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12. (a) Mazzocchi observed that alkenes with lower ionization potential fail to photoadd to N-methylphthalimide and explained this by electron transfer quenching action (large  $k_{M1}$ ) of alkenes with low oxidation potential<sup>12b</sup>; (b) P. H. Mazzocchi, S. Minamikawa, and M. Bowen, *J. Org. Chem.*, 9., 1713 (1978).

### Solid-State <sup>13</sup>C-NMR Studies of Bis(oxalato)dioxovanadate(V) Complexes

Man-Ho Lee

Department of Industrial Chemistry,  
Kyungpook National University, Taegu 702-701

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Vanadium(V) forms stable complexes with oxalate,<sup>1-4</sup> EDTA,<sup>5,6</sup> and a few other ligands. The rarity of vanadium (V) complexes is due to its strong oxidizing power with most ligands being oxidized by the metal center.

Oxalate as a bidentate ligand has been of great interest in coordination chemistry for a long time.<sup>7</sup> Oxalic acid is known to form irregular octahedral complexes with vanadium (V), and their structures having been assigned on the basis of X-ray diffraction studies<sup>1,2</sup> are shown in Figure 1. In this paper we report the solid-state <sup>13</sup>C-NMR spectra of (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·2H<sub>2</sub>O and K<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O and discuss them with relation to the structures. And <sup>13</sup>C-NMR spectra of the complexes in solution are also discussed.

Solid (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·2H<sub>2</sub>O and K<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O

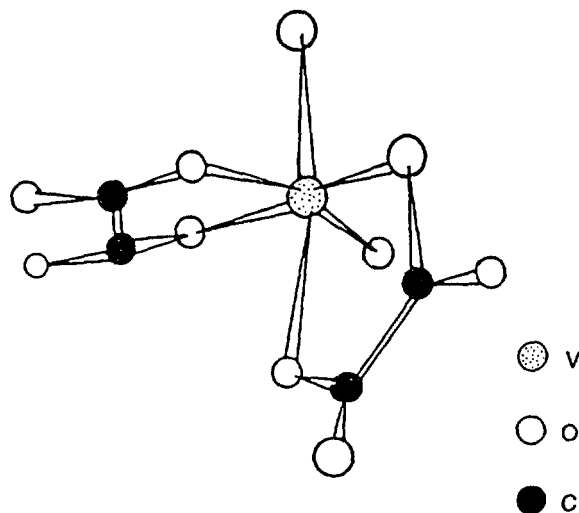


Figure 1. Irregular octahedral geometry of [VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]<sup>3-</sup> ion.

