Structural characterization of vanadium terpyridine complexes for the study of in-situ ligand cyclization reaction

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Abstract. Vanadyl complex [V^IV(hmfc)(terpy)]·3.5H_2O (1) (hmfc=5-hydroxy-3-methyl-2(5H)-furanone-5-carboxylate; terpy=2,2':6',2'-terpyridine) has been isolated, which the hmfc ligand was formed through in-situ cyclization of lactate. X-ray structural analysis shows that hydroxyfuranone carboxylate chelates to vanadium through hydroxy group and carboxy group. Under the same condition, a peroxo vanadium terpyridine [V^IV(O_2)(terpy)(H_2O)]Cl·H_2O (2) could also be isolated, which is directly formed by molecular oxygen. In addition, a mixed-valence complex [V_2O_5(terpy)_2]Cl·9H_2O (3) was isolated with two dimensional water units. These three complexes were characterized by elemental analysis, IR, UV-Vis, EPR, TGA, bond valence calculations and X-ray structural analyses. The formation of hydroxyfuranone carboxylate ligand may provide a new approach for one-pot synthesis of γ-hydroxy butenolide derivatives.

Keywords: furanone, lactic acid, ligand assisted reaction, terpyridine, vanadium

1. Introduction

2(5H)-furanone, also known as γ-butenolide, is present in various natural products [1, 2] and served as chiral building blocks for the synthesis of diverse organic compounds [3]. Many functionally substituted derivatives of 2(5H)-furanone possess a wide range of biological activities, which include antibiotic [4], anticancer [5], pesticides [6], and plant growth regulators [7]. Except total synthesis, the most studied strategies for their preparations are cyclization of functional olefin, alkyne, and α-hydroxy ketone, as well as modification of the ring of furan derivatives or γ-butyro lactone [3, 8, 9]. The development of synthetic methods for assembling multi-substituted furanone with unique substituent patterns with simple conditions remains an important synthetic goal.

In another aspect, vanadium-based catalysts have been widely used as homogeneous or heterogeneous catalysts in various oxidation processes, which include oxidation of alkanes and alcohols, epoxidation, oxidative bromination and sulfoxidation [10, 11]. The relevance of vanadate-dependent enzymes in various biological catalytic processes [12] also stimulated research on vanadium based catalysis. Based on the special catalytic property of vanadium, in this report we used terpyridine as assisted ligand for the preparation of 5-hydroxy-3-methyl-2(5H)-furanone-5-carboxylate (hmfc) vanadium complex [VO(hmfc)(terpy)]·3.5H_2O (1), where hmfc ligand was formed through in-situ cyclization of lactate. As the reaction system was exposed to air, it can also activate dioxygen to form a peroxy vanadium complex [V^IV(O_2)(terpy)(H_2O)]Cl·H_2O (2) in a wide pH range. Moreover, a mixed-valence complex [V_2O_5(terpy)_2]Cl·9H_2O (3) was isolated under hydrothermal condition. Based on the
syntheses and structural studies of these complexes, the mechanism for the formation of "hmfc" ligand was discussed.

2. Experiment

2.1. Materials and instrumentation

In this work, reagents were of commercially analytical grade and distilled water was used as solvent. A Vario EL III CHN elemental analyser was used for elemental analyses (C, H and N). Infrared spectra were performed in the range 400–4000 cm⁻¹ in KBr plates on a Nicolet 380 FT-IR spectrometer. The solid diffused UV/Vis spectra were recorded in the 200–800 nm range using a Cary 5000 UV-visible-NIR spectrophotometer. Solid electron paramagnetic resonance (EPR) spectra were collected at 90 K on a Bruker EMX-10/12 spectrometer. pH value was measured by a PHB-8 digital pH meter. TG analyses were performed on a TG 209F1 instrument in N₂ atmosphere with a heating rate of 10°C min⁻¹.

