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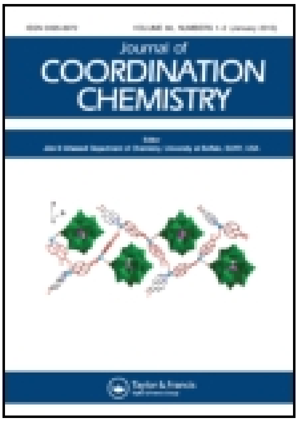

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NMR and theoretical study on the coordination interactions between peroxovanadium(V) complex and bisubstituted pyridine ligands

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NMR and theoretical study on the coordination interactions between peroxovanadium(V) complex and bisubstituted pyridine ligands

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To understand the substitution effects of pyridine ligands on coordination equilibrium, the coordination interactions between a series of bisubstituted pyridine ligands and peroxovanadium(V) $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ in solution have been investigated by multinuclear (^{1}H, ^{13}C, and ^{51}V) magnetic resonance and HSQC. A series of new six-coordinate peroxovanadate complexes $[OV(O_2)_2L]^{n-}$ ($L = \mathbf{2}$, **3**, **4**, $n = 1$ or 3) have been observed, and the coordination ability of the bisubstituted pyridines to peroxovanadium(V) is 3,4-dimethylpyridine (**2**) > 3,5-dimethylpyridine (**3**) > pyridine-3,5-dicarboxylate (**4**) ≫ 2,3-dimethylpyridine (**1**). The coordination interactions among title system have been further studied by DFT (density functional theory) calculations, and the results indicate that solvent may play an important role in these coordination interactions.

Keywords: Peroxovanadate; Bisubstituted pyridine ligands; Interaction; NMR; DFT-calculation

1. Introduction

Vanadium complexes, particularly vanadates and peroxovanadate compounds, have attracted tremendous attention owing to their potential applications in many fields such as inorganic cofactor, catalytic centers, models for haloperoxidases, insulin mimicry, anti-tumor drugs [1–6]. Therefore, investigation on coordination chemistry and biological mechanism of vanadium compounds has become very active. For example, Boruah [7] recently reported a series of new polymer-bound peroxo complexes of vanadium(V) exhibiting high activity with alkaline phosphatase. Tracey and co-workers [8] studied reactions between peroxovanadate complexes and a series of amino acids or peptides through NMR spectroscopy. Waidmann [9a] synthesized some oxo-peroxovanadium complexes and studied the complex formation mechanism. Similarly, Przybylski *et al.* [9b] obtained some

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*Corresponding author. Emails: fine_chem@163.com (X. Yu); pgyi@hnust.cn (P. Yi) biperoxovanadate-bipyridine complexes and studied their spectroscopic properties. Salifoglou's group [10a] explored the insulin mimetic activity of a ternary V(V)-citrate-(H_2O_2) system *in vitro*. At the same time, Przybylski *et al.* [10b] investigated the aqueous V(V)-peroxo-amino acid chemistry through the spectroscopic characterization. Sivak [11] studied the solid-state anion-Pi and Pi-Pi interactions in mono-peroxovanadium(V) complexes by both experimental and computational methods. Pombeiro [12a] and Ballistreri [12b] investigated the kinetics and oxidation mechanism of vanadate complexes containing pyrazine-2-carboxylic acid or picolinate. The V-51 NMR chemical shifts of peroxo forms of vanadium in haloperoxidases were calculated from QM/MM Models by Bühl's group [13]. Similarly, in our previous study, the interactions between peroxovanadate complexes and organic ligands were explored through spectroscopic investigations [14].

Ligands containing pyridine, such as 8-hydroxyquinoline [15], 2,6-pyridinedicarboxylate [16], 4,4′-bipyridine [17], 2,3-dihydroxy pyridine [18], methyl substituted 2-aminopyridines [19], and 4-(pyridin-2-yl)pyrimidine [20], are chelating-ligands which may facilitate coordination to the peroxovanadium(V) complex and produce new peroxovanadium(V) species. To expand our work in this area, herein we report an experimental and theoretical investigation on the coordination interaction between peroxovanadium(V) $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ and a series of bisubstituted pyridine ligands through multinuclear (^1H, ^{13}C, and ^{51}V) magnetic resonance, HSQC, and density functional theory (DFT) calculations, focusing our attention on two aspects: (i) understanding the substitution effect of ligands on the coordination equilibrium and (ii) probing the solution structures and coordination motifs of the newly formed complexes for a better understanding of complex formation.

