternary vanadium complexes containing noninnocent ligands.[26,37,42,49−51]

One common class of noninnocent ligands is *o*-dioxolene, also referred to as the catechol ligand. Catechols coordinate as a neutral or anionic ligand with an (OO) motif and in a bidentate fashion, as catecholate dianions (electronic spin state, $S = 0$), as semiquinonato monoanions ($S = {}^{1}/_{2}$), or as neutral *o*-benzoquinones ($S = 0$).[9,13,15,52−59] Pierpont reported an equilibrium between $M^{n+1}(Cat^{2-})$ (Cat = catechol) 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 has been reported from the excited state of an *o*-dioxolene-based chromophore to 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-*tert*-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 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,[36] we have conducted ^{51}V SSNMR investigations of a series of known *o*-dioxolane−oxovanadium(V) complexes with (ONN and OO) ancillary ligand donor sets.



SJZ00108

Figure 1. Redox noninnocent vanadium(V) catechol complex-**SJZ00108**.[36]

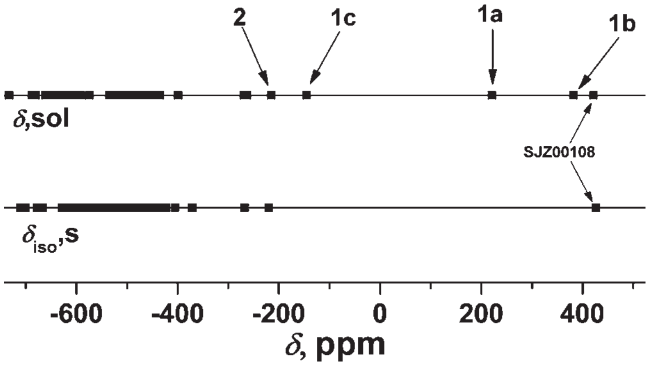


Figure 2. Comparison between the ^{51}V isotropic chemical shifts obtained from solid-state and solution NMR for all compounds reported thus far in the literature, demonstrating a missing domain in the solid-state NMR investigation.

Normal and redox-inactive (innocent) ligands are generally described as having a large energy gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). Noninnocent 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 noninnocent ligands decreases 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 the 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 the orbital energies resulted in the orbitals being no longer at the HOMO−LUMO gap.[64] Changes in the electronic properties of these systems by substitution on the catechol moiety with mononuclear Ti^{IV} or TiO_2 nanoparticles were not found to be reflected in the reduction potential in these complexes.[65] Vanadium catechol complexes in solution were, however, found to be sensitive to the subtle changes in the electronic structure[16] and therefore are excellent candidates to

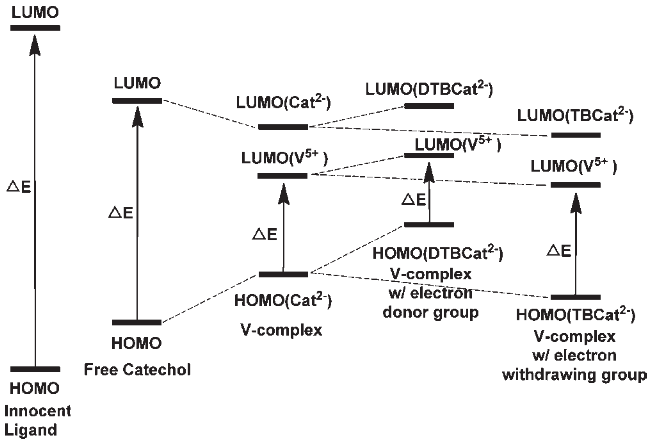


Figure 3. Qualitative presentation of molecular orbital energies and electronic excitation in free and vanadium-coordinated *o*-dioxolenes. For comparison, the separation between HOMO and LUMO for redox innocent ligands is also shown (left). The solid arrows correspond to the lowest-energy excitation in each system.

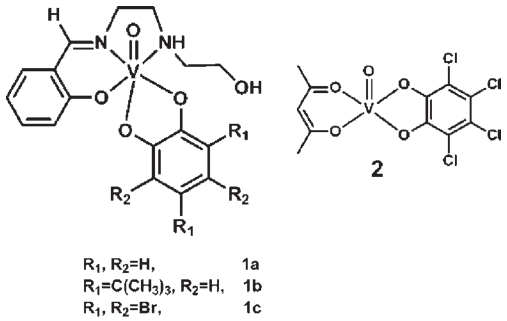


Figure 4. Molecular structures of the four vanadium(V) *o*-dioxolene compounds under investigation: [VO(hshed)(Cat)] [**1a**; hshed = *N*-salicylidenyl-*N*′-(2-hydroxyethyl)ethylenediamine], [VO(hshed)(DTBCat)] (**1b**; DTBCat = 3,5-di-*tert*-butylcatechol), [VO(hshed)(TBCat)] (**1c**; TBCat = tetrabromocatechol), and [VO(acac)(TCCat)] (**2**; acac = 2,4-pentanedionate and TCCat = tetrachlorocatechol).