2.2. Synthesis of [IVO(hmfc)(terpy)]·3.5H₂O (1)

Vanadyl sulphate (50 mg, 0.25 mmol) and terpyridine (58 mg, 0.25 mmol) were dissolved in the mixture of water and ethanol (10.0 mL, 1:1 by volume), lactic acid (108 mg, 1.0 mmol) was added with continue stirring. The pH of the solution was adjusted to 5.0 with ammonium hydroxide and set aside for two weeks to deposit yellow crystals of 1. The crystals were filtered and washed with water with yield (based on vanadium) 31 mg (23.9%). Anal. Calc. for C₃₁H₂₁N₆O₁₅V: C, 48.6; H, 4.3; N, 8.1. Found: C, 48.4; H, 4.2; N, 8.3, (%). IR (cm⁻¹): ν(C=O) 1726vs, ν₃(COO⁻) 1648 vs, ν₂(COO⁻) 1366m, ν(C=O–C) 1276s, ν(V=O) 945vs.

2.3. Synthesis of [IVO(O₂)(terpy)(H₂O)]Cl·H₂O (2)

Method 1: Vanadyl sulphate (50 mg, 0.25 mmol) and terpyridine (58 mg, 0.25 mmol) were dissolved in the mixture of water and ethanol (10.0 mL, 1:1 by volume), lactic acid (108 mg, 1.0 mmol) was added with continue stirring. The pH of the solution was adjusted to 8.0 with ammonium hydroxide and then re-adjusted to pH 3.0 with diluted hydrochloric acid. After one month, red crystals of 2 were isolated. Method 2: based on method 1, 30% H₂O₂ (110 μL, 1.0 mmol) was added to the above mixture. Red crystals of 2 were obtained after several days, which were filtered and washed with water with yield (based on vanadium) 75 mg (74.3%). Anal. Calc. for C₃₅H₁₅ClN₁₀O₅V: C, 44.6; H, 4.4; N, 9.1. Found: C, 44.8; H, 4.0; N, 9.4, (%). IR (cm⁻¹): ν(V=O) 964s, ν(O=O) 947s, ν(V–O) 586w, 570w.

2.4. Synthesis of [V₂O₅(terpy)₂]Cl₃·9H₂O (3)

V₂O₅ (46 mg, 0.25 mmol) and terpyridine (58 mg, 0.25 mmol) were dissolved in the mixture of water and ethanol (10.0 mL, 1:1 by volume), citric acid (192 mg, 1.0 mmol) was added with continue stirring. The pH value was adjusted to 2.0 with dilute hydrochloric acid. The mixture was placed in a Teflon-lined stainless steel bomb then heated at 443 K for 3 days and cooled with programed control. The solution was evaporated in air at room temperature for one month to grow yellow-green crystals of 3. The crystals were filtered and washed with water with yield (based on vanadium) 72 mg (65.1%). Elemental analysis (calc. for C₃₅H₆₀Cl₃N₁₀O₁₂V₂): C, 40.7; H, 4.6; N, 9.5%. Found: C, 40.6; H, 4.5; N, 9.4%. IR (cm⁻¹): ν(V=O) 963s, 947s, 927s.

2.5. X-ray crystallography

An Oxford Gemini CCD diffractometer, with graphite monochromatic Mo-Kα radiation (λ=0.71073 Å) and applied with multi-scan absorption corrections, was used for collections of the crystal data for 1–3 at 173 K. Olex2 and ShelXT were used to solve the structures and Shelxl crystallographic software package [13-15] and full-matrix least-squares on F² were applied to refined the structure. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were generated geometrically or located from differential Fourier maps and refined isotropically. For 1, the unit cell includes disordered solvent water molecules, 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 473 Å\(^3\) and the residual electron density amounted to 180 e per unit cell, corresponding to nearly 16 molecules of water per unit cell in 1 (2 molecules of water per molecule).

3. Results and Discussion

3.1. Synthesis

The reactions of vanadium sulphate with lactic acid and terpyridine are sensitive to pH variations, as demonstrated by a digital pH monitor. 1 was only isolated under weak acidic condition (pH=5~6), while 2 can be obtained easily under a wide range of pH value 2~7. 2 can be also separated from the mother liquor of 1. In this case, more lactic acid will increase the yield of 1, inhibiting the formation of peroxo vanadium complex 2. Direct addition of H\(_2\)O\(_2\) to the reaction mixture is favourable for the formation of 2. 3 was synthesized under hydrothermal condition with citric acid, it can be isolated along with 2, which indicate that the strong acidic condition is not favourable for the cyclization of lactate, but capable for the activation of oxygen. The synthesis process is shown in scheme 1.

