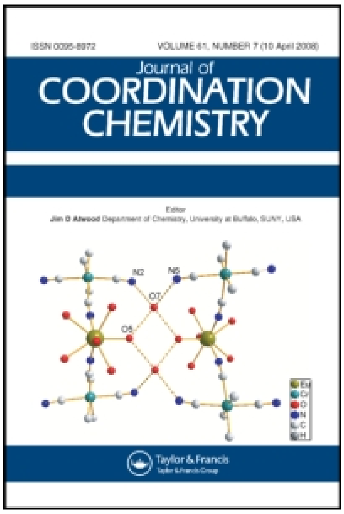

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NMR and theoretical study on the interaction between diperoxovanadate and 3-picoline derivatives

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NMR and theoretical study on the interaction between diperoxovanadate and 3-picoline derivatives

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To understand the substituent effects of 3-picoline derivatives on reaction equilibrium, the interactions between a series of 3-picoline-like ligands and $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ in solution were explored by multinuclear (^{1}H, ^{13}C, and ^{51}V) magnetic resonance, COSY, and HSQC in $0.15\,mol\,L^{-1}$ NaCl ionic medium for mimicking physiological conditions. The relative reactivity among the 3-picoline derivatives is 3-methyl pyridine > nicotinate > nicotinamide > ethyl nicotinate. Competitive coordination results in the formation of a series of new six-coordinated peroxovanadate species $[OV(O_2)_2L]^{n-}$ (L = 3-picoline derivatives, $n = 1$ or 2). Density functional calculations provide a reasonable explanation on the relative reactivity of the 3-picoline derivatives. Solvation effects play an important role in these reactions.

Keywords: Diperoxovanadate; 3-Picoline derivatives; Interaction; NMR; DFT-calculation

1. Introduction

Vanadium complexes, particularly vanadates and recently reported peroxovanadate compounds, have biological and industrial significance [1–4]. Vanadate is the inhibitor of Na^+, K^+-ATPases [5a]; some haloperoxidases such as chloroperoxidase (V-ClPO) from *Curvularia inaequaliz* contain vanadium in the active site [5b, 5c]. Insulin-mimicking ability of vanadium complexes attracts attention [1, 5d]. Moreover, vanadium compounds are widely employed as catalysts for reactions such as oxidation, epoxidation, and hydroxylation [5e, 5f]. Therefore, the coordination chemistry and biological mechanism of vanadium compounds have been the subject of extensive studies. For example, the mechanism of reactions of diperoxovanadium(V) compounds at physiological pH and the relevance to their DNA-photocleavage activities have been reported by Abu-Omar *et al.* [6]. Cuin *et al.* [7] synthesized vanadium complexes containing glycolic acid and studied their biological activity. A series of

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peroxovanadium complexes including amino acids was also synthesized and characterized by Gerbase *et al.* [8], and the ligand bonding properties were studied through different spectroscopic methods. Crans and Baran [9] also synthesized a series of oxovanadium(V) containing the hydroxylamido ligand (isoelectronic with hydrogen peroxide) and amino acids and then studied their spectral properties. Coordination reactions between peroxovanadate complexes and a series of amino acids or peptides have been explored by Tracey *et al.* [10] through NMR spectroscopy, obtaining formation constants and coordination mechanism in the solutions. Araujo and Brito [11] have used electromotrice force measurements together with UV-Vis to explore interactions between vanadium (III and IV) and organic ligands. Similarly, the interactions between peroxovanadate complexes and organic ligands were explored through detailed spectroscopic investigations in our previous papers [12–19].

Ligands containing a pyridine ring, such as 3-pyrid-3-ylbenzoic acid [20a, 20b], *p*-amino acetophenone isonicotinoyl hydrazone [20c], pyridine-3,5-dicarboxylate [20d], pyridine-2,6-dicarboxylate [20e], 3,5-bis(isonicotinamido)-benzoate [20f], are important building blocks for many transition metal complexes. In this work, NH_4VO_3/H_2O_2/3-picoline derivatives were studied using multinuclear (^1H, ^{13}C, and ^{51}V) magnetic resonance, COSY, and HSQC to probe the substitution group effects in the pyridine ring on the reaction equilibrium. DFT calculations provide a reasonable explanation for the experimental observations. Through the combined use of these methods, solution structures and coordination of all species in the interaction systems can be determined and a better understanding of the experimental phenomena can be achieved.

