Degradations of novel tetranuclear vanadyl glycollates to dinuclear species

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Abstract

Novel tetranuclear vanadyl glycollates $[\text{Ni}(\text{phen})_3]_2[\text{V}^{\text{IV}}_4\text{O}_4(\text{glyc})_6] \cdot 23\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3]_2[\text{V}^{\text{IV}}_4\text{O}_4(\text{glyc})_6] \cdot 16\text{H}_2\text{O}$ (**2**) have been obtained through the capture of bulky nickel phenanthroline cation (H_2glyc = glycollic acid, phen = 1,10-phenanthroline), and the mixed-ligand complex $[\text{V}^{\text{IV}}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4] \cdot 6\text{H}_2\text{O}$ (**3**) (bpy = 2,2'-bipyridine) was isolated with the addition of bpy under hydrothermal condition. Tetrameric **1** and **2** are easily oxidized to dimeric complex $[\text{Ni}(\text{phen})_3][\text{V}^{\text{V}}_2\text{O}_4(\text{glyc})_2] \cdot 5\text{H}_2\text{O}$ (**4**), while **3** with bipyridine is stable. The degradation process was traced by IR and XRD experiment. **1** ~ **4** feature bidentate glycollate that chelates to vanadium atom through α -alkoxy and α -carboxy groups, which were full characterized by elemental analysis, TG, IR, UV-vis, EPR, XRD and X-ray structural analyses. Bond valence calculation is also performed.

Keywords: Glycollate; Vanadyl; Bipyridine; Nickel phenanthroline; Degradations.

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1. Introduction

The vanadium complexes are found with multi-applications in catalysis [1-3], medicine [4-6] as well as in biochemistry [7-9]. The discovery of the alternative vanadium-dependent nitrogenase have shown that cofactor of V nitrogenase containing homocitrate bidentately bound to vanadium in the active site, which is proposed analogous to Mo nitrogenase [10-12], and appears to have much better catalytic activity in the conversion of carbon monoxide to ethylene with over 93% selectivity [13]. The peculiar properties prompted the studies of coordination chemistry of the model compounds for *R*-homocitrato vanadium complexes and its homologues.

Up to now, much work have been carried out to investigate the direct coordination chemistry of vanadium homocitrate [14,15], and its homologues citrate [15-27], malate [28, 29], lactate [28] or glycollate [28,30,31]. These α -hydroxycarboxylates bind to the vanadium atom through their α -alkoxy, α -carboxy and/or β -carboxy groups. Vanadium α -hydroxycarboxylates with unusual α -hydroxy coordination are also reported [29,32]. These crystalline compounds have dimeric cores or mononuclear forms. Besides the X-ray crystal structure studies, a number of solution studies have been carried out on vanadium(IV,V) - α -hydroxycarboxylate systems, aiming to delineate the distributions of species involved in solution, where VL, V_2L_2 and V_3L_2 products were proposed [33,34]. But vanadyl α -hydroxycarboxylates with multinuclear forms are rare [35,36]. Here novel tetranuclear vanadium(V/IV) glycollates $[Ni(phen)_3]_2[V^{IV}_4O_4(glyc)_6] \cdot 23H_2O$ (**1**), $[Ni(phen)_3]_2[V^{IV}_4O_4(glyc)_6] \cdot 16H_2O$ (**2**) and $[V^{IV}_4O_6(glyc)_2(bpy)_4] \cdot 6H_2O$ (**3**) are reported with different configurations coordinated by α -alkoxy and carboxy groups. The degradations of tetranuclear **1** and **2** to dinuclear vanadium(V) glycollate $[Ni(phen)_3][V^V_2O_4(glyc)_2] \cdot 5H_2O$ (**4**) in solid state and solution have been traced by IR and XRD experiments.

2. Experimental

2.1. Materials and instrumentation

All solvents and reagents were of commercially analytical grade and used without further purification. Nanopure-quality water was used throughout this work. Elemental analyses (C, H and N) were performed on a Vario EL III CHN elemental analyzer. TG analyses were performed on a TG 209F1 instrument in N₂ atmosphere with a heating rate of 10 °C min⁻¹. Infrared spectra were recorded in the range 400 ~ 4000 cm⁻¹ on a Nicolet 380 FT-IR spectrometer in KBr plates. The solid diffused UV/Vis spectra were recorded at 293K using a Cary 5000 UV-visible-NIR spectrophotometer in the 200 ~ 800 nm range. Solid electron paramagnetic resonance (EPR) spectra were analysed by a Bruker EMX-10/12 spectrometer using crystalline samples at 90 K. pH value was determined by PHB-8 digital pH meter. X-ray powder diffraction (XRD) analysis was carried out on a Panalytical X'pert PRO diffractometer scanning 2θ from 4° to 80°. Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$) obtained at 35 kV and 15 mA was used as the X-ray source.

