# Notes

## Solution and Solid-State NMR Studies of Vanadium(V)-Ethylenediaminetetraacetate Complexes

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NMR spectroscopy provide valuable informations on structure, coordination bond etc. of vanadium(V) complexes. Many carboxylic acids are known to form anhydrides with vanadate in solution, if they also have further hydroxyl or amine groups available for chelation. Oxalate[1-3] gives the simple mono- and bisoxalato species, presumably with *cis*-octahedral coordinaton. Also aminopolycarboxylates such as ethylenediaminetetraacetate (EDTA) form similar complexes.[4-6] However, α-hydroxycarboxylates such as lactate, glycerate etc. form a variety of derivatives, including simple esters, chelates having trigonal bipyramidal coordination, and two binuclear complexes with mixed coordination.[2,7,8]

The solid-state $^{13}$C-NMR study of vanadium(V) complexes has not been reported with the exception of bis(oxalato)-dioxovanadate(V)[3]. But in recent years $^{51}$V-NMR has emerged as a powerful tool for studying the local environment of vanadium in solid vanadia based catalysts[9] and some solid metavanadates.[10,11] The resulting $^{51}$V MAS spectra are not simple due to the simultaneous line-broadening effects arising from second-order quadrupolar and chemical shift anisotrpy (*ca.* 1000 ppm). Nevertheless, considerable information can be obtained by comparing the spectrum of the unknown solid with those of known crystals. The linewidths are not always large, because the quadrupolar coupling constant $e^2qQ/h$ may be modest in magnitude, *e.g.* 800 kHz for $V_2O_5$. The solid-state $^{51}$V-NMR study of vanadium(V) complex has not been reported elsewhere.

Of vanadium(V)-aminopolycarboxylate complexes Amos and Sawyer[4] reported first $^1$H-NMR (100 MHz) study of EDTA complex in solution. In the previous papers[5,6] we reported the studies on the interaction of vanadium(V) with some aminopolycarboxylates in aqueous soluton by $^{13}$C- and $^{51}$V-NMR spectroscopies. The structures of EDTA complexes have also been studied by X-ray diffraction method.[12,13] These complexes have *cis*-VO₂ group as oxalate complexes do. The structure of (NH₄)₃[VO₂Y] where Y[4-] represented a fully deprotonated ethylenediaminetetracacetate anion is shown in Figure 1. The vanadium atom of the complex anion is octahedrally complexed to two oxo ligands, two nitrogen atoms and two oxygen atoms from the two (protonated or unprotonated) actetate groups of the EDTA ligand. The complexes have a $C_2$ axis of symmetry passing through the vanadium and the center of ethylenic backbone.
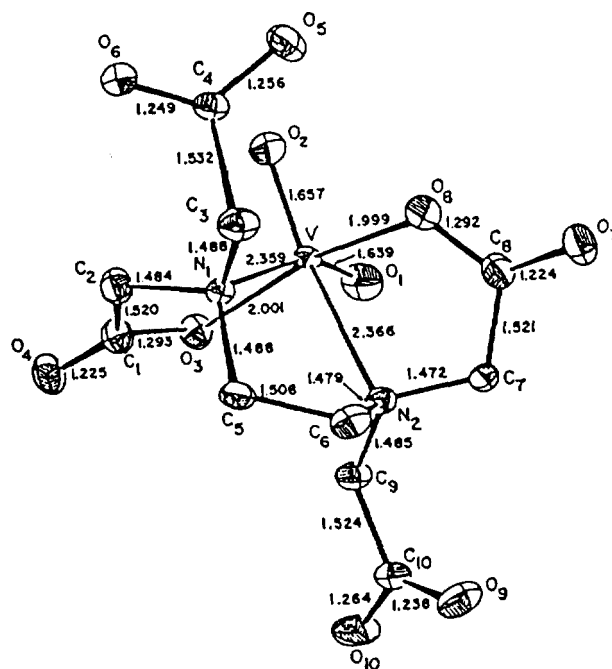


**Figure 1.** ORTEP of Na₃[VO₂Y] · 4H₂O carrying the pertinent bond distances(A).[13]

In this paper we reported the solution ($^1$H, $^{13}$C and $^{51}$V) and solid-state ($^{13}$C and $^{51}$V) NMR studies of three vanadium (V)-EDTA complexes, (NH₄)₃[VO₂Y], Na₃[VO₂Y]·4H₂O and (NH₄)[VO₂H₂Y]·3H₂O, and the spectra were discussed in relation with the structrues. The solid-state $^{51}$V-NMR spectra of vanadium(V) complexes were reported here at first time.

