Study on structural variation of oxalate-oxodiperoxovanadate(V) from solid state to solution using NMR spectroscopy and theoretical calculation

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A R T I C L E   I N F O

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A B S T R A C T

In order to understand the geometric structure of oxalate-diperoxovanadate(V) K₃[VO(O₂)₂(C₂O₄)]H₂O (abbr. bpV(ox)) in water, ⁵¹V and ¹³C NMR spectroscopy and density functional theory (DFT) calculations were employed to explore the difference with the solid structure of bpV(ox) from X-ray diffraction. It is suggested by the differences in the ⁵¹V and ¹³C isotropic chemical shifts between solid state and solution and verified by our DFT calculations that the geometry of bpV(ox) anion may undergo change upon dissolution. Besides, the ¹³C NMR spectra of the coordinated oxalate in bpV(ox) was first assigned with the help of DFT calculation. The combination of the NMR data and DFT calculations confirms that bpV(ox) is seven-coordinated pentagonal bipyramidal in solid, while it is six-coordinated pentagonal pyramidal when it dissolves in water. This study sheds some light on the coordination chemistry of peroxovanadium(V) complexes.

The coordination chemistry of vanadium compounds plays an important role in in vitro insulin-mimetic activity and in vivo blood glucose lowering activity [1,2]. The general coordination number of vanadium in complexes with multi-dentate ligands ranges from four to eight [3,4]. X-ray diffraction studies show that many monomeric oxoperoxovanadium complexes are commonly pentagonal bipyramidal [5,6]. In contrast, since vanadate readily undergoes coordination geometry changes [7,8], whether the coordination number of the complexes in solution is six or seven is still controversial [9–11]. ⁵¹V solid state NMR (SSNMR) spectroscopy has become an important analytical tool for studying vanadium compounds since it can provide valuable information on the local environment of vanadium nucleus [12]. The combination of SSNMR and computational methods is capable of providing unique structural information unavailable from single-crystal X-ray diffraction or other spectroscopic methods [13,14].

In order to understand the structural variation from the solid state to solution, we used multinuclear (⁵¹V and ¹³C) NMR to explore the structure of the complex K₃[VO(O₂)₂(C₂O₄)]H₂O (abbr. bpV(ox)), which has an insulin-mimetic bioactivity. Density functional theory (DFT) calculations were performed to interpret the experimental observations. Through the combination of NMR spectroscopy and theoretical calculations, a better understanding of the coordination chemistry of peroxovanadium(V) complexes can be achieved. It is found that the bpV(ox) anion has different geometry in the solid and solution state. The coordination number of the vanadium center changes from seven to six upon dissolution. This study sheds some light on the coordination chemistry of peroxovanadium(V) complexes.

Orange crystals of bpV(ox) were prepared using the method reported by Vuletic and Djordjevic [15]. The crystal structure data were consistent with that reported by Begin et al. [16]. The ⁵¹V MAS NMR spectra of solid bpV(ox) recorded on a 14.1 T NMR spectrometer with three different spinning rates. The spinning rate independent centerband at –713 ppm, as indicated by the asterisks in the spectra, represents the isotropic shift, which comprises of isotropic chemical shift and isotropic shift of the second-order quadrupolar interaction. The lineshape of the centerband, which is independent of the chemical shift anisotropy, strongly depends on the second-order quadrupolar interaction. The fitting of the centerband lineshape allows one to obtain the quadrupolar coupling constant C_Q, the asymmetry parameter of the electric field gradient (EFG) tensor η_Q, and the isotropic chemical shift δiso. The results are given in Table 1. From the numerical simulation, we obtained that the isotropic ⁵¹V chemical shift in the solid form of bpV(ox) is –704 ppm.

The solution ⁵¹V NMR spectrum of bpV(ox) in D₂O with a concentration of 0.02 mol/L was recorded at room temperature for comparison. The solution ⁵¹V chemical shift is –738 ppm. The ⁵¹V solution and solid state isotropic chemical shifts (–738 vs.
–704 ppm) differ by 34 ppm. This is attributed to the high sensitivity of chemical shielding at the vanadium nucleus with respect to the change of its local environment [12]. The discrepancy in $^{51}$V isotropic chemical shifts between the solid and solution states suggests that the geometry of the first coordination sphere of the vanadium center may undergo change when $\text{bpV(ox)}$ dissolves in water.