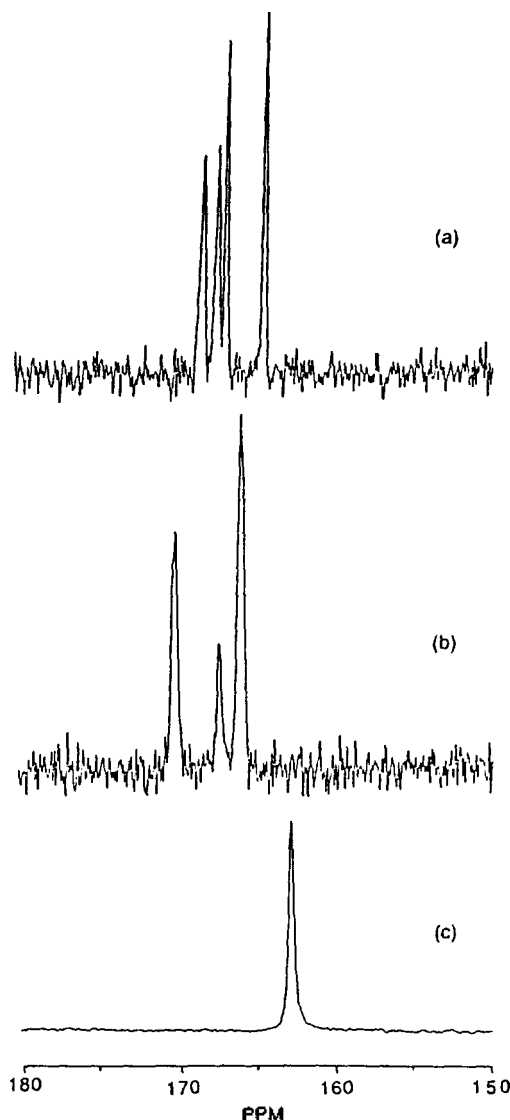
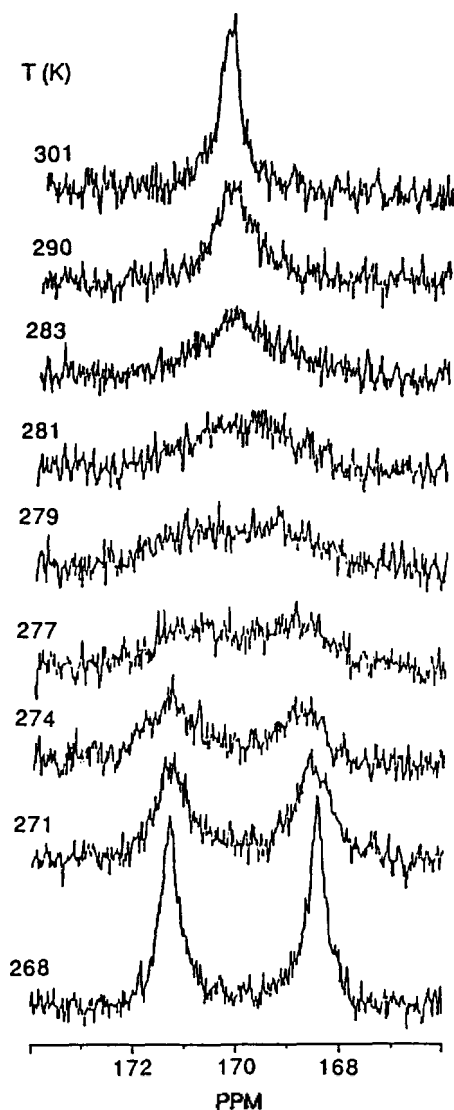


Figure 2. CP/MAS <sup>13</sup>C-NMR spectra (75.47 MHz) of solid (a) (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·2H<sub>2</sub>O, (b) K<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O, and (c) H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O.

were prepared by the method of Sathyanarayana, *et al.*<sup>8</sup> and by the method of Drew, *et al.*,<sup>2</sup> respectively.

<sup>13</sup>C NMR spectra of solid samples were recorded on a Bruker MSL-300 NMR spectrometer at 75.47 MHz with CP/MAS technique. A spectral width of 29411 Hz and an accumulation of ~200 transient with acquisition time of 0.85 s were used for obtaining <sup>13</sup>C spectra of the solid samples. The contact time was 2 ms and the delay between each scan was 5 s. Chemical shifts were measured relative to the carboxylic carbon in glycine and reported according to the relation  $\delta_{TMS} = \delta_{glycine} + 176.0$  ppm. <sup>13</sup>C-NMR spectra of solution samples were recorded on a Bruker AM-250 NMR spectrometer at 62.90 MHz. <sup>13</sup>C chemical shifts were measured relative to internal dioxane and reported according to the relation  $\delta_{DSS} = \delta_{dioxane} + 69.14$  ppm.

