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^{51}V NMR Studies of Vanadium(I) Complexes. Equilibria and Crystal Structure of Na[V(NO)(N(CH$_2$CH$_2$O)$_3$)] and its Derivatives

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Abstract

Vanadium(I) complexes of $[V(NO)L]^-$ (H_3L = trisethanolamine (H_3thea), tris(2-hydroxypropyl)amine (H_3thpa), nitrilotriacetic acid (H_3nta), *N,N*-bis(2-hydroxyethyl)glycine (H_3bheg) and *N*-(2-hydroxyethyl)iminodiacetic acid (H_3heia)) have been prepared in aqueous solution, and their ^{51}V NMR spectra were measured at 23 °C. The obtained chemical shift (δ) ranges from -67 to $+501$ ppm, while the linewidths at half-height fall within 3.6 KHz. The correlation of the chemical shift with the reciprocal of the d–d transition energy has been found. The equilibria of $[V(NO)(thea)]^-$ with CN^- were examined with ^{51}V NMR, from which the formation of $[V(NO)(CN)(thea)]^{2-}$ (δ = +184 ppm) and $[V(NO)(CN)_6]^{4-}$ (δ = -1284 ppm) was clearly recognized. A molecular structure of Na[V(NO)(thea)]·NaI·5H$_2$O has been determined: space group $P2_1/c$, a = 15.875(8), b = 11.181(3), c = 12.209(6) Å, β = 126.75(3)°, V = 1736.4 Å^3, Z = 4, R = 0.048, R_w = 0.070. The coordination geometry of the compound is approximately trigonal bipyramid, three oxygen atoms of thea^{3-} consitituting a coordination plane. Nitrogen atoms of thea and NO are apically coordinated to the V(I) atom.

Introduction

^{51}V NMR spectroscopy has been successfully used to investigate the structural and bonding properties of vanadium(V) complexes with the aid of high receptivity and sharp signal regardless of the quadrupolar nuclide [1–4]. In principle, diamagnetic vanadium complexes afford detectable ^{51}V NMR signals. There are, however, a few reports on ^{51}V NMR studies of the lower valent vanadium complexes. Nitrosyl complexes of vanadium(I) of the type $\{VNO\}^4$ [5] are intriguing because they are air-stable despite low valent oxidation state and especially because they have various coordination geometries [6, 7]. This variety of structure often leads to solutions containing several species, and thus the isolation of complexes followed by crystallographic determination is the principal procedure to characterize a complex of interest. In practice reaction solutions often give several ^{51}V signals [8, 9]. In order to characterize species in solution, the development of ^{51}V NMR spectroscopy for low-valent vanadium is of quite importance. Rehder and coworkers [4, 14] have measured ^{51}V NMR signals of various V(I) and V(-I) complexes, whose shielding ranges from -1200 to $+300$ ppm. The large shielding variations make it possible to characterize vanadium(I) complexes in solution.

We present the trigonal bipyramidal five coordinate nitrosyl vanadium(I) complexes and characterize the structure both in solution and in the solid state. The second purpose of this work is to examine the relationship between the chemical shift and the structure and to explore the coordination chemistry of the complexes in question through the pursuit of equilibrium behavior.

Experimental

All operations were carried out under an atmosphere of purified argon. NH$_4$VO$_3$ and quadridentate ligands below were purchased from Wako Chemicals Ltd.

$L = N(CH_2X)_2(CH_2Y)$

$X = Y = CH_2OH$; H_3thea

$X = CH_2OH$, $Y = COOH$; H_3bheg

$X = COOH$, $Y = CH_2OH$; H_3heia

$X = Y = COOH$; H_3nta

$N(CH(CH_3)CH_2OH)_3$; H_3thpa

Preparation of Vanadium Complexes

Na[V(thea)(NO)]·NaI·5H$_2$O (**1**) was prepared according to the literature [7]. NH$_4$VO$_3$ (117.0 mg) and H_3thea (0.14 ml) were dissolved in 5 ml of water. A solution of hydroxylammonium chloride (139.0 mg) and NaOH (200.0 mg) in 5 ml of water were added to this solution and stirred for 30 min. This

