



Solution and Solid-state Vanadium-51 NMR Studies of Vanadium (V) Complexes

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Abstract: Several dioxovanadate (V) complexes are synthesized and studied by solution and solid-state ^{51}V NMR spectroscopy. In the results, large ^{51}V chemical shift anisotropy ($\Delta\delta_a = -800 \sim -720$ ppm) and quadrupole coupling ($e^2qQ/h = 7.50 \sim 9.16$ MHz) were observed in the solid-state complexes. The isotropic chemical shifts of the solid samples are very close to the values obtained from solution measurements.

In recent years ^{51}V NMR has emerged as a powerful tool for studying the local environment of ^{51}V nuclei in solution¹ and solid-state.² The ^{51}V nucleus (spin $I = 7/2$, natural abundance 99.76%) has an electric quadrupole moment which interacts with the gradient of the intramolecular electric field. This interaction produces the so called quadrupolar effects of the first and second order in ^{51}V NMR spectra.³ The analysis of these effects allows one to measure the quadrupolar coupling constant e^2qQ/h and asymmetry parameter η_Q . These parameters directly characterize the gradient of the electric field which is created at the V nucleus by the surrounding atoms and thus can be related to distortions of the symmetry of the local environment of the V atom. As found recently, the principal components of the chemical shift tensor are also very sensitive to the type of local environment of ^{51}V nuclei.⁴

In general, three different types of interaction influence the ^{51}V NMR spectra of solid diamagnetic samples: (1) the dipole interaction of the magnetic moment of the ^{51}V nucleus with magnetic moment of other nuclei, leading to broad lines; (2) the

quadrupolar interaction of the ^{51}V nuclei with the electric field gradient, which splits the lines and contributes to the shift of the central ($m_I=1/2 \leftrightarrow -1/2$) lines; (3) the chemical shift interaction, which changes the position of the lines and makes them asymmetric. The line shape can be rather complicated due to simultaneous action of all three types of interaction. The dipolar interaction and the first order quadrupolar interaction do not depend on the spectrometer frequency ν_0 , while the second order quadrupolar effects are inversely proportional to ν_0 . The effects of the anisotropy of the chemical shift are directly proportion to ν_0 . Thus, at high enough ν_0 the second order quadrupolar effects are suppressed and can be neglected, while the effects of the chemical shift anisotropy become more pronounced and can be measured more precisely.

In this paper, we measure the chemical shift anisotropies and the quadrupolar coupling interactions of ^{51}V nuclei in several dioxovanadate (V) complexes from magic-angle-spinning (MAS) spectra of the powder samples. In our knowledge this is the first report to measure the chemical shift anisotropy and the quadrupolar coupling constant of ^{51}V in vanadium (V) complex.

EXPERIMENTAL

Materials

All reagent grade chemicals were used as received without further purification. Ammonium metavanadate, oxalic acid (H_2Ox), ethylenediaminetetraacetic acid (H_4EDTA), nitrilotriacetic acid (H_3NTA), and propylenediaminetetraacetic acid (H_4PDTA) were obtained from Aldrich Chemical Co. Dioxovanadate (V) complexes were prepared from the reaction of ammonium metavanadate and ligand in aqueous solution with the similar method reported elsewhere.⁵

NMR measurements

Solution ^{51}V spectra of samples were recorded on a JEOL GSX-400 spectrometer (105 MHz) at room temperature. Spinning (MAS and off-MAS) ^{51}V

spectra of powder samples were recorded on a Bruker MSL-400 spectrometer (105.25 MHz) at room temperature. Bruker high-speed probehead was used with rotors of 4 mm o.d. The angle in the off-MAS measurements was chosen so that the intensities of the spinning sidebands caused by the satellite transitions were negligible. The spinning axis used was inclined at 53.7° to the magnetic field. The spinning rate for MAS spectra was 10 kHz. The ordinary single pulse sequence with phase alternation was used with and without ^1H high-power decoupling during signal acquisition. ^1H high-power decoupling had negligible effect on the line shape. The $\pi/2$ pulse width for solution was set at $6.0 \mu\text{s}$. The pulse length was $1.0 \mu\text{s}$ and the repetition time was 1.0 s. Recovery time after the pulse transmission was $5 \mu\text{s}$.

Analysis of the Solid-state ^{51}V Spectra.

The line shape of the spectra and the intensity of the spinning side bands (SSBs) were analyzed using our own softwares written in Fortran. The powder averaging procedure incorporates the two-dimensional interpolation and partitioning all directions presented by Alderman *et.al.*⁶ The intensity of SSBs in MAS spectra produced by chemical shift anisotropy was calculated using the formula derived by Herzfeld and Berger.⁷ Chemical shift anisotropy was estimated from the SSB intensity using a least squares fitting,⁸ in which the procedure was based on Fenzke *et.al.*⁹ The detailed procedure is described elsewhere.¹⁰

RESULTS AND DISCUSSION

Magic angle spinning (MAS) can average the broadening effect of the first-order quadrupole interaction, giving rise a large number of SSBs. Chemical shift anisotropy is also averaged by MAS, which also results in SSBs. Therefore, one can

estimate the quadrupole coupling and the chemical shift anisotropy from analysis of the SSB intensity.¹¹

MAS ^{51}V spectrum of the $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ is shown in Fig. 1 (A). A large number of spinning sidebands are observed over a range wider than 1.0 MHz, which originate mainly from the satellite transitions broadened by the first-order quadrupole interaction. Several stronger signals in the central position are expected to originate from the central transition. The spread of the central transition reflects the magnitude of chemical shift anisotropy. We cannot separate the central transition from the satellite transitions owing to the severe overlapping. Each spinning sideband has its own fine structure originating

from the second-order quadrupole interaction. It is difficult to measure the whole spectrum with good quality experimentally, since there are a large number of SSBs each with fine structure spread over a wide frequency range.