$^{13}$C NMR spectroscopy was used to further investigate the structural variation of $\text{bpV(ox)}$. The solid state $^{13}$C MAS NMR spectrum of $\text{bpV(ox)}$ shows that the chemical shifts of the two carbon atoms are 167.8 and 165.6 ppm (Fig. 2a). Here, we differentiate the two carbons as C1 at 167.8 ppm and C2 at 165.6 ppm. Relative to 160.0 ppm (the chemical shift of H$_2$C$_2$O$_4$), the 7.8 and 5.6 ppm downfield shifts suggest that the two carbons experience different chemical environments. While in the $\text{bpV(ox)}$ solution, the chemical shifts of 173.4 and 168.0 ppm were observed for the two carbon atoms (Fig. 2b). The chemical shift difference between the two carbon atoms is 2.2 ppm in solid state and 5.4 ppm in solution. This suggests that the environments of the two carbon atoms are much more alike in solid state than in solution state, implying that solvent effects play an important role in the $^{13}$C chemical shifts of $\text{bpV(ox)}$ when it dissolves and the coordination number of the vanadium center may change. Note that, as Na$_2$C$_2$O$_4$ was added into the $\text{bpV(ox)}$ solution, the intensity of the peak at 173.4 ppm was enhanced significantly (Fig. 2c). This indicates that the chemical environment of one of the carbons in $\text{bpV(ox)}$ is similar to that of the carbons in Na$_2$C$_2$O$_4$ in solution. Based on the above experimental results, we suppose that the solution structure of $\text{bpV(ox)}$ anion is different from the solid state one and the coordination number of vanadium may change. The following DFT calculations give more support to our suggestion. What's more, the two carbon atoms of $\text{bpV(ox)}$ would be assigned.

DFT computations were performed to provide a better theoretical understanding of experimental observations [18]. Together with the experimental solid state structure data [16], some optimized bond parameters of $\text{bpV(ox)}$ anion are listed in Table 2. It can be seen that the optimized V=O$_1$ bond length is slightly shorter than the experimental one. The four V–O bond lengths (V–O$_2$, V–O$_3$, V–O$_4$, and V–O$_5$) are unequal in solid state, and V–O$_3$ and V–O$_4$ are slightly shorter due to less steric influence from the ligand. In the optimized structure, the V–O$_2$ and V–O$_5$ bond lengths are almost equal, so are the V–O$_3$ and V–O$_4$ bond lengths. For the bonds between vanadium and oxalate, the V–O$_6$ bond length in the optimized structure is slightly longer than the one in solid state, while the V–O$_7$ bond is broken, with the distance increasing from 2.251 to 4.988 Å. The bond angles related to the O$_7$ also change a lot in accordance. All these indicate that the $[\text{VO(O}_2\text{)}_2]$ group and the V–O$_6$ is rather stable from solid state to gas phase, while the V–O$_7$ bond is broken in gas phase, and possibly in solution state too, due to the relatively flexible structure of the coordination groups in oxalate.

The solid state structure and the optimized structure of $\text{bpV(ox)}$ anion are shown in Fig. 3. The main difference between them is in the manner in which the oxalate is coordinated: one is bidentately coordinated to vanadium with both two –OC(O)– groups, resulting in a seven-coordinated structure, while the other is monodentately coordinated to vanadium with only one –OC(O)– group, resulting in a six-coordinated structure. This result is in accordance with

<table>
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<th>Table 1</th>
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<tr>
<td>Solid state $^{51}$V NMR parameters for $\text{bpV(ox)}$ obtained from numerical simulations of $^{51}$V MAS NMR spectra: quadrupolar couplings ($C_Q$, $\eta_Q$), isotropic chemical shifts ($\delta_{iso}$), and chemical shielding anisotropies ($\delta_{anis}$). $\delta_{iso} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; $\delta_{anis} = \delta_{33} - \delta_{iso}$. The EFG parameters are $C_Q = \epsilon e^2 Q / h$, and $\eta_Q = (V_{11} - V_{22})/V_{33}$, where $\epsilon$ is the electron charge, $h$ is Planck’s constant, and $Q$ is the nuclear quadrupolar moment of $^{51}$V, –4.8 fm$^2$ [17].</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameters</th>
<th>$C_Q$ (MHz)</th>
<th>$\eta_Q$</th>
<th>$\delta_{iso}$ (ppm)</th>
<th>$\delta_{anis}$ (ppm)</th>
<th>$\delta_{11}$ (ppm)</th>
<th>$\delta_{22}$ (ppm)</th>
<th>$\delta_{33}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{bpV(ox)}$</td>
<td>4.8</td>
<td>0.90</td>
<td>–704</td>
<td>–920</td>
<td>–175</td>
<td>–313</td>
<td>–1624</td>
</tr>
</tbody>
</table>

Fig. 1. Solid state $^{51}$V MAS NMR spectra of $\text{bpV(ox)}$ at different spinning rates recorded on 14.1 T. (a) 15 kHz, (b) 21 kHz, and (c) 28 kHz.