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deep red color solution was transferred into a NMR sample tube or a cuvette for measurements. In order to isolate the complex, solid NaI(excess) was added at room temperature. The solution was allowed to stand at 3 °C for 24 h, after which the dark red crystals were filtered off (yield 345.0 mg, 70.4%). IR (KBr disc): ν_{NO} = 1504 cm^{-1}, ^{1}H NMR (20 mM in D_2O): 2.51(t) and 4.18(t) ppm. Electronic spectrum (H_2O): λ_{max} = 511 nm (ϵ = 240 M^{-1} cm^{-1}).

Other complexes were prepared in a similar way.

In order to obtain single crystals, the aqueous solution of **1**, which contains an amount of NaI less than in the case mentioned above, was transferred into a Schlenk tube, and this was kept at 5 °C. The dark red brick-shaped crystals were obtained for a week.

Crystallography

A crystal with dimensions of *c.* 0.3 × 0.3 × 0.3 mm was used for the determination and the collection of intensity data at 296 K. The cell dimensions and the diffraction intensities were measured on a Rigaku AFC-6B diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å).

Crystal Data

$C_6H_{22}N_2O_9VNa_2I$, M = 490.08, space group $P2_1/c$ (monoclinic), a = 15.875(8), b = 11.181(3), c = 12.209(6) Å, β = 126.75(3)°, Z = 4, D_c = 1.848 g cm^{-3}, μ = 23.89 cm^{-1}, $F(000)$ = 940.0.

All independent reflections within the range $2\theta < 45°$ were collected by the use of the ω–2θ scan mode and a scanning rate of 8° min^{-1}. Three reflections were monitored every 120 reflections. There was no significant variation of the intensities during data collection. The intensity data were converted to F_o data in the usual manner. No absorption correction was applied. The standard deviations, $\sigma(F_o)$, were estimated by counting statistics. A total of 1965 reflections with $|F_o| > 3\sigma(|F_o|)$ were used for the determination of the crystal structure.

Structure Determination

The structure was solved by the heavy-atom method and refined by block-diagonal least-squares refinement. Several cycles of refinement including anisotropic thermal parameters were carried out with the weighting scheme $w = 1/\sigma^2(F_o)$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 10. Toward the end of the development of the structure, substantially large anisotropic thermal parameters were obtained for three α-carbon atoms of thea^{3-}. The difference peaks were observed in positions that could be occupied by the carbon atoms. These sites were modeled as carbon atoms with an anisotropic thermal parameter, and the site occupancies of the two carbon atoms were refined, leading to values near 58% (type A) and 42% (type B) for two modes of thea^{3-} coordination. For the final refinement the multiplicities were fixed at those values. The significance of the two sites is verified by their stable refinement and by the fact that modeling these sites led to lowering of the R factors. The final R and R' values were 0.048 and 0.070, respectively. The final Fourier difference map showed no significant features. All calculations were performed on a FACOM M-382 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY [11]. The final atomic parameters for the non-hydrogen atoms are listed in Table 1.

NMR Measurements

A Jeol GSX-270 NMR spectrometer was used to obtain ^{1}H and ^{51}V NMR spectra. For ^{1}H NMR spectra, D_2O was used as a solvent. For ^{51}V NMR measurements operated at 71.00 MHz, 4000 transients were accumulated using a 4.5 μs (45°) pulse; 16 K data points were collected over a band width of 160 KHz. A probe temperature was set at 23 °C. ^{14}N NMR spectra operating at 80.79 MHz were recorded with a Jeol GSX-500 NMR spectrometer; 1000 transients were accumulated using a 35 μs (90°) pulse and 32 K data points were collected over a band width of 40 KHz. $(CH_3)_3Si(CH_2)_3SO_3Na$ was used as an internal reference for ^{1}H NMR, while

TABLE 1. Final atomic coordinates and isotropic thermal parameters with e.s.d.s in parentheses for Na[V(NO)(thea)]·NaI·5H_2O