2.2. Synthesis of $[Ni(phen)_3]_2[V_4O_4(glyc)_6] \cdot 23H_2O$ (**1**)

Nickel chloride hexahydrate (79 mg, 0.33 mmol) and phenanthroline monohydrate (198 mg, 1.0 mmol) were dissolved in water-ethanol solution (4.0 mL, 1:1 by volume). The solution was added to a mixture of excess glycollic acid (228 mg, 3.0 mmol), vanadyl sulfate (217 mg, 1.33 mmol) and hydrazine hydrochloride (53 mg, 0.5 mmol) in water (4.0 mL). The pH value was adjusted to 6.0 with potassium hydroxide (5.0 M). The mixture was stirred for 20 mins and evaporated at room temperature for several days. Deep-blue crystals were collected and washed with water to afford **1**. Yield: (based on vanadium) 262 mg (41.0%). Anal. Calc. for C₈₄H₁₀₆N₁₂O₄₅V₄Ni₂: C, 43.4; H, 4.6; N, 7.2. Found: C, 43.0; H, 3.9; N, 6.9 (%). IR (cm⁻¹): $\nu_{as}(CO_2)$, 1628vs, 1602s, 1517s; $\nu_s(CO_2)$, 1425s, 1356s; $\nu(V=O)$, 988s, 935s; $\nu(V-O-V)$, 849m.

2.3. Synthesis of $[Ni(phen)_3]_2[V_4O_4(glyc)_6] \cdot 16H_2O$ (**2**)

Complex **2** was synthesized by the same procedure as **1** with the absence of hydrazine hydrochloride. The deep-blue crystals were collected and washed with water to afford **2**. Yield: (based on vanadium) 160 mg (25.4%). Anal. Calc. for $C_{84}H_{92}N_{12}O_{38}V_4Ni_2$: C, 45.9; H, 4.2; N, 7.7. Found: C, 45.5; H, 4.1; N, 7.4 (%). IR (cm^{-1}): $\nu_{as}(CO_2)$, 1647s, 1517m; $\nu_s(CO_2)$, 1425s, 1345m; $\nu(V=O)$, 983m, 932s; $\nu(V-O-V)$ 849m.

2.4. Synthesis of $[V_4O_6(glyc)_2(bpy)_4] \cdot 6H_2O$ (**3**).

Vanadium pentoxide V_2O_5 (182 mg, 1.0 mmol), excess glycollic acid (230 mg, 3.0 mmol), and 2,2'-bipyridine (160 mg, 1.0 mmol) were dissolved in water (8.0 mL) with continually stirring. The pH value was adjusted to 5.0 with dilute potassium hydroxide (1.0 M). The mixture was placed in a Teflon-lined stainless steel bomb. The bomb was heated at 413 K for 4 days and cooled with programmed control. The dark brown precipitates were collected and washed with ethanol to afford **3**. Yield: (based on bpy) 86 mg, (28%). Anal. Calc. for $C_{44}H_{48}N_8O_{18}V_4$: C, 44.7; H, 4.1; N, 9.5. Found: C, 44.2; H, 3.4; N, 9.1 (%). IR (cm^{-1}): $\nu_{as}(CO_2)$, 1602s; $\nu_s(CO_2)$, 1380m; $\nu(V=O)$, 942s; $\nu(V-O-V)$, 766s.

2.5. Synthesis of $[Ni(phen)_3][V_2O_4(glyc)_2] \cdot 5H_2O$ (**4**)

The deep-blue crystals of **2** were set aside with their mother liquors for a half month, and pink crystals were collected and washed with water to afford of **4**. Yield: 220 mg from **2** (43.9%) (based on vanadium). Anal. Calc. for $C_{40}H_{38}O_{15}N_6V_2Ni$: C, 47.9; H, 3.8; N, 8.4. Found: C, 47.7; H, 3.5; N, 8.4 (%). IR (cm^{-1}): $\nu_{as}(CO_2)$, 1654s, 1587m, 1517s; $\nu_s(CO_2)$, 1426s, 1343s; $\nu(V=O)$, 932s; $\nu(V-O-V)$, 849s.

