

바나듐(V)-아미노폴리카르본산 착물의 탄소-13 및 바나듐-51 핵자기공명연구 (제 1 보)

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Carbon-13 and Vanadium-51 Nuclear Magnetic Resonance Studies of Vanadium(V)-Aminopolycarboxylic Acids (I)

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요 약. 탄소-13 및 바나듐-51 핵자기공명분광법을 이용하여 아미노폴리카르본산-바나듐(V) 착물의 용액 내에서의 구조에 대해 연구하였다. 이 때 사용한 리간드는 ethylenediaminetetraacetic acid (EDTA), *trans*-cyclohexanediaminetetraacetic acid (CDTA), 1,2-propylenediaminetetraacetic acid (PDTA), ethylenediaminediacetic acid (EDDA), 2-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), 및 nitrilotriacetic acid (NTA) 등이었다. 모든 리간드는 바나듐(V)과 시스-VO₂ 핵을 함유하는 정 8면체 구조의 1:1 착물을 생성하였다. 바나듐(V)에 대한 히드록시에틸기의 배위는 아세테이트기의 배위에 비해 덜 바람직함을 알 수 있었다. 그리고 EDDA 및 PDTA는 각각 2가지의 이성체착물들을 생성함을 알 수 있었다.

ABSTRACT. ¹³C and ⁵¹V NMR spectroscopy have been used to study the solution structures of the vanadium (V) complexes formed by ethylenediaminetetraacetic acid (EDTA), *trans*-cyclohexanediaminetetraacetic acid (CDTA), 1,2-propylenediaminetetraacetic acid (PDTA), ethylenediaminediacetic acid (EDDA), 2-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrilotriacetic acid (NTA). All of the complexes probably have octahedral structures containing *cis*-VO₂ core. The coordination of hydroxyethyl group is found to be less favored than that of acetate group. EDDA forms two isomers, α -*cis* and β -*cis*. PDTA also forms two structural isomers due to the methyl group in the ligand.

INTRODUCTION

Recently, there is increasing evidence that vanadium has a significant biological role¹⁻³. The Mo(IV)/Mo(V) or Mo(V)/Mo(IV) couple

is expected to be involved in the enzymatic oxidation-reduction reactions⁴. The chemistries of V(V)/V(IV) and Mo(VI)/Mo(V) are known to be similar, and vanadium can replace molybdenum in certain nitrogenases, although

with a subsequent decrease in enzyme effectiveness^{5~7}. The equilibrium and kinetic studies have been reported for some vanadium (V)-aminopolycarboxylic acid chelates^{8~14}. It is reported that most aminopolycarboxylic acids form only 1:1 complexes with vanadium (V). Kinetic studies of some peroxovanadium (V) complexes in aqueous solutions have also been reported^{15~19}.

According to the ¹H NMR study²⁰ ethylenediaminetetraacetic acid (EDTA) and N, N-dimethylethylenediaminediacetic acid (DMEDDA) form α -*cis* complexes with vanadium (V) in aqueous solution, while ethylenediaminediacetic acid (EDDA) forms α -*cis* and β -*cis* isomers (The terminology is suggested by Legg *et al.*²¹). ¹H NMR spectroscopy has proven useful for the studies of the numerous metal complexes with aminopolycarboxylic acid ligands such as EDTA^{22~28}. To date, however, virtually little attention has been given to study these complexes by ¹³C NMR spectroscopy. It is supposed that ¹³C NMR spectroscopy is particularly useful in the study of such metal chelate systems because the wide range of chemical shifts and narrow linewidths readily allow us to resolve individual carbon resonances in various structural forms. The ⁵¹V NMR spectroscopy has been primarily used to study the structures of isopolyvanadate ions in aqueous solution and the relatively narrow line widths are reported^{29~32}. But the ⁵¹V NMR study of vanadium(V) complex has not been carried out.

We plan to investigate the coordination of vanadium (V) to a number of aminopolycarboxylic acid ligands which contain various functional groups such as amine, carboxylate, hydroxyethyl, ether, *etc.* In this paper we report the ¹³C and ⁵¹V NMR studies of vanadium(V) complexes of ethylenediaminete-

traacetic acid(EDTA), *trans*-cyclohexanedi-aminetetraacetic acid (CDTA), 1,2-propylenediaminetetraacetic acid (PDTA), ethylenediaminediacetic acid (EDDA), 2-hydroxyethylethylenediaminetriacetic acid (HEDTA), diethylenetriaminepentaacetic acid(DTPA), and nitrilotriacetic acid (NTA) in the aqueous solution of pH 6.

