

# UC Davis

## UC Davis Previously Published Works

### Title

$\alpha$ -Hydroxy coordination of mononuclear vanadyl citrate, malate and S-citramalate with N-heterocycle ligand, implying a new protonation pathway of iron–vanadium cofactor in nitrogenase

### Permalink

<https://escholarship.org/uc/item/6ck3n897>

### Authors

Chen, Can-Yu  
Chen, Mao-Long  
Chen, Hong-Bin  
et al.

### Publication Date

2014-12-01

### DOI

10.1016/j.jinorgbio.2014.08.003

Peer reviewed



Published in final edited form as:

*J Inorg Biochem.* 2014 December ; 141: 114–120. doi:10.1016/j.jinorgbio.2014.08.003.

## $\alpha$ -Hydroxy coordination of mononuclear vanadyl citrate, malate and S-citramalate with N-heterocycle ligand, implying a new protonation pathway of iron-vanadium cofactor in nitrogenase

Can-Yu Chen<sup>a,b</sup>, Mao-Long Chen<sup>a</sup>, Hong-Bin Chen<sup>a</sup>, Hongxin Wang<sup>c</sup>, Stephen P. Cramer<sup>\*,c</sup>, and Zhao-Hui Zhou<sup>\*,a,c</sup>

<sup>a</sup>State Key Laboratory for Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

<sup>b</sup>College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou 310036 China

<sup>c</sup>Department of Chemistry, University of California, Davis, CA 95616, United States

### Abstract

Unlike the most of  $\alpha$ -alkoxy coordination in  $\alpha$ -hydroxycarboxylates to vanadium, novel  $\alpha$ -hydroxy coordination to vanadium(IV) has been observed for a series of chiral and achiral monomeric  $\alpha$ -hydroxycarboxylato vanadyl complexes [VO(H<sub>2</sub>cit)(bpy)]·2H<sub>2</sub>O (**1**), [VO(Hmal)(bpy)]·H<sub>2</sub>O (**2**), [VO(H<sub>2</sub>cit)(phen)]·1.5H<sub>2</sub>O (**3**), [VO(Hmal)(phen)]·H<sub>2</sub>O (**4**), and [VO(*S*-Hcitmal)(bpy)]·2H<sub>2</sub>O (**5**), [VO(H<sub>2</sub>cit)(phen)]<sub>2</sub>·6.5H<sub>2</sub>O (**6**), which were isolated from the reactions of vanadyl sulfate with  $\alpha$ -hydroxycarboxylates and *N*-heterocycle ligands in acidic solution. The complexes feature a tridentate citrate, malate or citramalate that chelates to vanadium atom through their  $\alpha$ -hydroxy,  $\alpha$ -carboxy and  $\beta$ -carboxy groups; while the other  $\beta$ -carboxylic acidic group of citrate is free to participate strong hydrogen bonds with lattice water molecule. The neutral  $\alpha$ -hydroxy group also forms strong intermolecular hydrogen bonds with water molecule and the negatively-charged  $\alpha$ -carboxy group in the environment. The inclusion of a hydrogen ion in  $\alpha$ -alkoxy group results in the formation of a series of neutral complexes with one less positive charge. There are two different configurations of citrate with respect to the *trans*-position of axial oxo group, where the complex with *trans*-hydroxy configuration seems more stable with less hindrance. The average bond distances of V–O<sub>hydroxy</sub> and V–O <sub>$\alpha$ -carboxy</sub> are 2.196 and 2.003 Å respectively, which are comparable to the V–O distance (2.15 Å) of homocitrate in FeV-cofactor of V-nitrogenase. A new structural model is suggested for *R*-homocitrato iron vanadium cofactor as VFe<sub>7</sub>S<sub>9</sub>C(*R*-Hhomocit) (H<sub>4</sub>homocit = homocitric acid) with one more proton in homocitrate ligand.

### Keywords

Citrate; malate; vanadyl; crystal structure; *R*-homocitrato iron vanadium cofactor; nitrogenase

\*Corresponding authors: Z. -H. Zhou: zhzhou@xmu.edu.cn; Tel.: +86 592 2184531; fax: +86 592 2183047; S. P. Cramer: spjcramer@ucdavis.edu; Tel.: +1 530 7526153.

## 1. Introduction

While the most extensively characterized Mo-nitrogenase contains both molybdenum (Mo) and iron (Fe) with *R*-homocitrato iron-sulfur-carbon-molybdenum cofactor MoFe<sub>7</sub>S<sub>9</sub>C(*R*-homocit) (H<sub>4</sub>homocit = homocitric acid) [1,2], some organisms have alternative nitrogenases containing Fe and vanadium(V), or Fe only. Although the V-alternative nitrogenase is inferred to have very similar structure with Mo-nitrogenase [3–6], it appears to have much better catalytic activity in the conversion of carbon monoxide to ethylene with over 93% selectivity [7,8], and becomes much interested recently [9]. It is proposed that homocitrate may facilitate the formation of intramolecular hydrogen bond between  $\alpha$ -alkoxy or  $\alpha$ -carboxy group with imidazole group in the histidine residue [10–12]. The introduction of hydrogen atom onto FeMo-cofactor is considered from the proton delivery side through the  $\beta$ - and  $\gamma$ -carboxy groups with water pool around homocitrate in the MoFe protein [13–16], while fewer comments are emphasized on the coordinated  $\alpha$ -alkoxy,  $\alpha$ -carboxy groups or their protonated forms that closed to the catalytic center for protonation. It seems that studies of the model compounds are needed for a better clarification. In the previous study of vanadium hydroxypolycarboxylate complexes, most of the investigations have addressed the coordination chemistry of citrate vanadates [17–25] and vanadyl complexes [25–31]. The mixed-ligand complexes have been reported as dimers [V<sub>2</sub>O<sub>3</sub>(phen)<sub>3</sub>(Hcit)]·5H<sub>2</sub>O, [V<sub>2</sub>O<sub>3</sub>(phen)<sub>3</sub>(Hcit)<sub>2</sub>(phen)<sub>3</sub>O<sub>3</sub>V<sub>2</sub>]·12H<sub>2</sub>O [32] and monomer [VO(H<sub>2</sub>cit)(bpy)]·1.5H<sub>2</sub>O [33] (H<sub>4</sub>cit = citric acid, phen = 1,10-phenanthroline, and bpy = 2,2'-bipyridine). The formers are coordinated by citrate with  $\alpha$ -alkoxy group, while the later is coordinated by citrate with  $\alpha$ -hydroxy group. In this publication, a series of mononuclear chiral and achiral  $\alpha$ -hydroxycarboxylato vanadyl complexes of malate, citrate and *S*-citramalate are examined with the aid of N-heterocycle ligands, which show unusual protonation in  $\alpha$ -alkoxy group. Different configurations in citrate are observed and the absolute configuration of vanadyl *S*-citramalate is assigned. Their relationship with homocitrate coordination in FeV-cofactor is also discussed.