2.6. X-ray crystallography

The crystal data for **1** ~ **4** were collected on an Oxford Gemini CCD diffractometer, with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 173 K. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined by

full-matrix least-squares on F^2 using the Shelxl crystallographic software package [37-39]. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were generated geometrically or located from differential Fourier maps and refined isotropically. For **1**, **2** and **4**, the unit cell includes a large region of disordered solvent water molecules respectively, which could not be modelled as discrete atomic sites. PLATON/SQUEEZE was employed to calculate the diffraction contribution of the solvent molecules, and to produce a set of solvent-free diffraction intensities. The SQUEEZE calculations showed a total solvent accessible area volume of 890.7 Å³ in **1**, 618.8 Å³ in **2**, 525.8 Å³ in **4**, and the residual electron density amounted to 229 e in **1**, 163 e in **2**, 105 e in **4** per unit cell, corresponding to nearly 23 molecules of water in **1**, 16 molecules of water in **2** and 5 molecules of water in **4** respectively.

3. Results and Discussion

3.1. Syntheses

The reactions of vanadium sulfate with excess H₂glyc are sensitive to pH variations, as demonstrated by a digital pH monitor. **1** and **2** were obtained in weak acid solution. Decrease of pH value will result in the formation of an oxidized dimeric complex **4**. Hydrazine hydrochloride supposedly creates additional osmotic effects leading to a structure with higher water content in the formation of **1**, while its absence will be suitable for the formation of **2**. It is noteworthy that the products are trapped by bulky cation Ni(phen)²⁺ as counteranion in aqueous solution. **3** was obtained through the hydrothermal process at 413 K. One-pot reaction is preceded by the reaction of vanadium pentoxide and excess H₂glyc (1 : 3) in the presence of N-heterocycle ligand, where bipyridine should not be excess. **1** ~ **4** are only slightly soluble in water. It is interesting to note that **1** and **2** can gradually transform to **4**.

3.2. Crystal structures of **1** ~ **4**

The molecular structures of **1**, **2** and **4** consist of $[\text{Ni}(\text{phen})_3]^{2+}$ cations, tetrameric anion of $[\text{V}_4\text{O}_4(\text{glyc})_6]^{2-}$ or dimeric anion $[\text{V}_2\text{O}_4(\text{glyc})_2]^{2-}$ and crystal water molecules, while **3** consists of a neutral tetrameric molecule and crystal water molecules. Detail crystallographic data are given in Table 1. The ORTEP plots of the $[\text{V}_4\text{O}_4(\text{glyc})_6]^{2-}$ anions in **1** and **2**, and the neutral molecule of $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4]$ in **3** are shown in Figures 1 ~ 3. The ORTEP diagram of $[\text{V}_2\text{O}_2(\text{glyc})_2]^{2-}$ anion in **4** is shown in Figure S1. The comparisons of their frameworks are shown in Figure 4 for the dimeric and tetrameric complexes. Selected bond distances and angles for **1** ~ **4** are listed in Tables S1 ~ S4.

[Table 1]

[Figures 1 ~ 4]

The structure of tetranuclear anion in **1** can be considered as a coupling product of two asymmetric units $[\text{VO}(\text{glyc})_2\text{VO}(\text{glyc})]$. Each vanadium atom is hexa-coordinated in a distorted octahedral geometry. Besides the terminal oxygen, V1 atom is chelated by one glycollate, and V2 atom is chelated by two glycollates where one of its α -alkoxy oxygen atoms bridges with neighboring V2a atom. Similar structure can be found in some vanadium alkoxides listed in Table S5. The $\text{V}-\text{O}(\mu_3\text{-alkoxido})$ distances (2.03 ~ 2.28 Å) and $\text{V}-\text{O}(\mu_3\text{-alkoxido})-\text{V}$ angles (95.6 ~ 105.3°) in **1** are similar with those of common alkoxido(oxido)vanadium complexes (distances 1.94 ~ 2.41 Å and angles 86.2 ~ 109.7°). The comparisons for the configurations of two $\text{V}=\text{O}_{\text{terminal}}$ groups [40] show that they contain the same modes of *anti*-coplanar, twist and *syn*-coplanar, except V^{3+} containing complexes. Moreover, the structure is outcome of the dense hexagonal packing of cations and anions. Such packing is widespread and can be found not only in alkoxides of vanadium but typical for all 3d metal alkoxides [41].

