Square Pyramidal Dialkoxo-Bound Monooxo−Vanadium(V) Complex and Its Behavior in Solution

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Introduction

Interest in vanadium chemistry has increased since the recognition of the involvement of vanadium ions in many important biological systems.[1] The distinctive preference of the vanadium ion for N/O donor atom types has prompted the synthesis and characterization of many model complexes containing N/O donor ligands, the spectroscopic properties and solution behavior of which have been investigated.[2] A short vanadium−oxygen bond length (1.72 Å) for the coordination environment of the vanadium(V) center in vanadate-dependent bromoperoxidase, based on the EXAFS,[3] increased interest in alkoxo-bound vanadium(V) model complexes. In addition, crystallographic studies on chloroperoxidase (at 2.1-Å resolution) showed a five-coordinate trigonal bipyramidal vanadium center as an active site, where three nonprotein oxygen atoms are situated at short distances from the vanadium(V) center (average 1.65 Å).[4] While five-coordinate monooxo−vanadium(IV) model complexes[5,6] are common, only a few five-coordinate monooxo−vanadium(V) model complexes[5b,6,7] are known. In this study, we report the synthesis and structural characterization of a five-coordinate square pyramidal dialkoxo-bound monooxo−vanadium(V) complex and its behavior in solution.

Experimental Section

Materials. The following were used as received with no further purification: salicylhydrazide (shz), vanadium(III) acetylacetonate, chloroform-*d*, and tetrabutylammonium tetrafluoroborate ($TBABF_4$) from Aldrich, Inc.; methanol (MeOH) and ethanol (EtOH) from Carlo Erba.

Instrumentation. C, H, N, and V determinations were performed by the Elemental Analysis Laboratory of the Korean Institute of Basic Science. Infrared spectra were recorded as KBr pellets in the range 4000−600 cm^{-1} on a Bio-Rad FT-IR spectrometer. The solution IR spectra were recorded between KBr plates. Absorption spectra were obtained using a Perkin−Elmer Lambda spectrometer. ^1H NMR spectra were obtained using a Varian-300 spectrometer and ^{51}V NMR spectra were obtained using a Bruker DMX 600 spectrometer. Positive-ion electron spray ionization (ESI) mass spectrum was obtained using a JEOL HX110A/HX110A tandem mass spectrometer in ethanol. Room-temperature magnetic susceptibilities of well-ground solid samples were measured by using an Evans balance.[8] All the electrochemical measurements described in this study were carried out at room temperature using the BAS CV-50W with a conventional three-electrode configuration. The working electrode was a glassy carbon disk (GC, electrochemical area = 0.064 cm^2) freshly polished with activated aluminum oxide (150 mesh, 58 Å, Aldrich) before use. The reference and counter electrodes were Ag/AgCl (3 M KCl) and Pt gauze, respectively. All the potentials mentioned in this paper were referenced to Ag/AgCl.

Synthesis: V(V)O(Hacshz)(OEt), 1. ($Hacshz^{2-}$ is a doubly deprotonated dianionic acetylacetosalicylhydrazone). A 0.234-g (1.53-mmol) sample of shz was dissolved in 15 mL of ethanol. When a 0.531-g (1.52-mmol) sample of vanadium(III) acetylacetonate was added to the solution, the solution changed its color to dark brown. After 20 min of stirring, the solution was filtered. Slow evaporation of the filtrate solution over 3 days produced dark brown crystals (0.270 g, 51.4%). Anal. Calcd for VO(Hacshz)(OEt) ($C_{14}H_{17}N_2O_5V$) (fw = 344.24): C, 48.85; H, 4.98; N, 8.14; V, 14.80. Found: C, 48.88; H, 4.92; N, 8.21; V, 14.6. IR (KBr, cm^{-1}): ν 998 vs $\nu_{V=O}$. ^1H NMR (300 MHz, $CDCl_3$): **A** form. δ 11.00 (s), 1H for phenolic proton; 7.82 (d), 7.31 (t), 6.95 (d), 6.87 (t), 4H for phenyl protons; 5.66 (s), 1H for −CH−; 5.39 (m), 2H for $V-OCH_2CH_3$; 2.42 (s), 2.23 (s), 6H for two methyl groups; 1.57 (t), 3H for $V-OCH_2CH_3$. **B** form. δ 10.04 (s), 1H for CH_3CH_2OH; 7.22 (t), 7.01 (d), 6.87 (d), 6.61 (t), 4H for phenyl protons; 5.57 (s), 1H for −CH−; 3.65 (qr), 2H for $HOCH_2CH_3$; 2.42 (s), 1.82 (s), 6H for two methyl groups; 1.17 (t), 3H for free $HOCH_2CH_3$. Ratio **A**:**B** = 4:1. ^{51}V NMR (157.7 MHz, $CDCl_3$): **A** form. δ −519.98. **B** form. δ −514.21. Ratio **A**:**B** = 4.7:1. ^{51}V NMR (157.7 MHz, MAS): δ −511.68. ESI mass spectrum: *m*/*z* of $[VO(Hacshz)(OEt) + H]^+$, 345. UV−vis (CH_3Cl) [λ_{max} (ϵ)]: 240 (13 300 M^{-1} cm^{-1}), 267 (18 800 M^{-1} cm^{-1}), 339 (12 200 M^{-1} cm^{-1}), 390 nm (shoulder, 6600 M^{-1} cm^{-1}).