## 2. Experimental

### 2.1. Preparation of [VO(H<sub>2</sub>cit)(bpy)]·2H<sub>2</sub>O (1)

Vanadyl sulfate VOSO<sub>4</sub>·xH<sub>2</sub>O (0.083 g, 0.51 mmol) and excess citric acid monohydrate (0.22 g, 1.0 mmol) was dissolved in 20 mL of water-ethanol (1:1 in volume) with concentrated ammonium hydroxide (0.50 mL). 2,2'-Bipyridyl (0.080 g, 0.51 mmol) was added to the solution with continual stirring. The mixture turned from dark blue to green yellow. The pH value was adjusted to 2.0 with dilute hydrochloric acid (1.0 M). The solution was filtered and evaporated for several days to deposit grey yellow crystals at room temperature. The precipitate was collected and washed with ethanol to afford **1** (0.11 g, 47% yield based on vanadium). Found (calc for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>10</sub>V): C, 42.5 (42.8); H, 3.9 (3.7); N, 5.7 (6.0%). IR (KBr, cm<sup>-1</sup>):  $\nu_{as}(\text{CO}_2\text{H})$ , 1720<sub>m</sub>;  $\nu_{as}(\text{CO}_2)$ , 1604<sub>vs</sub>;  $\nu_s(\text{CO}_2)$ , 1446<sub>m</sub>, 1386<sub>s</sub>, 1346<sub>m</sub>;  $\nu(\text{V}=\text{O})$ , 988<sub>m</sub>, 952<sub>m</sub>. The data are similar to that of [VO(H<sub>2</sub>cit)(bpy)]·1.5H<sub>2</sub>O [33]

## 2.2. Preparation of [VO(Hmal)(bpy)]·H<sub>2</sub>O (2)

VOSO<sub>4</sub>·xH<sub>2</sub>O (0.083 g, 0.51 mmol) and excess racemic malic acid (0.14 g, 1.0 mmol, H<sub>3</sub>mal = *R,S*-malic acid) was dissolved in 20 mL of water–ethanol (1:1 in volume) with concentrated ammonium hydroxide (0.50 mL). 2,2′-Bipyridyl (0.081 g, 0.52 mmol) was added to the solution with continual stirring. The mixture turned from dark blue to green yellow. The pH value was adjusted to 3.0 with dilute hydrochloric acid (1.0 M), and the solution was changed into light blue. The solution was filtrated and evaporated for several days. The grey yellow precipitate was collected and washed with ethanol to afford **2** (0.074 g, 39% yield based on vanadium). Found (calc for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>7</sub>V): C, 45.3 (45.1); H, 3.5 (3.8); N, 7.7 (7.5%). IR (KBr, cm<sup>-1</sup>): ν<sub>as</sub>(CO<sub>2</sub>), 1660<sub>vs</sub>, 1639<sub>vs</sub>; ν<sub>s</sub>(CO<sub>2</sub>), 1396<sub>s</sub>; ν(V=O), 971<sub>s</sub>.

## 2.3. Preparation of [VO(H<sub>2</sub>cit)(phen)]·1.5H<sub>2</sub>O (3)

VOSO<sub>4</sub>·xH<sub>2</sub>O (0.16 g, 1.0 mmol) and excess citric acid monohydrate (0.47 g, 2.2 mmol) was dissolved in 20 ml water–ethanol (1:1 in volume) with potassium hydroxide (5.0 M, 2 mL). 1,10-Phenanthroline monohydrate (0.20 g, 1.0 mmol) was added to the solution with continual stirring. The mixture turned from dark blue to green yellow. The pH value was adjusted to 2.0 with dilute hydrochloric acid (1.0 M). The solution was filtrated and evaporated for several days, and the solution turned to light blue color. The light blue precipitate was collected and washed with ethanol to afford **3** (0.25 g, 55% based on vanadium). Found (calc. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O<sub>9.5</sub>V): C, 46.3 (46.6); H, 3.9 (3.7); N, 5.7 (6.0%). IR (KBr, cm<sup>-1</sup>): ν<sub>as</sub>(CO<sub>2</sub>H), 1727<sub>m</sub>; ν<sub>as</sub>(CO<sub>2</sub>), 1631<sub>vs</sub>; ν<sub>s</sub>(CO<sub>2</sub>), 1426<sub>m</sub>, 1383<sub>s</sub>, 1342<sub>m</sub>; ν(V=O), 979<sub>m</sub>.

## 2.4. Preparation of [VO(Hmal)(phen)]·H<sub>2</sub>O (4)

VOSO<sub>4</sub>·xH<sub>2</sub>O (0.084 g, 0.51 mmol) and excess racemic malic acid (0.14 g, 1.0 mmol) was dissolved in 20 ml water–ethanol (1:1 in volume) with concentrated ammonium hydroxide (0.50 mL). 1, 10-Phenanthroline monohydrate (0.10 g, 0.50 mmol) was added to the solution with continual stirring. The mixture turned from dark blue to green yellow. The pH value was adjusted to 3.0 with dilute hydrochloric acid (1.0 M). The solution was filtered and evaporated for several days, and the solution turned to light blue color. The light blue precipitate was collected and washed with ethanol to afford **4** (0.080 g, 40% based on vanadium). Found (calc. for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>7</sub>V): C, 48.2 (48.4); H, 3.5 (3.6); N, 6.8 (7.1%). IR (KBr, cm<sup>-1</sup>): ν<sub>as</sub>(CO<sub>2</sub>), 1636<sub>vs</sub>; ν<sub>s</sub>(CO<sub>2</sub>), 1424<sub>m</sub>, 1395<sub>s</sub>, 1344<sub>w</sub>; ν(V=O), 981<sub>m</sub>.

## 2.5. Preparation of [ VO(S-Hcitmal)(bpy)]·2H<sub>2</sub>O (5)

VOSO<sub>4</sub>·xH<sub>2</sub>O (34 mg, 0.21 mmol) and *S*-citramalic acid (59 mg, 0.40 mmol, H<sub>3</sub>citmal = *S*-citramalic acid) was dissolved in 20 ml water–ethanol (1:1 in volume) with potassium hydroxide (5.0 M, 0.40 mL). 2,2′-Bipyridine (32 mg, 0.21 mmol) was added to the solution with continual stirring. The mixture turned from dark blue to green yellow. The pH value was adjusted to 3.0 with dilute hydrochloric acid (1.0 M). The solution was filtered and evaporated for several days, and the solution turned to light blue colour. The grey yellow precipitate was collected and washed with ethanol to afford **5** (13 mg, 39% based on vanadium). IR (KBr, cm<sup>-1</sup>): ν<sub>as</sub>(CO<sub>2</sub>), 1647<sub>vs</sub>; ν<sub>s</sub>(CO<sub>2</sub>), 1446<sub>m</sub>, 1381<sub>s</sub>; ν(V=O), 978<sub>m</sub>.

## 2.6. Preparation of $[\text{VO}(\text{H}_2\text{cit})(\text{phen})]_2 \cdot 6.5\text{H}_2\text{O}$ (**6**)

Ammonium vanadate (0.24 g, 2.0 mmol) and citric acid monohydrate (0.27 g, 1.3 mmol) were dissolved in 20 ml  $\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$  (1:1 in volume) with ammonium hydroxide (0.50 mL). 1,10-Phenanthroline monohydrate (0.61 g, 3.1 mmol) was added to the solution with continual stirring. Hydrazine hydrochloride (0.057 g, 0.50 mmol) was added to reduce vanadate(V). The mixture turned from green yellow to dark blue. The pH value was adjusted to 1.5 with dilute hydrochloric acid (1.0 M). The solution was filtrated and evaporated for several days. The blue precipitate was collected and washed with ethanol to afford **6** (0.23 g, 35% based on citric acid). Found (calc. for  $\text{C}_{36}\text{H}_{41}\text{N}_4\text{O}_{22.5}\text{V}_2$ ): C, 43.5 (43.6); H, 4.0 (4.2); N, 6.0 (5.7%). IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{as}}(\text{CO}_2\text{H})$ , 1727<sub>m</sub>;  $\nu_{\text{as}}(\text{CO}_2)$ , 1629<sub>vs</sub>, 1603<sub>vs</sub>;  $\nu_{\text{s}}(\text{CO}_2)$ , 1429<sub>m</sub>, 1385<sub>s</sub>, 1342<sub>m</sub>;  $\nu(\text{V}=\text{O})$ , 979<sub>m</sub>.