EXPERIMENTAL

All of the ligands utilized were commercially available. PDTA was obtained from LaMont Laboratories and recrystallized from hot water before use. DTPA and CDTA were obtained from Geigy Industrial Chemicals and used as received. The remaining ligands were obtained from Aldrich Chemical Company and used as received. Ammonium metavanadate, NH₄VO₃, was obtained from Matheson Coleman and Bell. The ligands were used as free acids or sodium salts.

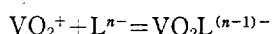
Sample solutions for NMR were prepared by dissolving the weighed amounts of ligand and NH₄VO₃ into in 20 % D₂O/80 % H₂O by addition of 50 % NaOH solution to provide solution of 0.5M in ligand. After dissolving the pH of the solution was adjusted to 6.0 \pm 0.2 with 50 % NaOH solution and concentrated H₂SO₄. ¹³C NMR spectra were obtained on a Varian XL-100 FT spectrometer (25.16 MHz) at 40°C. A sweep width of 5120 Hz and an accumulation of 1000-10000 transients with acquisition time of 0.800 sec(8191 data points) were normally used. The samples were run in 10 mm tubes with broad band proton noise decoupling. Chemical shifts were measured relative to internal dioxane and reported relative to external TMS using the relation $\delta_{\text{TMS}} = \delta_{\text{Dioxane}} + 67.73 \text{ ppm}$.

⁵¹V NMR spectra were obtained on a Bruker WM 250 FT spectrometer(67.76 MHz). A sweep width of 20 kHz and pulse length of 10 μ sec

were used. The spectra were obtained from the accumulation of ~ 1000 transients with acquisition time of 0.102 sec. The chemical shifts were measured relative to external VOCl_3 . The samples were also run in 10 mm tubes at $40 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Vandium(V) which has d^0 electronic configuration forms octahedral complex with aminopolycarboxylic acid (d^2sp^3 bonding) by the reaction:



where L^{n-} represents the ligand anion of aminopolycarboxylic acid. The formation of mononuclear vanadium(V) species in aqueous solution is limited by the ease of formation of polynuclear vanadates. The principal mononuclear species is thought to be the aquated dioxovanadium ion, VO_2^+ , which is formed when metavanadate solution is acidified³³. The studies of the dioxovanadium(V) complexes are rare. The main obstacle appears to be uncertainty regarding the precise nature of vanadium(V) species present in solution. This is also due to the fact that the free dioxovanadium ion, VO_2^+ , readily hydrolyzes to HVO_5^{4-} and VO_3^- , and also polymerizes in moderately acidic solution. In addition the VO_2^+ is often reduced by some organic substances in acidic media.

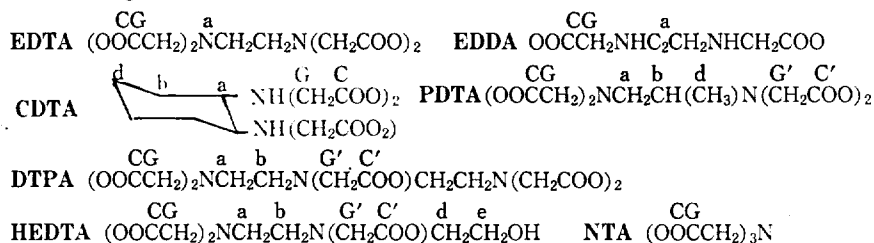
In this study we chose pH 6 to form the dioxovanadium(V) complexes with aminopolycarboxylic acids in aqueous solution because vanadium(V)-EDTA complex is reported to be stable around pH 6 by kinetic study³⁴. It is supposed that at higher pH OH^- displaces the coordinated carboxyl group from the metal ion and thereby the complex hydrolyzes to vanadium(V) and free ligand. The pH of the solution can also affect the kind of complex species formed.

