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Interactions between diperoxovanadate complex and amide ligands in aqueous solution

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Abstract

Multinuclear (^{1}H, ^{13}C, ^{14}N, and ^{51}V) NMR spectroscopy has been used to study the reactions between the diperoxovanadate complex $K_3[OV(O_2)_2(C_2O_4)] \cdot H_2O$ (abbr. bpV(ox)) and ethylenediamine or diethylamine in aqueous solution. The interaction between bpV(ox) and diethylamine was very weak and no new complex was formed. However, bpV(ox) reacted with ethylenediamine giving a new product in which ethylenediamine attached to the vanadium atom via one nitrogen atom in a monodentate manner. Diffusion ordered spectroscopy (DOSY) measurements and theoretical calculations proved the formation of new product in bpV(ox) and ethylenediamine. The vanadium atoms in both $[OV(O_2)_2(C_2O_4)]^{3-}$ and $[OV(O_2)_2(en)]^-$ species are six coordinated in solution state.
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1. Introduction

Recent studies on vanadium compounds as antidiabetic agents have increased interest in vanadium coordination chemistry and in biological mechanism of vanadium compounds [1–4]. However, because of the complex chemistry of vanadium compounds under physiological conditions, the active species has remained elusive, and the mechanism by which peroxo complexes of vanadium mimic-insulin is not fully understood. Investigation on how peroxovanadate interacts with amide ligands may provide some helpful information for understanding the biological mechanism.

The solid state structures have been determined for a large number of mono- and di-peroxovanadium(V) complexes by X-ray diffraction. These studies showed that the most common geometry for the monomeric oxoperoxo complexes is pentagonal bipyramidal and that the peroxo groups are always bound in the equatorial plane relative to the axial oxo ligand. The remaining equatorial and apical positions in the coordination shell are occupied by other ligands [5]. However, the complex structure in solid state and in solution state may be different. Further studies

of the actual processes involved in solution require an understanding of the basic chemistry of peroxovanadates, such as their interactions with amide ligands. NMR has been intensively used in the study of vanadium(V)/H_2O_2 systems and has proved to be successful in the structural characterization of the species in solution [6–13]. ^{51}V NMR is an important method in characterizing and analyzing vanadium(V) compounds [14–20]. By using a reference scale, ^{51}V NMR techniques could be sufficiently advanced in studying structures and coordination environments of known or unknown vanadium(V) compounds [21,22]. DOSY can be used to identify the individual components in a mixture. In this paper, the interactions between bpV(ox) and amide ligands, ethylenediamine and diethylamine, in aqueous solution was studied by various NMR techniques. Theoretical calculations were performed to elucidate the experimental observations. Through the combination of these methods, a better understanding of the experimental phenomena was achieved.

2. Experimental and theoretical

2.1. Materials and preparations

The chemicals deuterium oxide (D_2O), H_2O_2, V_2O_5, NaCl, oxalic acid, ethylenediamine, and diethylamine were analytic grade reagents. The ionic medium mimicking the ionic strength
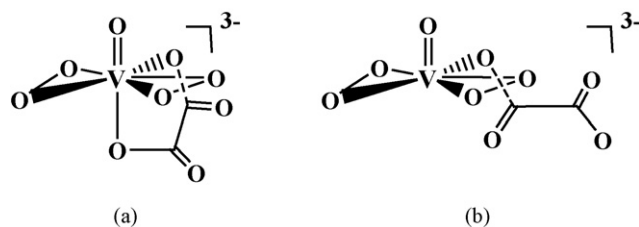
Fig. 1. Structural sketches of bpV(ox) anion in: (a) solid state and (b) solution state.

of human blood, 0.15 mol/L NaCl·D$_2$O solution at 25 °C, was adopted in all experiments. The K$_3$[OV(O$_2$)$_2$(C$_2$O$_4$)]·2H$_2$O was prepared and characterized according to the method reported previously [23]. The structural sketches of its anion in solid and solution state were shown in Fig. 1(a) and (b), respectively.

