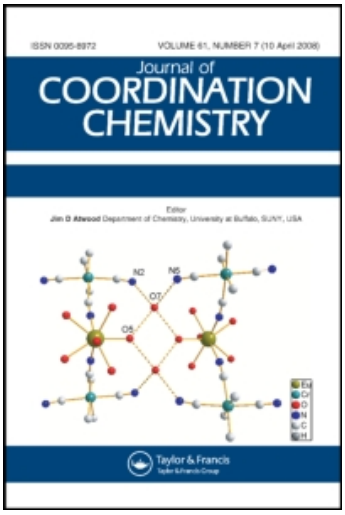


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# The structure, stability, and reactivity of oxalato-monoperoxovanadium(V) in solution

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In order to understand the solution chemistry of an oxalato-monoperoxovanadium(V) complex ($K_3[VO(O_2)(C_2O_4)_2]\cdot ½H_2O$, mpVox), the solid and solution-state NMR characteristics, transformation behavior, and exchange phenomena in the solution are described in this article. NMR experimental and theoretical results indicated that the vanadium of mpVox in solid and solution state are seven coordinate. However, some geometric parameters tend to change upon dissolution. The dynamic transformation of mpVox in solution was investigated using NMR, IR, and UV-Vis. The reduction product is oxalato-bisoxovanadate. Concentration, pH, and temperature affect this transformation. $^{51}V$ NMR investigation on the system of mpVox with picolinc acid showed that two oxalates are substituted to produce $[VO(O_2)(ox)(pic)]^{2-}$ and $[VO(O_2)(pic)_2]^-$.

*Keywords*: Vanadium; Spectroscopy; Solution structure; Transformation; Interactions

## 1. Introduction

Peroxovanadium complexes have received interest as orally administered drugs for the treatment of diabetes mellitus [1–4]. Also, they are key intermediates in the action of haloperoxidases and in other biologically significant oxidations [5–7]. Most peroxovanadium complexes are stable in solution when they are stored in cold and dark conditions at neutral or slightly basic pH. However, they may decompose to vanadate species at lower pH or with irradiation [8]. Such lability may compromise the effectiveness of these compounds as therapeutic agents. For example, with two equivalents of glutathione or other thiols, the dipicolinato-peroxovanadate forms dipicolinato-oxovanadate and vanadate, which are both insulin-mimetic vanadium compounds [9, 10]. Stability and redox are thus critical to the insulin-mimetic

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peroxovanadates under physiological conditions and should be considered in developing vanadium-based oral insulin-mimetic agents [11–13]. Although several studies have demonstrated the metabolic effects of vanadium during the past two decades, the knowledge about its functional mechanism is still limited [14–17].

Because of the great importance of peroxovanadium complexes in biological systems, it is necessary to investigate their solution chemistry. Monomeric peroxo complexes, including oxoperoxovanadium complexes [18] and oxodiperoxotungsten complexes [19], are commonly pentagonal bipyramidal with the peroxo groups bound in the equatorial plane relative to the axial oxo ligand. The ligands are bound to metal bidentate through oxygen or nitrogen. However, it is known that vanadium(V) is stereochemically flexible with geometries ranging from tetrahedral and octahedral to trigonal pyramidal and pentagonal bipyramidal, and thermodynamically plausible [20–22]. Our previous work showed that oxalato-diperoxovanadium(V) is seven-coordinate pentagonal bipyramidal in the solid state, the same as the oxodiperoxotungsten(VI) complexes [19]. However, oxalato-diperoxovanadium(V) changes to six-coordinate pentagonal pyramidal when dissolved in water [23]. The coordination chemistry of peroxovanadium complexes plays an important role in *in vitro* insulin-mimetic activity and *in vivo* antidiabetic blood-glucose-lowering activity [24–29]. To understand the active mechanism, clear picture about coordination chemistry of peroxovanadium complexes is necessary. Based on Yu's [22] study on the interactions between diperoxovanadate and picolinamide-like ligands, we investigated the monoperoxovanadium complexes. We chose oxalato-monoperoxovanadium(V) ($K_3[VO(O_2)(C_2O_4)_2]\cdot \frac{1}{2}H_2O$, mpVox) as a model to study solution-state properties and interaction with picolinic acid to gain insight into the solution chemistry of monoperoxovanadates. The structure of mpVox was investigated using multinuclear NMR spectroscopy and density functional theory (DFT) calculations. The $^{13}C$ NMR spectra were assigned with the help of DFT calculation. The stability and reduction of mpVox were investigated using NMR, IR, and UV-Vis spectra. The influences of concentration, pH, and temperature are discussed.