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 *tert*-butyl group, the HOMO is raised more than the LUMO, and the HOMO−LUMO gap is decreased in the complex; this is illustrated in Figure 3. In contrast, substitution by bromo substituents lowers the HOMO and LUMO.[66] However, because 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 because 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 noninnocent ligands.[66] Density functional theory (DFT) calculations generally predict the NMR parameters accurately. However, when a ligand is noninnocent with large ^{51}V isotropic chemical shifts, the experimentally observed deshielding 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 CSA tensors) can effectively describe the electronic properties of the complexes with redox noninnocent ligands. We also performed quantum chemical characterization of one of these complexes and found limited agreement between the values calculated and experimentally measured. Our experimental results were used to provide the information needed for application of ^{51}V SSNMR parameters in characterizing the electronic properties of systems containing noninnocent 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 CSA 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 ^{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%), and tetrachloro-*o*-quinone (97%) were purchased from Sigma-Aldrich. Sodium hydroxide was purchased from Fisher Scientific. All reagents were commercially available and were used as received. Solvents were ACS-grade and were 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.

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 five-coordinate 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 the spectra were in agreement with previous reports.[16,57]

Solution ^{51}V NMR Spectroscopy. 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$_3$ (δ_{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 T3MAS probe was employed for all solid-state NMR experiments. Neat VOCl$_3$ was used as an external reference (δ_{iso} = 0.0 ppm).[71] This sample was also used to determine the 90° pulse width, which was set to 4.0 μs ($\gamma B_1/2\pi \approx$ 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 magic-angle-spinning (MAS)

Table 1. Experimental ^{51}V NMR Parameters for Six- and Five-Coordinate Vanadium(V) *o*-Dioxolene Compounds (**1a**–**1c** and **2**)[a,b]

	solid state											solution
compound	C_Q/MHz ± 0.1	η_Q ± 0.05	δ_{iso}/ppm ±5	δ_σ/ppm ±30	η_σ ± 0.05	δ_{11}/ppm ±30	δ_{22}/ppm ±30	δ_{33}/ppm ±30	α/deg ±10	β/deg ±15	γ/deg ±30	δ_{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	−1	−314	0.65	−314	54	258	45	45	90	−145[16]
2	4.1	0.77	−219	−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 and 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 $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_\sigma = \delta_{zz} - \delta_{iso}$, and $\eta_\sigma = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$ according to the Haeberlen–Mehring–Spiess convention.[37] Here δ_{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 **1a**[a,b]

	Solid state										Solution
method	C_Q/MHz	η_Q	δ_{iso}/ppm	δ_σ/ppm	η_σ	δ_{11}/ppm	δ_{22}/ppm	δ_{33}/ppm	α/deg	β/deg	γ/deg	δ_{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 (nonoptimized)	7.76	0.38	−16.3	−472.0	0.82	413.2	26.2	−488.3	89	109	69	
B3LYP/TZV (nonoptimized)	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 $|\delta_{xx} - \delta_{iso}| \leq |\delta_{yy} - \delta_{iso}| \leq |\delta_{zz} - \delta_{iso}|$ and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_\sigma = \delta_{zz} - \delta_{iso}$, and $\eta_\sigma = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$ according to the Haeberlen–Mehring–Spiess convention.[16] Here δ_{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.

SSNMR spectra were acquired at ω_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 μs 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 a baseline correction. The isotropic chemical shifts were determined by analyses of the spectra collected at different MAS frequencies. The ^{51}V CSA (δ_σ, η_σ) and quadrupolar (C_Q, η_Q) parameters as well as the relative tensor orientations described by the Euler angles (α, β, and γ) were extracted by numerical simulations of the spinning-sideband patterns using the *SIMPSON*[72] software package. The best-fit values are shown in Table 1.

In this work, the chemical shift parameters are defined such that $|\delta_{xx} - \delta_{iso}| \leq |\delta_{yy} - \delta_{iso}| \leq |\delta_{zz} - \delta_{iso}|$ and $\delta_{iso} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_\sigma = \delta_{zz} - \delta_{iso}$, and $\eta_\sigma = (\delta_{yy} - \delta_{xx})/(\delta_{zz} - \delta_{iso})$ according to the Haeberlen–Mehring–Spiess convention.[37] δ_{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 $|V_{ZZ}| \geq |V_{YY}| \geq |V_{XX}|$, e is the electron charge, and h is Planck's constant.