The formation of complexes was easily detected by the appearance of a set (or sets) of new resonances which were distinct from the free ligand resonances over a range of metal-ligand ratios. The resonance lines of ^{13}C NMR were generally sharp and therefore consistent with the slow exchange of ligand between bound and unbound states on NMR time scale. All of the ligands studied formed quite strong complexes with vanadium(V) at pH 6 as judged by the virtually complete conversion of unbound to bound resonances in the solution. The ^{13}C chemical shift data for the ligands in free and complexed forms are shown in Table 1. The new resonance peaks of ^{51}V NMR were also appeared in the vanadate solutions when complexes were formed as shown in Table 2. The ^{51}V NMR chemical shifts of the complexes ranged from -509.3 to -524.6 ppm relative to VOCl_3 , which were downfield from that (-541.2 ppm)³⁰ of tetrahedral VO_4^{3-} . The downfield resonance is probably due to the decreased electron density on vanadium, which reflects the stronger oxo bonding in octahedral vanadium-aminopolycarboxylic acid complexes than in the tetrahedral VO_4^{3-} . The ^{51}V NMR resonance peaks were well separated when structural isomers of the complexes were formed as shown typically in Fig. 1. EDDA formed two isomers with vanadium(V) which resonate at -523.4 and -512.5 ppm, respectively.

Aqueous solutions of the most vandium(V) complexes at pH 6 retained their initial yellow color and were stable about one month before taking a green tint. However, the solutions of vanadium(V) complexes of the ligands such as EDDA and HEDTA containing OH or NH groups turned slightly green after standing for 1 or 2 days, indicating oxidation of the ligands by vanadium(V). The oxidation was often acid-catalyzed to give a paramagnetic blue VO^{2+}

Table 1. ^{13}C chemical shifts(ppm) of free ligands and complexed ligands (U: unbonded, B: bonded).

Ligand or Complex	Assignment ^a											
	C(U)	C(B)	C'(U)	C'(B)	G(U)	G(B)	G'(U)	G'(B)	a	b	d	e
EDTA ²⁻	173.50				58.98				52.59			
[VO ₂ EDTA] ³⁻	177.79	182.83			62.05	63.86			54.87			
EDDA	172.44				50.96				44.70			
[VO ₂ EDDA(I)] ⁻		184.31				55.14			49.82			
[VO ₂ EDDA(II)] ⁻		184.10				59.02			48.50			
		180.87				57.47			49.82			
CDTA ²⁻	175.32				55.56				63.56	25.33	24.99	
[VO ₂ CDTA] ³⁻	179.54	182.94			54.91	60.67			65.34	26.81	25.42	
PDTA ²⁻	173.03		174.19		59.35		55.67		57.61	58.06	11.85	
[VO ₂ PDTA(I)] ³⁻	179.56	183.07	179.56	183.07	57.85	66.53	53.26	63.08	60.73	57.85	12.29	
[VO ₂ PDTA(II)] ³⁻	177.31	182.16	177.99	183.52	57.44	66.29	53.03	62.85	62.08	59.50	12.62	
DTPA ³⁻	171.73		179.44		58.29		57.52		54.14	50.43		
[VO ₂ DTPA] ³⁻	177.59	182.68		181.08	58.89	63.64		62.07	54.97	54.12		
	171.35				60.56				55.45	51.55		
HEDTA ⁻	175.70		175.19		58.91		57.44		52.62	52.35	58.36	57.44
[VO ₂ HEDTA] ²⁻	177.77	182.79		182.31	61.81	63.68		62.04	54.98	54.46	61.56	58.56
NTA ²⁻	171.45				58.52							
[VO ₂ NTA] ²⁻		180.75				66.31						

^a Structural assignment:Table 2. ^{51}V NMR chemical shift data of vanadium (V) complexes.

Complex	Chemical shift(ppm) ^a	Half-width(Hz)
[VO ₂ EDTA] ³⁻	-522.9	1,050
[VO ₂ EDDA(I)] ⁻	-512.5	670
[VO ₂ EDDA(II)] ⁻	-523.4	700
[VO ₂ CDTA] ³⁻	-509.8	1,470
[VO ₂ PDTA(I)] ³⁻	-509.3	930
[VO ₂ PDTA(II)] ³⁻	-518.8	730
[VO ₂ DTPA] ³⁻	-524.6	1,870
[VO ₂ HEDTA] ²⁻	-523.0	1,030
[VO ₂ NTA] ²⁻	-509.3	430

^a Relative to VOCl₃; positive is downfield.

species.