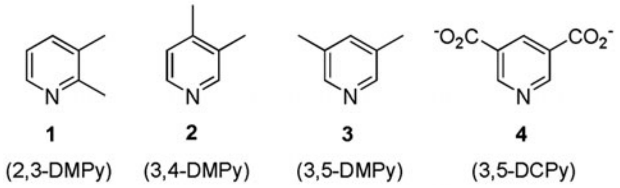
2. Experimental

2.1. *Spectroscopies*

All spectra were recorded on a Bruker AV-II 500 MHz NMR spectrometer. 3-(Trimethylsilyl)-propanesulfonic acid sodium salt was used as an internal reference for ^1H and ^{13}C chemical shifts. ^{51}V chemical shift was measured relative to the external standard $VOCl_3$ with upfield shifts considered negative. All pH measurements were measured by a pHS-2 digital pH-meter (Shanghai Leici Device Works, China) with a combinational glass calomel electrode.

2.2. *Materials and preparations*

The reagents D_2O, H_2O_2 (30%, fresh and stored at 0 °C), NaCl, $NaHCO_3$, NH_4VO_3, 2,3-dimethylpyridine (abbr. 2,3-DMPy, **1**), 3,4-dimethylpyridine (abbr. 3,4-DMPy, **2**), and 3,5-DMPy (**3**) were commercially available (Sinopharm Chemical Reagent Co., Ltd.) and used without purification. The pyridine-3,5-dicarboxylate (abbr. 3,5-DCPy, **4**) can be obtained by mixing $NaHCO_3$ and nicotinic acid with 2:1 M ratio. Organic ligands are shown in scheme 1. The ionic medium was chosen to represent the physiological condition, 0.15 mol/L NaCl/D_2O solution at 20 °C in all NMR experiments. To form the ternary system of NH_4VO_3/H_2O_2/bisubstituted pyridine ligands, NH_4VO_3 and H_2O_2 were first mixed in D_2O to produce $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ (bpV) followed by



Scheme 1. Structures of bisubstituted pyridine ligands.

addition of the ligands. The NMR samples are recorded after at least 4 h to let coordination interactions reach equilibriums.

2.3. *Computational method*

Geometries of the newly formed complexes were optimized using the B3P86 method [21–24]. The Wadt and Hay core-valence effective core potential [25] was used for vanadium (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 were used [27]. The single-point solvation energy was calculated using polarizable continuum models (PCM [28, 29]) at each optimized gas-phase geometry. Harmonic frequencies were calculated to confirm the equilibrium geometries that correspond to energy minima. All calculations were carried out with Gaussian 03 program suite [26].

3. Results and discussion

3.1. *^{51}V NMR studies on coordination reactions*

The starting sample is a mixture of NH_4VO_3 and H_2O_2 with 1 : 5 M ratio in D_2O (0.2 mol/L vanadate concentration) with ^{51}V NMR peak at −692 ppm assigned to $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(H_2O)]^-$ according to previous reports [5d, 14, 20] (figure 1). When 3,5-dimethylpyridine is added to bpV solution, a new single peak appears at −712 ppm, assigned to $[OV(O_2)_2(3,5\text{-DMPy})]^-$. Its intensity increases with increasing quantity of 3,5-dimethylpyridine (from 0 to 0.6, 1.0, and finally 2.0 equivalents) before reaching a maximum, as shown in figure 1(b)–(d). With addition of 3,5-dimethylpyridine, the peak at −692 ppm slightly moves to upfield, whereas the peak at −712 ppm hardly moves, resulting from the change of pH (from 4.0 → 7.6) [5d, 14b]. The small new peak at −732 or −755 ppm might be assigned to $[HVO(O_2)_3]^{2-}$ and $[HV_2O_3(O_2)_4]^{3-}$, respectively, according to the literature [20]. When the molar ratio of 3,5-dimethylpyridine to bpV reaches 2 : 1, almost all bpV is converted to $[OV(O_2)_2(3,5\text{-DMPy})]^-$.