DFT Calculations. Quantum chemical calculations for the structurally characterized VO(hshed)(Cat) complex (**1a**) were performed with DFT in *Gaussian03*.[73] The ^{51}V magnetic shielding and EFG tensors were computed using the B3LYP functional and several basis sets (6-311+G, 6-311++G, TZV, TZVP, and Wachters+f). Calculations were carried

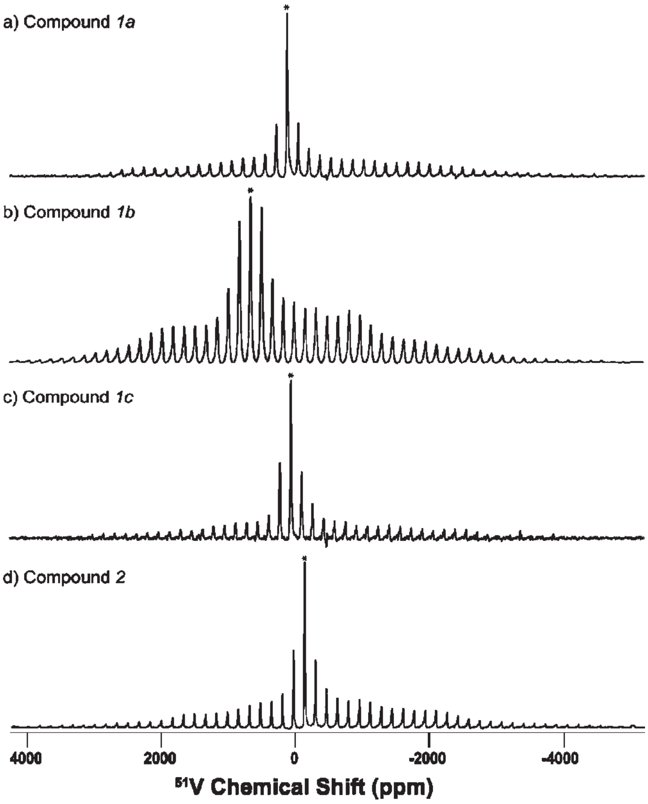


Figure 5. ^{51}V SSNMR spectra of the four vanadium(V) *o*-dioxolene compounds of the series V^VO(hshed) (**1a**−**1c**; a−c) and [VO(acac)-(TCCat)] (**2**; d) obtained at a magnetic field of 9.4 T with a MAS frequency of 17 kHz. A total of 8192 scans were accumulated for each spectrum, and the pulse delay was 1.0 s.

out using either the nonoptimized 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** and **2**; Figure 4). Compound **1a** contains a redox-active catechol ligand in a bidentate dianionic mode of coordination to the oxovanadium(V) center, resulting in a downfield chemical shift of 221 ppm for this noninnocent complex (Table 1). Upon the introduction of *tert*-butyl groups to the catechol ring (**1b**), further downfield chemical shift (at 382 ppm) is observed (Table 1). Introducing electron-withdrawing bromo substituents to the catechol moiety (**1c**) results in an upfield shift (−145 ppm). The five-coordinate 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 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 MAS SSNMR investigations. The ^{51}V MAS NMR spectra of the four oxovanadium(V) catecholato compounds (**1a**−**1c** and **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** and **2**) recorded at the MAS frequency of 17 kHz. The CSA and quadrupolar NMR parameters, as well as the relative orientation, were extracted by fitting the ^{51}V MAS NMR 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, **1b** at 531 ppm, **1c** at −1 ppm, and **2** at −219 ppm. These results show that the noninnocent 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 CSA, δ_σ, does not vary to as large of an extent as the isotropic shifts and is in the range of 243−437 ppm for these complexes. Analysis of the individual CSA tensor components, δ_{11}, δ_{22}, and δ_{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** and **2** and other known vanadium(V) complexes were plotted as a function of the solution chemical shifts (Figure 7).[26−38,49] The linear relationship shows that the expected correlation between solid-state (δ_{iso}) and solution isotropic chemical shifts (δ) generally holds, although significantly more scatter in the current data is observed for these noninnocent complexes.

