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. 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. A short vanadium–oxygen bond length (1.7 Å) for the coordination environment of the vanadium(V) center in vanadate-dependent bromoperoxidase, based on the EXAFS, increased interest in the interaction of vanadium(V) ion with nonprotein oxygen atoms as an active site, where three nonprotein oxygen atoms are situated at short distances from the vanadium(V) center (average 1.65 Å). While five-coordinate monooxo–vanadium(V) model complexes are common, only a few five-coordinate monooxo–vanadium(V) model complexes 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: salicylaldehyde (shz), vanadium(III) acetylacetonate, chloroform-d, and tetrabutylammonium tetrafluoroborate (TBABF4) from Aldrich, Inc.; methanol (MeOH) and ethanol (EtOH) from Carlo Erba.

Instrumentation. C, H, and N 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. H NMR spectra were obtained using a Varian-300 spectrometer and ⁵¹V 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. 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 cm²) 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⁻ is a doubly deprotonated diatomic acetylacetoxyalcoholide). 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%). Anal. Calc'd for VO(Hacshz)(OEt) (C₁₄H₁₇N₂O₅V) (fw 554): 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 ν C–O, H NMR (300 MHz, CDCl₃): A form, δ 11.00 (s), 1H for phenolic proton; 7.82 (d), 7.31 (d), 6.95 (d), 6.87 (t), 4H for phenyl protons; 5.66 (s), 1H for −CH−; 5.39 (m), 2H for V−O−CH₂−; 2.42 (s), 2.23 (s), 6H for two methyl groups; 1.57 (t), 3H for V−O−CH₃, B form, δ 10.04 (s), 1H for CH₃OH; 7.22 (t), 7.01 (d), 6.87 (d), 6.61 (t), 4H for phenyl protons; 5.57 (s), 1H for −CH−, 3.65 (q), 2H for HOCH₂CH₃; 2.42 (s), 1.82 (s), 6H for two methyl groups; 1.17 (t), 3H for free HOCH₂CH₃, Ratio A:B = 4.1. ⁵¹V NMR (157.7 MHz, CDCl₃): A form, δ −519.98, B form, δ −514.21. Ratio A:B = 4.71. ⁵¹V NMR (157.7 MHz, MAS): δ −511.68. ESI mass spectrum: m/z [VO(Hacshz)(OEt)]⁺, 345. UV–vis (CH₂Cl₂) [Δmax (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 F² by full-matrix least-squares techniques with

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Table 1. Crystal Data and Structure Refinement for 1

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Scheme 1

Scheme 1 shows the reaction of shz with acetylacetone in situ (Scheme 1). Similar N-acylation of salicylhydrazide was observed. Magnetic susceptibility measurement of complex 1 indicated that the metal ion of the complex is diamagnetic d⁰ vanadium(V). During the reaction, the vanadium ion was air-oxidized to dialkoxy-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. The 1H NMR spectrum of complex 1 showed a characteristic δ = 1.567(3) ppm.

Results and Discussion

Preparation and Characterization of Complex 1. VO(Hacshz)(OEt), 1, could be synthesized using vanadium acetylacetone and shz in a one-pot reaction. Acetylacetylcolosalicylhydrazone (H₃acshz) was formed via a Schiff base condensation of acetonate and shz in a one-pot reaction. Acetylacetosalicyl-

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 diacetylacetylcolosalicylhydrazone (Hacshz⁻) serves as a tridentate ligand to form five- and six-membered chelating rings. An ethedox 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. 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 bipyramid. 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, 1 – 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 1H NMR spectrum of complex 1 in CDCl₃ gave two sets of bands at an approximate...
They interpreted their results with two coordination environments of octahedral monoalkoxo-bound monooxo-vanadium(V) complexes with pyrazolylpyridine bidentate chelating ligands.13 They reported a similar solution behavior of octahedral monoalkoxo-bound monooxo-vanadium(V) complexes with pyrazolylpyridine bidentate chelating ligand. 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 were broadened, the minor set of bands disappeared (Figure 2b). In addition, the coordinated ethoxide bands at 5.3 and 1.57 ppm were broadened, and the bands corresponding to ethoxy protons of the major species broadened, and the bands corresponding to ethoxy protons of the major species broadened, 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. 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 were broadened, and the bands corresponding to ethoxy protons of the major species broadened, and the bands corresponding to ethoxy protons of the major species broadened, increased.

The ESI mass spectrum of complex 1 in ethanol gave a band corresponding to only a monomeric complex ion, [VO(Hacshz)2(OEt) + H]+. Therefore, we assigned the major set of bands as those of monomeric form A as in the solid-state structure. 51V NMR spectrum of complex 1 in CDCl3 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 1H 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. 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. 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. 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 alkoxo-bridged dimer. It is well-known that alkoxides usually form dimeric complexes. 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.

Cyclic voltammetric measurements were performed in a chloroform solution containing 10 mM complex 1 and 0.1 M TBABF4 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 major 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. The reduction potential of the major species, approximately −50 mV, is comparable to that of the monoalkoxo dioxo square pyramidal V(V) complex, [salamp][V(V)O2(salamp)]. 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 and monooxo μ-oxo square pyramidal V(V) complex. It is likely that the reduction peak at −350 mV results from a V(IV)/V(III) couple.

Notes

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 Hacshz, where Hacshz 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, 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.