## 2. Experimental

### 2.1. *Preparation of mpVox*

Red crystals of mpVox were prepared using the method reported by Stomberg [30]. $KVO_3$ (1.38 g), $K_2C_2O_4\cdot H_2O$ (1.84 g), and $H_2C_2O_4\cdot 2H_2O$ (1.16 g) were dissolved in 10 mL 30% $H_2O_2$ at 0°C. The solution was left for evaporation at 4°C. Prism crystals were obtained within 1 week. $\delta\,^{51}V$ NMR ($D_2O$): −596 ppm. $\delta\,^{13}C$ NMR ($D_2O$): 166.7, 168.3 ppm. IR (KBr, $cm^{-1}$): $\nu$(O–H) 3475 vs, $\nu_{as}$(COO) 1719, 1708, 1675 vs, 1656 m, $\nu_s$(COO) 1432 vs, 1400 vs, 1271, $\nu$(V=O) 948 vs, $\nu$(O–O) 933 s, $\nu$(V–OO) 545 s. UV-Vis: 424 nm ($\varepsilon = 1.0\times10^3\,L\,mol^{-1}\,cm^{-1}$). X-ray: triclinic, $P\bar{1}$.

### 2.2. *Transformation of mpVox*

Crystals of mpVox were picked out and put in a beaker with some mother liquid at 4°C. The transformation product of mpVox was recorded by X-ray, NMR, IR, and UV-Vis. Two mpVox solutions with the concentration of 0.2 and 0.5 mol $L^{-1}$ were prepared.

The pH of the mpVox solution with the concentration of 0.2 mol $L^{-1}$ was about 5.5. An appropriate amount of oxalic acid was added into the mpVox solution to adjust the pH to 1.0. Variable temperature (VT) $^{51}V$ NMR was performed to investigate the temperature effect.

### 2.3. *Interaction of mpVox with picolinic acid*

A series of different molar equivalents of picolinic acid (from 0.5 to 1.0, 1.5, 2.0, 3.0, and 4.0 equivalents with respect to vanadium) were added into the mpVox solution and $^{51}V$ NMR spectra were recorded.

### 2.4. *Spectroscopic methods*

The solid-state NMR experiments were performed on a Bruker DMX 300 NMR spectrometer ($B_0 = 7.0$ T) using a 4.0 mm Bruker double resonance MAS probe. The solid-state $^{51}V$ MAS NMR spectra were recorded at 10 and 14.5 kHz. The $^{51}V$ isotropic chemical shifts were referenced to neat $VOCl_3$ (assigned to 0 ppm). The solid-state $^{13}C$ MAS NMR spectra were recorded at 6.0 kHz. The $^{13}C$ isotropic chemical shifts were referenced to the carbonyl carbon of glycine (assigned to 173.2 ppm).

Solution $^{51}V$ and $^{13}C$ NMR spectra were recorded on a Bruker AV300 FT NMR spectrometer. Trimethylsilylpropanesulfonic acid sodium salt (DSS) was used as an internal reference for $^{13}C$ chemical shifts. The $^{51}V$ chemical shifts were measured relative to external $VOCl_3$.

IR spectra were recorded as nujol mulls between KBr plates using a Nicolet Avatar IR-360 spectrometer. Electronic spectra were recorded on a UV-240 spectrophotometer. Crystal structural data of mpVox were collected on a Bruker Smart Spex CCD diffractometer with graphite-monochromated Mo-K$\alpha$ radiation at 293 K.



### 2.5. *Computational details*

The geometry of mpVox anion was optimized using B3LYP hybrid density functional [31–34]. Vibrational frequencies were calculated at the same level of theory to ensure that the optimized geometry was a true local minimum. For O and C, 6-311G(d,p) basis set was used. For V, LANL2DZ was used. The $^{13}C$ chemical shielding values were calculated based on the X-ray crystal structure and the optimized structure for solid and solution state, respectively. The GIAO technique was employed to circumvent the gauge-origin problem [35]. Solvation effects were taken into account by using polarizable continuum model (PCM [36]) on the optimized geometry. The chemical shieldings were converted to chemical shifts with respect to the reference compound TMS calculated at the same level of theory. All calculations were carried out with Gaussian 03 program suite [37].