^{51}V NMR Parameters of the VO(hshed)(Cat) Complex (1a): DFT. To understand the experimental ^{51}V SSNMR 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) (**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 (δ_σ agrees to within 90 ppm and η_σ 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

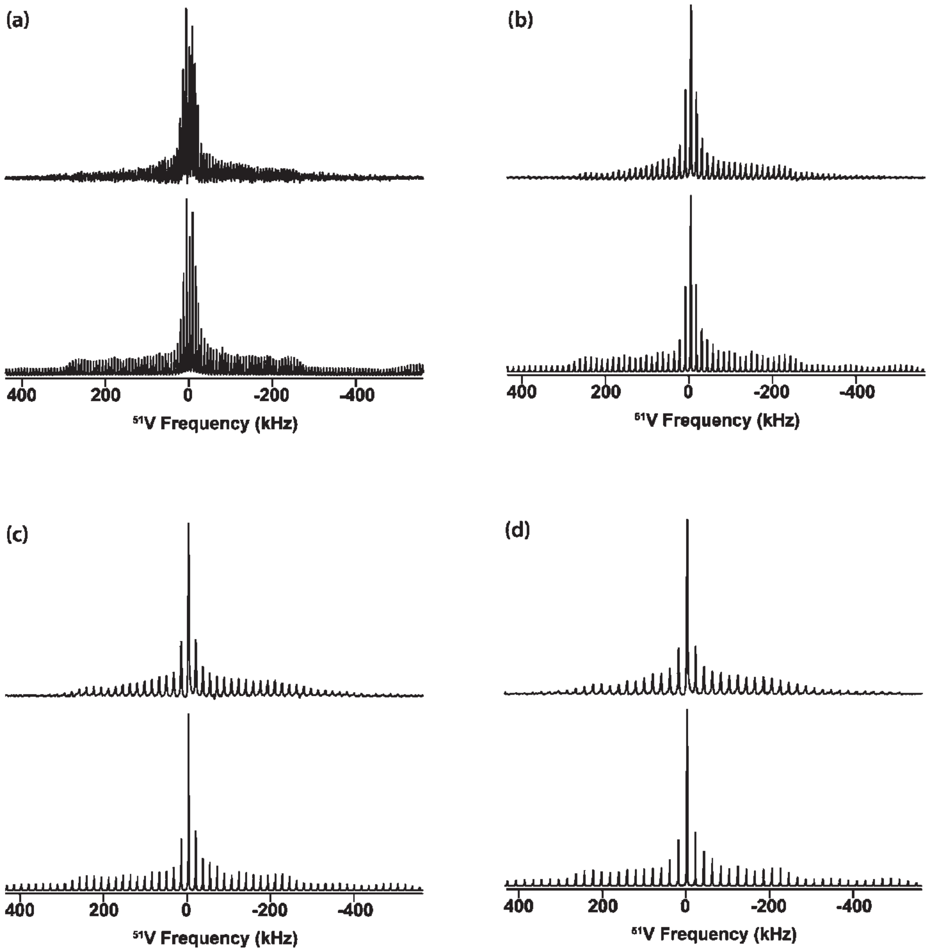


Figure 6. Experimental (top) and simulated (bottom) ^{51}V SSNMR spectra of [VO(hshed)(Cat)] acquired at the MAS frequencies of (a) 7 kHz, (b) 13 kHz, (c) 17 kHz, and (d) 20 kHz. The spectra were simulated with SIMPSON with the parameters listed in Table 1.

4.0 MHz, and for the different basis sets, 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 vanadium(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 ^{51}V MAS 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 SSNMR 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 CSA provides fundamental information about the electronic structure of these systems as well as documents a less traditional method for gaining information on these challenging systems.

The ternary vanadium(V) catechol complexes (**1a**−**1c** and **2**) examined in this work contain one co-ligand in addition to one catechol moiety and, as a result, have unusual electronic properties. Solution NMR spectroscopy of noninnocent vanadium complexes has been reported;[16] however, no generalized understanding of the relationships between the different NMR parameters and the electronic structure in such compounds has 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 (δ_{iso}) and in solution (δ) of vanadium complexes formed from innocent ligands. The ^{51}V NMR chemical shifts for these complexes are in the range of −300 to −700 ppm.[18,38,67] However, unusual electronic properties have been found in complexes formed from redox noninnocent ligands such as catechols[16,75] and hydroxylamines.[67] In these systems, strong deshielding of the metal nucleus is observed, with the chemical shift range dramatically extending outside the −300 to −700 ppm region,