The maximum oxidation state of vanadium is +5. Vanadium(V) forms two oxo species, VO³⁺ and VO₂⁺. The former unit is found in the oxyhalides. The second species, VO₂⁺, is not well characterized. The structural determination by X-ray diffraction methods for the crystalline oxalato(H₂Ox) chelate, (NH₄)₃(VO₂(Ox)₂)³⁵, and EDTA(H₄Y) chelates, NH₄(VO₂H₂A)·3H₂O³⁶ and Na₃(VO₂A)·4H₂O³⁷, have been reported. A consistent stereochemical pattern for the dioxovanadium(V) complexes emerged from these studies, indicating that all three complexes had irregular octahedral geo-

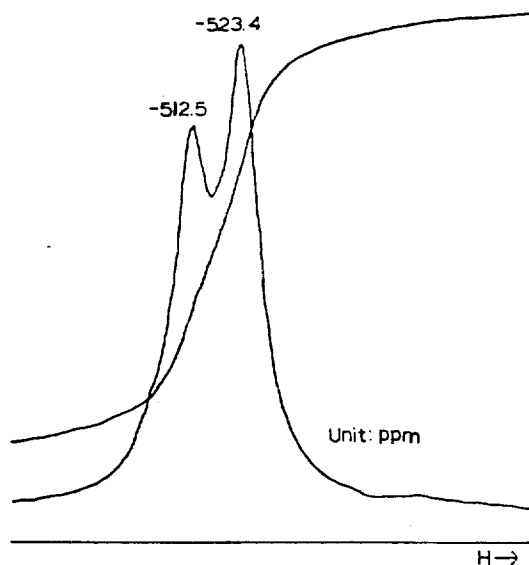


Fig. 1. ^{51}V NMR spectrum of the solution containing 0.5 M NH_4VO_3 and 0.5 M EDTA at pH 6.

metry with two double-bonded oxygen atoms *cis* to each other. The VO_2 group was strongly kinked: the OVO angles ranged from 104 to 107°.

Vanadium(V)-EDTA. Vanadium(V), with two of its coordination sites occupied by oxygen atoms, probably has an octahedral configuration with four available coordination sites. Hence, the donor atoms of multidentate ligands will compete for these bonding sites. In the ^{13}C NMR spectra of Fig. 2 five peaks are appeared when EDTA complex is formed. Two peaks appeared at 63.86 and 182.83 ppm are assigned to the carbon atoms of the bound acetate groups. Two peaks appeared at 62.05 and 177.79 ppm are assigned to the carbon atoms of the unbound acetate groups, and the peak appeared at 54.87 ppm is assigned to the carbon atoms of the ethylenic backbone. Thus, the four available coordination sites of the VO_2^+ ion are occupied by two nitrogen and two acetate oxygen atoms of EDTA, and two other acetate groups are free to rotate about C-N bonds. The complex,

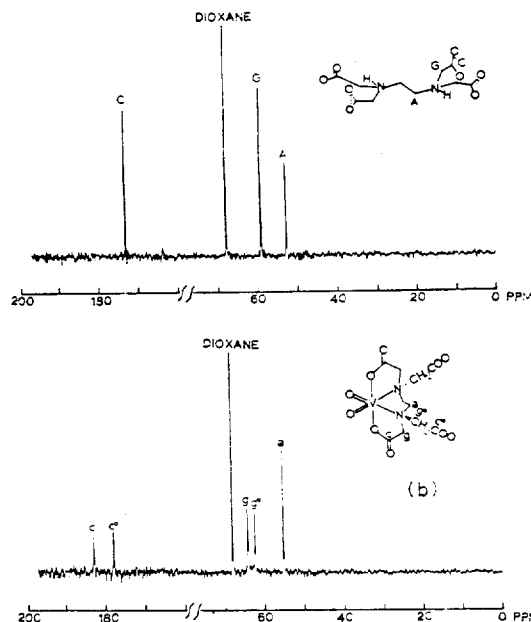


Fig. 2. ^{13}C NMR spectra of the solutions containing (a) 0.5 M EDTA and (b) 0.5 M NH_4VO_3 and 0.5 M EDTA at pH 6.