According to figure 1, since only the peroxo species existed in the reaction system, the NMR spectra just displayed the range between −650 and −800 ppm in the following study. Likewise, when the same molar quantity of bisubstituted pyridine ligands was added to peroxovanadate solutions, shown in figure 2, the area of bpV peak decreased and a new peak appeared at −715 ppm for 3,4-dimethylpyridine {assigned to $[OV(O_2)_2(3,4\text{-DMPy})]^-$},

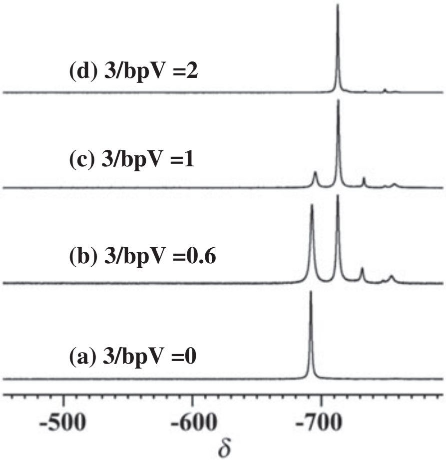


Figure 1. ^{51}V NMR spectra of the coordination system of NH_4VO_3/H_2O_2/3,5-dimethylpyridine. The total concentration of vanadate species is 0.2 mol/L. The pH of the systems (a)–(d) are 4.0, 5.8, 6.8, and 7.6, respectively.

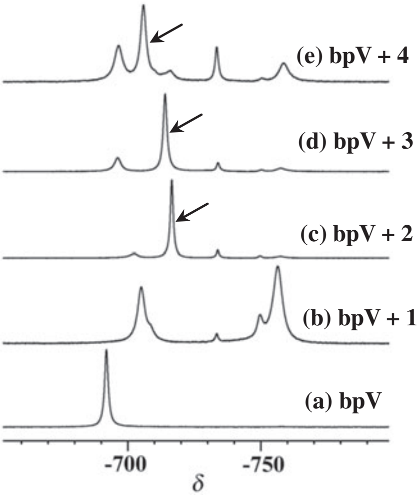


Figure 2. ^{51}V NMR spectra of the coordination system of NH_4VO_3/H_2O_2/bisubstituted pyridines with 1:5:1 molar ratio in D_2O solution. The total concentration of vanadate species is 0.2 mol/L. Peaks of the newly formed $[OV(O_2)_2L]^-$ (L = **2**–**4**) species are indicated by arrows. The pH of the systems (a)–(e) are 4.0, 7.1, 7.1, 6.8, and 5.8, respectively.

−705 ppm for pyridine-3,5-dicarboxylate {assigned to $[OV(O_2)_2(3,5\text{-DCPy})]^-$}, and 2,3-dimethylpyridine has no affinity. For 2,3-dimethylpyridine, new-formed peaks are at −748 ppm {assigned to $[(OV(O_2)_2)_2(\mu\text{-O})]^{4-}$} [30] and −755 ppm {assigned to $[HV_2O_3(O_2)_4]^{3-}$}. For pyridine-3,5-dicarboxylate, the new-formed peak at -757 ppm was assigned to $[HV_2O_3(O_2)_4]^{3-}$ in the coordination system. According to Pettersson's work, pH of these reaction systems was 4.0 ~ 7.1, which could form the stable peroxovanadate species [5d]. Judged from the ratio of bpV peak areas before and after coordination, the coordination ability of organic ligands to diperoxovanadate is 3,4-dimethylpyridine > 3,5-dimethylpyridine > pyridine-3,5-dicarboxylate with 2,3-dimethylpyridine having no affinity.

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

The ^{1}H and ^{13}C NMR spectral data of the coordination system of bpV (0.2 mol/L) and bisubstituted pyridine ligands with different molar ratio in sodium chloride deuterium oxide solution are listed in Supplementary material.