All of the vanadium(V) complexes in solution show similar patterns in $^1$H spectra. In the complexes the four available coordination sites of the VO₂ are occupied by two nitrogen and two acetate oxygen atoms of EDTA as shown in Figure 1. Two other acetate groups are not bonded to vanadium. Because the bonded nitrogen is asymmetric, the methylene protons on a nonbonded acetate group as well as a bonded acetate group are nonequivalent. Hence, an AB splitting pattern is expected for the nonbonded as well as for the bonded acetate groups. For example, the wide AB patern, centered at 3.93 ppm, arises from the bonded acetate groups and the AB pattern, centered at 3.97 ppm, arises from the nonbonded acetate groups in the $^1$H spectrum of (NH₄)₃[VO₂Y][4-]. The ethylenic backbone protons of the ligand also show complicated A₂B₂ pattern in the range of 2.9-3.3 ppm. No attempt has been made to analyze the A₂B₂ pattern. In the spectrum of Na₃[VO₂Y]·4H₂O there are small impurity peaks, indicating some hydrolysis of the complex in the solution. The $^1$H chemical shifts and coupling constants of the vanadium(V) complexes are summarized in Table 1. All of the vanadium (V) complexes in solution also show similar patterns in $^{13}$C spectra. The $^{13}$C chemical shifts of the vanadium(V) complexes are summarized in Table 2. For example, five peaks of almost equal intensity appear in the $^{13}$C spectra of

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**Table 1.** ¹H-NMR Chemical Shifts[a] (in ppm) and Coupling Constants (in Hz) of Acetate Groups in Vanadium(V) Complexes

| Complex[b] | CH₂COO(U)[c] | CH₂COO(B)[c] | NCH₂CH₂N |
|---|---|---|---|
| (NH₄)₃[VO₂Y] | 3.97(18.3) | 3.93(17.2) | 2.9-3.3 |
| Na₃[VO₂Y] · 4H₂O | 3.98(17.7) | 3.94(17.3) | 2.9-3.3 |
| (NH₄)[VO₂H₂Y] · 3H₂O | 3.97(17.8) | 4.18(18.4) | 2.8-3.4 |

[a] Relative to external TMS. [b] Y⁴⁻ = (⁻OOCCH₂)₂NCH₂CH₂N(CH₂-COO⁻)₂. [c] B: bound, U: unbound.

**Table 2.** ¹³C Chemical Shifts[a] (in ppm) of Vanadium(V) Complexes in Solution

| Complex[b] | COO (U)[c] | COO (B)[c] | CH₂ (U)[c] | CH₂ (B)[c] | NCH₂-CH₂N |
|---|---|---|---|---|---|
| (NH₄)₃[VO₂Y] | 177.75 | 182.79 | 61.78 | 63.66 | 54.71 |
| Na₃[VO₂Y] · 4H₂O | 177.82 | 182.82 | 61.77 | 63.64 | 54.65 |
| (NH₄)[VO₂H₂Y] · 3H₂O | 173.85 | 182.10 | 60.97 | 61.25 | 54.77 |

[a] Relative to external TMS. [b] Y⁴⁻ = (⁻OOCCH₂)₂NCH₂CH₂N(CH₂-COO⁻)₂. [c] B: bound, U: unbound.

**Table 3.** Solution and Solid-State ⁵¹V Chemical Shifts[a] (in ppm) of Vanadium Complexes

| Complex[b] | δ (solution) | δᵢ (solid)[c] | |
|---|---|---|---|
| (NH₄)₃[VO₂Y] | −517.7 | −525 | −539 |
| Na₃[VO₂Y] · 4H₂O | −518.0 | −523 | −538 |
| (NH₄)[VO₂H₂Y] · 3H₂O | −524.3 | −489 | −504 |

[a] Relative to external VOCl₃. [b] Y⁴⁻=(⁻OOCCH₂)₂NCH₂CH₂N(CH₂-COO⁻)₂. [c] δᵢ: isotropic shift.