Atom	x	y	z	β_{eq}
I	0.8633(0)	0.3099(1)	0.4463(1)	3.03(4)
V	0.7041(1)	−0.1815(1)	0.4289(1)	1.45(4)
Na(1)	0.5795(2)	0.1077(3)	0.4098(3)	2.37(13)
Na(2)	0.4349(3)	−0.1428(3)	−0.0501(3)	2.33(11)
C(1)	0.7520(6)	−0.0666(9)	0.6675(8)	3.02(36)
C(2)	0.8324(6)	−0.3816(8)	0.5828(9)	3.37(35)
C(3)	0.8750(6)	−0.0655(9)	0.4523(9)	3.26(39)
C(4A)	0.8560(12)	−0.0669(15)	0.6936(14)	2.99(60)
C(4B)	0.8446(18)	−0.1423(23)	0.7242(19)	3.75(91)
C(5A)	0.8823(14)	−0.2859(14)	0.6883(17)	3.34(58)
C(5B)	0.9124(16)	−0.2827(17)	0.6353(23)	3.67(81)
C(6A)	0.9316(11)	−0.1421(15)	0.5794(15)	2.70(59)
C(6B)	0.9110(16)	−0.0628(19)	0.5959(20)	3.21(82)
N(1)	0.8604(5)	−0.1667(6)	0.6165(7)	2.11(27)
N(2)	0.5815(5)	−0.1906(5)	0.2827(6)	1.76(25)
O(1)	0.4889(4)	−0.1925(5)	0.1744(5)	2.22(21)
O(2)	0.6706(4)	−0.0881(5)	0.5264(5)	1.94(21)
O(3)	0.7660(4)	−0.0998(5)	0.3589(5)	2.31(21)
O(4)	0.7296(4)	−0.3449(5)	0.4695(5)	2.13(21)
O(13)	0.6537(4)	0.1138(5)	0.2884(5)	2.48(21)
O(14)	0.6136(5)	−0.4292(5)	0.5627(6)	2.68(20)
O(15)	0.4737(4)	−0.1485(5)	0.4498(5)	2.35(20)
O(16)	0.5791(4)	−0.4900(5)	0.2629(5)	2.63(20)
O(17)	0.7217(5)	0.2564(7)	0.5878(6)	3.70(27)

CH_3NO_2/C_6D_6 (4/1 vol./vol.) and neat $VOCl_3$ were external standard for ^{14}N and ^{51}V NMR, respectively.

Results and Discussion

Crystal Structure

Figure 1 illustrates the molecular structure of $[V(NO)(thea)]^-$, where the atom-numbering scheme is also given. This form has near C_3 symmetry with a three fold axis coincident with the V–N(1) axis of the molecule. There are two forms of disorder present in the structure. From the view down to the V–N(1) axis, two different (clockwise and counter clockwise) forms are recognized, which are defined according to the translation (twist) of the helices. Both forms coexist with almost equal populations (52:48). This type of disorder likely happens because the interconversion of the two forms may take place without any restriction in solution. The coordination about the V^I is trigonal bipyramid, which involves three oxygen of $thea^{3-}$ at the equatorial positions and two nitrogens of $thea^{3-}$ and NO at the axial positions. Selected bond distances and angles are presented in Table 2. Wieghardt *et al.* [6] recently determined the structure of $Na[V(NO)(thea)]\cdot NaClO_4\cdot 4H_2O$ (1′) by X-ray crystallography. **1** and **1′** have a difference in composition about the inorganic anion and water. The molecular structure of **1′**, which has no disorder, is essentially similar to that of the clockwise form of **1**. The $V-N_1$ and $V-N_2$ bond distances of **1′** are in good agreement with that of **1**. These complexes are commonly characterized by (i) linear V–N–O linkage (177.2(5)° and 178.9(7)° for **1** and **1′**, respectively), and (ii) a short $V-N_2$ bond distance (1.684(5) and 1.696(7) Å for **1** and **1′**, respectively). This leads to the conclusion that NO acts as the electron donor [12] toward transition metals and formally considered to be NO^+, the formal oxidation state of the vanadium being +I. The trigonal-bipyramidal structure found here is rare among low valent vanadium complexes [13].