We attempted to extract only the signals from the central transition by use of off-MAS technique. Fig. 1 (B) shows the off-MAS spectrum of the $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$, giving central transition. Signals from the satellite transitions are broadened by the first-order quadrupole interaction, and thus can be eliminated experimentally. The first-order quadrupole interaction does not work on this transition, and therefore we have to consider the chemical shift anisotropy and the second-order quadrupole interaction. The former is responsible for the SSB intensities and the latter for the fine structure of each SSB. We analyzed the SSB intensities and line shapes of the off-MAS spectrum

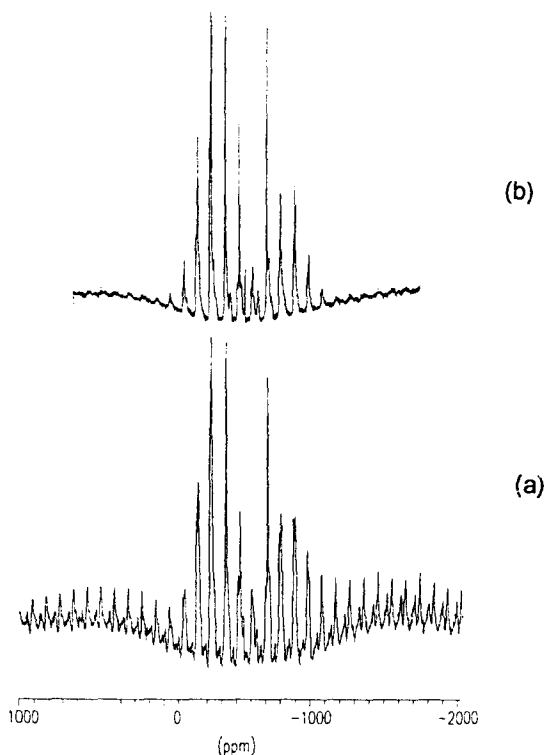


Fig. 1. (a)MAS and (b)off-MAS ^{51}V NMR spectra of $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$

measured at a Larmor frequency of 105.25 MHz to obtain chemical shift anisotropy. Next we obtain quadrupole coupling and chemical shift anisotropy from the lineshape obtained by summing up the isotropic peak and the spinning sidebands. Refinements of the parameters were carried out by simulating mainly the off-MAS spectra measured at two magnetic field strength and the static spectrum.

Table 1. Parameters of chemical shift anisotropy and quadrupole coupling of ^{51}V

Complex ^a	δ_{iso} (ppm)	$\Delta\delta_{\text{a}}$ (ppm)	η_{c}	e^2qQ/h (MHz)	η_{Q}	α (deg.)	β (deg.)	γ (deg.)	δ_{sol} (ppm)
1	-507.0	-800	0.04	8.80	0.75	0	3	0	-504.3
2	-502.0	-760	0.06	7.50	0.33	0	0	0	-503.5 -515.5
3	-518.4	-720	0.06	7.50	0.50	0	2	0	-517.7
4	-513.0	-800	0.06	8.75	0.49	0	3	0	-518.0
5	-480.8	-870	0.06	9.16	0.48	0	0	0	-524.3
6	-534.0	-730	0.28	7.84	0.50	0	5	0	-534.4
7	-547.4	-740	0.28	8.15	0.70	0	10	0	-534.5
Error	0.5	10	0.02	0.05	0.02	30	2	30	0.5

^a1; $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$, 2; $(\text{NH}_4)_3[\text{VO}_2\text{PDTA}] \cdot \text{H}_2\text{O}$, 3; $(\text{NH}_4)_3[\text{VO}_2\text{EDTA}]$,
4; $\text{Na}_3[\text{VO}_2\text{EDTA}] \cdot 4\text{H}_2\text{O}$, 5; $(\text{NH}_4)_3[\text{VO}_2\text{EDTA}] \cdot 3\text{H}_2\text{O}$, 6; $(\text{NH}_4)_3[\text{VO}_2\text{Ox}_2] \cdot 4\text{H}_2\text{O}$
7; $\text{K}_3[\text{VO}_2\text{Ox}_2] \cdot 3\text{H}_2\text{O}$.

The parameters of chemical shift anisotropy and quadrupole coupling obtained are listed in Table 1. Dioxovanadate (V) complexes show the large chemical shift anisotropy ($\Delta\delta_{\text{a}} = -800 \sim -720$ ppm) for ^{51}V atom. The components of the ^{51}V chemical shift tensor are very sensitive to the type of atoms in the first coordination sphere of the V atom. The isotropic chemical shifts (δ_{iso}) of the solid samples are very close to the values (δ_{sol}) obtained from solution. ^{51}V resonance peak in solid-state is essentially not shifted in frequency from the solution value except by outer-sphere interaction. It is interesting to note the nearly axial symmetry of chemical shift tensors, which reflect the strong deshielding environment of both nitrogen and oxygen donor atoms. The values of eulerian angles (α, β, γ) indicate that the principal axes of chemical shift tensor and quadrupole interaction tensor are almost the same.

Distortion of octahedron results in an increase of the electric field gradient at V nucleus, giving large quadrupole coupling constant ($e^2qQ/h = 7.50 \sim 9.16$ MHz) in the complexes. In general, the larger $\Delta\delta_a$ value corresponds to the larger values of QCC.

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