



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

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INTRODUCTION

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 ($m_1 = 1/2 \leftrightarrow -1/2$) 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 in $\text{H}_2\text{O}-\text{D}_2\text{O}$ (90:10 v/v) 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

RESULTS AND DISCUSSION

Solution ^{51}V NMR spectroscopy

The complexes show ^{51}V peaks whose chemical shifts fall in the range of -503.5 and -534.4 ppm relative to VOCl_3 as shown in Table 1, indicating octahedral geometry.¹ The half-widths of oxalate complexes are smaller than other complexes, due to the increase of symmetry in the structure of oxalate complexes. PDTA complex show two ^{51}V peaks at -503.5 and -515.5 ppm, indicating isomerization of the complex in aqueous solution.

Decoupling had negligible effect on the line shape. The $\pi/2$ pulse width for solution was set at 6.0 μs . The pulse length was 1.0 μs and the repetition time was 1.0 s.

Recovery time after the pulse transmission was 5 μ s. The chemical shifts were referenced to external VOCl_3 . Details of the measurements were described in the previous paper.⁶

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.*⁷ The intensity of SSBs in MAS spectra produced by chemical shift anisotropy was calculated using the formula derived by Herzfeld and Berger.⁸ Chemical shift anisotropy was estimated from the SSB intensity using a least squares fitting,⁹ in which the procedure was based on Fenzke *et al.*¹⁰ The detailed procedure is described elsewhere.¹¹

Solid-state ^{51}V NMR spectroscopy

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.¹² MAS and off-MAS ^{51}V spectra of the powder $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ are 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 might be originated from the central transition. The large shielding anisotropy at high magnetic field (9.4 T) causes the MAS spectra to be broken up into centerbands and an extensive set of spinning side bands,

Table 1. ^{51}V chemical shifts of dioxovanadate(V) complexes in solution

Complex	δ (ppm) ^a	Half-width (Hz)
$(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$	-504.3	480
$(\text{NH}_4)_3[\text{VO}_2\text{PDTA}] \cdot \text{H}_2\text{O}$		
(I)	-503.5	1290
(II)	-515.5	1050
$(\text{NH}_4)_3[\text{VO}_2\text{EDTA}]$	-517.7	910
$\text{Na}_3[\text{VO}_2\text{EDTA}] \cdot 4\text{H}_2\text{O}$	-518.0	960
$(\text{NH}_4)[\text{VO}_2\text{H}_2\text{EDTA}] \cdot 3\text{H}_2\text{O}$	-524.3	1150
$(\text{NH}_4)_3[\text{VO}_2\text{Ox}_2]$	-534.4	290
$\text{K}_3[\text{VO}_2\text{Ox}_2] \cdot 3\text{H}_2\text{O}$	-534.1	320

^aRelative to external VOCl_3 .

which are spaced by integer multiples of the spinning frequency. We cannot separate the central transition from the satellite transitions due to the severe overlapping. Thus, we measured off-MAS ^{51}V spectra, as shown in Fig. 1(b, c) to obtain only the signals from the central transitions.¹³ These signals are ascribed to the central transition. The first-order quadrupole interaction does not work on the central transition ($1/2 \leftrightarrow -1/2$), and therefore the chemical shift anisotropy and the second-order quadrupole interaction influence the line shape and the chemical shift of ^{51}V signal. We analyzed the SSB intensities and line shapes of the off-MAS spectra to obtain chemical shift anisotropy and the quadrupole coupling data, summarized in Table 2.

We have also measured the ^{51}V spectra for static samples as shown in Fig. 2. Static signals from the satellite transitions are not clearly observed and the line shape of the central transition is governed dominantly by chemical shift anisotropy. We have simulated the static spectra to check and confirm validity of the parameters obtained from analyses of the off-MAS spectra.

Dioxovanadate (V) complexes show the large chemical shift anisotropy ($\Delta\delta_a = -800 \sim -720$ 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

Table 2. Parameters of chemical shift anisotropy and quadrupole coupling of ^{51}V

Complex ^a	δ_{iso} (ppm)	$\Delta\delta_a$ (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: $\text{NH}_4[\text{VO}_2\text{H}_2\text{EDTA}] \cdot 3\text{H}_2\text{O}$, 6: $(\text{NH}_4)_3[\text{VO}_2\text{Ox}_2] \cdot 4\text{H}_2\text{O}$,

7: $\text{K}_3[\text{VO}_2\text{Ox}_2] \cdot 3\text{H}_2\text{O}$.