According to the bond lengths in solid (NH<sub>4</sub>)<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·2H<sub>2</sub>O and K<sub>3</sub>[VO<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>]·3H<sub>2</sub>O determined by X-ray diffraction studies<sup>1,2</sup> two oxo oxygens in both complexes have short V=O bonds (1.628(2)-1.648(2) Å) which indicate strong



**Figure 3.**  $^{13}\text{C}$ -NMR spectra (62.90 MHz) of  $(\text{NH}_4)_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$  in 20%  $\text{D}_2\text{O}$ -80%  $\text{H}_2\text{O}$  at various temperatures.

multiple bond character. The remaining four metal-oxygen (carboxylate) bonds are longer and fall into two groups depending on whether or not they are *trans* to a  $\text{V}=\text{O}$  bond. The *trans* V-O bonds are significantly longer (2.158(2)-2.235(2) Å) than the other pair (1.972(2)-2.009(2) Å). This serves as a good illustration of the structural *trans* effect.<sup>1</sup> This  $\sigma$  bond strength weakening is reflected throughout the rest of the anion as the strongest of the inner C-O bonds are adjacent to the weaker V-O bonds. The terminal carbon-oxygen bond lengths (1.220(3)-1.241(4) Å) are slightly shorter than the inner C-O bonds (1.257(3)-1.291(3) Å) but comparable to the C=O double bond length found in aldehydes and ketones.<sup>2</sup> Thus, the carboxylates in the complexes are classified to two groups: those that are *cis* to and those that are *trans* to V=O bonds.

As shown in Figure 2(a), solid  $(\text{NH}_4)_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$  shows two sets of  $^{13}\text{C}$  signals: one set (164.6, 167.2 ppm)

is assigned to  $^{13}\text{C}$ 's in the C=O groups *trans* to the V=O and the other set (167.7, 168.6 ppm) is assigned to  $^{13}\text{C}$ 's in the C=O groups *cis* to the V=O. The intensity variation between two sets of signals is typical for long delays between scans (5-20 s). The intensity variation is therefore a result of different cross polarization during the chosen CP time (2 ms). As shown in Figure 2(b), solid  $\text{K}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$  also shows two sets of  $^{13}\text{C}$  signals: one set (166.4, 170.6 ppm) is assigned to  $^{13}\text{C}$ 's in the C=O groups which are *trans* to the V=O, and other set (166.4, 167.7 ppm) is assigned to the  $^{13}\text{C}$ 's in the C=O groups *cis* to the V=O. From the signal intensity it is supposed that two signals coincide accidentally at 166.4 ppm. We assigned the observed  $^{13}\text{C}$  signals of the complexes to *cis* and *trans* carboxylates on the basis of their intensities and V-O bond lengths. As shown in Figure 2 (c), solid oxalic acid,  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , shows only one  $^{13}\text{C}$  signal at 162.7 ppm. We expect that  $^{13}\text{C}$  chemical shifts of the solid complexes are also influenced by the environment of the  $[\text{VO}_2(\text{C}_2\text{O}_4)_2]^{3-}$  anion such as type of cations, hydrogen bonding of water molecules, etc. But as far as now the further assignment of  $^{13}\text{C}$  signals is impossible because of lack of the solid-state  $^{13}\text{C}$ -NMR data.

When solid  $(\text{NH}_4)_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$  was dissolved in water it showed different  $^{13}\text{C}$ -NMR spectra at various probe temperatures as shown in Figure 3. The complex showed only one  $^{13}\text{C}$  signal (169.97 ppm) at higher temperature (300 K) indicating the occurrence of fast exchange between two types of carboxylate groups (*cis* and *trans* to V=O) in the solution. But below the coalescence temperature (281 K) the  $^{13}\text{C}$  signal is splitted to two signals (168.48, 171.37 ppm) because of slow exchange between two carboxylates on NMR time scale. Of course the chemical exchange between two carboxylates are impossible in the solid sample. Solid  $\text{K}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2] \cdot 3\text{H}_2\text{O}$  also gave similar spectra as shown in Figure 3 when dissolved the complex in water.

In conclusion, the solid-state  $^{13}\text{C}$ -NMR spectroscopy is very useful to obtain information about the bond character in the vanadium(V) complexes.

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