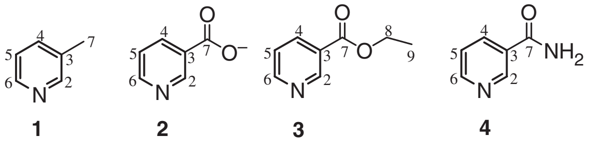
2. Experimental

2.1. *Spectroscopies*

All spectra were recorded on a Bruker AV-II 500 MHz NMR spectrometer. DSS (3-(trimethylsilyl)-propanesulfonic acid sodium salt) was used as an internal reference for ^1H and ^{13}C chemical shifts. The ^{51}V chemical shift was measured relative to the external standard $VOCl_3$ with upfield shifts considered negative.

2.2. *Materials and preparations*

D_2O, H_2O_2 (30%), NaCl, $NaHCO_3$, NH_4VO_3, 3-methyl pyridine (abbr. 3-Me-py, **1**), nicotinic acid, ethyl nicotinate (abbr. Et-nic, **3**), and nicotinamide (abbr. nicamide, **4**) were commercial products used without purification. Nicotinate (abbr. nic, **2**) can be obtained by mixing $NaHCO_3$ and nicotinic acid with 1 : 1 molar ratio. The atom numbers of organic ligands are shown in scheme 1. Ionic medium, $0.15\,\mathrm{mol\,L^{-1}}$ NaCl/D_2O solution at 20°C in all NMR experiments, was chosen to represent physiological conditions. To form the ternary system of NH_4VO_3/H_2O_2/3-picoline derivatives, NH_4VO_3 and H_2O_2 were first mixed in D_2O to produce $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ (abbr. bpV) followed by the addition of the ligands.



Scheme 1. Structures of 3-picoline derivatives.

2.3. *Computational method*

The geometries of the newly formed complexes were optimized using the B3LYP method [21–24]. The Wadt and Hay [25] core-valence effective core potential was used for the metal center (13 explicit electrons for neutral V) with the valence double zeta contraction of the basis functions (denoted as Lanl2dz in Gaussian [26]). For O, N, C, and H the standard 6-31+G* basis sets developed by Hariharan and Pople [27] were used. The single point solvation energy was calculated using polarizable continuum models (PCM [28, 29]) at each optimized gas phase geometry. Vibrational frequencies were calculated to ensure that each minimum is a true local minimum (only real frequencies). All calculations were carried out with the Gaussian 03 program suite [26].

3. Results and discussion

3.1. *^{51}V NMR studies on the interaction systems*

The starting sample is a mixture of NH_4VO_3 and H_2O_2 with 1 : 5 molar ratio and 0.2 mol L^{-1} vanadate concentration in D_2O. Its ^{51}V NMR spectrum has a peak at −692 ppm, shown in figure 1, which was assigned to bpV according to previous reports [12–19]. After 3-picoline is added to the bpV solution, a new single peak appears at about −712 ppm, assigned to $[OV(O_2)_2(\text{3-Me-pic})]^-$. Its intensity increases with increasing quantity of 3-Me-py (from 0.5 to 1.0, 1.5, and finally 2.0 equivalents) before reaching a maximum, as shown in figure 1(b)–(e). Moreover, with the addition of 3-Me-py, the peak at −692 ppm slightly moves upfield, whereas the peak at −712 ppm hardly moves, perhaps due to the change of pH [15]. The small new peak at −732 or −755 ppm is assigned to $[V(O_2)_3]^-$ or $[[OV(O_2)_2]_2]^{2-}$, respectively [13]. When the molar ratio between 3-Me-py and bpV reaches 2 : 1, almost all bpV is converted to $[OV(O_2)_2(\text{3-Me-pic})]^-$.