## 2.7. X-Ray structure determinations

Crystals of **1** ~ **3** in oil were analyzed with a Bruker Smart Apex CCD area detector diffractometer with graphite monochromate Cu-K $\alpha$  radiation ( $\lambda = 1.54180 \text{ \AA}$ ) at 296 K or Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 223 K for **5** and 296 K for **6** respectively. The data were corrected for absorption using SADABS program. The structures were solved by SHELXS in the WinGX program and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all of the nonhydrogen atoms with SHELX-97 [34,35]. Hydrogen atoms were located from a difference Fourier map and refined isotropically. Detail crystallographic data are given in Tables S1 ~ S4 in supporting information.

## 2.8. Physical measurements

The pH value was measure by a potentiometric method with a digital PHB-8 pH meter. Infrared spectra were recorded as Nujol mulls between KBr plates on a Nicolet 360 FT-IR spectrometer. Elemental analyses were performed with an EA 1100 elemental analyzer. The electronic spectra were recorded on a Shimadzu UV 2501 spectrophotometer with an integrating sphere for reflectance spectroscopy. X-ray photoelectron spectra (XPS) were recorded on a Quantum 2000 Scanning ESCA Microprobe electron spectrometer using Al K $\alpha$  radiation with a pass energy of 46.95 eV. The binding energy (BE) scale was regulated by setting the C 1s transition at 284.6 eV (accuracy of BE was  $\pm 0.1$  eV). EPR spectra of the complexes were collected at different temperature on a Bruker EMX-10/12 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in DMSO solution at 298 K on a Bruker AV400 spectrometer using 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal reference.

## 3. Results and Discussion

### 3.1. Syntheses and solubilities

Dinuclear or tetranuclear vanadium  $\alpha$ -hydroxycarboxylate complexes such as dioxovanadates(V)  $[\text{VO}_2(\text{H}_2\text{cit})]_2^{2-}$  [18,19],  $[\text{V}_2\text{O}_4(\text{R,S-H}_2\text{homocit})_2]^{2-}$  ( $\text{H}_4\text{homocit}$  = homocitric acid) [20],  $[\text{VO}_2(\text{Hcit})]_2^{4-}$  [21–24],  $[\text{VO}_2(\text{cit})]_2^{6-}$  [24–26],  $[\text{VO}_2(\text{Hmal})]_2^{2-}$  [27]; vanadyl citrate complexes of  $[\text{V}_2\text{O}_2(\text{Hcit})(\text{cit})]^{3-}$  [28,29] and  $[\text{VO}(\text{cit})]_2^{4-}$  [25,30,31]; and mixed-valence oxovanadium<sup>IV</sup> complexes of  $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})] \cdot 5\text{H}_2\text{O}$ ,  $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})_2(\text{phen})_3\text{O}_3\text{V}_2] \cdot 12\text{H}_2\text{O}$ , and  $[\text{V}_2\text{O}_3(\text{phen})_3(\text{R,S-H}_2\text{homocit})]\text{Cl} \cdot 6\text{H}_2\text{O}$

have previously been reported. These complexes have  $V_2(V)O_4$ ,  $V_2(IV)O_2$  or  $V_2(IV/V)O_3$  cores. The malate, citrate or homocitrate group binds to the vanadium atoms through its  $\alpha$ -alkoxy and  $\alpha$ -carboxy, and/or  $\beta$ -carboxy groups. With the available structural data, the present study shows that malate, citrate or *S*-citramalate chelates to the vanadium atom through  $\alpha$ -hydroxy,  $\alpha$ -carboxy, and  $\beta$ -carboxy groups in **1** ~ **3**, **5** and **6**. The ligand in **5** is in *S*-configuration, its vanadium center can be assigned as  $d^0$ -configuration. Moreover, compound **6** has two configurations of **6A** and **6B**. Configuration in **6A** is similar with **3**, while **3** and **6A** are in different configurations with **6B** as shown in Scheme 1.

Unlike the reaction of vanadium(III) chloride with bipyridine and citric acid [33], direct reaction of vanadyl sulfate with excess  $H_3mal$ ,  $H_4cit$  or *S*- $H_3citmal$  is delicately sensitive to pH adjustment, as demonstrated by a digital pH monitor. The reaction takes place in the presence of bpy or phen in an aqueous ethanol solution. Increase of pH value will result in the formation of dimeric or tetrameric species like phenanthroline citrato vandate(V/IV)  $[V_2O_3(phen)_3(Hcit)_2(phen)_3O_3V_2] \cdot 12H_2O$ . Insufficient supplies of the organic acids are unfavorable for the coordination of malate or citrate ligand. Dissolution of vanadyl sulfate is finished in the presence of an alkaline solution.

Compound **6** was synthesized from the reaction of ammonium vanadate,  $H_4cit$  and phen in a molar ratio of 2: 1: 3, while hydrazine hydrochloride acted as a reductant and the pH value was maintained at 1.5.

Compounds **1** ~ **6** are insoluble in water and ethanol. There is no signal for their solution NMR. While compounds **1**, **2** and **4** are sparingly soluble in DMSO.  $^{13}C$  NMR spectra in deuterated DMSO are showed in Figure S1 with long time superposition. The spectra reveal the decomposition of the complexes into free ligand in DMSO solution. The resonances at 74.0 (**1**), 68.4 (**2**) and 68.2 ppm (**4**) were assigned to the  $\alpha$ -carbon of the free citrate or malate respectively, and the signals at 172.8 (**1**), 173.3 (**2**) and 173.9 ppm (**4**) in downfield regions were assigned to the  $\beta$ -carboxy group of citrate or malate, and the resonance located at downfield [176.0 (**1**), 176.0 (**2**) and 177.6 ppm (**4**)] were attributed to the central carboxy carbon of citrate or malate [ $H_4cit$ , 179.3 $_{\alpha}$ -carboxy, 176.0 $_{\beta}$ -carboxy, 75.9 $_{\alpha}$ -hydroxy, 46.1 $_{CH_2}$ ]. Other resonances between 110 to 160 ppm were assigned to the carbons of bpy or phen. These resonances were in consistent with those of the free citrate or malate, bpy or phen ligand, which are the results for the decomposition of compounds **1**, **2** or **4**.

### 3.2. Crystal structures

The crystal structures of **1** ~ **3**, **5** and **6** consist of neutral molecules and crystallized water molecules, while compound **4** was synthesized and isolated as light blue powder without crystal structure. Its molecular formula was established based on elemental analysis, infrared, NMR and EPR spectra. The ORTEP diagrams of the neutral molecules of **1**, **2**, and **5** are shown in Figures S2 ~ S4 in the supporting information (SI). The environments of **3** and **6** with hydrogen bonds between  $\alpha$ -hydroxy and water molecule,  $\alpha$ -carboxy group are shown in Figures 1 and 2 respectively. Selected bond distances and angles for **1** ~ **3**, **5** and **6** are listed in Tables S1 ~ S4. The neutral molecule contains a monomeric vanadyl complex with N-heterocycle ligand and malate, citrate or citratemalate ligand. The vanadium atom is

six-coordinated in a distorted octahedral geometry. The malate, citrate or citratemalate ligand chelates to the vanadium atom as a tridentate ligand via its  $\alpha$ -hydroxy,  $\alpha$ -carboxy and one of the  $\beta$ -carboxy oxygen atoms, whereas the other  $\beta$ -carboxylic acid group is free for citrate ligand. The free carboxylic acidic group participates in strong intermolecular hydrogen bonds with lattice water molecules [**1**, O7 $\cdots$ O1w 2.61(1); **3**, O7 $\cdots$ O1w 2.84(1); **6**, O7 $\cdots$ O2w 2.63(1) and O17 $\cdots$ O3w 2.65(1) Å] in Table 1. The  $\alpha$ -hydroxy group also forms strong hydrogen bonds with the negatively-charged  $\alpha$ -carboxy groups, forming one dimensional chain (Figure S5). Especially, the lattice water molecules form one dimensional zigzag water chains in compound **1**. The strong hydrophilic chain may be related to the hydrophobic packing by  $\pi$ - $\pi$  interaction, which is resulted from strongly binding heterocyclic (N-) ligands of bpy and phen in the vanadium inner coordination shell. Packing diagram of [VO(H<sub>2</sub>cit)(bpy)]·2H<sub>2</sub>O (**1**) showing hydrophobic  $\pi$ - $\pi$  interaction of bpy is shown in supporting information Figure S6.