## 3. Results and discussion

### 3.1. *Coordination structure of mpVox in solid and solution*

The mpVox crystal that we obtained was consistent with the previous reports [18]. The solid-state structure of mpVox anion is shown in figure 1, together with atomic labels.

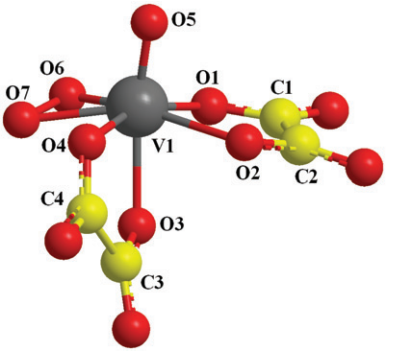


Figure 1. Structure view and atomic numbering of $[VO(O_2)(C_2O_4)_2]^{3-}$.

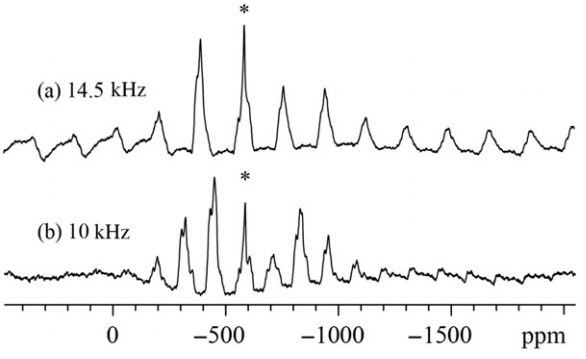


Figure 2. Solid-state $^{51}V$ MAS NMR spectra of mpVox recorded at 7.0 T with spinning rates of (a) 14.5 kHz and (b) 10 kHz.



The vanadium is coordinated by seven oxygens in a pentagonal bipyramid. The equatorial plane is defined by the peroxo oxygens and three oxygens from two oxalates. Figure 2 shows the $^{51}V$ MAS NMR spectra of mpVox recorded at the spinning rates of 14.5 and 10 kHz. The spinning-rate independent center band at −586 ppm, as indicated by asterisks in the spectra, represents the isotropic shift. The solution-state $^{51}V$ NMR spectrum of mpVox in $D_2O$ was recorded for comparison. The solution-state $^{51}V$ chemical shift is −596 ppm. The solution and solid-state isotropic chemical shifts differ by 10 ppm. This variation implies some difference in structures between solid and solution. Geometric optimization of mpVox anion was also performed and the results are listed in table 1. The optimized $V{=}O_5$ bond length is slightly shorter than the experimental one. The optimized $V–O_6$ and $V–O_7$ bond lengths are almost equal, although in solid state the $V–O_6$ is 0.408 Å, shorter than $V{-}O_7$. Similarly, the $V{-}O_1$, $V{-}O_2$, and $V{-}O_4$ bond lengths are unequal in solid state but tending to be closer in the optimized structure. The difference of geometric structure between calculated and experimental data are reasonable because solvent effects were taken into account by using PCM considered on the optimized geometry. Therefore, it can be obtained that the vanadium remains seven coordinate in the solution. This indicates that the coordination manner of mpVox anion is unchanged when it dissolves in water. So the change of $^{51}V$ chemical shift from solid state to solution is attributed to the change

Table 1. Geometric parameters for mpVox (distances in Å and angles in degree).