The structure of tetranuclear anion in **2** consists of one $[\text{V}_2\text{O}_2(\text{glyc})_2]$ unit connected by two $[\text{VO}(\text{glyc})_2]$ units. The V2 atom exists in distorted octahedral configuration, which is chelated

by a bidentate glycollate and its α -alkoxy oxygen served as a bridging atom connects with V2a atom. The V1 atom in $[\text{VO}(\text{glyc})_2]$ has a tetragonal geometry. It is coordinated by two glycollates via α -alkoxy and carboxy oxygen atoms, forming two five membered chelate rings. The two units $[\text{VO}(\text{glyc})_2]$ coordinate to the two vanadium atoms of $[\text{V}_2\text{O}_2(\text{glyc})_2]$ via their α -alkoxy oxygens. Due to the same dense hexagonal packing mode of cations and anions, the structure of anion in **2** with a $[\text{V}_4\text{O}_4]$ ring is thus closely related to **1** (see Figure 4). In the $[\text{V}_4\text{O}_4]$ ring of **1**, V1 connect with O1 with the distance of 2.251 Å, while V1 and O8 in complex **2** could not connect with each other because of the longer distance of 3.822 Å. The discrete of V1 and O8 in **2** is caused by the tetragonal coordination geometry of V1 atom.

Complex **3** consists of two *trans*-oxo- $[\text{V}_2\text{O}_3(\text{glyc})(\text{phen})_2]$ units. The vanadium atom in each unit exists in a distorted N_2O_4 octahedral geometry. Besides one terminal oxygen atom, V2 atom is coordinated by one glycollate through α -carboxy and α -alkoxy groups, where α -alkoxy atom acts as a bridging group, two nitrogen atoms from bpy and one of the nitrogen atoms is at the *trans*-position of terminal oxygen, and a triply bridging oxygen atom which links with the other two vanadium centers. Besides the terminal oxygen atom, V1 atom is coordinated by two nitrogen atoms from bpy, one α -alkoxy atom from glycollate and two bridging oxygen atoms. The V1...V1a distances are in the order of 3.083(2) Å, a distance that implicates a weak interaction between two metal centers. Complex **3** has a ladder-like $[\text{V}_4\text{O}_4]$ ring. Locating at each side of the “ladder”, two planes of bpy groups are generally parallel to each other and the average distance 3.711 Å is longer than the distances 3.5726 Å [42] and 3.4 ~ 3.5 Å [43] reported in literatures.

[Table 2]

As shown in Tables S1 ~ S4, the V–O distances in **1** ~ **4** vary systematically. The short V–O distances in range 1.588(3) ~ 1.627(2) Å are in agreement with the double-bond character. For the tetranuclear complexes of **1** ~ **3**, the V–O (alkoxy) distances with an

average value of 2.040 Å are comparable to that of $V^{IV}_2O_2$ binuclear complexes (2.047av Å). The V–O (carboxy) distances 2.015 Å are shorter than those of $V^{IV}_2O_2$ binuclear complexes (2.049 av Å) reported in Table 2. For the dinuclear complex **4**, the V–O (alkoxy) distances (1.982av Å) and V–O (carboxy) distances (1.980av Å) are comparable with the corresponding distances in $V^V_2O_4$ core reported. In the vanadyl α -hydroxycarboxylates, the bond distances of α -alkoxy and α -carboxy to vanadium(IV) are longer than those of vanadium(V) α -hydroxycarboxylates, indicating weak binding of α -alkoxy and α -carboxy groups to the vanadium atom in low oxidation state. All of the reported $V^{V/IV}$ –O (alkoxy) and $V^{V/IV}$ –O (carboxy) distances are shorter than that found in V-nitrogenase (2.15 Å) in lower oxidation state.