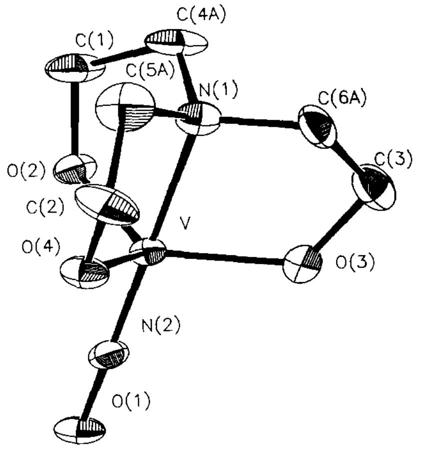

Fig. 1. ORTEP drawing of the entire molecule of $[V(NO)(thea)]^-$ with thermal ellipsoids at the 50% level. One of the two conformations of the chelate ring (clockwise form) is drawn.

TABLE 2. Principal bond distances (Å) and angles (°) with e.s.d.s in parentheses

Bond	Length (Å)	Bond	Length (Å)
V–N(1)	2.152(5)	V–N(2)	1.681(5)
V–O(2)	1.884(7)	V–O(3)	1.880(8)
V–O(4)	1.873(6)	N(2)–O(1)	1.258(6)
Bond	**Angle (°)**	**Bond**	**Angle (°)**
N(1)–V–N(2)	179.0(3)	N(1)–V–O(2)	82.3(3)
N(1)–V–O(3)	82.1(3)	N(1)–V–O(4)	82.20(22)
N(2)–V–O(2)	96.8(3)	N(2)–V–O(3)	97.7(3)
N(2)–V–O(4)	98.72(24)	O(2)–V–O(3)	116.1(3)
O(3)–V–O(4)	120.35(32)	O(2)–V–O(4)	118.14(31)
V–N(2)–O(1)	177.3(6)		

Spectroscopic Properties

The ^1H NMR spectrum of an aqueous solution (pH = 11) of **1** gives sharp signals, indicative of diamagnetism of the complex, whose coordination shifts ($\delta_{coord} = \delta_{obs} - \delta_{metal\text{-}free}$) are −0.21 and +0.52 ppm for NCH_2 and OCH_2, respectively. Other derivatives of **1** also exhibit well-resolved sharp signals. Consequently, the electronic configuration of a vanadium(I) ion is in the singlet state, enabling us to observe their ^{51}V NMR spectra. Figure 2 reveals

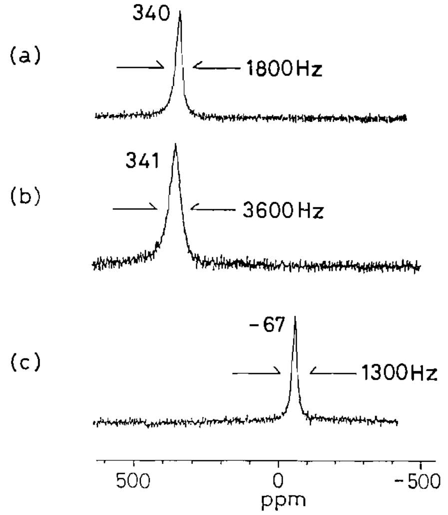

Fig. 2. ^{51}V NMR Spectra at 23 °C of aqueous solution of (a) $[V(NO)(thea)]^-$, (b) $[V(NO)(thpa)]^-$, and (c) $[V(NO)(nta)]^-$. The concentration of complexes is 20 mM, and 4000 scans are used for all the solutions.

