



Degradations of novel tetranuclear vanadyl glycollates to dinuclear species



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ABSTRACT

Novel tetranuclear vanadyl glycollates $[\text{Ni}(\text{phen})_3]_2[\text{V}_4^{\text{IV}}\text{O}_4(\text{glyc})_6] \cdot 23\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3]_2[\text{V}_4^{\text{IV}}\text{O}_4(\text{glyc})_6] \cdot 16\text{H}_2\text{O}$ (**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 $[\text{V}_4^{\text{IV}}\text{O}_6(\text{glyc})_2(\text{bpy})_4] \cdot 6\text{H}_2\text{O}$ (**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 $[\text{Ni}(\text{phen})_3][\text{V}_2^{\text{IV}}\text{O}_4(\text{glyc})_2] \cdot 5\text{H}_2\text{O}$ (**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.

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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 has 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-homocitrate 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 $[\text{Ni}(\text{phen})_3]_2[\text{V}_4^{\text{IV}}\text{O}_4(\text{glyc})_6] \cdot 23\text{H}_2\text{O}$ (**1**), $[\text{Ni}(\text{phen})_3]_2[\text{V}_4^{\text{IV}}\text{O}_4(\text{glyc})_6] \cdot 16\text{H}_2\text{O}$ (**2**) and $[\text{V}_4^{\text{IV}}\text{O}_6(\text{glyc})_2(\text{bpy})_4] \cdot 6\text{H}_2\text{O}$ (**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 $[\text{Ni}(\text{phen})_3][\text{V}_2^{\text{IV}}\text{O}_4(\text{glyc})_2] \cdot 5\text{H}_2\text{O}$ (**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 N_2 atmosphere with a heating rate of $10^\circ\text{C min}^{-1}$. Infrared spectra were recorded in the range $400\text{--}4000\text{ cm}^{-1}$ on a Nicolet 380 FT-IR spectrometer in KBr plates. The solid diffused UV/Vis spectra were recorded at 293 K using a Cary 5000 UV–Vis–NIR spectrophotometer in the $200\text{--}800\text{ nm}$ 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

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2θ from 4° to 80° . Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) obtained at 35 kV and 15 mA was used as the X-ray source.

2.2. Synthesis of $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6] \cdot 23\text{H}_2\text{O}$ (**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 glycolic 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 min 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 $\text{C}_{84}\text{H}_{106}\text{N}_{12}\text{O}_{45}\text{V}_4\text{Ni}_2$: C, 43.4; H, 4.6; N, 7.2. *Found*: C, 43.0; H, 3.9; N, 6.9%. IR (cm^{-1}): $\nu_{\text{as}}(\text{CO}_2)$, 1628 vs, 1602 s, 1517 s; $\nu_{\text{s}}(\text{CO}_2)$, 1425 s, 1356 s; $\nu(\text{V}=\text{O})$, 988 s, 935 s; $\nu(\text{V}-\text{O}-\text{V})$, 849 m.

2.3. Synthesis of $[\text{Ni}(\text{phen})_3]_2[\text{V}_4\text{O}_4(\text{glyc})_6] \cdot 16\text{H}_2\text{O}$ (**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 $\text{C}_{84}\text{H}_{92}\text{N}_{12}\text{O}_{38}\text{V}_4\text{Ni}_2$: C, 45.9; H, 4.2; N, 7.7. *Found*: C, 45.5; H, 4.1; N, 7.4%. IR (cm^{-1}): $\nu_{\text{as}}(\text{CO}_2)$, 1647 s, 1517 m; $\nu_{\text{s}}(\text{CO}_2)$, 1425 s, 1345 m; $\nu(\text{V}=\text{O})$, 983 m, 932 s; $\nu(\text{V}-\text{O}-\text{V})$ 849 m.

2.4. Synthesis of $[\text{V}_4\text{O}_6(\text{glyc})_2(\text{bpy})_4] \cdot 6\text{H}_2\text{O}$ (**3**)

Vanadium pentoxide V_2O_5 (182 mg, 1.0 mmol), excess glycolic 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 programed control. The dark brown precipitates were collected and washed with ethanol to afford **3**. Yield: (based on bpy) 86 mg (28%). *Anal. Calc.* for $\text{C}_{44}\text{H}_{48}\text{N}_8\text{O}_{18}\text{V}_4$: C, 44.7; H, 4.1; N, 9.5. *Found*: C, 44.2; H, 3.4; N, 9.1%. IR (cm^{-1}): $\nu_{\text{as}}(\text{CO}_2)$, 1602 s; $\nu_{\text{s}}(\text{CO}_2)$, 1380 m; $\nu(\text{V}=\text{O})$, 942 s; $\nu(\text{V}-\text{O}-\text{V})$, 766 s.

2.5. Synthesis of $[\text{Ni}(\text{phen})_3][\text{V}_2\text{O}_4(\text{glyc})_2] \cdot 5\text{H}_2\text{O}$ (**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 **4**. Yield: 220 mg from **2** (43.9%) (based on vanadium). *Anal. Calc.* for $\text{C}_{40}\text{H}_{38}\text{O}_{15}\text{N}_6\text{V}_2\text{Ni}$: C, 47.9; H, 3.8; N, 8.4. *Found*: C, 47.7; H, 3.5; N, 8.4%. IR (cm^{-1}): $\nu_{\text{as}}(\text{CO}_2)$, 1654 s, 1587 m, 1517 s; $\nu_{\text{s}}(\text{CO}_2)$, 1426 s, 1343 s; $\nu(\text{V}=\text{O})$, 932 s; $\nu(\text{V}-\text{O}-\text{V})$, 849 s.

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 \AA^3 in **1**, 618.8 \AA^3 in **2**, 525.8 \AA^3 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 H_2glyc 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 $\text{Ni}(\text{phen})^{2+}$ 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 H_2glyc (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 Figs. 1–3. The ORTEP diagram of $[\text{V}_2\text{O}_2(\text{glyc})_2]^{2-}$ anion in **4** is shown in Fig. S1. The comparisons of their frameworks are shown in Fig. 4 for the dimeric and tetrameric complexes. Selected bond distances and angles for **1–4** are listed in Tables S1–S4.

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 \AA) and $\text{V}-\text{O}(\mu_3\text{-alkoxido})-\text{V}$ angles (95.6–105.3 $^\circ$) in **1** are similar with those of common alkoxido(oxido)vanadium complexes (distances 1.94–2.41 \AA and angles 86.2–109.7 $^\circ$). 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

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