| Bond | $V_1$–$O_5$ | $V_1$–$O_6$ | $V_1$–$O_7$ | $V_1$–$O_1$ | $V_1$–$O_2$ | $V_1$–$O_3$ | $V_1$–$O_4$ | $O_6$–$O_7$ |
|---|---|---|---|---|---|---|---|---|
| X-ray | 1.645 | 1.656 | 2.064 | 1.997 | 2.201 | 2.139 | 2.013 | 1.386 |
| DFT | 1.611 | 1.874 | 1.905 | 2.071 | 2.118 | 2.235 | 2.055 | 1.417 |
| Angle | $O_1$–$V_1$–$O_4$ | $O_1$–$V_1$–$O_7$ | $O_3$–$V_1$–$O_2$ | $O_3$–$V_1$–$O_7$ | $O_3$–$V_1$–$O_4$ | $O_5$–$V_1$–$O_6$ | $O_5$–$V_1$–$O_7$ | $O_5$–$V_1$–$O_1$ |
| X-ray | 158.05 | 127.42 | 75.88 | 82.91 | 76.58 | 104.24 | 104.68 | 102.31 |
| DFT | 152.33 | 121.75 | 80.14 | 85.79 | 74.81 | 102.37 | 100.67 | 96.63 |
| Angle | $O_5$–$V_1$–$O_2$ | $O_5$–$V_1$–$O_3$ | $O_6$–$V_1$–$O_1$ | $O_6$–$V_1$–$O_4$ | $O_6$–$V_1$–$O_7$ | $O_6$–$V_1$–$O_3$ | $O_6$–$V_1$–$O_2$ | $O_5$–$V_1$–$O_4$–$C_4$ |
| X-ray | 89.40 | 161.30 | 88.14 | 105.28 | 41.82 | 92.79 | 161.52 | 147.57 |
| DFT | 90.18 | 166.82 | 78.04 | 123.75 | 44.04 | 90.28 | 151.39 | 178.72 |

Table 2. Comparison of the experimental and calculated $^{13}C$ NMR chemical shifts of mpVox (in ppm).

| State | Solid | | Solution | | |
|---|---|---|---|---|---|
| Carbon | $\delta_{cal}$ | $\delta_{exp}$ | $\delta_{cal}$ | $\delta_{cal,pcm}$ | $\delta_{exp}$ |
| $C_1$ | 171.5 | 169.6 | 174.3 | 175.1 | 168.3 |
| $C_2$ | 167.6 | 166.9 | 171.2 | 172.6 | 166.7 |
| $C_3$ | 165.9 | 165.6 | 169.6 | 171.2 | 166.7 |
| $C_4$ | 167.5 | 166.9 | 174.2 | 175.3 | 168.3 |



of local environment around vanadium nucleus, such as the relative positions of coordination atoms, intermolecular H-bonding of the peroxide to the water of crystallization, and possibly the solvent effects [38].

Besides $^{51}V$ NMR, $^{13}C$ NMR is effective to characterize the coordination structure. Due to the equivalence of the two carbon sites, the $H_2C_2O_4$ should have only one $^{13}C$ NMR peak. The experimental result verifies from this expectation, with signal at 160.0 ppm in the $^{13}C$ MAS NMR spectrum at a spinning rate of 6 kHz. The solid-state $^{13}C$ MAS NMR spectrum of mpVox at the same spinning rate shows that chemical shifts of the four carbons are 169.6, 166.9, and 165.6 ppm, indicating that the four carbons are not equivalent. Similarly, the solution-state $^{13}C$ NMR spectrum of mpVox shows that chemical shifts are 168.3 and 166.7 ppm. To assign these two $^{13}C$ NMR spectra, DFT calculations were performed.

The calculated $^{13}C$ chemical shifts of mpVox anion are listed in table 2. The results show that the chemical shifts of $C_1$, $C_2$, $C_3$, and $C_4$ in solid state are 171.5, 167.6, 165.9, and 167.5 ppm, respectively. According to this result, we assigned the peak at 169.6 ppm to $C_1$, the peak at 165.6 ppm to $C_3$, and the peak at 166.9 ppm to $C_2$ and $C_4$. For the solution state, the chemical shifts of $C_1$ and $C_4$ are close to each other, while $C_2$ and $C_3$ form another group. Therefore, we assigned the peak at 168.3 ppm to $C_1$ and $C_4$, and the peak at 166.7 ppm to $C_2$ and $C_3$. The theoretical $^{13}C$ chemical shifts of solid-state mpVox are in good agreement with the experimental ones, while those of solution have slightly larger deviations, which may be due to factors not rigorously taken into account in solution state. As shown in table 2, an overall mean absolute deviation (MAD) of 0.5, 0.9, and 1.1 ppm are obtained for solid-state mpVox, the solution-state one without