$[\text{VO}_2\text{EDTA}]^{3-}$, has a C_2 axis of symmetry passing through the vanadium atom and the center of ethylenic backbone, resulting in *cis*- VO_2 geometry. The ^{51}V NMR shows one resonance at -522.9 ppm when the complex is formed. This result is consistent with the ^{13}C NMR data. Two nitrogen atoms of the free EDTA at pH 6 are almost completely protonated. Thus, displacement of two bound protons by VO_2^+ produces substantial downfield shift of the carbon atoms in vicinity of the coordination sites when complexation occurs.

Vanadium(V)-CDTA. CDTA has been used as an excellent masking agent for many metal ions. Especially in the spectrophotometric determination of vanadium(V) with xylenol orange³⁸ or 4-(2-pyridylazo)-resorcinol (PAR)^{39,40}, CDTA prevents the interference of many metal ions. EDTA does not show such a selective masking behavior as CDTA does and prevents the color reaction of vanadium(V). Therefore,

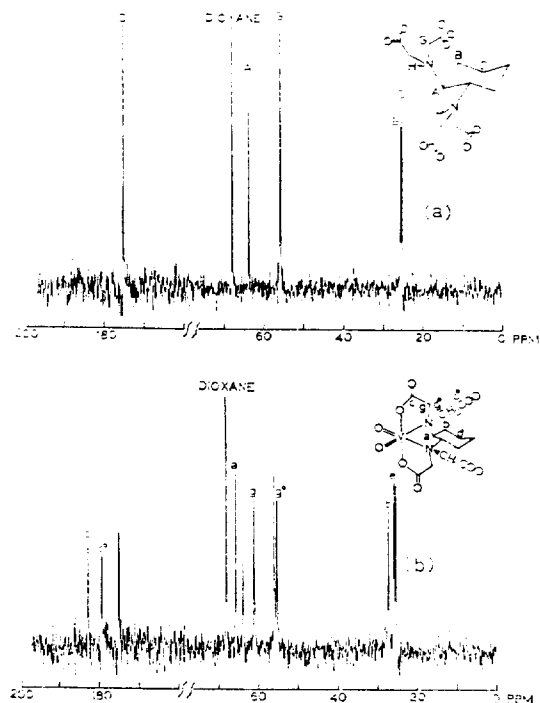


Fig. 3. ^{13}C NMR spectra of the solutions containing (a) 0.5 M CDTA and (b) 0.5 M NH_4VO_3 and 0.5 M CDTA at pH 6.

CDTA is supposed to show a special action toward vanadium(V) in that the stability order of CDTA- and EDTA-complexes of vanadium(V) is the reverse of that found for many metal ions. This is exceptional because metal-CDTA complexes are usually more stable than the corresponding EDTA complexes⁴¹. The ^{13}C NMR spectra of CDTA and its vanadium(V) complex are shown in Fig. 3. It is evident that ^{13}C resonance lines of the free ligand are superimposed on those of the complex in Fig. 3(b), indicating the presence of the free CDTA in the solution. It may be due to the fact that CDTA complex is usually formed or dissociated slowly. In the complex the bound acetate groups resonance at 60.67 and 182.94 ppm and the unbound acetate groups resonance at 54.91 and 179.54 ppm. It is also assigned that the carbons of the cyclohexane ring reso-

nance at 25.42, 16.81 and 65.34 ppm. It is assumed that the four available coordination sites of VO_2^+ are occupied by two nitrogen and two acetate oxygen atoms, and two other acetate groups are free as in EDTA complex. $[\text{VO}_2\text{CDTA}]^{3-}$ has also a symmetrical structure. The ^{51}V NMR spectra shows a resonance peak at -509.8 ppm when the complex is formed.

According to the chemical bond model studies, the exceptionally low stability of $[\text{VO}_2\text{CDTA}]^{3-}$ compared to $[\text{VO}_2\text{EDTA}]^{3-}$ can be largely attributed to the steric hindrance between the free acetate groups and the hydrogen atoms on the b carbons in the cyclohexane ring.

Vanadium(V)-PDTA. Since PDTA can be labelled by its optical activity, it is useful in carrying out the ligand exchange studies with metal complexes and in investigating the principle of stereospecific limitation in the complex. In PDTA the methyl substituent on the ethylenic backbone causes two iminodiacetic (IDA) groups to become chemically different and the acetate carbons of each IDA group become magnetically inequivalent upon coordination.