The cations in **1**, **2** and **4**, $[Ni(phen)_3]^{2+}$ are composed of a common Ni(II) phenanthroline complex in an octahedral configuration. The two phen are parallel to each other and the rings of each phenanthroline are involved in π – π stacking in an offset or parallel-displaced mode [44]. The anions and the cations of **1**, **2**, and **4** fill each interspace while the neutral molecules of **3** stack by face-to-face π – π interactions through parallel pyridine rings. The strong intermolecular interactions of **3** (interplanar distance 3.662 Å) contribute to the stability of the structure. The packing diagrams are shown in Figures S2 ~ S5.

3.3. TGA

TGA curves of polycrystalline samples of **1** and **2** and derivative of mass loss are shown in Figures S6a and b. **1** and **2** lose about 16.4 wt. % and 12.4 wt. % at 110 °C respectively. The low water mass losses were caused by their dehydration in room temperature. Moreover, the decompositions occurred from 300 to 400 °C with mass % losses of 16.6 % for **1** and 15.5% for **2**.

3.4. IR and UV-visible spectroscopies

FT-infrared spectra show well-resolved strong and sharp absorptions for the coordinated

glycollates of **1** ~ **4** in Figure S7. Antisymmetric stretching vibrations $\nu_{as}(\text{COO}^-)$ are observed between 1517 and 1654 cm^{-1} . The corresponding symmetric stretches $\nu_s(\text{COO}^-)$ appear between 1343 and 1426 cm^{-1} . All of the carboxy absorptions are shifted to lower frequencies with respect to those of free glycollic acid. The frequency difference $\Delta[\nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)]$ [45] was greater than 200 cm^{-1} , which is consistent with the monodentate coordinated carboxy group, and in agreement with those observed from X-ray structural analysis. The aforementioned tentative assignments were in consonance with previous reports on α -hydroxycarboxylato complexes [14,15,17,21,28]. Moreover, the peaks around 932 ~ 988 cm^{-1} are assigned to V=O bond, which is in consistent with the values observed for the V-O containing dinuclear species [14,18,21,30].

The solid diffused reflectance UV-visible spectra of **1**, **2** and **4** show nearly the same absorptions around 216, 254, 296, 329 nm in Figure S8. Above 400 nm, the weak absorptions can be observed at 580, 558 and 525 for **1**, **2** and **4** respectively. **3** shows the absorptions at 215, 256, 296, 329 nm, and a wide absorption in the range of 360 ~ 600 nm respectively. The absorptions above 360 nm can be assigned for d-d transitions of vanadium glycollate, and the features below 360 nm can be attributed to charge-transfer or $\pi \rightarrow \pi$ bands [46].

3.5. Bond valence calculations

Theoretical bond valence calculations [47, 48] give the valences 4.315, 4.267 for **1**, 4.261, 4.390 for **2**, 4.303, 4.204 for **3**, and 5.145, 5.203 for **4** respectively, which indicate that V sites are in +4 oxidation state in **1** ~ **3**, and +5 oxidation state in **4**. This is further supported by EPR experiment at 90 K. The EPR spectra of **1** and **2** appear to be anisotropic while **3** appears to be isotropic as shown in Fig. 5. The vanadyl complexes of **1** and **2** display axis-symmetric EPR spectra, and the g values obtained are $g_{//}$ 3.1061, $g_{\perp}$ 1.9802, g 4.3356 for **1**; and $g_{//}$ 3.1663, $g_{\perp}$ 1.9602, g 4.3361 for **2** respectively. As for complex **3**, the g value obtained is 1.9707. The bands centered on g 1.9802, 1.9602, 3.1061, 3.1663 and 1.9707 that exhibit S =

$\frac{1}{2}$ signals, which are consistent with a $3d^1$ metal center V^{4+} . The weak bands centered on g 4.3356 and 4.3361 are signals of NMR tube (g 4.3371). However, none of the spectrum shows any resolved hyperfine structures determined by the ^{51}V nuclear spin ($I = 7/2$, $S = \frac{1}{2}$) [49]. The missing of hyperfine structures is presumably determined by strong spin-spin interactions and spin-orbit coupling interactions.