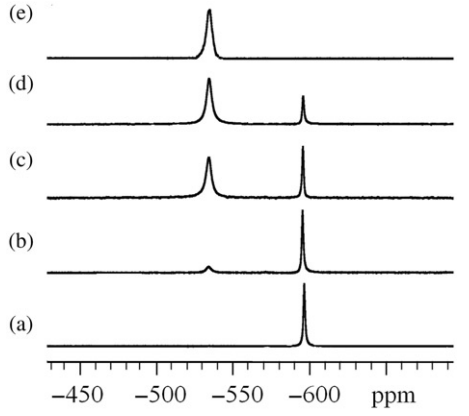


Figure 3. $^{51}V$ NMR spectra of mpVox solution (0.2 mol $L^{-1}$) recorded (a) immediately after preparation, (b) 2 weeks later, (c) 6 weeks later, (d) 8 weeks later, and (e) 12 weeks later.



PCM, and the solution-state one with PCM, respectively. In general, the calculated isotropic $^{13}C$ NMR shifts agree well with the experimental values, and the solvent effects play an important role in solution. Furthermore, with the help of theoretical calculations, the two $^{13}C$ NMR spectra can be reasonably assigned.

### 3.2. *Stability of mpVox*

Since stability is important for vanadium compounds as diabetic drugs [39], we explored the stability of mpVox by measuring the variations of its $^{51}V$ NMR, $^{13}C$ NMR, IR, and UV-Vis spectra with time in neutral pH at room temperature. The time-dependent $^{51}V$ NMR spectra were given in figure 3. The $^{51}V$ chemical shift of pure mpVox is −596 ppm (figure 3a). In 2 weeks, the peak at −596 ppm is predominant with only a small peak at −535 ppm (figure 3b). The integral area ratio of the peak −596 ppm to the peak −535 ppm (figure 3b) was 4 : 1. Six weeks later, the peaks at −596 and −535 ppm coexisted and the integral area ratio became 1 : 2 (figure 3c) and 1 : 4 (figure 3d). Twelve weeks later, mpVox transformed entirely (figure 3e).

Time-dependent $^{13}C$ NMR spectra of mpVox solution are shown in figure 4. Initially, there are two peaks with chemical shifts of 168.3 and 166.7 ppm (figure 4a). At 4 weeks, one new peak appears at 167.7 ppm (figure 4b). At the end, only a broad peak at 167.7 ppm remains (figure 4c), which corresponds to the transformation product recorded in figure 3e. The IR and UV-Vis measurements also reveal such transformation. In the IR spectra, $\nu$(V=O) 948 $cm^{-1}$, $\nu$(O–O) 933 $cm^{-1}$, and $\nu$(V–OO) 545 $cm^{-1}$ are the three characteristic peaks of mpVox. As time elapses, the V=O vibrational peak (948 $cm^{-1}$) exhibits blue shift and splits into two peaks at 923 and 894 $cm^{-1}$, implying that the transformation product has two V=O groups. At the same time, both $\nu$(O–O) and $\nu$(V–OO) disappear, indicating the loss of peroxo group –O–O–. In the UV-Vis spectra, the characteristic peak of V–OO in 424 nm diminishes in the transformation product, as shown in figure 5, indicating no peroxo group in **2**. From these spectroscopic results, we conclude that the transformation product is a bisoxo compound without peroxo. The transformation product was separated and its unit

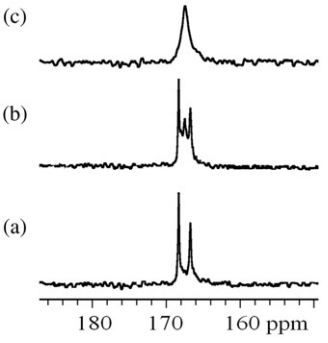


Figure 4. $^{3}$C NMR spectra of mpVox solution (0.2 mol L$^{-1}$) recorded (a) immediately after preparation, (b) 4 weeks later, and (c) 12 weeks later.

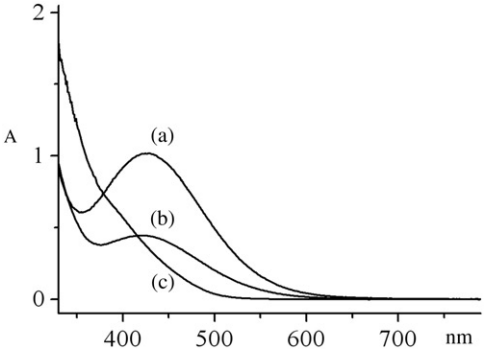


Figure 5. UV-Vis spectra of mpVox solution (0.2 mol L$^{-1}$) recorded (a) immediately after preparation, (b) 4 weeks later, and (c) 12 weeks later.