In the previous reports, the chelation of malate or citrate complexes with vanadium or molybdenum results in the coordination of  $\alpha$ -alkoxy group from the deprotonation of  $\alpha$ -hydroxy group. Even the homocitrate chelation is supposed to have  $\alpha$ -alkoxy coordination to molybdenum in iron molybdenum cofactor of nitrogenase. Based on the coordination modes of vanadyl citrate, malate and *S*-citramalate, it is reasonable to propose that bidentate chelation of homocitrate ligand through  $\alpha$ -hydroxy and  $\alpha$ -carboxy ligands with one less positive charge, and the  $\alpha$ -hydroxy group participates with strong hydrogen bonds with water molecules.

The V=O distances in **1** ~ **3** and **5** are in the range of 1.573(5)–1.604(3) Å, in agreement with the double bond character. The V–O distances in **1** ~ **3** and **5** vary systematically according to its bond types in Table 2. The V–O <sub>$\alpha$ -hydroxy</sub> distances are in the range of 2.172(5)–2.297(3) Å with an average value of 2.196(6) Å, which is comparable to the V–O distance (2.15 Å) in homocitrate FeV-cofactor of V-nitrogenase [4]. They are much longer than those of vanadyl citrates [1.984(8) Å], and also much longer than Rb<sub>4</sub>[V<sub>2</sub>O<sub>2</sub>(tart)<sub>2</sub>]·2H<sub>2</sub>O [2.001(5) Å] and (NH<sub>4</sub>)[VO(ehba)(Hehba)]·2H<sub>2</sub>O (H<sub>2</sub>ehba = 2-ethyl-2-hydroxy butyric acid) [36,37]. These are attributed to the protonation of  $\alpha$ -alkoxy group and the *trans* influence of the terminal oxygen. The V–O <sub>$\alpha$ -carboxy</sub> distances are in range 1.983(3)–2.146(5) Å with an average value of 2.003(6) Å. They are comparable with those of dinuclear vanadyl complexes (Table 2). The V–O <sub>$\beta$ -carboxy</sub> distances are in range 1.978(4)–2.020(5) Å with an average value of 1.990(6) Å. They are comparable to those of dinuclear citrate vanadyl complexes [1.997(7)<sub>av</sub> Å].

The structure of **6** consists of two parts of mononuclear vanadyl citrates denoted as A and B. Part B is different from part A in their configuration. In part A, the molecular structure is similar to that of **3**. The vanadium atom is six-coordinated in a distorted octahedral geometry with N<sub>2</sub>O<sub>4</sub> coordination, which contains a terminal oxygen atom, two nitrogen atoms from phen and three oxygen atoms from citrate. The  $\alpha$ -hydroxy group of citrate ligand coordinates to vanadium atom in *trans* position to the terminal oxygen with an angle of O(1)–V(1)–O(8) 175.5(3)°, while the  $\alpha$ -carboxy group of citrate coordinates to vanadium ion in *cis* position to the terminal oxygen with an angle of O(2)–V(1)–O(8) 100.7(3)°. In part B, the vanadium atom is also six-coordinated in a distorted octahedral geometry with



$N_2O_4$  coordination. The axial oxygen atom is *trans* to the  $\alpha$ -carboxy oxygen atom and *cis* to  $\alpha$ -hydroxy oxygen atom [O(11)–V(2)–O(18), 97.9(2)° and O(12)–V(2)–O(18), 171.5(3)°]. The distance of V–O $_{\alpha\text{-carboxy}}$  in **B** [2.146(5) Å] becomes longer than those in **A** and compounds **1** ~ **3** and **5** [1.955(6) – 2.003(3) Å]. This is because the *trans* influence of axial oxygen oxo group. The distance of V–O $_{\alpha\text{-hydroxy}}$  in **B** [2.026(5) Å] shows shorter than those in **A** and compounds **1** ~ **3** and **5** [2.172(5) – 2.297(3) Å] without the *trans* influence of axial oxygen oxo group. Moreover, it is interesting to note that achiral citrate is in different configurations of *R* and *S* respectively after coordination with vanadium. The formulae of **6** can thus be assigned as [ $\Delta$ VO(*R*-H<sub>2</sub>cit)(phen)] [VO(*S*-H<sub>2</sub>cit)(phen)]·6.5H<sub>2</sub>O (**6**). Further attempts to isolate the *B* configuration in compounds **1** ~ **5** was unsuccessful, which may be resulted from the unstable configuration in *B*.

### 3.3. IR and UV-visible Spectroscopies

To assist the structural analysis, the FT-infrared spectra of **1** ~ **5** are shown in Figure S7, with well-resolved strong and sharp absorption bands for the carboxy and/or carboxylic acid group of the coordinated citrate, malate and *S*-citramalate. Antisymmetric stretching vibrations  $\nu_{\text{as}}(\text{CO}_2^-)$  were observed between 1660 and 1600  $\text{cm}^{-1}$ , while the vibrations of  $\nu(\text{CO}_2\text{H})$  were observed between 1730 and 1710  $\text{cm}^{-1}$  for citrate complexes. The corresponding symmetric stretches  $\nu_{\text{s}}(\text{CO}_2^-)$  appeared between 1450 and 1375  $\text{cm}^{-1}$ . All of the carboxy absorptions were shifted to lower frequencies with respect to those of H<sub>3</sub>mal, H<sub>4</sub>cit or *S*-H<sub>3</sub>citmal. The frequency difference [ $\nu_{\text{as}}(\text{CO}_2^-)$ – $\nu_{\text{s}}(\text{CO}_2^-)$ ] [38] was greater than 200  $\text{cm}^{-1}$ , which is consistent with a carboxy group coordinated to the metal ion in monodentate fashion, and in agreement with those observed in X-ray structural analysis. The aforementioned assignments were also in consonance with previous reports of the other mononuclear citrate complexes like iron and manganese [39,40]. The features in the region of 950–990  $\text{cm}^{-1}$  indicate the existence of V=O, which is in consistent with the values observed for the other vanadyl complexes [28–32].

The diffused reflectance UV-visible spectra of **1** ~ **3** were recorded in the solid state (Figure S8). The spectra show several bands at 242, 296, 544 and 715 nm for **1**, 250, 299, 322, 430, 552 and 735 nm for **2**, 225, 265, 299, 420, 558 and 745 nm for **3**. Bands in the range of 715–745 nm are assigned to d-d transitions, and the bands in the in the range of 420–558 nm region can be assigned to metal-to-ligand charge transfer. The bands below 350 nm region should be the  $\pi$ – $\pi$  transition [41].

### 3.4. Bond valence calculation and bio-relevance

Besides the structural inference, the vanadium covalency assignments were also supported by an X-ray photoelectron spectroscopy (XPS) analysis of V2p energy level as shown in Figure 3. The strong peaks at 515.8 and 523.3 eV for **1** correspond to vanadium 2p<sub>3/2</sub> and 2p<sub>1/2</sub> in the oxidation states of IV [42], while L-edge XPS is one of the best methods to define the oxidation states of transition metals. Theoretically, bond valence calculations [43,44] also give consistent valences (4.0, 3.9 and 3.8 for **1** ~ **3**, 3.9 for both **5** and **6** respectively).