For 2,3-dimethylpyridine, due to no affinity to bpV, there is only one group peak in its ^{1}H or ^{13}C NMR spectrum. For other bisubstituted pyridines, there are two groups in each ^{1}H and ^{13}C NMR spectra. One group was assigned to free ligand and the other to coordinated pyridine, that is, the ligand of the new species formed in the coordination system. According to assignments of ^{1}H and ^{13}C NMR signals of the bpV-bisubstituted pyridine coordination system, NMR signals can also be assigned through the HSQC spectrum, which is displayed in figure 3. Based on the chemical shifts and/or the relative areas of the ^{1}H, ^{13}C, and ^{51}V peaks, the newly formed species $[OV(O_2)_2L]^-$ (L = bisubstituted pyridine ligands) can be concluded to be six-coordinate. Notably, single-crystal X-ray crystallographic analysis further confirmed that six-coordinated can also be observed in the complex $[OV(O_2)_2(\text{imidazole})]^-$, in which imidazole has a similar coordination to bisubstituted pyridine ligands in this work [31].

3.3. *Theoretical study on the coordination interactions*

NMR spectra data of the coordination system indicated that the newly formed species $[OV(O_2)_2L]^{n-}$ are six-coordinate. We suggest the possible coordination modes as follows after analyzing the NMR spectra of the coordination system, shown in scheme 2.

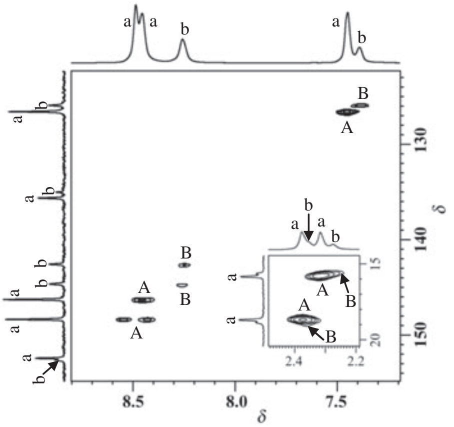
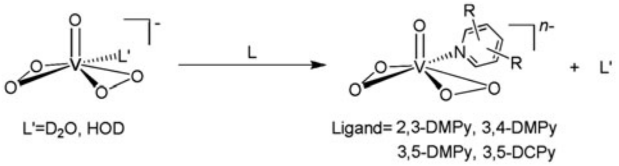


Figure 3. HSQC spectrum of the bpV and 3,4-DMPy in aqueous solution. The molar ratio of bpV and 3,4-DMPy 1 : 1. a or b label the signals from the coordinated or free 3,4-DMPy; A or B label the cross peaks from the coordinated or free 3,4-DMPy.



Scheme 2. Structures of newly-formed peroxovanadate species.

Table 1. Dominant bond distances of peroxo species optimized at B3P86/6–31 + G^* level (Å).

Ligands	V=O_1	Deviation/%[a]	V–N	Deviation/%[a]	V–O_2	Deviation/%[a]	V–O_3	Deviation/%[a]	V–O_4	Deviation/%[a]	V–O_5	Deviation/%[a]
2,3-DMPy	1.600	−0.19	2.239	7.03	1.843	−1.23	1.841	−1.29	1.868	−2.81	1.858	−1.38
3,4-DMPy	1.600	−0.19	2.162	3.35	1.844	−1.18	1.839	−1.39	1.870	−2.71	1.862	−1.17
3,5-DMPy	1.600	−0.19	2.168	3.63	1.844	−1.18	1.839	−1.39	1.870	−2.71	1.862	−1.17
3,5-DCPy	1.601	−0.12	2.192	4.78	1.842	−1.29	1.841	−1.29	1.883	−2.03	1.881	−0.16
Imidazole	1.603	0	2.092	0	1.866	0	1.865	0	1.922	0	1.884	0

[a] Compared to the experimental result of the peroxo species V-im from reference [31].