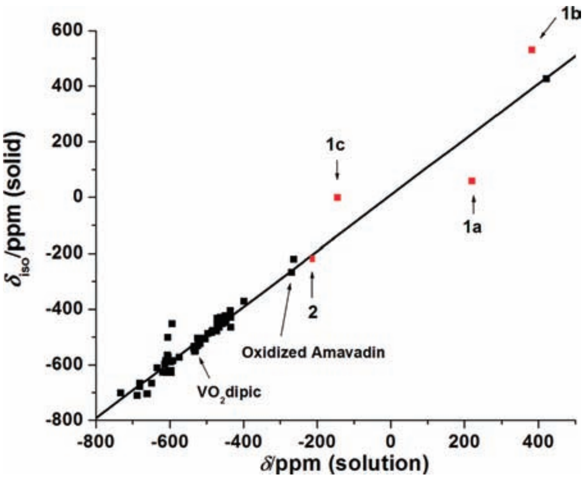


Figure 7. Plot of the solution ^{51}V NMR isotropic chemical shifts versus experimentally obtained SSNMR chemical shifts for all of the compounds reported hitherto in the literature along with the results reported in this study, establishing a linear correlation between the different methods of investigations: solid state versus solution.

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** and **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 seven-coordinate geometry with dipicolinic acid ligands.[28] In comparison, six-coordinate compounds typically show somewhat larger quadrupolar coupling constants, in the range of 3.0−6.3 MHz.[27,33,34,36,38] Five- and eight-coordinate 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 (Bolte, S.; Ooms, K.; Renirie, R.; Wever, R.; Polenova, T., 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 six-coordinate, while **2** is a five-coordinate 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 distributions 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 CSA 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 application of the ^{51}V SSNMR parameters in characterizing the electronic properties of systems containing noninnocent ligands and having chemical shifts outside the range of −300 to −700 ppm, where no data were available before this work (Figure 2). Solution and solid-state isotropic chemical shifts exhibit linear correlations 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 structures are the same. On the other hand, there is no relationship between the isotropic chemical shift (either solution or solid state) and the CSA, which is due to the fact that the individual CSA tensor values (δ_{11}, δ_{22}, and δ_{33}) vary widely within this series of complexes (see Table 1). All of the CSA tensors are rhombic, and it is 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 molecular orbitals 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 **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 δ_σ is only predicted to within 90 ppm using the 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 vanadium-51(V) complexes with noninnocent ligands has been attributed to several possible factors:[66] (i) that the paramagnetic contributions in the closed-shell wave functions are severely underestimated; (ii) that a temperature-dependent paramagnetic term arises from nonzero spin density at the metal due to the mixing of vanadium(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 "noninnocent" ligand character resulting in strong deshielding is due to not only the bidentate catechol ligand but also the coligand tridentate salicylideneaminato Schiff base,[66] which is consistent with an earlier work by Pecoraro et al.[16] The X-ray crystal structures for the other compounds are needed before detailed quantum chemical analyses of compounds **1b**, **1c**, and **2** and 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, σ, at the NMR-active nucleus is defined as the sum of the generally positive diamagnetic (σ_{dia}) component and a paramagnetic (σ_{para}) component (eq 1):

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

For the majority of metal-containing complexes, the σ_{dia} term is controlled by the core electrons and thus is 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 σ_{dia} but instead tune the σ_{para} term and thus the shielding.[77−80] The σ_{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 (ΔE) between the HOMO and LUMO in these complexes. In fact, σ_{para} varies inversely with ΔE, and it also contains a $\langle r^{-3}\rangle$ term, indicating that only the orbitals near the metal center need to be considered.[16,28] The overlap of the ligand's valence π 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 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 the σ_{para} term of eq 1.

The small energy gap between the HOMO and LUMO in vanadium catechol complexes makes these systems ideally suited for analysis of electronic effects using ^{51}V SSNMR spectroscopy. Electronic excitation in free catechol is attributed to the transition from π HOMO to π^* 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 noninnocent nature of these ligands results in little separation between the HOMO and 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.[16,81] These calculations revealed that the small HOMO−LUMO gap and the effect on σ_{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). Because insufficient information is available for compounds with chemical shifts outside the range −300 to −700 ppm and because 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**, δ(solution) = 221 ppm/δ_{iso}(solid) = 58 ppm, is halfway between that in the vanadium(V) complexes examined previously and complex **SJZ00108**[36] (Figure 1). The introduction of *tert*-butyl groups to the catechol ring (**1b**) results in electron redistribution within the complex, increasing the energies of both HOMO and LUMO in **1b**. Because 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** [δ(solution) = 382 ppm/δ_{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** [δ(solution) = −145 ppm/δ_{iso}(solid) = −1 ppm]. These three compounds are the first examples of complexes with ^{51}V chemical shifts in this range. Furthermore, the dramatic variation in the 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 vanadium(V) complexes, little change in the 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 noninnocent ligand with another redox-inactive oxygen-rich coligand. 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). In contrast, replacing bromo substituents by chloro substituents on the catechol moiety has very little influence on the ^{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 SSNMR spectroscopy. The objective with this work was to address whether SSNMR observables, quadrupolar and CSA tensors, can effectively describe the electronic properties of the metal complexes containing redox noninnocent 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 using 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 CSA 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 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 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.