Fig. 2. Solid state $^{13}$C MAS NMR spectrum (a), and solution $^{13}$C NMR spectra of $\text{bpV(ox)}$ (b) as well as $\text{bpV(ox)}$ added with Na$_2$C$_2$O$_4$ (c).
the deduction from $^{51}$V and $^{13}$C NMR experimental observation: the coordination structure of bpV(ox) anion may change when it dissolves in water. 

The calculated $^{13}$C chemical shifts of bpV(ox) anion show that the chemical shifts of C$_1$ and C$_2$ in solid state are 168.6 and 165.1 ppm, respectively, in good agreement with the experimental measurement (167.8 and 165.6 ppm). It supports our assignment of two $^{13}$C peaks in solid state NMR spectrum. That is, the peak at 167.8 ppm is from C$_1$ and the peak at 165.6 ppm is from C$_2$. It also implies that the carbon in the apical position trans to V=O is more shielded than that in the equatorial plane cis to V=O.

The experimentally observed $^{13}$C chemical shifts of bpV(ox) in solution were 173.4 and 168.0 ppm, while the calculated ones are 184.9 and 181.3 ppm (without PCM), or 185.3 and 180.4 ppm (with PCM). It implies that the solution structure would be the optimized six-coordinated structure from crystal. Compared to the solid state, the deviations of the calculated values from the experimental ones become larger in solution state. However, the experimental and calculated $^{13}$C chemical shifts of Na$_2$C$_2$O$_4$ without/with PCM are 173.5 and 183.5/184.5 ppm, respectively. This is in good agreement with the calculated one with PCM (4.9 ppm). It supports our assignment of two $^{13}$C peaks in solid state NMR spectrum.

The calculated $^{13}$C chemical shifts of bpV(ox) anion show that the chemical shifts of C$_1$ and C$_2$ in solid state are 168.6 and 165.1 ppm, respectively, in good agreement with the experimental measurement (167.8 and 165.6 ppm). It supports our assignment of two $^{13}$C peaks in solid state NMR spectrum. That is, the peak at 167.8 ppm is from C$_1$ and the peak at 165.6 ppm is from C$_2$. It also implies that the carbon in the apical position trans to V=O is more shielded than that in the equatorial plane cis to V=O.

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In conclusion, bpV(ox) is pentagonal bipyramidal in the solid state, while it is pentagonal pyramidal in solution. The coordination number of vanadium center changes from seven to six upon dissolution. In addition, DFT calculation results support the hypothesis that the carbon in the apical position, trans to V=O, is more shielded than that in the equatorial plane cis to V=O. In summary, the present work showed that a combination of NMR spectroscopy and DFT calculation provides a useful tool for investigating the coordination structure of peroxovanadium(V) complexes in solution.

### Acknowledgments

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### References


### Table 2

Some geometric parameters of the solid state and optimized structures of bpV(ox) anion (distances in Å and angles in degree).

<table>
<thead>
<tr>
<th>bpV(ox)</th>
<th>Method</th>
<th>V-O$_1$</th>
<th>V-O$_2$</th>
<th>V-O$_3$</th>
<th>V-O$_4$</th>
<th>V-O$_5$</th>
<th>V-O$_6$</th>
<th>O$_1$-V-O$_6$</th>
<th>O$_1$-V-O$_7$</th>
<th>O$_6$-V-O$_7$</th>
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<tr>
<td>X-ray</td>
<td>1.622</td>
<td>1.934</td>
<td>1.866</td>
<td>1.856</td>
<td>1.911</td>
<td>2.060</td>
<td>2.251</td>
<td>90.3</td>
<td>164.4</td>
<td>74.1</td>
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<tr>
<td>DFT</td>
<td>1.606</td>
<td>1.875</td>
<td>1.907</td>
<td>1.904</td>
<td>1.868</td>
<td>2.084</td>
<td>4.988</td>
<td>100.1</td>
<td>124.2</td>
<td>24.2</td>
</tr>
</tbody>
</table>

![Fig. 3. Structures of bpV(ox) anion. (a) Seven-coordinated solid state structure and (b) optimized six-coordinated structure.](image-url)
The geometry of the bpV(ox) anion was optimized using the B3LYP hybrid density functional. For O and C, 6-311G(d,p) was used. For V, 6-31G* basis set with an additional f function was used. Experimental crystal data were directly used for solid state $^{13}$C chemical shielding calculation, whereas the optimized structure was used for solution $^{13}$C chemical shielding calculation. Solvent effects were taken into account for solution state by using polarizable continuum model on optimized geometry.