X-ray Crystallography. A dark brown crystal of complex **1** was mounted on a glass fiber. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71069 Å) on a Siemens SMART CCD equipped with a graphite crystal, incident-beam monochromator. Data were collected at room temperature. Lp and absorption corrections were applied to the data. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with

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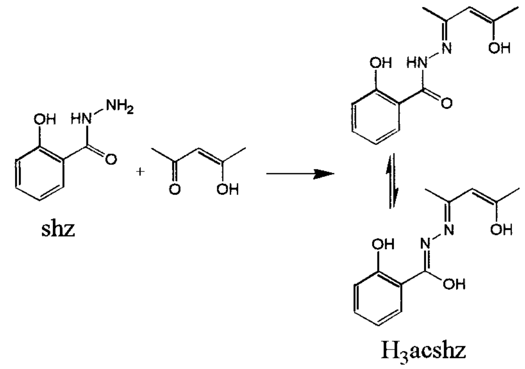
Table 1. Crystal Data and Structure Refinement for **1**

formula	$C_{14}H_{17}N_2O_5V$
fw	344.24
temp	293(2) K
cryst syst, space group	monoclinic, $P2_1/c$
unit cell dimens	$a = 10.4210(2)$ Å, $\alpha = 90°$ $b = 15.0591(3)$ Å, $\beta = 114.309(1)°$ $c = 10.7892(1)$ Å, $\gamma = 90°$
V	1543.04(5) $Å^3$
Z, calcd density	4, 1.482 mg/m^3
abs coeff	0.667 mm^{-1}
cryst size	0.45 × 0.35 × 0.20 mm
θ range for data colln	2.14°−22.50°
reflctns collctd/unique	6056/2025 [R(int) = 0.0574]
data/restraints/params	2025/0/250
goodness-of-fit on F^2	1.273
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0578, wR2 = 0.1303
R indices (all data)^a	R1 = 0.0629, wR2 = 0.1332
largest diff peak and hole	0.328 and −0.354 e $Å^{-3}$

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$.

Scheme 1



SHELX97.[9] All non-hydrogen atoms were refined anisotropically; all hydrogen atoms were found on a difference Fourier map and refined with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. Crystal and intensity data are given in Table 1.

Results and Discussion

Preparation and Characterization of Complex 1. VO(Hacshz)(OEt), **1**, could be synthesized using vanadium acetylacetonate and shz in a one-pot reaction. Acetylacetosalicylhydrazone (H_3acshz) was formed via a Schiff base condensation reaction of shz with acetylacetonate in situ (Scheme 1). Similar *N*-acylation of salicylhydrazide was observed.[10] Magnetic susceptibility measurement of complex **1** indicated that the metal ion of the complex is diamagnetic d^0 vanadium(V). During the reaction, the vanadium ion was air-oxidized to dialkoxo-bound monooxo−vanadium(V) from its initial 3+ oxidation state to a final 5+ oxidation state in ethanol solution. It is well-known that the alkoxy group can stabilize the high oxidation state.[5b,6a,7,11] The IR spectrum of complex **1** showed a characteristic V=O stretching band at 998 cm^{-1}.[12] The ethanol solution of complex **1** gave a peak at *m*/*z* 345 in the ESI mass spectrum. The peak corresponds to a mononuclear complex ion, [VO(Hacshz)(OEt) + H]$^+$. The solid-state ^{51}V NMR spectrum of complex **1** showed a band at −511.68 ppm.