In addition, the X-band solid state EPR spectra of **1**, **2**, and **4** exhibit one broad band centered on 2.0 at 250 K and two or three bands at 100 K with a resolved hyperfine structure as shown in Figure 4, presumably determined by strong spin-spin interactions. Better resolution has been obtained at lower temperature. The broad line is modulated by a multi-line hyperfine anisotropic contribution determined by the  $^{51}\text{V}$  nuclear spin ( $I = 7/2$ ,  $S = 1/2$ ), and indicative of the complex being mononuclear and the metal center being in an axial environment [45], consistent with a  $\text{V}^{4+}$ .

The neutral  $\alpha$ -hydroxy coordination in vanadyl hydroxycarboxylates is different from the previous  $\alpha$ -alkoxy coordination in model molybdenum  $\alpha$ -hydroxycarboxylates [46,47], which may change the charge balance of homocitrate and FeMoco surrounding around the  $\alpha$ -hydroxy group. We have also noted there is a sketch that shows both  $\alpha$ -hydroxy and  $\alpha$ -alkoxy groups in FeMoco for selection in recent review, but not further comment is added [48]. Here several accurate structural methods for small molecules converge in the determination of the proton in the  $\alpha$ -hydroxy group of hydroxycarboxylates. Although there is a large gap between the coordination chemistry of mononuclear  $\alpha$ -hydroxycarboxylato vanadium/molybdenum with the biological homocitrate system, and the vanadyl hydroxycarboxylates of citrate, malate or *S*-citramalate does not involve *R*-homocitrate, the present formation of unsymmetric mononuclear hydroxycarboxylato vanadyl compounds **1** ~ **6** could still be related to the coordination of homocitrate FeV-cofactor in nitrogenase [5, 49], that may show an unusual neutral  $\alpha$ -hydroxy coordination in low oxidation state (+3 ~ +4) [50] as shown in Scheme 2.

## 4. Conclusions

The syntheses, spectral and structural characterization of compounds **1** ~ **6** show that monomeric vanadyl species existed in distorted  $\text{N}_2\text{O}_4$  octahedron from N-heterocycle ligand and  $\alpha$ -hydroxypolycarboxylate. The  $\alpha$ -hydroxypolycarboxylate ligands coordinate tridentately to the central vanadium with  $\alpha$ -hydroxy,  $\alpha$ -carboxy and  $\beta$ -carboxy oxygen atoms with two different configurations. The unique  $\alpha$ -hydroxy and the free  $\beta$ -carboxylic acid groups of citrate ligand participate in strong hydrogen bonds in the model compounds, implying a new protonation pathway of iron-vanadium cofactor  $\text{VFe}_7\text{S}_9\text{C}(\text{R-Hhomocit})$  in nitrogenase.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgments

We thank the National Science Foundation of China (21073150), the National Basic Research Program of China (2010CB732303), (US) National Institute of General Medical Sciences (GM-65440 to SPC), US DOE Office of Biological and Environmental Research (SPC) for the generous supports of this research.

## Appendix A. Supplementary material

CCDC numbers 937507–937511 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data

Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/\\*\\*\\*\\*](http://dx.doi.org/****).

## Abbreviations

<b>H<sub>4</sub>cit</b>	citric acid
<b>H<sub>3</sub>mal</b>	<i>R,S</i> -malic acid
<b>H<sub>3</sub>citmal</b>	<i>S</i> -citramalic acid
<b>H<sub>4</sub>homocit</b>	homocitric acid
<b>phen</b>	110-phenanthroline
<b>bpy</b>	2,2'-bipyridine
<b>H<sub>2</sub>ehba</b>	2-ethyl-2-hydroxy butyric acid
<b>neo</b>	2,9-dimethyl-1,10-phenanthroline,
<b>DSS</b>	2,2-dimethyl-2-silapentane-5-sulfonate
<b>XPS</b>	X-ray photoelectron spectra

## References

1. Spatzal T, Aksoyoglu M, Zhang L, Andrade SLA, Schleicher E, Weber S, Rees DC, Einsle O. *Science*. 2011; 334:940. [PubMed: 22096190]
2. Einsle O, Tezcan FA, Andrade SLA, Schmid B, Yoshida M, Howard JB, Rees DC. *Science*. 2002; 297:1696–1700. [PubMed: 12215645]
3. Hales BJ, Case EE, Morningstar JE, Dzeda MF, Mauterer LA. *Biochemistry*. 1986; 25:7251–7264. [PubMed: 3026449]
4. Strange RW, Eady RR, Lawson D, Hasnain SS. *J Synchrotron Rad*. 2003; 10:71–75.
5. Eady RR. *Chem Rev*. 1996; 96:3013–3030. [PubMed: 11848850]
6. Fay AW, Blank MA, Lee CC, Hu Y, Hodgson KO, Hedman B, Ribbe MW. *J Am Chem Soc*. 2010; 132:12612–12618. [PubMed: 20718463]
7. Hu YL, Lee CC, Markus MW. *Science*. 2011; 333:753–755. [PubMed: 21817053]
8. Chi L, Hu YL, Markus MW. *Angew Chem*. 2012; 51:1947–1949. [PubMed: 22253035]
9. Darnajoux R, Constantin J, Miadlikowska J, Lutzoni F, Bellenger JP. *New Phytologist*. 2014; 202:765–771. [PubMed: 24641550]
10. Grönberg KLC, Gormal CA, Durrant MC, Smith BE, Henderson RA. *J Am Chem Soc*. 1998; 120:10613–10621.
11. Seefeldt LC, Dance IG, Dean DR. *Biochemistry*. 2004; 43:1401–1409. [PubMed: 14769015]
12. Zhou ZH, Zhao H, Tsai KR. *J Inorg Biochem*. 2004; 98:1787–1794. [PubMed: 15522406]
13. Dance I. *Chem Commun*. 2013; 49:10893–10907.
14. Dance I. *Biochemistry*. 2006; 45:6328–6340. [PubMed: 16700544]
15. Dance I. *J Am Chem Soc*. 2005; 127:10925–10943. [PubMed: 16076199]
16. Jia HP, Quadrelli EA. *Chem Soc Rev*. 2014; 43:547–564. [PubMed: 24108246]
17. Elzbleta LC, Daniele S, Eugenio G, Giovanni M. *Dalton Trans*. 2008:4903–4916. [PubMed: 18766223]
18. Wright DW, Humiston PA, Orme-Johnson WH, Davis WM. *Inorg Chem*. 1995; 34:4194–4197.