Likewise, when the same molar quantities of other 3-picoline derivatives were added to the peroxovanadate solutions, shown in figure 2, the area of the bpV peak decreased and a new peak appeared at about −707 ppm for $[OV(O_2)_2(\text{nic})]^{2-}$, −701 ppm for $[OV(O_2)_2(\text{Et-nic})]^-$, and −702 ppm for $[OV(O_2)_2(\text{nicamide})]^-$. Judged from the difference of the ratio of bpV peak areas before and after the reaction, different ligands have different equilibrium constants. Based on the following reaction equation:

$$\text{bpV} + \text{L} = \text{bpV(L)}$$

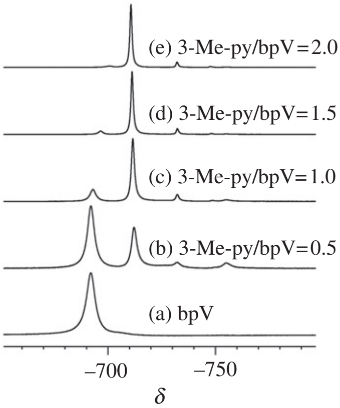


Figure 1. ^{51}V NMR spectra of NH_4VO_3/H_2O_2/3-Me-py. The total concentration of vanadate species is $0.2\,mol\,L^{-1}$ and the bpV refers to $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$.

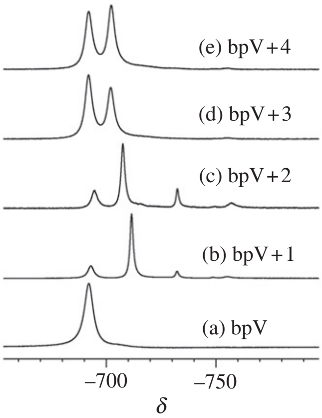


Figure 2. ^{51}V NMR spectra of NH_4VO_3/H_2O_2/3-picoline derivatives with 1 : 5 : 1 molar ratio in D_2O solution. The total concentration of vanadate species is $0.2\,mol\,L^{-1}$ and the bpV refers to $[OV(O_2)_2(D_2O)]^-/[OV(O_2)_2(HOD)]^-$.

the equilibrium constant of different reactions could be calculated according to the following equation:

$$K = [\mathrm{bpV(L)}]/[\mathrm{L}][\mathrm{bpV}], \quad \text{where L = 3-picoline derivatives.}$$

As a result, the equilibrium constants are 57, 34, 8, and $12\,mol\,L^{-1}$ for **1**, **2**, **3**, and **4**, respectively. Based on equilibrium constants, the order of interaction of 3-picoline derivatives with diperoxovanadate is 3-Me-py > nic > nicamide > Et-nic.

3.2. *Assignments of ^{1}H and ^{13}C NMR data of the interaction systems*

There are two groups of 3-picoline derivative peaks in every ^{1}H and ^{13}C NMR spectra. One was assigned to the free ligands and the other to coordinated 3-picoline derivative.

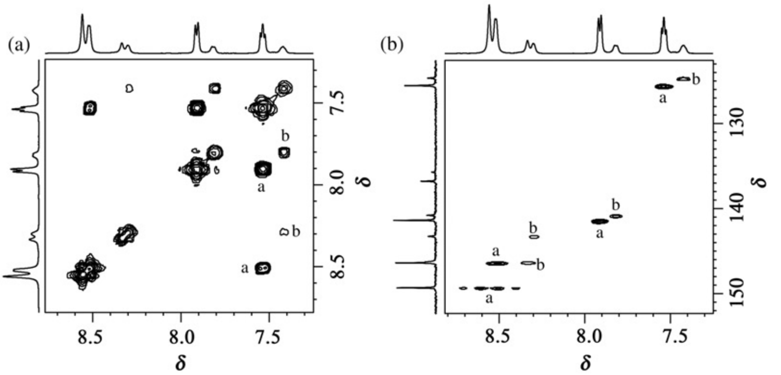
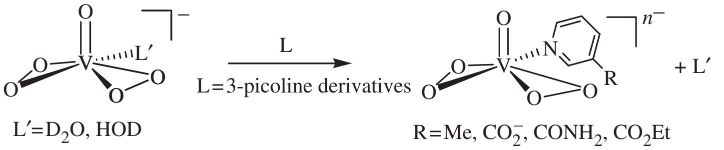