The ^{13}C NMR spectra of PDTA and its complex are shown in Fig. 4. Coordination of PDTA to vanadium(V) produces two structural isomers which are different in the methyl position in the complexes, being identified from the fact that two sets of new resonance lines are appeared in the ^{13}C NMR spectrum and two resonance peaks are also appeared in the ^{51}V NMR spectrum. The intensity ratio of two isomers is not exactly one because of the preference of the methyl group for the equatorial position to axial position. In the region of carboxylate resonance of the ^{13}C NMR there are six lines of which two have twice intensities of the others. This fact indicates the presence of eight carboxylate carbons in the com-

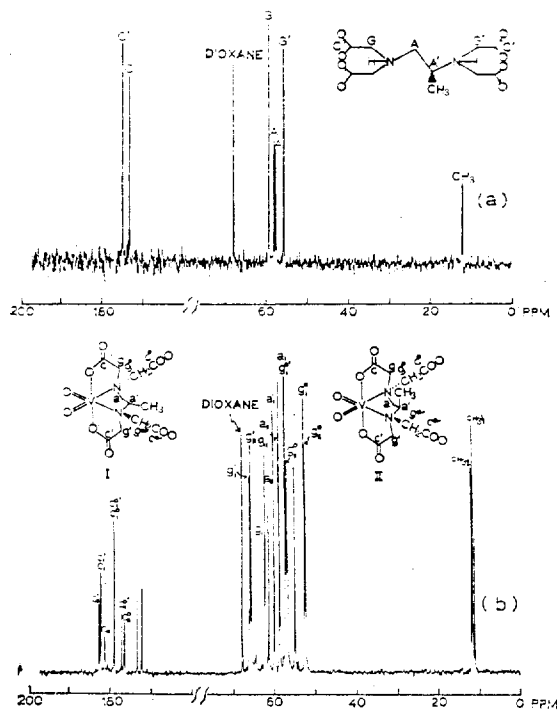


Fig. 4. ^{13}C NMR spectra of the solutions containing (a) 0.5 M PDTA and (b) 0.5 M NH_4VO_3 and 0.5 M PDTA at pH 6.

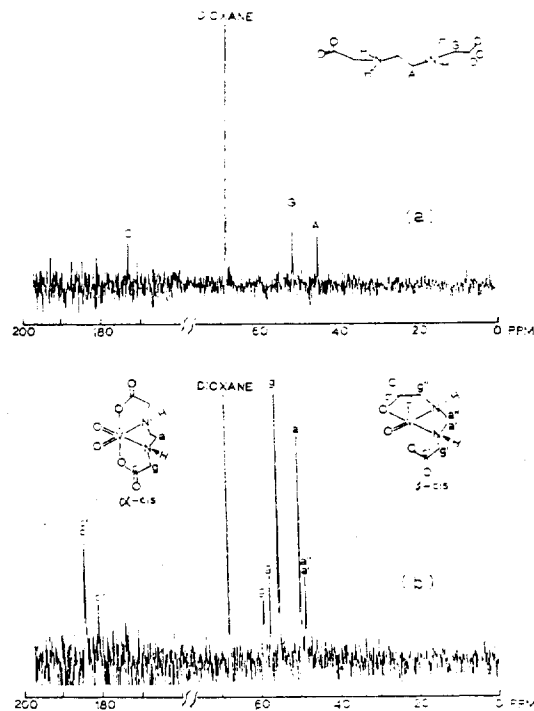


Fig. 5. ^{13}C NMR spectra of the solution containing (a) 0.5 M EDDA and (b) 0.5 M NH_4VO_3 and 0.5 M EDDA at pH 6.

plexes. Because the ligand-metal bond has a long life time compared to NMR time scale, the interconversion between two isomers may occur slowly at room temperature.

Vanadium(V)-EDDA. EDDA is a quadridentate ligand which contains two nitrogen and two acetate oxygen atoms. The ^{13}C NMR spectra of EDDA and its vanadium(V) complex are shown in Fig. 5. It is evident that two isomers of EDDA complex are formed, because two sets of ^{13}C NMR resonance lines whose intensities are almost equal are appeared. The isomer(I) shows three resonances of carbons at 49.82, 55.14 and 184.31 ppm, indicating a symmetrical structure in which two acetate groups are magnetically equivalent. Therefore, the isomer(I) is assigned to α -cis complex. The isomer(II) which is assigned to β -cis complex shows six resonances of carbons at 48.50,

49.82, 57.47, 59.02, 180.87 and 184.10 ppm. The β -isomer has an unsymmetrical structure. The ^{51}V NMR of EDDA complex shows two resonance peaks at -512.5 and -523.4 ppm as shown in Table. 2. indicating the formation of two isomers.