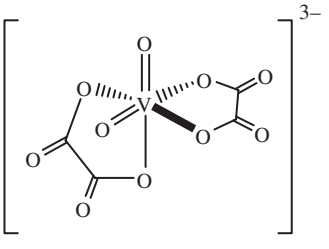


Figure 6. Structure view of $[VO_2(C_2O_4)_2]^{3-}$ anion.

cell parameters ($a = 7.798$ Å, $b = 7.853$ Å, $c = 11.515$ Å, $\alpha = 91.32°$, $\beta = 94.02°$, $\gamma = 110.36°$, and $V = 658.60$ Å$^3$) are consistent with the previous report [40].

It has a distorted octahedral geometry wherein the angle between the two oxo ligands is 90°. The structure view of its anion $[VO_2(C_2O_4)_2]^{3-}$ is shown in figure 6. When mpVox transformed completely, we added $H_2O_2$ to the solution and found that $[VO_2(C_2O_4)_2]^{3-}$ was converted to mpVox reversibly. In the $^{51}$V NMR spectra, the peak at −535 ppm was gradually converted to −596 ppm, as given in figure 3(a)–(e).

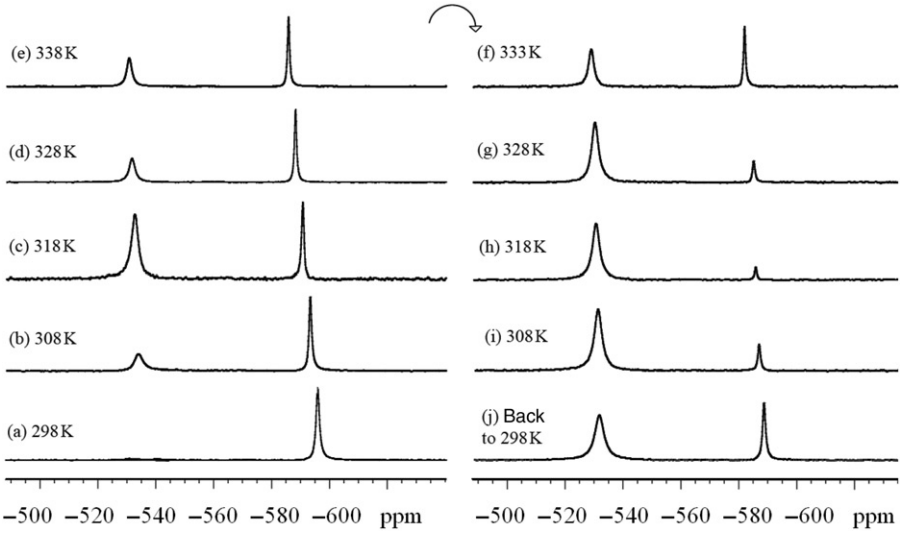


Figure 7. $^{51}$V VT NMR spectra of mpVox solution (0.2 mol $L^{-1}$). Temperature increases in the left column and then decreases in the right column.



It takes about 12 weeks for mpVox (0.2 mol $L^{-1}$) to completely change into $[VO_2(C_2O_4)_2]^{3-}$ at room temperature. When the solution concentration is 0.5 mol $L^{-1}$, the time interval shortens to about 8 weeks. The higher the concentration, the shorter the transformation period. The transformation rate also greatly increases in a very acidic environment. When oxalic acid was added to adjust the pH to 1.0, the transformation would finish in a minute. The effect of temperature was investigated by VT NMR. Figure 7 shows the $^{51}$V VT NMR spectra of the mpVox solution (0.2 mol $L^{-1}$). It can be seen that the influence of temperature on mpVox transformation is nonlinear. Higher temperature does not mean higher transformation efficiency. The optimal temperature for the transformation of mpVox at 0.2 mol $L^{-1}$ concentration is 318 K. The solution does not return to the same state when the temperature is decreased.