[Figure 5]

4. Degradations of tetrameric vanadyl complexes to dimeric vanadate

4.1. Degradation in solution

As stated in experimental section, crystals of **4** could be obtained from the solution of complex **2**. Hence, XRD experiment was carried out to trace the degradation in solution from **2** to **4**. In Figure 6, three strong peaks at 7.560° , 8.395° and 10.500° found in **2** (experiment) are consistent with the simulated XRD pattern of **2** at 7.582° , 8.340° and 10.478° . They weakened in 2a and 2b, and almost disappeared in 2c. On the contrary, the peaks at 7.899° and 10.116° emerged in 2a and 2b and become stronger in 2c. They are corresponding to complex **4** at 7.838° and 10.022° . It seems that the transformation happened in an early stage and almost completed after a half month.

[Figure 6]

4.2. Degradation in solid state

Besides the conversion in solution, degradation can be also found in solid state. Tetrameric **1** in solid state was tracing by IR under heating condition. As shown in Figure 7, obvious changes can be observed in the range of 1120 and 930 cm^{-1} after 0.5 h. The peaks at 1121 , 1061 , 990 and 934 cm^{-1} weakened or even disappeared while the peaks at 1077 and 969 cm^{-1} strengthened. As time went on, the changes were small which indicate that the conversion takes place in the early stage. After 26 h, the spectrum is very similar to that of the spectrum in **4**. Inconsistent spectrum may be caused by the other product from the

degradation in the oxidate process shown in equation (1). To further identify the final product, the compound was washed with water, then collected to measure by XRD experiment. In Figure S9, the XRD pattern of the product is consistent with that of complex **4**. It confirms that dimeric vanadate is the final product.

[Figure 7]

As shown in the experimental section, vanadyl glycollates favor rhombic dimeric structure **4** as a stable framework [28,30,31,50]. The number of rhombic dimeric unit, to some extent, reflects the stability of the structure. As shown in Figure 4, complex **1** contains five rhombus units, while **2** and **3** contain one and three rhombus unit respectively. It seems that the stability of **3** remains in middle among the three compounds. But in actually, **3** shows a special stability in the same condition (Figure S10) due to the hydrophobic packing by π - π interaction, which is the result from strong binding heterocyclic ligands of bpy in the vanadium coordination shell.

5. Conclusions

In summary, we have obtained three novel tetranuclear vanadyl (IV) glycollates, where **1** and **2** are trapped by bulky nickel phenanthroline cations and **3** was isolated with the addition of bpy under hydrothermal condition. X-ray structural analyses of **1** ~ **4** show that tetrameric and dimeric species existed in distorted octahedral, quadrangular pyramid and trigonal bipyramid configurations. Glycollate ligands coordinate bidentately to the central vanadium with α -alkoxy and α -carboxy oxygen atoms. The monodentate coordination of α -carboxy group is supported by IR analysis. EPR spectra indicate that the vanadium sites are in +4 oxidation state in **1** ~ **3** and +5 oxidation state in **4**. **1** and **2** are vulnerable to be oxidized to dimeric **4**, which was further traced by IR and XRD experiments, while **3** is stable due to the

strongly binding N-heterocyclic ligand of bpy. The degradation process reflects a possible way of utilizing polyvanadium in biological process.

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Figures and Table Options

Figure 1. The ORTEP plot of the anion in $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 23\text{H}_2\text{O}$ (**1**) at the 30% probability levels, showing incomplete double-cubane configuration.

Figure 2. The ORTEP plot of the anion in $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 16\text{H}_2\text{O}$ (**2**) at the 30% probability levels, showing butterfly configuration.

Figure 3. The ORTEP plot of $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4]\cdot 6\text{H}_2\text{O}$ (**3**) at the 30% probability levels.

Figure 4. The frameworks of $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 23\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 16\text{H}_2\text{O}$ (**2**), $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4]\cdot 6\text{H}_2\text{O}$ (**3**) and $[\text{Ni}(\text{phen})_3][\text{V}_2\text{O}_4(\text{glyc})_2]\cdot 5\text{H}_2\text{O}$ (**4**).

Figure 5. EPR spectra of solid $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 23\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 16\text{H}_2\text{O}$ (**2**) and $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4]\cdot 6\text{H}_2\text{O}$ (**3**) at 90 K.

Figure 6. Qualitative XRD tracing of the conversion from $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 16\text{H}_2\text{O}$ (**2**) to $[\text{Ni}(\text{phen})_3][\text{V}_2\text{O}_4(\text{glyc})_2]\cdot 5\text{H}_2\text{O}$ (**4**) in solution at different times. (2a, 2b and 2c are the XRD patterns for the samples collected from solution after 1.5, 7 and 15 days).