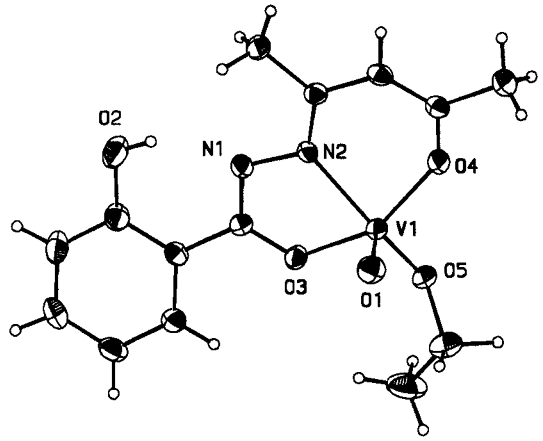


Figure 1. ORTEP drawing of complex **1**, VO(Hacshz)(OEt), with thermal ellipsoids at the 30% probability level.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**

V1−O1	1.567(3)		
V1−O3	1.935(3)	V1−N2	2.092(3)
V1−O4	1.857(3)	V1−O5	1.744(3)
C2−C7	1.467(6)	N1−C7	1.311(5)
N1−N2	1.400(5)	N2−C8	1.320(5)
C8−C10	1.413(6)	C10−C11	1.343(6)
O4−C11	1.320(5)		
O3−C7	1.302(5)		
O1−V1−O3	101.701(6)	O1−V1−O4	103.261(7)
O1−V1−O5	107.461(7)	O1−V1−N2	101.041(5)
O4−V1−O3	149.431(4)	O5−V1−O3	89.981(3)
O3−V1−N2	74.661(2)	O5−V1−O4	99.031(4)
O4−V1−N2	83.451(3)	O5−V1−N2	149.881(5)
V1−O5−C13	134.2(4)		

Intramolecular Hydrogen Bond

donor	hydrogen	acceptor	D−H	H···A	D···A	∠D−H···A
O2	H2O	· · · N1	0.80(7)	1.89(7)	2.590(5)	145(7)

Crystal Structure of Complex 1. An ORTEP drawing of complex **1** is shown in Figure 1. Complex **1** is a square pyramidal dialkoxo-bound monooxo−vanadium(V) complex. Doubly deprotonated dianionic acetylacetosalicylhydrazone (Hacshz^{2-}) served as a tridentate ligand to form five- and six-membered chelating rings. An ethoxide anion occupied the remaining basal site of the square pyramidal oxovanadium(V) ion. The vanadium−ethoxy oxygen bond length (V1−O5, 1.744(3) Å) is 0.2 and 0.1 Å shorter than the other vanadium−oxygen bond lengths (V1−O3, 1.953(3); V1−O4, 1.857(3) Å) in the complex (Table 2). The vanadium−oxo oxygen bond length (V1−O1, 1.567(3) Å) is similar to the value reported for analogous structures.[6a] The vanadium ion is displaced about 0.444(2) Å from the basal plane of the square pyramidal dialkoxo-bound monooxo−vanadium(V) complex. This square pyramidal feature of dialkoxo-bound monooxo−vanadium(V) complex is contradictory to that of other tripodal alkoxo-bound monooxo five-coordinate V(V) complexes that are often close to trigonal bipyramidal.[7] There are no other groups near the open face of the square pyramidal complex in the crystal structure. The nearest intermolecular contact from the vanadium atom is the symmetry-related O2 atom (symmetry code: $1 - x, -y, 1 - z$) at 3.363 Å. We could see only one hydrogen bond (Table 2), a phenolic hydrogen atom of the ligand participating in the intramolecular hydrogen bond to form a pseudo six-membered ring.

Solution Behavior of Complex 1. The ^{1}H NMR spectrum of complex **1** in $CDCl_3$ gave two sets of bands at an approximate