Vanadium(V)-HEDTA. HEDTA has six donor atoms, two nitrogens, three acetate oxygens and a hydroxyethyl oxygen, which compete to form octahedral complex with VO_2^+ . This ligand will show lower affinity to metal ions than EDTA because of the decrease in the basicity of the nitrogen bound to the hydroxyethyl group. The ^{13}C NMR spectra of HEDTA and its complex are shown in Fig. 6. There are three resonance lines in the carboxylate region of the complex: two (182.31 and 182.79 ppm) are assigned to the bound groups and one (177.77 ppm) is assigned to the unbound

group. The coordination of $\text{CH}_2\text{CH}_2\text{OH}$ arm of the ligand is supposed not to occur in the complex, because the chemical shift of the hydroxy-bearing carbon is not great (less than 1 ppm) when the complex is formed. The VO_2^+ ion showed a greater affinity for the acetate oxygen than for hydroxyethyl oxygen if the coordination is available. ^{51}V NMR spectrum of the complex, $[\text{VO}_2\text{HEDTA}]^{2-}$, showed a resonance peak at -523.0 ppm, indicating an octahedral structure.

Vanadium(V)-DTPA. DTPA has eight donor atoms, three nitrogens and five acetate oxygens, which can coordinate to metal ion. The ^{13}C NMR spectra of DTPA and its complex are shown in Fig. 7. The earlier ^1H ⁴² and ^{13}C ⁴³ NMR studies of protonation of the free ligand found the end nitrogens to be more protonated than the center nitrogen at intermediate pH

values. DTPA forms only 1:1 complex with VO_2^+ . In ^{13}C NMR of the complex four resonance lines appeared in the carboxylate region: Two (181.08 and 182.68 ppm) are assigned to the bound groups, one (177.59 ppm) is assigned to the unbound group of the bound IDA moiety, and one (171.35 ppm) having twice intensity of the others is assigned to the unbound carboxylate of the unbound IDA moiety. Thus, VO_2^+ coordinates to the center and a terminal nitrogens and two acetate oxygens. One IDA moiety does not participate in the coordination. After coordination the unbound terminal nitrogen of the ligand is still protonated.

Vanadium(V)-NTA. NTA is a quadradenate ligand, containing a nitrogen and three acetate oxygens. The ^{13}C NMR spectra of NTA and its complex are shown in Fig. 8. In the spectra of complex two resonance lines are

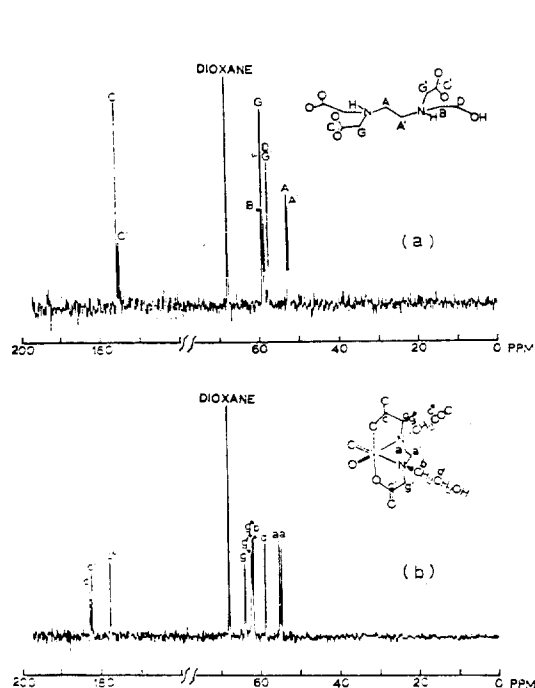


Fig. 6. ^{13}C NMR spectra of the solutions containing (a) 0.5 M HEDTA and (b) 0.5 M NH_4VO_3 and 0.5 M HEDTA at pH 6.