Figure 7. Qualitative IR tracing of the conversion from $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 23\text{H}_2\text{O}$ (**1**) to $[\text{Ni}(\text{phen})_3][\text{V}_2\text{O}_4(\text{glyc})_2]\cdot 5\text{H}_2\text{O}$ (**4**) in solid state at different times heated at 70 °C.

Table 1. Crystallographic data for $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 23\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6]\cdot 16\text{H}_2\text{O}$ (**2**), $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4]\cdot 6\text{H}_2\text{O}$ (**3**) and $[\text{Ni}(\text{phen})_3][\text{V}_2\text{O}_4(\text{glyc})_2]\cdot 5\text{H}_2\text{O}$ (**4**).

Table 2. Comparisons of V–O distances (Å) in dimeric citrato, malato, lactato and glycollato vanadium complexes.

Table 1. Crystallographic data for [Ni(phen)₃]₂[V₄O₄(glyc)₆]·23H₂O (**1**), [Ni(phen)₃]₂[V₄O₄(glyc)₆]·16H₂O (**2**), [V₄O₆(glyc)₂(bpy)₄]·6H₂O (**3**) and [Ni(phen)₃][V₂O₄(glyc)₂]·5H₂O (**4**)

	1	2	3	4
Empirical formula	C ₈₄ H ₁₀₆ N ₁₂ O ₄₅ V ₄ Ni ₂	C ₈₄ H ₉₂ N ₁₂ O ₃₈ V ₄ Ni ₂	C ₄₄ H ₄₈ N ₈ O ₁₈ V ₄	C ₄₀ H ₃₈ O ₁₅ N ₆ V ₂ Ni
Formula weight	2324.98	2198.87	1180.66	1003.35
Temperature, K	173(2)			
Wavelength	0.71073 Å			
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ /c	<i>P</i> $\bar{1}$
Unit cell dimensions				
a, Å	13.5345(7)	12.468(1)	12.8063(9)	12.4886(4)
b, Å	14.5915(8)	14.3664(9)	9.5831(4)	13.6362(5)
c, Å	15.7255(6)	15.359(1)	20.064(1)	14.9658(5)
α, °	109.657(4)	106.509(7)	90	76.898(3)
β, °	104.259(4)	101.800(7)	102.874(6)	66.721(3)
γ, °	105.151(5)	102.881(6)	90	75.259(3)

$V, \text{\AA}^3$	2625.2(2)	2463.5(4)	2400.4(3)	2241.2(2)
Z	1	1	2	2
D (calculated), g/cm^3	1.471	1.482	1.634	1.487
Abs. coeff., mm^{-1}	0.787	0.829	0.840	0.898
$F(000)$	1202.0	1132.0	1208	1028.0
Crystal size, mm	0.20×0.20×0.15	0.30×0.25×0.10	0.20×0.16×0.06	0.30×0.30×0.20
θ range for data collection, °	2.91 ~ 29.99	2.91 ~ 29.98	2.92 ~ 27.00	2.994 ~ 30.04
Reflections collected	21126	22756	10902	21148
Independent reflections	10300	12320	5170	11319
R_{int}	0.0434	0.0477	0.0707	0.0221
Data / restraints / parameters	10300 / 0 / 559	12320 / 0 / 559	5170 / 0 / 334	11319 / 0 / 540
GOF on F^2	1.097	1.067	1.022	1.033
Final R indices $R_1 [I > 2\sigma(I)]$	0.0579	0.0748	0.0981	0.0418
$R_2 [I > 2\sigma(I)]$	0.1356	0.1546	0.2233	0.1105
Largest diff. peak and hole, $\text{e\AA}^{-3}$	0.37 / -0.43	0.42 / -0.62	1.221 / -0.839	0.41 / -0.41

Table 2. Comparisons of V–O distances (Å) in dimeric citrato, malato, lactato and glycollato vanadium complexes.