TABLE 3. Observed spectroscopic properties of vanadium complexes[a]

Complex	δ (^{51}V)[b]	($\Delta\nu_{1/2}$[c])	δ (^{14}N)[d]	$\tilde{\lambda}_{max} \times 10^{-4}$ (cm^{-1})
Na[V(NO)(thea)]	+340	(1800)	+11.96	1.96
Na[V(NO)(thpa)]	+341	(3600)		1.96
Na[V(NO)(nta)]	−67	(1300)	+1.08	2.45
Na[V(NO)(heia)]	−127	(2100)	+2.03	2.44
Na[V(NO)(bheg)]	+501	(2200)[e]	+4.26	1.40

[a]Aqueous solutions. [V^+] = 20 mM for ^{51}V NMR, and 50 mM for ^{14}N NMR. [b]Shifts in ppm, referenced against neat $^{51}VOCl_3$. Error limit ±2 ppm. [c]Linewidths at half-height in Hz. Error limit ±150 Hz. [d]Shifts in ppm, referenced against $CH_3{}^{14}NO_2$/benzene-d_6 (vol./vol. 4/1). Error limit ±0.5 ppm. [e]Main peak. Another minor peak is observed at +626 ppm.

the ^{51}V NMR spectra of their aqueous solutions. For all these cases, a single signal was observed except for a sharp signal at ~ −500 ppm with a small intensity. The latter signal is attributed to the starting vanadium(V) species. The observed chemical shifts and the linewidths of the main signals are listed in Table 3. There are two characteristic features of these spectra. (i) The ^{51}V shift values spread over +501 ~ −67 ppm. Vanadium(I) complexes having a single NO commonly give a chemical shift between −300 and −1200 ppm [4]. On the other hand, dinitrosyl complexes shift considerably downfield up to +300 ppm [4, 14]. Hence, the present result is the first example showing that mononitrosyl vanadium complexes afford a downfield shift much more than those so far synthesized. (ii) The linewidths ($\Delta\nu_{1/2}$) are significantly broad, ranging from 1.3 to 3.6 kHz. This is due to the lower symmetric coordination environment around the vanadium ion, which accelerates the quadrupolar relaxation rate. In Table 3, there is no apparent correlation between δ and the combination of carboxylate and alcoholate groups. For metal nuclides having d-electrons, the paramagnetic deshielding term contributes significantly to the observed chemical shift [1, 3, 4]. The factors influencing this term are formalized as follows.

$$\delta_{para} = \text{const} \times \Delta E^{-1}[r^{-3}]_{3d}C(3d)^2 \qquad (1)$$

ΔE is the mean excitation energy, r the distance of the vanadium-3d electrons from the nucleus, and C the LCAO coefficient for the 3d orbitals taking part in the electronic transitions. The ligand field transition energy may correspond to the ΔE term. Hence, $\tilde{\lambda}_{max}$ can be regarded as ΔE. Inspection of Table 3 reveals that δ has a good correlation with d–d transition energies ($\tilde{\lambda}_{max}$ values); δ shows a downfield shift with decreasing $\tilde{\lambda}_{max}$. The vanadium complexes used here have the same geometry (trigonal bipyramidal) and N_2O_3 donor set, and consequently ΔE is the major factor in eqn. (1).

^{51}V NMR spectra of **1** show apparent pH dependence. At a strong acidic solution (pH < 1), no signals are observed, while a single signal with $\Delta\nu_{1/2}$ = 200 Hz appears at −559 ppm in the range of pH 3 ~ 4. This sharp signal is characteristic of vanadium(V) species, as has been suggested by Wieghardt *et al.* [6]. On raising the pH (4 ~ 5), this signal disappears and no signals are recognized. At pH > 5, a broad signal at +340 ppm grows, which is ascribed to **1**, and the formation of **1** is completed at pH > 8. At present, the NMR-silent species at the intermediate pH region are not identified, being under investigation.

Equilibrium with CN^-

Upon addition of CN^-, **1** react with CN^- to give vanadium complexes having various coordination numbers of CN^-. Figure 3 shows the titration behavior of ^{51}V NMR spectra. As the CN^- concentration increases, the signal at +340 ppm of **1** de-