19. Wright DW, Chang RT, Mandal SK, Armstrong WH, Orme-Johnson WH. *J Biol Inorg Chem.* 1996; 1:143–151.
20. Zhou ZH, Yan WB, Wan HL, Tsai KR, Wang JZ, Hu SZ. *J Chem Crystallogr.* 1995; 25:807–811.
21. Zhou ZH, Zhang H, Jiang YQ, Lin DH, Wan HL, Tsai KR. *Trans Met Chem.* 1999; 24:605–609.
22. Tsaramyrsi M, Kavousanaki D, Raptopoulou CP, Terzis A, Salifoglou A. *Inorg Chim Acta.* 2001; 320:47–59.
23. Kaliva M, Giannadaki T, Salifoglou A, Raptopoulou CP, Terzis A. *Inorg Chem.* 2002; 41:3850–3858. [PubMed: 12132908]
24. Kaliva M, Raptopoulou CP, Terzis A, Salifoglou A. *J Inorg Biochem.* 2003; 93:161–173. [PubMed: 12576278]
25. Zhou ZH, Wan HL, Hu SZ, Tsai KR. *Inorg Chim Acta.* 1995; 237:193–197.
26. Aureliano M, Tiago T, Gândara RMC, Sousa A, Moderno A, Kaliva M, Salifoglou A, Duarte RO, Moura JGG. *J Inorg Biochem.* 2005; 99:2355–2361. [PubMed: 16219359]
27. Biagioli M, Strinna-Erre L, Micera G, Panzanelli A, Zema M. *Inorg Chim Acta.* 2000; 310:1–9.
28. Burojevic S, Shweky I, Bino A, Summers DA, Thompson RC. *Inorg Chim Acta.* 1996; 251:75–79.
29. Tsaramyrsi M, Kaliva M, Salifoglou A, Raptopoulou CP, Terzis A, Tangoulis V, Giapintzakis J. *Inorg Chem.* 2001; 20:5772–5779.
30. Rehder D, Pessoa JC, Geraldies CFGC, Castro MMCA, Kabanos T, Kiss T, Meier B, Micera G, Pettersson L, Rangel M, Salifoglou A, Turel I, Wang DR. *J Biol Inorg Chem.* 2002; 7:384–396. [PubMed: 11941496]
31. Velayutham M, Varghese B, Subramanian S. *Inorg Chem.* 1998; 37:1336–1340. [PubMed: 11670342]
32. Chen CY, Zhou ZH, Chen HB, Huang PQ, Tsai KR, Chow YL. *Inorg Chem.* 2008; 47:8714–8720. [PubMed: 18722422]
33. Jodaian V, Mirzaei M, Arca M, Aragoni MC, Lippolis V, Tavakoli E, Langeroodi NS. *Inorg Chim Acta.* 2013; 400:107–114.
34. Farrugia LJ. *J Appl Crystallogr.* 1999; 32:837–838.
35. Sheldrick, GM. *SHELX-97, Programs for Crystal Structure Analysis.* University of Göttingen; Germany: 1997.
36. Wroblewski JT, Thompson MR. *Inorg Chim Acta.* 1988; 150:269–277.
37. Barr-David G, Hambley TW, Irwin JA, Judd RJ, Lay PA, Martin BD, Bramley R, Nixon NE, Hendry P, Ji JY, Baker RSU, Bonin AM. *Inorg Chem.* 1992; 31:4906–4908.
38. Deacon GB, Philips R. *Coord Chem Rev.* 1980; 33:227–250.
39. Matzapetakis M, Raptopoulou CP, Tsohos A, Papefthymiou B, Moon N, Salifoglou A. *J Am Chem Soc.* 1998; 120:13266–13267.
40. Matzapetakis M, Raptopoulou CP, Terzis A, Lakatos A, Kiss T, Salifoglou A. *Inorg Chem.* 1999; 38:618–619.
41. Kovalevsky AY, Gembicky M, Novozhilova IV, Coppens P. *Inorg Chem.* 2003; 42:8794–8802. [PubMed: 14686859]
42. Silversmit G, Depla D, Poelman H, Marin GB, De Gryse R. *J Electron Spectrosc Relat Phenom.* 1991; 57:189–197.
43. Brown ID, Altermatt D. *Acta Crystallogr.* 1985; B41:244–247.
44. Chen MD, Zhou ZH, Hu SZ. *Chinese Sci Bull.* 2002; 47:978–981.
45. Smith TM, LoBrutto R, Pecoraro VL. *Coord Chem Rev.* 2002; 228:1–18.
46. Zhou ZH, Hou SY, Cao ZX, Wan HL, Ng SW. *J Inorg Biochem.* 2004; 98:1037–1044. [PubMed: 15149813]
47. Li DM, Xing YH, Li ZC, Xu JQ, Song WB, Wang TG, Yang GD, Hu NH, Jia HQ, Zhang HM. *J Inorg Biochem.* 2005; 99:1602–1610. [PubMed: 15951017]
48. Hoffmann BM, Lukoyanov D, Yang ZY, Dean DR, Seefeldt LC. *Chem Rev.* 2014; 114:4041–4062. [PubMed: 24467365]
49. Ruttimann C, Rangaraj P, Shah VK, Ludden PW. *J Biol Chem.* 2001; 276:4522–4526. [PubMed: 11053414]