Figure 3. COSY and HSQC spectra of pyridine ring resonances of NH_4VO_3/H_2O_2/3-Me-py with 1 : 5 : 1 molar ratio in D_2O solution. The total concentration of vanadate species is $0.2\,mol\,L^{-1}$. (a) Coordinated ligands; (b) free ligands.



Scheme 2. Structures of newly formed peroxovanadate species.

In the interaction systems, some peaks in the pyridine ring overlapped with close chemical shifts, making assignments of the ^1H and ^{13}C NMR spectra difficult. Therefore, we used 2-D NMR spectra to make the assignments, as shown in figure 3 (the NH_4VO_3/H_2O_2/3-Me-py system was used as an example). In the COSY, correlation was observed between the peaks $8.52 \rightarrow 7.54 \rightarrow 7.91$ ppm, which was assigned to 6-H, 5-H, and 4-H, respectively (the atom number shown in scheme 1), and the single peak located in 8.56 or 2.36 ppm was assigned to 2-H or 7-H, respectively. Based on the results of COSY spectrum, the chemical shift of 2-C, 4-C, 5-C, 6-C, or 7-C is 149.3, 141.4, 125.5, 146.3, or 17.63 ppm, respectively. The only quaternary carbon atom (3-C) is located in 136.8 ppm. Through the combined use of multinuclear and 2-D NMR technologies, the ^1H and ^{13}C NMR spectral assignments of other interaction systems are listed in the "Supplementary material". According to the chemical shifts and/or the relative areas of the ^1H, ^{13}C, and ^{51}V peaks, we suggest that the newly formed species $[OV(O_2)_2L]^-$ (L = 3-picoline derivatives) is six-coordinate.

3.3. *Theoretical study on the reaction products*

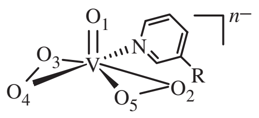
After analyzing the NMR spectra of the interaction systems, possible reaction modes are shown in scheme 2. Accompanied by the dissociation of a water molecule, a six-coordinate species $[OV(O_2)_2L]^{n-}$ forms. The structures of the newly formed species were optimized using the B3LYP method. The results confirmed that the newly formed species $[OV(O_2)_2L]^{n-}$ are six-coordinate. Five oxygens coordinating to vanadium form

Table 1. Selected bond distances of peroxovanadate species optimized at B3LYP/6-31+G* level (Å).

Ligands	V=O1	Error (%)	V–N	Error (%)	V–O2	Error (%)	V–O3	Error (%)	V–O4	Error (%)	V–O5	Error (%)
1	1.608	0.31	2.209	5.59	1.856	−0.54	1.850	−0.80	1.883	−2.03	1.875	−0.42
2	1.611	0.50	2.228	6.50	1.849	−0.91	1.854	−0.59	1.893	−1.51	1.878	−0.27
3	1.608	0.31	2.200	5.16	1.852	−0.75	1.849	−0.86	1.883	−2.03	1.875	−0.42
4	1.605	0.12	2.210	5.64	1.862	−0.21	1.849	−0.86	1.880	−2.19	1.877	−0.32
Imidazole[a]	1.603		2.092		1.866		1.865		1.922		1.884	

[a]Data from reference [30].

Table 2. Characteristic IR peaks of peroxovanadate species at B3LYP/6-31+G* level (cm^{-1}).