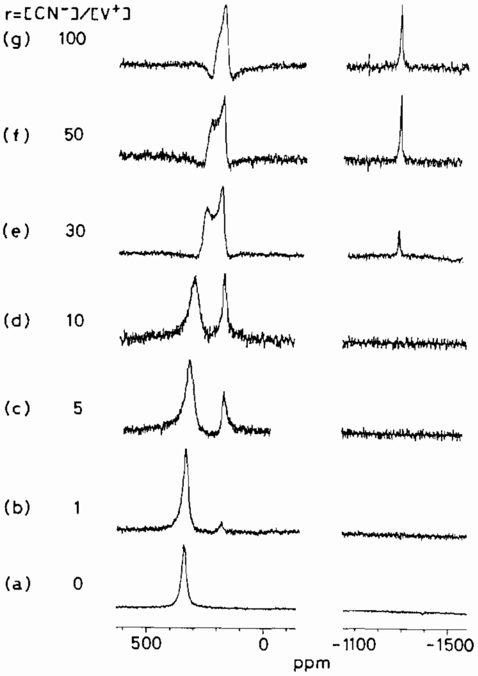

Fig. 3. Dependence of ^{51}V NMR spectra on the concentration of cyanide ion. A 20 mM solution of [V(NO)(thea)]$^-$ is titrated with CN^-.

creases, moving to an upfield region with line-broadening. Concurrently, a new signal A increases near +184 ppm. During the titration, no shift of signal A was observed. At r ([CN]/[V]) = 100, a single signal B is obtained at *c.* 176 ppm. In the course of this titration, a new signal C also appears at −1284 ppm, which is quite sharp ($\Delta\nu_{1/2}$ = 600 Hz). We have synthesized $K_4[V(CN)_6(NO)]$ according to the literature method [15]. This aqueous solution provides a ^{51}V NMR signal at −1282 ppm, which corresponds well to the signal C obtained with a large excess of CN^-. Hence the signal C is undoubtedly attributable to seven-coordinate $[V(CN)_6(NO)]^{4-}$.

We also monitored this formation process with ^{1}H NMR. Until r is 10, no signals of metal-free thea^{3-} are recognized. When r increases from 10 to 100, two kinds of signals appeared, with a decrease of the signals of **1**, which are ascribed to metal-free and partly coordinated thea^{3-}. ^{14}N NMR measurements were done to examine whether NO still binds vanadium or not. For all the titrated conditions, the signal of coordinated NO was observed, whose shifts fall within the range of coordinated NO^+ [16]. This confirms that no dissociation of NO takes place. **1** gives the ^{14}N NMR signal of NO at +11.96 ppm, which did not disappear but shifted downfield on addition of CN^-, indicating the presence of chemical exchange phenomena among complexes having various coordination numbers of CN^-. Octahedral six-coordinate $[V(NO)(thea)(CN)]^{2-}$ has been synthesized by adding CN^- to a solution of **1**, and crystallographically characterized [6].

On the basis of the crystallographic and NMR results, the species generated by CN^- addition could be specified. $[V(NO)(thea)(CN)]^{2-}$ (**2**) readily forms in a low concentration of CN^-. Once **2** forms, CN^- is substituted for an oxygen atom of the coordinated thea^{3-} stepwise: the possible structures are $[V(NO)(thea)(CN)_n]^{-(n+1)}$, where thea^{3-} takes an interesting role as a tridentate (n = 2) and bidentate (n = 3) chelating ligand. The ^{51}V NMR signal B reveals that several species in solution encounter the fast chemical exchange, while the signal A comes from a species which is inactive to chemical exchange. At the present stage the signal A is possibly assigned to **2**, and the averaged signal B is ascribed to $[V(NO)(thea)(CN)_n]^{-(n+1)}$ (n = 2 or 3). Finally ^{51}V NMR spectra should be mentioned in the case of a large excess CN^-. From $r > 100$ both signals B and C are observed and as these intensities do not change significantly it is difficult to get the spectrum of pure $[V(NO)(CN)_6]^{4-}$ by this titration. This indicates that the formation constant of $[V(NO)(CN)_6]^{4-}$ is not relatively large, which may be associated with a rare seven-coordinate compound. In conclusion, the following scheme for the equilibria is given.

$$[V(NO)(thea)]^- \overset{CN^-}{\rightleftharpoons}$$

$$[V(NO)(thea)(CN)_n]^{-(n+1)} \overset{CN^-}{\rightleftharpoons} [V(CN)_6(NO)]^{4-}$$

(n = 2 and 3)

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