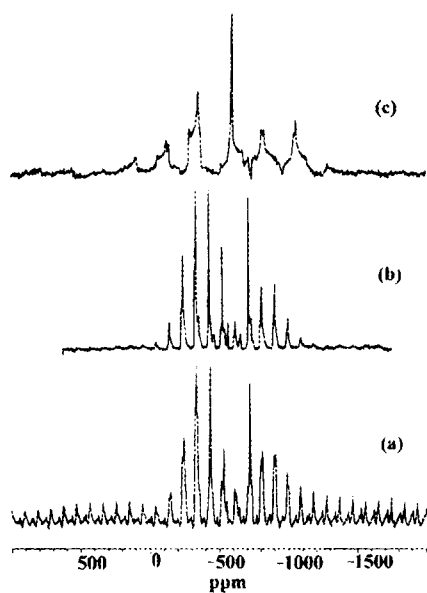


Fig. 1. ^{51}V NMR spectra of the powder $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$. (a) MAS and (b) Off-MAS spectra measured at 105.25 MHz and (c) Off-MAS spectra at 52.64 MHz. The spinning rates were (a, b) 10.00 kHz (c) 12.00 kHz.

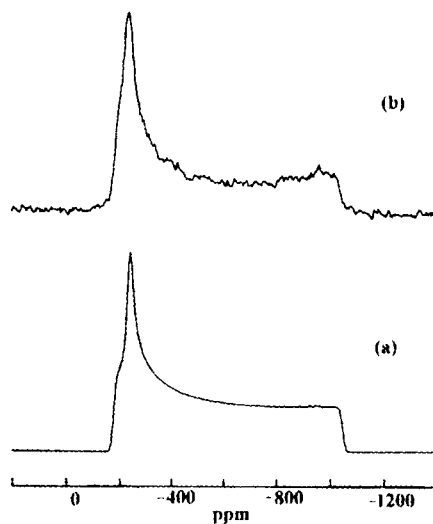


Fig. 2. (a) Calculated and (b) observed static ^{51}V NMR spectra of the powder $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ at 105.25 MHz.

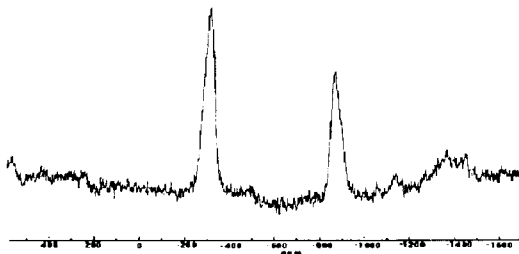


Fig. 3. Static ^{51}V NMR spectra of the single crystal $(\text{NH}_4)_2[\text{VO}_2\text{NTA}]$ at 105.25 MHz.

except by outer-sphere interaction. It is interesting to note the nearly axial symmetry of chemical shift tensors, which reflect similar deshielding environments for both nitrogen and oxygen donor atoms. The stronger the distortion from a regular octahedron, the larger the value of $\Delta\delta_a$. 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. It seems to expect a correlation between $\Delta\delta_a$ and quadrupole coupling for the complexes. The static ^{51}V spectrum of a single crystal is shown in Fig. 3, indicating two distinguishable signals which means two magnetically inequivalent but chemically identical vanadium sites. These sites are generated by the 2_1 symmetry operator within the unit cell.⁶

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REFERENCES

1. O. W. Howarth, *Prog. NMR Spectrosc.* **22**, 43 (1990) and references are therein.
2. O. B. Lapina, V. M. Mastikhin, A. A. Shubin, V. N. Krasilnikov, and K. I. Zamaraev, *Prog. NMR Spectrosc.* **24**, 457 (1992) and references are therein.
3. D. Rehder, *Bull. Magn. Reson.* **4**, 33 (1982).
4. H. Eckert, and I. E. Wachs, *J. Phys. Chem.* **93**, 6796 (1989).
5. L. Przyborowski, G. Schwarzenbach, and Th. Zimmermann, *Helv. Chim. Acta.* **48**, 1556 (1965).
6. M. -H. Lee, N. H. Heo, and S. Hayashi, *Polyhedron.* **17**, 55 (1998).
7. D. W. Alderman, M. S. Solum, and D. M. Grant, *J. Chem. Phys.* **84**, 3717 (1986).
8. J. Herzfeld, and A. E. Berger, *J. Chem. Phys.* **73**, 6021 (1980).

9. S. Hayashi and K. Hayamizu, *Chem. Phys.* **157**, 381 (1991).
10. D. Fenzke, B. Maess, and H. Pfeifer, *J. Mag. Reson.* **88**, 172 (1990).
11. S. Hayashi, *Magn. Reson. Chem.* **34**, 791 (1996).
12. M. Mehring, "Principles of High Resolution NMR in Solids" Springer-Verlag, Berlin, 1983.
13. E. Oldfield, R. A. Kinsey, B. Montez, T. Ray and K. A. Smith, *J. Chem. Soc. Chem. Commun.* 254 (1982).