### 3.3. *Interaction of mpVox with picolinic acid*

The interaction of mpVox and picolinic acid was probed by $^{51}$V NMR. Figure 8 displays the variation of $^{51}$V NMR spectra of mpVox solution with the addition of picolinic acid. When 0.25 equivalent picolinic acid is added, a new peak at −614 ppm appears with about 25% intensity of mpVox. When the amount of picolinic acid increases, the peak at −596 ppm decreases and the peak at −614 ppm becomes stronger (figure 8b–d). When 1.0 equivalent picolinic acid is added, the integral area ratio of −596 to −614 ppm becomes 5 : 95. Another new peak is recorded at −630 ppm with an intensity of about 10% of all vanadates (figure 8e). When more picolinic acid is added, −596 ppm becomes weaker and weaker and finally only those species corresponding to peaks at −614 and −630 ppm remain, as shown in figure 8(f)–(h). The new peaks at $\delta_v$ −614 and −630 ppm were assigned to $[VO(O_2)(ox)(pic)]^{2-}$ and $[VO(O_2)(pic)_2]^-$ (pic = picolinic acid anion), respectively.

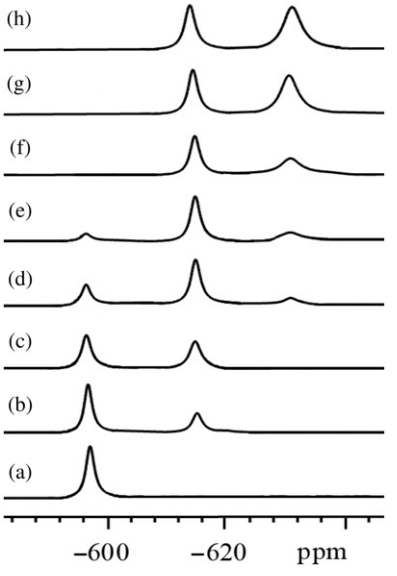


Figure 8. $^{51}V$ NMR spectra of mpVox and picolinic acid, from bottom to top: the mol equivalent of picolinic acid is (a) 0, (b) 0.25, (c) 0.5, (d) 0.75, (e) 1.0, (f) 1.25, (g) 1.5, and (h) 2.0.



According to the above $^{51}V$ NMR spectra, we suggest the exchange process as follows: (1) The mpVox dissolves in $D_2O$ or $H_2O$ and forms $[VO(O_2)(C_2O_4)_2]^{3-}$. (2) Picolinic acid attacks the vanadium of $[VO(O_2)(C_2O_4)_2]^{3-}$ accompanied by the loss of a $C_2O_4^{2-}$, producing $[VO(O_2)(ox)(pic)]^{2-}$. (3) The picolinic acid further attacks the vanadium of $[VO(O_2)(ox)(pic)]^{2-}$ accompanied by the loss of another $C_2O_4^{2-}$, producing $[VO(O_2)(pic)_2]^-$.

## 4. Conclusions

The structure, stability, and reactivity of mpVox in aqueous solution were investigated by multinuclear ($^{51}V$ and $^{13}C$) NMR spectroscopy and DFT calculations. The solid-state $^{13}C$ NMR spectrum of the coordinated oxalate was assigned with the help of DFT calculations. The discrepancy ($\Delta\delta = 10$ ppm) between solid and solution $^{51}V$ isotropic chemical shifts suggests that the geometry of the first coordination sphere of the vanadium center may change when mpVox dissolves in water. Both experimental and theoretical results indicate that mpVox anion has similar seven-coordinate structures in solution and solid state. However, upon dissolution, the bond lengths between vanadium and the coordinated atoms change to make the geometry more symmetric. Compared to the results of the diperoxovanadate complex $[VO(O_2)_2L]^-$ ($L = C_2O_4^{2-}$, $D_2O$ or HOD) with a six-coordinate solution structure [13], the monoperoxovanadium complex in this article is very different.

The mpVox undergoes dynamic changes in solution, leading to a reduced product with the loss of peroxy group (–O–O–). Concentration, pH, and temperature affect this transformation. Spectroscopic results (NMR, IR, and UV-Vis) show that

$[VO_2(C_2O_4)_2]^{3-}$ can be converted to $[VO(O_2)(C_2O_4)_2]^{3-}$ reversibly upon the addition of hydrogen peroxide. Reaction between mpVox and picolinc acid shows that oxalate can be exchanged by picolinate. The substitution behavior of picolinate in this article is in accord with the interactions between picolinamide-like ligands and diperoxovanadate complex studied before [22].

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