■ ASSOCIATED CONTENT

S Supporting Information. Experimental and simulated ^{51}V SSNMR spectra (9.4 T) of the three vanadium(V) *o*-dioxolene compounds of the series V^{V}O(hshed) (**1a**−**1b**) and [VO(acac)-(TCCat)] (**2**) acquired at the MAS rates of 13, 17, and 20 kHz. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: crans@lamar.colostate.edy (D.C.C.), tpolenov@mail.chem.udel.edu (T.P.).

■ ACKNOWLEDGMENT

D.C.C. acknowledges financial support of the National Science Foundation (Grants CHE-0628260 and CHE-0750079). T.P. acknowledges financial support of the National Science Foundation (Grant CHE-0750079) and the National Institutes of Health (Grant P30RR031160 from NCRR).

■ REFERENCES

(1) Jorgensen, C. K. *Coord. Chem. Rev.* **1966**, *1*, 15.

(2) Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L. *Chem. Rev.* **2004**, *104*, 939.

(3) Thorstensen, K.; Romslo, I. *Biochem. J.* **1990**, *271*, 1.

(4) Klabunde, T.; Krebs, B. *Struct. Bonding (Berlin)* **1997**, *89*, 177.

(5) Wang, Y.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. *Science* **1998**, *279*, 537.

(6) Mukhopadhyay, S.; Mandal, S. K.; Bhaduri, S.; Armstrong, W. H. *Chem. Rev.* **2004**, *104*, 3981.

(7) Kaim, W.; Schwederski, B. *Coord. Chem. Rev.* **2010**, *254*, 1580.

(8) Ward, M. D.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **2002**, 275.

(9) Pierpont, C. G. *Coord. Chem. Rev.* **2001**, *216*, 99.

(10) Pierpont, C. G.; Lange, C. W. *Prog. Inorg. Chem.* **1994**, *41*, 331.

(11) Wang, P. G.; Xian, M.; Tang, X. P.; Wu, X. J.; Wen, Z.; Cai, T. W.; Janczuk, A. J. *Chem. Rev.* **2002**, *102*, 1091.

(12) Cass, M. E.; Gordon, N. R.; Pierpont, C. G. *Inorg. Chem.* **1986**, *25*, 3962.

(13) Cass, M. E.; Greene, D. L.; Buchanan, R. M.; Pierpont, C. G. *J. Am. Chem. Soc.* **1983**, *105*, 2680.

(14) Chang, H. C.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 130.

(15) Chatterjee, P. B.; Bhattacharya, K.; Kundu, N.; Choi, K. Y.; Clerac, R.; Chaudhury, M. *Inorg. Chem.* **2009**, *48*, 804.

(16) Cornman, C. R.; Colpas, G. J.; Hoeschele, J. D.; Kampf, J.; Pecoraro, V. L. *J. Am. Chem. Soc.* **1992**, *114*, 9925.

(17) Attia, A. S.; Pierpont, C. G. *Inorg. Chem.* **1998**, *37*, 3051.

(18) Lapina, O. B.; Khabibulin, D. F.; Shubin, A. A.; Terskikh, V. V. *Prog. Nucl. Magn. Reson. Spec.* **2008**, *53*, 128.

(19) Plevin, M. J.; Bryce, D. L.; Boisbouvier, J. *Nat. Chem.* **2010**, *2*, 466.

(20) Tran, T. T.; Herfort, D.; Jakobsen, H. J.; Skibsted, J. *J. Am. Chem. Soc.* **2009**, *131*, 14170.

(21) Ellis, P. D.; Lipton, A. S. *Annu. Rep. NMR Spectrosc.* **2007**, *60*, 1.

(22) Rovnyak, D.; Baldus, M.; Wu, G.; Hud, N. V.; Feigon, J.; Griffin, R. G. *J. Am. Chem. Soc.* **2000**, *122*, 11423.

(23) Weiss, J. W. E.; Bryce, D. L. *J. Phys. Chem. A* **2010**, *114*, 5119.

(24) Bryce, D. L. *Dalton Trans.* **2010**, *39*, 8593.

(25) Brown, C.; Achey, R.; Fu, R. Q.; Gedris, T.; Stiegman, A. E. *J. Am. Chem. Soc.* **2005**, *127*, 11590.