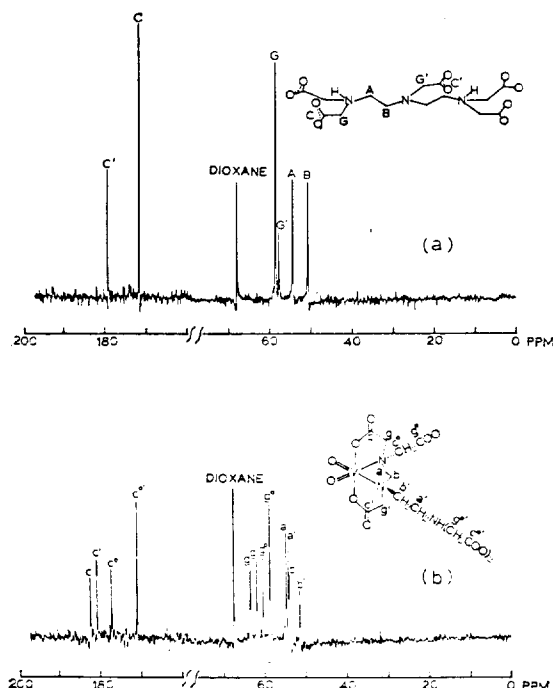


Fig. 7. ^{13}C NMR spectra of the solutions containing (a) 0.5 M DTPA and 0.5 M NH_4VO_3 and 0.5 M DTPA at pH 6.

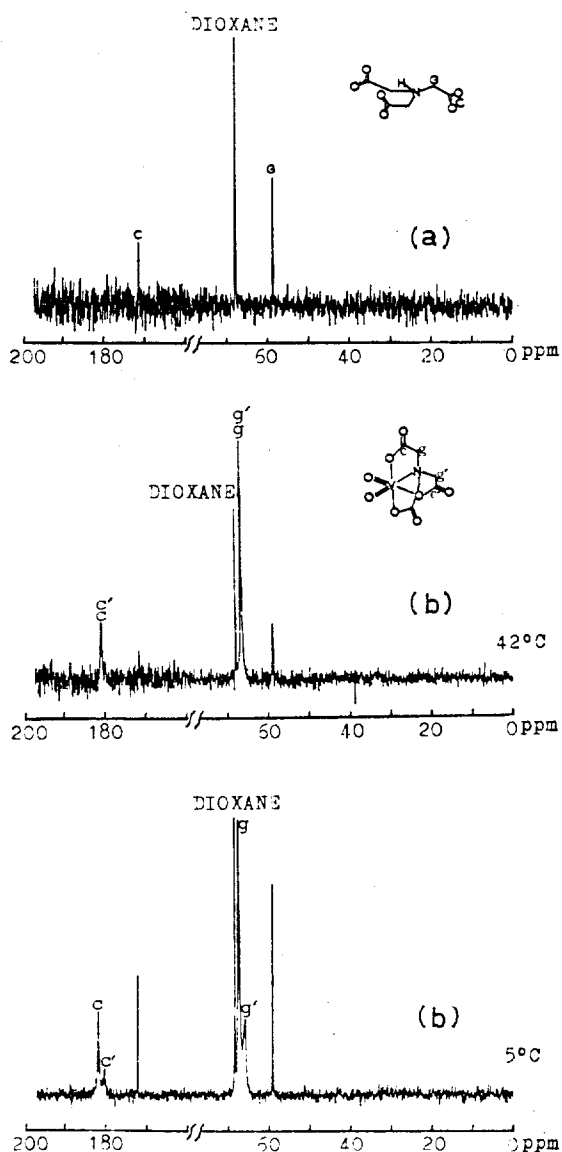


Fig. 8. ^{13}C NMR spectra of the solutions containing (a) 0.5 M NTA and (b) 0.5 M NH_4VO_3 and 0.5 M NTA at pH 6.

appeared at 66.31 and 180.75 ppm at room temperature, but each line is separated into two lines with 2:1 area ratio at 5°C. Therefore, it is supposed that the rapid exchange between acetate groups in the complex occurs on NMR time scale and the averaged lines are produced at room temperature. The low temperature spec-

trum shows that the exchange process is slowed sufficiently to permit observation of small chemical difference between the acetate groups *trans* to and *cis* to the oxo ligand.

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