(NH₄)₃[VO₂Y]. Four are asigned to the carbons of two kinds of acetate groups; unbound (177.75 and 61.78 ppm) and bound (182.79 and 63.66 ppm) acetate groups.[5] The carbons of unbound acetate groups resonate at higher magnetic field than those of bound acetate groups do. And one (54.71 ppm) is assigned to the carbons of ethylenic backbone. The unbound acetate groups in (NH₄)[VO₂H₂Y]·3H₂O resonate at higher field, indicating protonatation of these groups. The ⁵¹V chemical shifts of the vanadium(V) complexes in solution are given in Table 3. All of the complexes show almost identical ⁵¹V chemical shifts, indicating that they have same coordination geometry. The peaks occurring at −517.7-524.3 ppm are assigned to the octahedral complex. These ⁵¹V shifts are very close to −536 ppm of bis(oxalato)dioxovanadate² which is known as a octahedral complex. The difference of chemical shifts between EDTA and oxalate complexes is most likely due to the electron-donating ability of the ligands.

The CP/MAS ¹³C chemical shifts of the solid complexes are summarized in Table 4. According to the X-ray structures of Na₃[VO₂Y]·4H₂O¹³ and (NH₄)[VO₂H₂Y]·3H₂O¹² the crystals have four molecules in the unit cells (space group P2₁/n); the unit cell contains four crystallographically equivalent molecules with each having a two-fold axis of symmetry passing through the vanadium and the center of ethylenic backbone. The ¹³C spectra show four peaks in carboxylate region;

**Table 4.** CP/MAS ¹³C Chemical Shifts[a] (in ppm) of Vanadium(V) Complexes

| Complex[b] | COO (U)[c] | COO (B)[c] | CH₂ (U)[c] | CH₂ (B)[c] | NCH₂-CH₂N |
|---|---|---|---|---|---|
| (NH₄)₃[VO₂Y] | 174.16 172.96 | 179.27[d] | 57.14 | 62.85 | 54.45 |
| Na₃[VO₂Y] · 4H₂O | 175.04 173.65 | 180.18 178.98 | 59.03 57.31 | 61.52[d] | 55.65 48.23 |
| (NH₄)[VO₂H₂Y] · 3H₂O | 174.05 172.74 | 182.89 181.81 | 52.23 | 61.48 | 50.48 |

[a] Relative to external TMS. [b] Y⁴⁻ = (⁻OOCCH₂)₂NCH₂CH₂N(CH₂COO⁻)₂. [c] B: bound, U: unbound. [d] Overlapped peak.
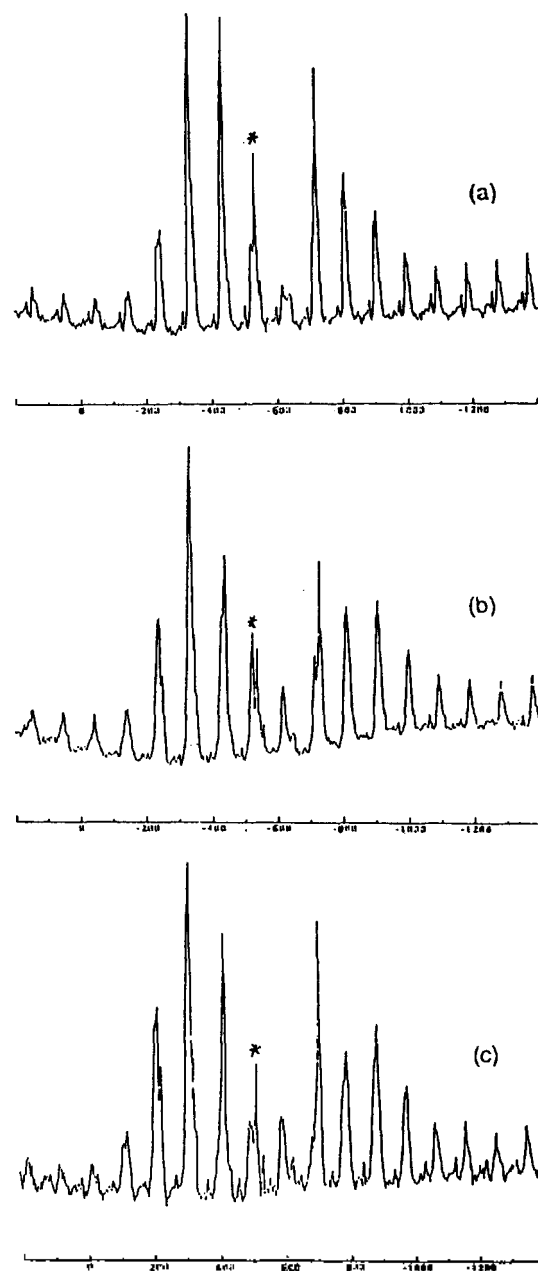