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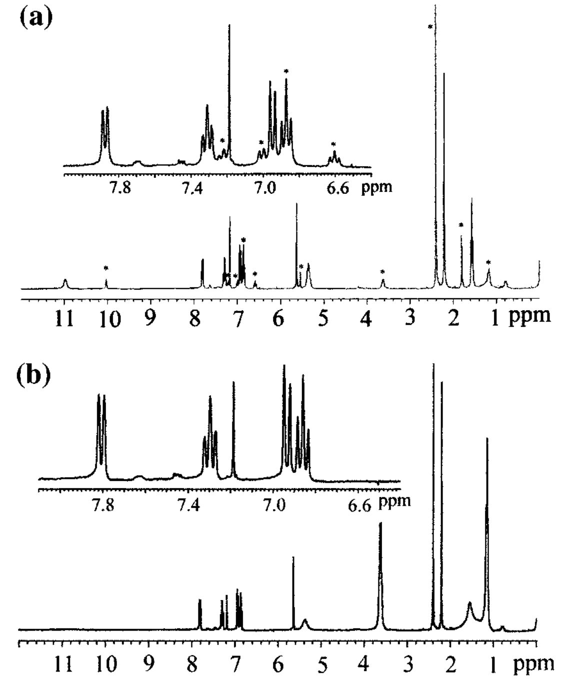

Figure 2. ^{1}H NMR spectra of complex **1** in $CDCl_3$. Insets present the expansion of four phenyl proton bands. (a) A minor set of bands is indicated with an asterisk. Integration of the bands at 2.42 and 6.87 ppm showed that the bands from the two species overlapped at the same positions. (b) Spectrum after adding 10 μL of ethanol to the chloroform solution. The minor set of bands disappeared, the bands corresponding to ethoxy protons of the major species broadened, and the bands corresponding to ethanol protons increased.

4:1 ratio (Figure 2a). This suggests that two species exist in a chloroform solution. Recently, Glas et al. reported a similar solution behavior of octahedral monoalkoxo-bound monooxo–vanadium(V) complexes with pyrazolylpyridine bidentate chelating ligand.[13] They interpreted their results with two coordination isomers in equilibrium based on NMR studies. When we added a small amount of ethanol to the chloroform solution of complex **1**, the minor set of bands disappeared (Figure 2b). In addition, the coordinated ethoxide bands at 5.3 and 1.57 ppm[6a] broadened and the free ethanol bands at 3.5 and 1.5 ppm increased. The ESI mass spectrum of complex **1** in ethanol gave a band corresponding to only a monomeric complex ion, [VO(Hacshz)-(OEt) + H]$^+$. Therefore, we assigned the major set of bands as those of monomeric form A as in the solid-state structure. ^{51}V NMR spectrum of complex **1** in $CDCl_3$ also showed two bands at an approximate ratio of 4.7:1 and the minor band disappeared in the presence of a small amount of ethanol, as in the ^{1}H NMR spectrum. This suggests that two species exist in the chloroform solution, and whatever the minor species is, it converts to the monomeric form in the presence of a small amount of ethanol.

Glas et al. proposed a coordination isomerism for their octahedral monoalkoxo-bound monooxo–vanadium(V) complexes based on the NMR study.[13] However, in this study, the vanadium ion is coordinated by a chelating tridentate ligand, so the occurrence of a coordination isomerism is not plausible. One of the possible structures for a minor species is a bis μ-oxo dimer.[14] If the minor species is a μ-oxo dimer, there would be a significant difference in the V=O stretch of the dimeric species compared to that of the monomeric species.[15] However, there was no significant change in the V=O stretch of complex **1** in chloroform solution compared to that of the monomeric species in the solid state. We could exclude the possibility of a bis μ-oxo dimer as a minor species. Another possible structure for a minor species is an alkoxy-bridged dimer. It is well-known that alkoxides usually form dimeric complexes.[6c,16] However, we could exclude the possibility of an ethoxide-bridged dimer as a minor species because there is only one set of bands for a coordinated ethoxide group. If the minor species is an ethoxy-bridged dimer, there should be another set of bands for two bridging ethoxide groups. The other possible structure for minor species is a chain structure where a phenolate oxygen atom of the neighboring monomeric species would link vanadium centers of the monomeric species. We could also exclude the possibility of a phenolate-linked chain structure. If phenolate was coordinated to the vanadium ion in the minor species, a phenolate ligand to vanadium metal charge-transfer band would have had to disappear when a small amount of ethanol was added to the chloroform solution of complex **1**. However, there was no recognizable change in the UV–vis spectrum of complex **1** in the chloroform solution after the addition of a small amount of ethanol to the solution.