2.2. Spectroscopy

All NMR spectra were obtained from a Varian Unity plus 500 MHz NMR spectrometer operating at 500.4 MHz for ^{1}H, 125.7 MHz for ^{13}C, 36.1 MHz for ^{14}N, and 131.4 MHz for ^{51}V NMR. The solvent for ^{1}H, ^{13}C, ^{14}N and ^{51}V NMR spectra was D$_2$O. ^{51}V NMR chemical shifts were relative to external reference VOCl$_3$ which was assigned to 0 ppm. ^{14}N chemical shifts were measured relative to the external standard NH$_3$. Baseline corrections were applied to all spectra before integrals were obtained. DOSY was recorded by using a z-gradient probe, which delivers a maximum gradient strength of 30 G/cm. The gradient compensated stimulated echo spin lock (GCSTESL) [24] was used for acquiring DOSY spectra. The typical experimental parameters for a ^{1}H DOSY spectrum were as follows: gradient duration $\delta = 2$ ms, gradient strength $G = 3$ G/cm, spin lock time $\tau_{SL} = 1.5$ ms, and time interval $\tau = 2.3$ ms. Diffusion coefficient was generally achieved by stepwise ramping up of the amplitudes of pulsed field gradients (PFGs), and diffusion times were optimized for every experiment. The typical time required for a 2D ^{1}H DOSY spectrum was approximately 0.8 h (16 scans, relaxation delay 4 s). Reference deconvolution and baseline correction were used to compensate experimental imperfections for all DOSY spectra. The spectrum editing for different component was performed by selecting a specific diffusion row that corresponds to a 1D ^{1}H NMR spectrum of the component.

2.3. Computational method

All the geometries were optimized by using the B3LYP hybrid density functional, which includes a mixture of Hartree-Fock exchange with Becke88 exchange functional under generalized gradient approximation plus a mixture of Vosko–Wilk–Nusair local correlation functional and Lee–Yang–Parr nonlocal correlation functional [25,26]. The Wadt and Hay core-valence effective core potential [27] was used for the metal center (13 explicit electrons for neutral V) with the valence double-ζ contraction of the basis functions (denoted as Lanl2dz in Gaussian [28]). For O, N, C, and H, the standard 6-
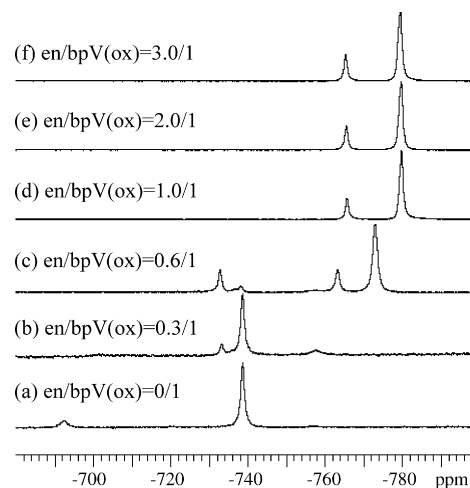

Fig. 2. ^{51}V NMR spectra of bpV(ox) (0.2 mol/L) and ethylenediamine with different molar ratio in NaCl (0.15 mol/L)·D$_2$O solution. The spectra from (a) to (f) correspond to the addition of ethylenediamine from 0 to 0.3, 0.6, 1.0, 2.0, and finally 3.0 equiv., respectively.

31 + G* basis sets developed by Hariharan and Pople [29] were used. The solvation effect was further considered using polarizable continuum model (PCM) [30] at each optimized gas phase geometry. All calculations were carried out with the Gaussian 98 program suite. Vibrational frequencies were calculated to ensure that each minimum in the gas phase is a true local minimum (only real frequencies). All energies reported in this work are ΔG (298 K) in kcal/mol.

3. Results and discussions

3.1. Reaction of bpV(ox) with ethylenediamine

3.1.1. Reaction processes monitored by ^{51}V NMR

The reaction process of bpV(ox) and ethylenediamine was probed by ^{51}V NMR. The results are shown in Fig. 2. There were two peaks in the ^{51}V NMR spectrum of bpV(ox) solution, locating at −692 and −738 ppm, respectively (Fig. 2(a)). The peak at −738 ppm was assigned to bpV(ox) [31], and the peak at −692 ppm was assigned to [OV(O$_2$)$_2$(H$_2$O)]$^-$ [7,8]. The pH value of the aqueous solution was 4.0. When ethylenediamine was added to bpV(ox) solution, the pH value rose up from 4.0 to 13.0 with the increase of the quantity of ethylenediamine. The variation of species in solution could be seen from Fig. 2(b)–(f). As shown in Fig. 2(b), when 0.3 equiv. ethylenediamine was added, the peak at −692 ppm disappeared and two new peaks at −757 and −732 ppm appeared with small intensity. The peak at −757 ppm arose from dimmer [(OV(O$_2$)$_2$)$_2$OH]$^{3-}$ and the peak at −732 ppm was assigned to triperoxovanadate [V(OH)(O$_2$)$_3$]$^{2-}$. When 0.6 equiv. ethylenediamine was added, the pH rose to about 8.0. The intensity of the peak at −732 ppm increased relatively, and the peak at −757 ppm moved to −762 ppm which belonged to diperoxovanadate [OV(OH)(O$_2$)$_2$]$^{2-}$. It is worth noting that a new peak appeared at −774 ppm in Fig. 2(c). It was assigned to [OV(O$_2$)$_2$(en)]$^-$. If more ethylenediamine was added, the peaks