(26) Rehder, D.; Polenova, T.; Buhl, M. *Annu. Rep. NMR Spectrosc.* **2007**, *62*, 49.

(27) Bolte, S. E.; Ooms, K. J.; Polenova, T.; Baruah, B.; Crans, D. C.; Smee, J. J. *J. Chem. Phys.* **2008**, *128*.

(28) Ooms, K. J.; Bolte, S. E.; Smee, J. J.; Baruah, B.; Crans, D. C.; Polenova, T. *Inorg. Chem.* **2007**, *46*, 9285.

(29) Smee, J. J.; Epps, J. A.; Ooms, K.; Bolte, S. E.; Polenova, T.; Baruah, B.; Yang, L. Q.; Ding, W. J.; Li, M.; Willsky, G. R.; la Cour, A.; Anderson, O. P.; Crans, D. C. *J. Inorg. Biochem.* **2009**, *103*, 575.

(30) Huang, W. L.; Todaro, L.; Francesconi, L. C.; Polenova, T. *J. Am. Chem. Soc.* **2003**, *125*, 5928.

(31) Huang, W. L.; Todaro, L.; Yap, G. P. A.; Beer, R.; Francesconi, L. C.; Polenova, T. *J. Am. Chem. Soc.* **2004**, *126*, 11564.

(32) Chen, L.; Kaiser, J. M.; Polenova, T.; Yang, J.; Rienstra, C. M.; Mueller, L. J. *J. Am. Chem. Soc.* **2007**, *129*, 10650.

(33) Nica, S.; Buchholz, A.; Rudolph, M.; Schweitzer, A.; Waechtler, M.; Breitzke, H.; Buntkowsky, G.; Plass, W. *Eur. J. Inorg. Chem.* **2008**, 2350.

(34) Gutmann, T.; Schweitzer, A.; Wachtler, M.; Breitzke, H.; Blichholz, A.; Plass, W.; Buntkowsky, G. *Phys. Chem. Chem. Phys.* **2008**, *222*, 1389.

(35) Schweitzer, A.; Gutmann, T.; Wachtler, M.; Breitzke, H.; Buchholz, A.; Plass, W.; Buntkowsky, G. *Solid State Nucl. Magn. Reson.* **2008**, *34*, 52.

(36) Pooransingh, N.; Pomerantseva, E.; Ebel, M.; Jantzen, S.; Rehder, D.; Polenova, T. *Inorg. Chem.* **2003**, *42*, 1256.

(37) Pooransingh-Margolis, N.; Renirie, R.; Hasan, Z.; Wever, R.; Vega, A. J.; Polenova, T. *J. Am. Chem. Soc.* **2006**, *128*, 5190.

(38) Fenn, A.; Wachtler, M.; Gutmann, T.; Breitzke, H.; Buchholz, A.; Lippold, I.; Plass, W.; Buntkowsky, G. *Solid State Nucl. Magn. Reson.* **2009**, *36*, 192.

(39) Skibsted, J.; Nielsen, N. C.; Bildsoe, H.; Jakobsen, H. J. *J. Am. Chem. Soc.* **1993**, *115*, 7351.

(40) Lapina, O. B.; Khabibulin, D. F.; Shubin, A. A.; Bondareva, V. M. *J. Mol. Catal. A: Chem.* **2000**, *162*, 381.

(41) Skibsted, J.; Jacobsen, C. J. H.; Jakobsen, H. J. *Inorg. Chem.* **1998**, *37*, 3083.

(42) Buhl, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 142.

(43) Spengler, J.; Anderle, F.; Bosch, E.; Grasselli, R. K.; Pillep, B.; Behrens, P.; Lapina, O. B.; Shubin, A. A.; Eberle, H. J.; Knozinger, H. *J. Phys. Chem. B* **2001**, *105*, 10772.

(44) Jenkins, J. E.; Creager, M. S.; Lewis, R. V.; Holland, G. P.; Yarger, J. L. *Biomacromolecules* **2010**, *11*, 192.

(45) Holland, G. P.; Cherry, B. R.; Jenkins, J. E.; Yarger, J. L. *J. Magn. Reson.* **2010**, *202*, 64.

(46) Creager, M. S.; Jenkins, J. E.; Thagard-Yeaman, L. A.; Brooks, A. E.; Jones, J. A.; Lewis, R. V.; Holland, G. P.; Yarger, J. L. *Biomacromolecules* **2010**, *11*, 2039.

(47) Butler, A.; Danzitz, M. J.; Eckert, H. *J. Am. Chem. Soc.* **1987**, *109*, 1864.

(48) Vilter, H.; Rehder, D. *Inorg. Chim. Acta Bioinorg. Chem.* **1987**, *136*, L7.