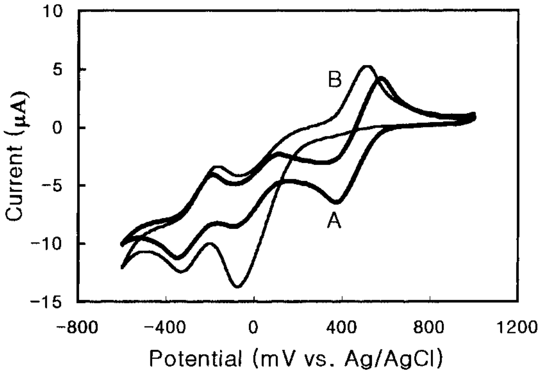

Figure 3. Cyclic voltammograms of complex **1** in (A) chloroform and (B) 10% (v/v) ethanol containing 0.1 M $TBABF_4$.

Cyclic voltammetric measurements were performed in a chloroform solution containing 10 mM complex **1** and 0.1 M $TBABF_4$ at 10 mV s^{-1}. Figure 3A shows three reduction peaks at ≈400 (630 mV versus NHE), −50, and −350 mV. Figure 3B demonstrates a cyclic voltammogram when 10% (v/v) ethanol was added. It is obvious that the peak at 400 mV completely disappeared and the reduction current at −50 mV increased instead. This result indicates that the minor species is more easily reduced than the major species. The variation of reduction potentials of vanadium complexes depending on the coordination environment has been previously reported.[2a,5b,6,17] The reduction potential of the major species, approximately −50 mV, is comparable to that of the monoalkoxo dioxo square pyramidal V(V) complex, [salampr][V(V)O_2(salamp)].[6c] The effect of the dialkoxo monooxo group in the major species on the reduction potential is comparable to that of the monoalkoxo dioxo group. The reduction potential of the minor species, on the other hand, corresponds to the values of the monooxo monoalkoxo square pyramidal V(V) complex[6a] and monooxo μ-oxo square pyramidal V(V) complex.[6b] It is likely that the reduction peak at −350 mV results from a V(IV)/V(III) couple.

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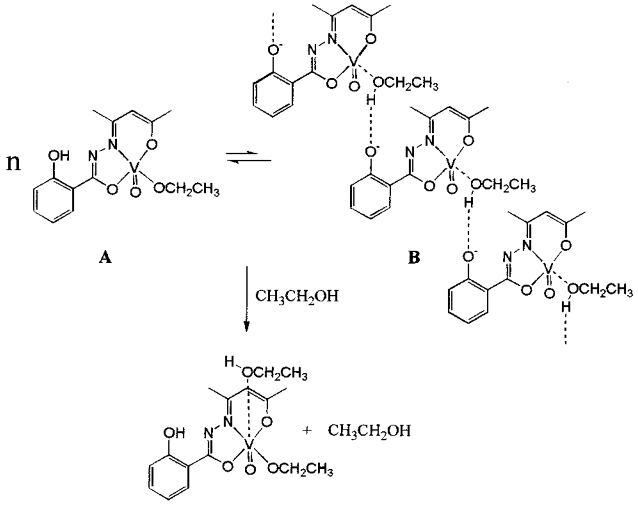
Scheme 2



In the chloroform solution, we could observe not only the protons of the ethoxide group but also the protons of the ethanol group. While the chemical shifts of the ethyl and methyl protons of the ethanol are very close to those of the free ethanol, that of the alcoholic proton is downshifted to 10.04 ppm and the shape of the band is pretty sharp. We propose that some of the deprotonated phenolic protons would move to the coordinated ethoxy oxygen and the minor species to be the monooxo monoalkoxo square pyramidal V(V) complex, form B, as shown in Scheme 2. The ethanol is weakly coordinated to the vanadium center and the intermolecular hydrogen bond between the ethanol and the phenolate oxygen atom of the neighboring molecule forms a hydrogen-bonded structure.

In conclusion, we have obtained the crystal structure of a mononuclear square pyramidal dialkoxo-bound monooxo–vanadium(V) complex **1** with a potential pentadentate ligand H$_3$acshz, where Hacshz^{2-} served as only a dianionic tridentate chelating ligand. The phenolic hydrogen atom of the ligand formed an intramolecular hydrogen bond with the imine nitrogen atom. In the chloroform solution, complex **1** exists in two forms. The major form is a monomeric species, as in the solid-state structure, and whatever the minor species is,[18] it converts to the monomeric form A in the presence of a small amount of ethanol.

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Supporting Information Available: An ORTEP drawing with complete atomic numbering and an X-ray crystallographic file in CIF format for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) We still do not have any conclusive evidence for the structure of a minor species.