50. Fisher K, Filworth MJ, Newton WE. *Biochemistry*. 2006; 45:4190–4198. [PubMed: 16566593]

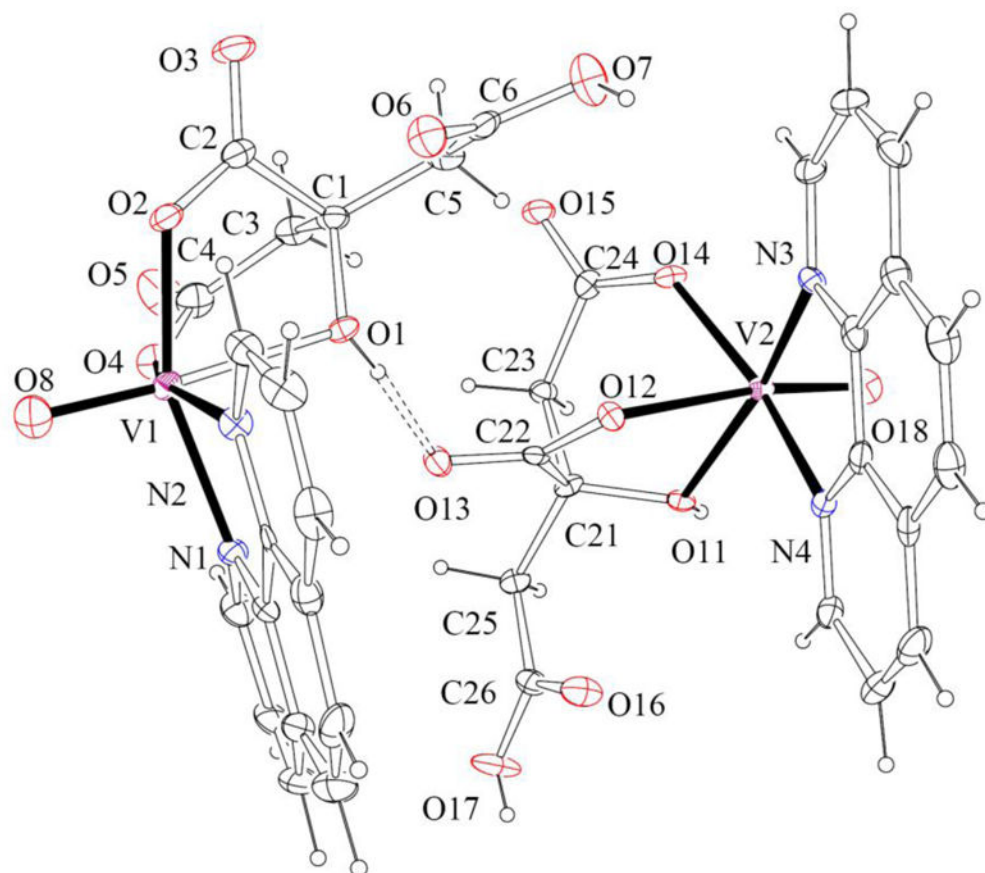
Author Manuscript

Author Manuscript

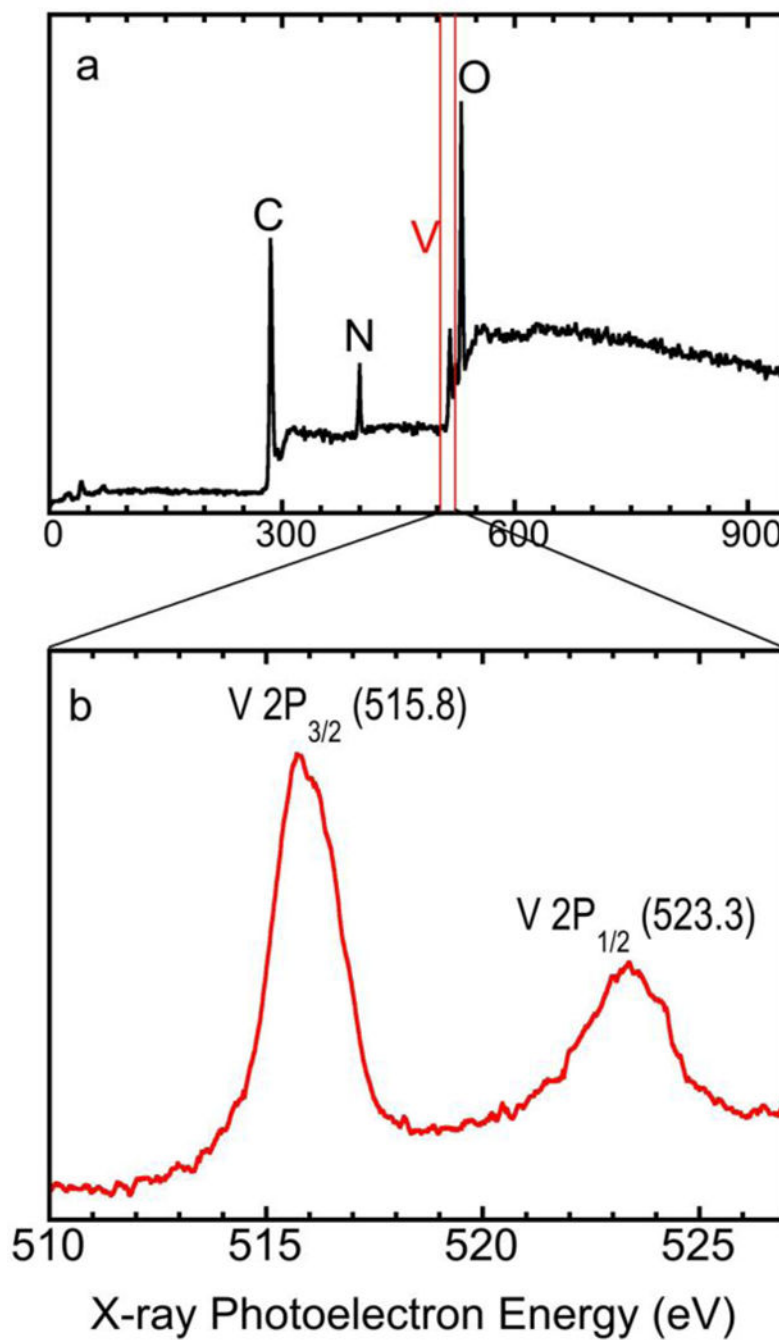
Author Manuscript

Author Manuscript



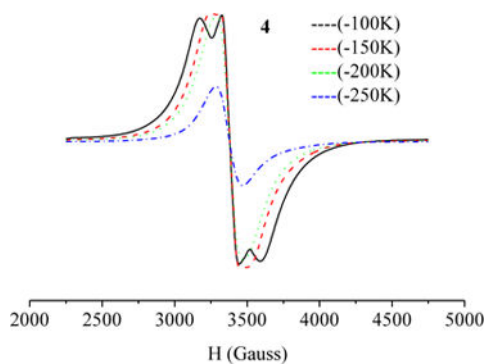
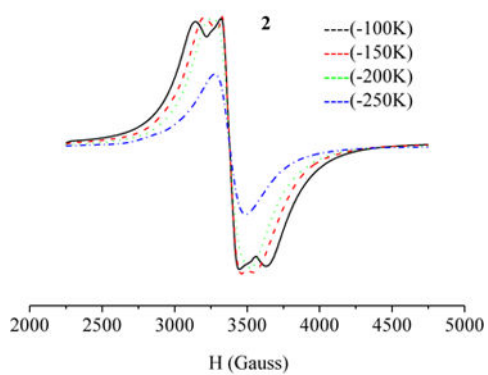
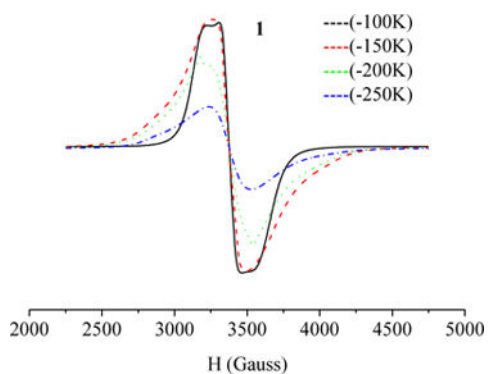


**Figure 2.** Ortep plot of [VO(H<sub>2</sub>cit)(phen)]<sub>2</sub>·6.5H<sub>2</sub>O (**6**) showing hydrogen bond between  $\alpha$ -hydroxy and  $\alpha$ -carboxy groups.



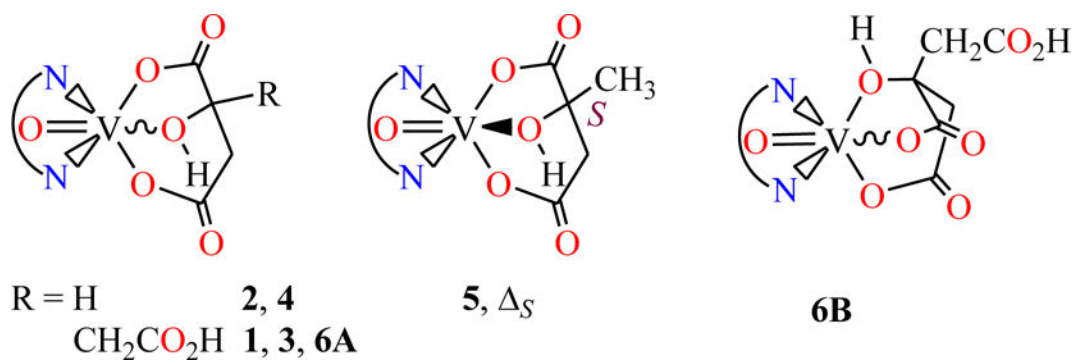
**Figure 3.**  
The X-ray photoelectron spectra of vandyl citrate  $[\text{VO}(\text{H}_2\text{cit})(\text{bpy})]\cdot 2\text{H}_2\text{O}$  (**1**).