A six-coordinate $[OV(O_2)_2L]^{n-}$ (L = bisubstituted pyridine ligands) forms accompanied by dissociation of water. The structures of the newly formed species were optimized using the B3P86 method. The DFT-calculation found a distorted pentagonal pyramid forms though the five oxygens coordinated to vanadium and nitrogen in pyridine ring. In the structure of $[OV(O_2)_2L]^{n-}$, the N in pyridine coordinated to V locates in the equatorial plane. The dominant bond distances of peroxovanadate species are listed in table 1. The bond length variance for different ligands is within the range of reported ones for diperoxovanadate complexes [14b]. The peroxo species containing V-im is interesting because of the same six-coordinate metal center [31]. Compared to typical bond distances in different peroxovanadate species, the V=O or V–O bond length is near to the similar crystal structure with deviation within 2.81% [31]. However, for V–N bond, the deviation of the bond length ranges from 3.35 to 7.03%, which may have something to do with the electron donating of pyridine. The stronger interaction between metal center and imidazole may explain the shorter V–N bond length. At the same time, the characteristic IR peaks of different peroxo species V-pyr agree well with the experimental result of similar structure (the max related deviation within 8.19%), shown in table 2 [31].

The coordination ability of bisubstituted pyridines to bpV in solution depends not only on the intrinsic bonding strength between $[OV(O_2)_2]^-$ and L, but also the solvent effect. The four coordination reactions studied here are as follows:

$$2,3\text{-DMPy} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(2,3\text{-DMPy})]^- + H_2O \tag{1}$$

$$3,4\text{-DMPy} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(3,4\text{-DMPy})]^- + H_2O \tag{2}$$

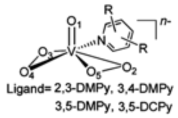
$$3,5\text{-DMPy} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(3,5\text{-DMPy})]^- + H_2O \tag{3}$$

$$3,4\text{-DCPy} + [OV(O_2)_2(H_2O)]^- \rightarrow [OV(O_2)_2(3,4\text{-DMPy})]^- + H_2O \tag{4}$$

The free energy changes of the coordination reactions 1–4 are listed in table 3. These data indicate that the reactions are not possible in the gas phase but thermodynamically favorable in the solution based on the free energy changes. Changes resulting from the solvation effects for these four reactions are 11.30, 12.88, 12.22, and 98.08 kcal/mol for free energy, respectively. Obviously, solvation plays an important role, especially for reaction 4. Comparison of the free energies of reactions 1–4 in solution shows that:

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

Table 2. Characteristic IR peaks of peroxovanadate species at B3P86/6–31 + G^* level (cm^{-1})[a].

Species	Ligands	$V{=}O_1$	Deviation/%[b]	$V{-}O_2/O_3/O_4/O_5$	Deviation/%[b]
	2,3-DMPy	995	4.74	945	8.03
	3,4-DMPy	996	4.84	942	7.71
	3,5-DMPy	997	4.94	943	7.81
	3,5-DCPy	1028	8.19	934	6.72
	Imidazole	950	0	875	0

[a] Frequency scaling factor is 0.9558.

[b] Compared to the experimental result of the peroxo species V-im from reference 31.

Table 3. The free energy changes of reactions 1–4 (kcal/mol).

Coordination reactions	ΔG (gas)	ΔG (sol.)	Solvation effects
Reaction 1	4.09	−7.21	11.30
Reaction 2	1.85	−11.03	12.88
Reaction 3	1.55	−10.67	12.22
Reaction 4[a]	89.97	−8.11	98.08

[a] The large free energy variation for reaction 4 is due to the negative charged character of 3,5-DCPy ligand, which has a strong interaction with water and then may stable the product.

This order is in agreement with the relative coordination ability of bisubstituted pyridines to bpV observed experimentally. The calculated G (reaction 1) is negative; however, the $[OV(O_2)_2(2,3\text{-DMPy})]^-$ species has not been observed by NMR, indicating that the dynamics (steric effect, etc.) may affect reaction 1.

4. Conclusions

Multinuclear NMR spectroscopy and DFT calculations were employed to study coordination interactions between diperoxovanadate and a series of disubstituted pyridine ligands. The coordination ability of the disubstituted pyridine ligands to diperoxovanadate follows the order: 3,4-dimethylpyridine > 3,5-dimethylpyridine > pyridine-3,5-dicarboylate ≫ 2,3-dimethylpyridine. The differences of coordination ability are attributed at least in part to the solvent effect on the equilibria.

Acknowledgments

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