Complex	V–O (α -alkoxy)	V–O (α -carboxy)	V–O $\square$ (β -carboxy)	Reference
[Ni(phen) ₃] ₂ [V ₄ O ₄ (glyc) ₆]·23H ₂ O (1)	2.080(3) _{av}	2.001(3) _{av}		This work
[Ni(phen) ₃] ₂ [V ₄ O ₄ (glyc) ₆]·16H ₂ O (2)	2.016(3) _{av}	1.999(3) _{av}		This work
[V ₄ O ₆ (glyc) ₂ (bpy) ₄]·6H ₂ O (3)	2.024(5) _{av}	2.045(5)		This work
Average	2.040(5)	2.015(5)		
V(IV)				
K ₃ [V ₂ O ₂ H(cit) ₂]·7H ₂ O	1.976(5) _{av}	1.981(6)	1.976(7) _{av}	[22]
(Hneo) ₃ [V ₂ O ₂ H(cit) ₂]·4H ₂ O	1.984(4) _{av}	2.137(4) _{av}	1.989(4) _{av}	[19]
Na ₄ [V ₂ O ₂ (cit) ₂]·6H ₂ O	2.089(2) _{av}	2.038(2)	2.025(2) _{av}	[17]
Na ₄ [V ₂ O ₂ (cit) ₂]·12H ₂ O	2.108(2) _{av}	2.039(2)	2.017(2) _{av}	[22]
(NH ₄) ₄ [V ₂ O ₂ (cit) ₂]·2H ₂ O	2.077(2) _{av}	2.049(2) _{av}	2.029(2) _{av}	[22]
Average	2.047(5)	2.049(6)	2.007(7)	
V(V)				
[Ni(phen) ₃][V ₂ O ₄ (glyc) ₂]·5H ₂ O (4)	1.982(2) _{av}	1.980(2) _{av}		This work
Cs ₂ [V ₂ O ₄ (lact) ₂]·2H ₂ O	1.979(4) _{av}	1.977(4) _{av}		[28]
K ₂ [V ₂ O ₄ (glyc) ₂]	1.979(3)	1.973(3)		[31]
(NH ₄) ₂ [V ₂ O ₄ (glyc) ₂]	1.978(5) _{av}	1.993(6) _{av}		[30]
Rb ₂ [V ₂ O ₄ (glyc) ₂]	1.980(2) _{av}	1.979(2)		[28]
Cs ₂ [V ₂ O ₄ (Hmal) ₂]	1.990(4) _{av}	1.977(4)		[28]

$\text{K}_2[\text{V}_2\text{O}_4(\text{H}_2\text{cit})_2] \cdot 4\text{H}_2\text{O}$	1.986(2) _{av}	1.980(3)	[16, 18]
$(\text{NH}_4)_2[\text{V}_2\text{O}_4(\text{H}_2\text{cit})_2] \cdot 2\text{H}_2\text{O}$	1.988(2) _{av}	1.974(3)	[18]
$\text{Na}_2[\text{V}_2\text{O}_4(\text{H}_2\text{cit})_2] \cdot 2\text{H}_2\text{O}$	1.984(3)	1.957(3)	[23]
$\text{Na}_2\text{K}_2[\text{V}_2\text{O}_4(\text{Hcit})_2] \cdot 9\text{H}_2\text{O}$	1.984(4) _{av}	1.979(4) _{av}	[21]
$\text{K}_4[\text{V}_2\text{O}_4(\text{Hcit})_2] \cdot 5.6\text{H}_2\text{O}$	1.994(2) _{av}	1.966(2)	[24]
$(\text{NH}_4)_4[\text{V}_2\text{O}_4(\text{Hcit})_2] \cdot 4\text{H}_2\text{O}$	1.997(1) _{av}	1.977(2)	[25]
$\text{K}_2(\text{NH}_4)_4[\text{V}_2\text{O}_4(\text{cit})_2] \cdot 6\text{H}_2\text{O}$	1.983(2) _{av}	1.981(2)	[17, 26]
$(\text{NH}_4)_6[\text{V}_2\text{O}_4(\text{cit})_2] \cdot 6\text{H}_2\text{O}$	1.984(2) _{av}	1.981(2)	[25]
$\text{K}_2[\text{V}_2\text{O}_4(R,S\text{-H}_2\text{homocit})_2] \cdot 6\text{H}_2\text{O}$	1.980(8) _{av}	1.959(8) _{av}	[14]
Average	1.985(8)	1.975(8)	

$\text{VFe}_7\text{S}_9\text{C}(R\text{-Hhomocit})(S\text{-cys})(N\text{-His})$	2.15	[55]
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Figure1

Figure2

Figure3

Figure4

(1)

(2)

(3)

(4)

Figure5

Figure6

Figure7