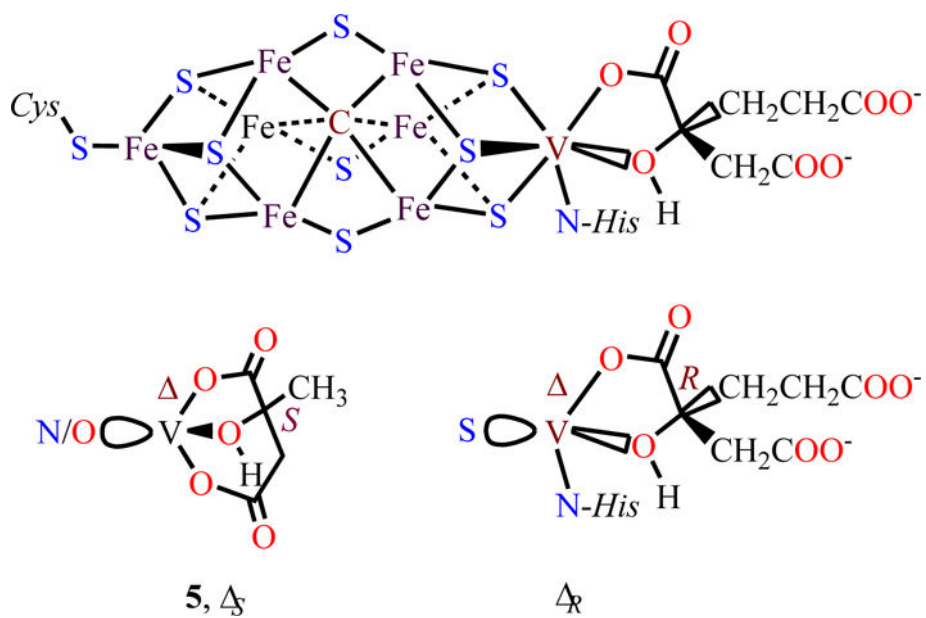


**Figure 4.**

The electron paramagnetic resonance spectra of vanadyl citrates and malates [VO(H<sub>2</sub>cit)(bpy)]·2H<sub>2</sub>O (1), [VO(Hmal)(bpy)]·H<sub>2</sub>O (2), [VO(H<sub>2</sub>cit)(phen)]·1.5H<sub>2</sub>O (3) and [VO(Hmal)(phen)]·H<sub>2</sub>O (4)

**Scheme 1.**

Typical mononuclear coordination modes of chiral and achiral  $\alpha$ -hydroxycarboxylate with vanadium(IV) in the text.

**Scheme 2.**

Sketch map of FeVco with the coordination of  $\alpha$ -hydroxy group and tentative assignment of the absolute configuration in vanadium center based on the structure of FeMo-protein [1].

**Table 1**

Strong hydrogen bonds observed in [VO(H<sub>2</sub>cit)(bpy)]·2H<sub>2</sub>O (**1**), [VO(Hmal)(bpy)]·H<sub>2</sub>O (**2**), [VO(H<sub>2</sub>cit)(phen)]·1.5H<sub>2</sub>O (**3**), [VO(*S*-Hcitmal)(bpy)]·2H<sub>2</sub>O (**5**) and [VO(H<sub>2</sub>cit)(phen)]<sub>2</sub>·6.5H<sub>2</sub>O (**6**)

Interaction	H···A(Å)	D···A(Å)	D—H···A (°)	Symmetry operation
<b>Compound 1</b>				
O(1)—H(1)···O(3)′	2.00	2.610	128	$x, 0.5-y, 0.5+z$
O(7)—H(2)···O(1) <sub>w</sub>	1.77	2.615	169	$x, y, z$
<b>Compound 2</b>				
O(1)—H(1)···O(5)′	1.75	2.557	160	$0.5+x, -0.5-y, z$
O(11)—H(2)···O(15)′	1.72	2.575	172	$0.5+x, -0.5-y, z$
<b>Compound 3</b>				
O(1)—H(1)···O(3)′	1.86	2.683	163	$-0.5+x, -y, z$
O(7)—H(2)···O(1) <sub>w</sub>	2.06	2.841	151	$x, y, z$
<b>Compound 5</b>				
O(1)—H(1)···O(15)	1.84	2.565	165	$x, y, z$
O(11)—H(2)···O(3)′	1.94	2.675	162	$x, y, 1+z$
<b>Compound 6</b>				
O(1)—H(1)···O(13)	1.86	2.576	141	$x, y, z$
O(11)—H(2)···O(15)′	1.89	2.507	167	$x-y, 2+x, -z$
O(7)—H(3)···O(2) <sub>w</sub>	2.01	2.63	130	$x, y, z$
O(17)—H(4)···O(3) <sub>w</sub>	1.81	2.65	167	$x, y, z$

**Table 2**

Comparisons of V–O distances (Å) in malato, citrato and *S*-citramalato vanadyl complexes (neo = 2,9-dimethyl-1,10-phenanthroline)

Complex	V–O ( $\alpha$ -hydroxy)	V–O ( $\alpha$ -carboxy)	V–O ( $\beta$ -carboxy)	Reference
[VO(H <sub>2</sub> cit)(bpy)]·2H <sub>2</sub> O ( <b>1</b> )	2.197(5)	1.993(4)	1.988(5)	This work
[VO(H <sub>2</sub> cit)(bpy)]·1.5H <sub>2</sub> O	2.209(3)	1.994(3)	1.985(4)	[33]
[VO(Hmal)(bpy)]·H <sub>2</sub> O ( <b>2</b> )	2.222(2) 2.228(2)	1.992(2) 1.983(2)	1.993(2) 2.001(2)	This work
[VO(H <sub>2</sub> cit)(phen)]·1.5H <sub>2</sub> O ( <b>3</b> )	2.209(4)	1.983(3)	1.981(4)	
[VO( <i>S</i> -Hcitmal)(bpy)]·2H <sub>2</sub> O ( <b>5</b> )	2.172(3) 2.297(3)	2.003(3) 1.987(4)	1.975(3) 1.978(4)	
[VO(H <sub>2</sub> cit)(phen)] <sub>2</sub> ·6.5H <sub>2</sub> O ( <b>6</b> )	2.203(5) 2.026(5)	1.947(5) 2.146(5)	1.990(5) 2.020(5)	
Average	<b>2.196(6)</b>	<b>2.003(6)</b>	<b>1.990(6)</b>	
K <sub>2</sub> [V <sub>2</sub> O <sub>4</sub> (H <sub>2</sub> cit) <sub>2</sub> ]·4H <sub>2</sub> O	1.986(2) <sub>av</sub>	1.980(3)		[18,20]
Na <sub>2</sub> K <sub>2</sub> [V <sub>2</sub> O <sub>4</sub> (Hcit) <sub>2</sub> ]·9H <sub>2</sub> O	1.984(4) <sub>av</sub>	1.979(4) <sub>av</sub>		[21–23]
K <sub>2</sub> (NH <sub>4</sub> ) <sub>4</sub> [V <sub>2</sub> O <sub>4</sub> (cit) <sub>2</sub> ]·6H <sub>2</sub> O	1.983(2) <sub>av</sub>	1.981(2)		[24–26]
K <sub>2</sub> [V <sub>2</sub> O <sub>4</sub> ( <i>R,S</i> -H <sub>2</sub> homocit) <sub>2</sub> ]·6H <sub>2</sub> O	1.980(8) <sub>av</sub>	1.959(8) <sub>av</sub>		[19]
Average	<b>1.984(8)</b>	<b>1.974(8)</b>		
Cs <sub>2</sub> [V <sub>2</sub> O <sub>4</sub> (Hmal) <sub>2</sub> ]	1.990(4) <sub>av</sub>	1.977(4)		[27]
K <sub>3</sub> [V <sub>2</sub> O <sub>2</sub> H(cit) <sub>2</sub> ]·7H <sub>2</sub> O	1.976(5) <sub>av</sub>	1.981(6)	1.976(7) <sub>av</sub>	[29]
(Hneo) <sub>3</sub> [V <sub>2</sub> O <sub>2</sub> H(cit) <sub>2</sub> ]·4H <sub>2</sub> O	1.984(4) <sub>av</sub>	2.137(4) <sub>av</sub>	1.989(4) <sub>av</sub>	[28]
Na <sub>4</sub> [V <sub>2</sub> O <sub>2</sub> (cit) <sub>2</sub> ]·6H <sub>2</sub> O	2.089(2) <sub>av</sub>	2.038(2)	2.025(2) <sub>av</sub>	[25,30,31]
Average	<b>2.016(5)</b>	<b>2.052(6)</b>	<b>1.997(7)</b>	
VFe <sub>7</sub> S <sub>9</sub> C( <i>R</i> -Hhomocit)( <i>S</i> -cys)( <i>N</i> -His)		<b>2.15</b>		[7]