**Figure 2.** CP/MAS ⁵¹V-NMR spectra of (a) (NH₄)₃[VO₂Y], (b) Na₃[VO₂Y] · 4H₂O and (c) (NH₄)[VO₂H₂Y] · 3H₂O.

two are assigned to two unbound carboxylate groups and other two are assigned to bound carboxylate groups. $^{13}C$ chemical shifts of solid complexes are influenced by the environment of vanadium(V), such as type of cation, hydrogen bonding of water molecule, etc. There are substantial differences between the solid-state and solution $^{13}C$ spectra of sample. In general, the multiple signals could arise from either an induced nonequivalence in the solid-state where the site symmetry is lower than the molecular symmetry or because the unit cell contains molecules which are magnetically nonequivalent.[14] It may be possible to distinguish these two possibilities from the X-ray structure. But the complexes show two sets of resonances, which correspond to the two magnetically inequivalent (but chemically identical) molecules generated by the $2_1$ symmetry operation within the unit cell.[15] The MAS $^{51}V$ spectra of the vanadium(V) complexes are shown in Figure 2, and the center bands are indicated by asterisk. All of the complexes show similar sideband patterns. The large shielding anisotropy at high magentic field (9.4 T) causes the spectra to be broken up into centerbands and an extensive set of spinning sidebands, which are spaced by integer multiples of the spinning frequency. The isotropic chemical shift frequencies are independent of the spinning speed and can easily be identified by varying the spinning rate. All of the complexes show two discernible $^{51}V$ patterns, corresponding two magnetically inequivalent sites. The results are also consistent with those of CP/MAS $^{13}C$ spectra. The isotropic chemical shift values obtained from the solid-state measurements, compared to those in solution, are summarized in Table 3. From the proximity of $^{51}V$ chemical shifts in solution and solid-state complexes, we guess that the geometries in the solid-state might also be retained in the solution. In conclusion, NMR spectroscopy has been proved to be a powerful tool in the characterization of solution and solid-state vanadium(V) complexes.

## Experimental

**Preparation of vanadium(V) complexes.** The vanadium complexes, $(NH_4)_3[VO_2Y]$, $Na_3[VO_2Y] \cdot 4H_2O$ and $(NH_4)$ $[VO_2H_2Y] \cdot 3H_2O$, were prepared by the method of Przyborowski *et al.*[16]

**NMR measurements.** $^1H$, $^{13}C$ and $^{51}V$ spectra of samples in $D_2O$ were recorded on a JEOL GSX-400 NMR spectrometer at 400, 100.5 and 105 MHz, respectively, at 298 K. $^{13}C$ spectra of solid samples (*ca.* 0.2 g) were recorded on a Bruker MSL-300 spectrometer (75.47 MHz) with CP/MAS technique at room temperature. A spectral width of 29411 Hz and an accumulation of *ca.* 200 transients with an acquisition time of 0.85 s were used. The contact time was 2 ms and the delay between each scan was 5 s. MAS $^{51}V$ spectra of the vanadium(V) complexes were recorded on a Bruker MSL-400 spectrometer (105 MHz) at room temperature using a spin rate of 10 kHz. The ordinary single pulse sequence was used without $^1H$ dipolar decoupling. The $^1H$ and $^{13}C$ chemical shifts are referenced to external TMS. And $^{51}V$ shifts are referenced to external $VOCl_3$.

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## Isopinocampheylhaloborane-Methyl Sulfide as Regioselective Monohydroboration Reagent. Synthesis of Aldehydes and Ketones from Alkynes in High Isomeric Purity

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Thexylhaloborane-methyl sulfide (ThxBHX·SMe$_2$, X=Cl, Br, I) appeared to be exceptionally valuable monohydroboration reagents for the selective hydroboration of alkynes of different structural types.[1] These reagents monohydroborate both internal and terminal alkynes cleanly with high regio- and stereospecificity to provide a valuable synthetic route to isomerically pure aldehydes and ketones.