(49) Crans, D. C.; Smee, J. J.; Gaidamauskas, E.; Yang, L. Q. *Chem. Rev.* **2004**, *104*, 849.

(50) Butler, A.; Walker, J. V. *Chem. Rev.* **1993**, *93*, 1937.

(51) Rehder, D.; Holst, H.; Priebsch, W.; Vilter, H. *J. Inorg. Biochem.* **1991**, *41*, 171.

(52) Cornman, C. R.; Kampf, J.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 1981.

(53) Pierpont, C. G.; Attia, A. S. *Collect. Czech. Chem. Commun.* **2001**, *66*, 33.

(54) Chatterjee, P. B.; Abtab, S. M. T.; Bhattacharya, K.; Endo, A.; Shotton, E. J.; Teat, S. J.; Chaudhury, M. *Inorg. Chem.* **2008**, *47*, 8830.

(55) Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *J. Am. Chem. Soc.* **1982**, *104*, 5092.

(56) Cornman, C. R.; Kampf, J.; Lah, M. S.; Pecoraro, V. L. *Inorg. Chem.* **1992**, *31*, 2035.

(57) Galeffi, B.; Postel, M.; Grand, A.; Rey, P. *Inorg. Chim. Acta* **1987**, *129*, 1.

(58) Kabanos, T. A.; White, A. J. P.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Chem. Commun.* **1992**, 17.

(59) Kabanos, T. A.; Slawin, A. M. Z.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1992**, 1423.

(60) Persson, P.; Bergstrom, R.; Lunell, S. *J. Phys. Chem. B* **2000**, *104*, 10348.

(61) Duncan, W. R.; Prezhdo, O. V. *J. Phys. Chem. B* **2005**, *109*, 365.

(62) Yin, C. X.; Finke, R. G. *J. Am. Chem. Soc.* **2005**, *127*, 13988.

(63) Sanchez de Armas, R.; San Miguel, M. A.; Oviedo, J.; Marquez, A.; Sanz, J. F. *Phys. Chem. Chem. Phys.* **2011**, *13*, 1506.

(64) Li, S. C.; Wang, J. G.; Jacobson, P.; Gong, X. Q.; Selloni, A.; Diebold, U. *J. Am. Chem. Soc.* **2009**, *131*, 980.

(65) Creutz, C.; Chou, M. H. *Inorg. Chem.* **2008**, *47*, 3509.

(66) Geethalakshmi, K. R.; Waller, M. P.; Buhl, M. *Inorg. Chem.* **2007**, *46*, 11297.

(67) Ooms, K. J.; Bolte, S. E.; Baruah, B.; Choudhary, M. A.; Crans, D. C.; Polenova, T. *Dalton Trans.* **2009**, 3262.

(68) Zhang, Y.; Gascon, J. A. *J. Inorg. Biochem.* **2008**, *102*, 1684.

(69) Schneider, C. J.; Zampella, G.; Greco, C.; Pecoraro, V. L.; De Gioia, L. *Eur. J. Inorg. Chem.* **2007**, 515.

(70) Zampella, G.; Fantucci, P.; Pecoraro, V. L.; De Gioia, L. *Inorg. Chem.* **2006**, *45*, 7133.

(71) Harris, R. K.; Becker, E. D.; De Menezes, S. M. C.; Goodfellow, R.; Granger, P. *Pure Appl. Chem.* **2001**, *73*, 1795.

(72) Bak, M.; Rasmussen, J. T.; Nielsen, N. C. *J. Magn. Reson.* **2000**, *147*, 296.

(73) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(74) Bryliakov, K. P.; Karpyshev, N. N.; Fominsky, S. A.; Tolstikov, A. G.; Talsi, E. P. *J. Mol. Catal. A: Chem.* **2001**, *171*, 73.

(75) Frank, P.; Robinson, W. E.; Kustin, K.; Hodgson, K. O. *J. Inorg. Biochem.* **2001**, *86*, 635.

(76) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699.

(77) Kanda, K.; Nakatsuji, H.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 5888.

(78) Nakatsuji, H.; Kanda, K.; Endo, K.; Yonezawa, T. *J. Am. Chem. Soc.* **1984**, *106*, 4653.

(79) Schreckenbach, G. *J. Chem. Phys.* **1999**, *110*, 11936.

(80) Wilson, P. J.; Amos, R. D.; Handy, N. C. *Phys. Chem. Chem. Phys.* **2000**, *2*, 187.

(81) Mondal, J. U.; Schultz, F. A.; Brennan, T. D.; Scheidt, W. R. *Inorg. Chem.* **1988**, *27*, 3950.