Species	Ligands	V=O1	Error (%)	V–O2/O3/O4/O5	Error (%)
 R = Me, CO_2^-, $CONH_2$, CO_2Et	**1**	986	3.79	932	6.51
	2	977	2.84	928	6.06
	3	984	3.58	930	6.29
	4	990	4.21	933	6.63
	Imidazole[a]	950		875	

[a]Data from reference [30].

a distorted pentagonal pyramid with nitrogen in pyridine coordinating to vanadium in the equatorial plane. The selected bond distances of peroxovanadate species are listed in table 1. Bond length variance for different organic ligands is within the range reported for diperoxovanadate complexes [13]. The peroxovanadate species containing imidazole has the same six-coordinated metal center. Compared to typical bond distances in different peroxovanadate species, the V=O or V–O bond length is close to the crystal structure within 2.19% [30]. However, the error of the V–N bond length ranges from 5.16 to 6.50, which may indicate more electron donation than pyridine; the stronger interaction between metal center and imidazole may give the shorter V–N bond length. Characteristic IR peaks of different peroxovanadate species agree well with the experimental data (table 2). The maximum related error is within 6.63% [30].

The reactivity of 3-picoline derivatives in solution depends on intrinsic bonding strength between $[OV(O_2)_2]^-$ and L and solvation effects. The four reactions studied here are:

$$\text{3-Me-pic} + [OV(O_2)_2(H_2O)]^- \rightarrow \left[OV(O_2)_2(\text{3-Me-pic})\right]^- + H_2O \tag{1}$$

$$\text{nic} + \left[OV(O_2)_2(H_2O)\right]^- \rightarrow \left[OV(O_2)_2(\text{nic})\right]^{2-} + H_2O \tag{2}$$

$$\text{Et-nic} + \left[OV(O_2)_2(H_2O)\right]^- \rightarrow \left[OV(O_2)_2(\text{Et-nic})\right]^- + H_2O \tag{3}$$

$$\text{nicamide} + \left[OV(O_2)_2(H_2O)\right]^- \rightarrow \left[OV(O_2)_2(\text{nicamide})\right]^- + H_2O \tag{4}$$

The free energy and enthalpy changes of reactions (1)–(4) are listed in table 3, indicating that the reactions are almost impossible in the gas phase but thermodynamically favorable in solution. Both the free energy and enthalpy changes have the same trend in solution. The changes resulting from solvation effects for these four

Table 3. The free energy and enthalpy changes of the coordination reactions (1)–(4) (kcal mol^{-1}).

Coordination reactions	ΔG(gas)	ΔH(gas)	ΔG(sol.)	ΔH(sol.)
Reaction (1)	3.03	1.56	−8.22	−8.56
Reaction (2)[a]	47.7	46.2	−7.54	−8.01
Reaction (3)	3.22	1.57	−5.31	−5.93
Reaction (4)	−0.88	−2.07	−6.22	−6.11

[a] The large free energy variation for reaction 2 is due to the negative charged nic, which has a strong interaction with water and then may stabilize the product.

reactions are 11.25, 55.24, 8.53, and 5.34 kcal mol^{-1} for free energy and 10.12, 54.21, 7.50, and 4.04 kcal mol^{-1} for enthalpy, respectively. Obviously, solvation effects play an important role, especially for reaction 2. Comparison of the free energies and enthalpies of reactions (1)–(4) in solution shows that:

$$\Delta G(\text{reaction 1}) < \Delta G(\text{reaction 2}) < \Delta G(\text{reaction 4}) < \Delta G(\text{reaction 3})$$

in agreement with the relative reactivity between 3-picoline derivatives and bpV observed experimentally.

4. Conclusions

In this article, several NMR experimental techniques were employed to study the interactions between diperoxovanadate complex and a series of 3-picoline derivatives in solution. The results indicate that new six-coordinated peroxovanadate species are formed. The coordination capability among the ligands is: 3-Me-py > nic > nicamide > Et-nic. Solvation effects play an important role in the reaction equilibrium.

Acknowledgments

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