\[ \text{Scheme 1. Syntheses of 1~3.} \]

3.2. Crystal structures of 1~3

The molecular structure of 1 consists of a neutral monomeric molecule and crystal water molecules, while 2 consists of a cation, a chloride ion and crystal water molecules and 3 consists of a dimeric cation. Detail crystallographic data were given in table S1. Selected bond distances and angles for 1~3 were listed in tables S2. The ORTEP plots of the neutral molecule of 1 and the cations in 2 and 3 were shown in Fig. 1~3.
Table S1. Crystallographic data for [VO(hmfc)(terpy)]·3.5H₂O (1), [VO(O₂)(terpy)(H₂O)]Cl·H₂O (2) and [V₂O₃(terpy)₂]Cl₃·9H₂O (3).

|                         | 1                                           | 2                                           | 3                                           |
|-------------------------|---------------------------------------------|---------------------------------------------|---------------------------------------------|
| Empirical formula       | C₂₁H₂₂N₃O₉₅V                               | C₁₅H₁₅ClN₃O₅V                              | C₃₀H₄₅Cl₁₃N₁₂O₁₂V₂                         |
| Formula weight          | 519.35                                      | 403.69                                      | 884.91                                      |
| Temperature, K          | 173.0                                       | 173.0                                       | 173.0                                       |
| Wavelength, Å           |                                              | 0.71073                                     |                                              |
| Crystal system          | Monoclinic                                  | Triclinic                                   | Triclinic                                   |
| Space group             | C2/c                                        | P ⠣                                        | P ⠣                                        |
| Unit cell dimensions    |                                             |                                             |                                             |
| a, Å                    | 17.5951(5)                                  | 8.1636(5)                                   | 9.5181(6)                                   |
| b, Å                    | 12.9266(4)                                  | 9.0880(9)                                   | 13.343(1)                                   |
| c, Å                    | 19.9935(7)                                  | 11.822(1)                                   | 15.447(1)                                   |
| α, °                    | 90                                           | 77.486(8)                                   | 85.832(6)                                   |
| β, °                    | 96.530(3)                                   | 80.788(6)                                   | 84.140(6)                                   |
| γ, °                    | 90                                           | 73.697(7)                                   | 84.690(6)                                   |
| V, Å³                   | 4517.9(2)                                    | 817.2(1)                                    | 1939.2(2)                                   |
| Z                       | 8                                            | 2                                           | 2                                           |
| D (calculated), g/cm³   | 1.527                                        | 1.641                                       | 1.516                                       |
| Abs. coeff., mm⁻¹       | 0.500                                        | 0.803                                       | 0.754                                       |
| F(000)                  | 2144.0                                       | 412.0                                       | 910.0                                       |
| Crystal size, mm        | 0.3×0.2×0.15                                 | 0.4×0.2×0.2                                 | 0.2×0.2×0.1                                 |
| 2θ range for data collection, ° | 4.298 to 61.706 | 5.228 to 59.894 | 4.318 to 49.994 |
| Reflections collected   | 11536                                        | 6756                                        | 12898                                       |
| Independent reflections | 6323                                         | 4071                                        | 6840                                        |
| Rint                    | 0.0357                                       | 0.0285                                      | 0.0521                                      |
| Data / restraints / parameters | 6323/4/304          | 4071/2/240                                  | 6840/8/489                                  |
| GOF on F²               | 1.067                                        | 1.023                                       | 1.055                                       |
| Final R indices R₁ [I > 2σ(I)] | 0.0600                                | 0.0421                                      | 0.0785                                      |
| R₂ [I > 2σ(I)]          | 0.1299                                       | 0.0887                                      | 0.1795                                      |
| Largest difference / peak and hole, eÅ³ | 0.34/-0.34                          | 0.57/-0.39                                  | 1.00/-0.91                                  |
**Table S2.** Selected bond distances (Å) and angles (º) for \([\text{VO(hmfc)(terpy)}\cdot 3.5\text{H}_2\text{O}] (1), \text{[VO(O}_2\text{)(terpy)}(\text{H}_2\text{O})]\text{Cl⋅H}_2\text{O} (2)\) and \([\text{V}_2\text{O}_3(\text{terpy})_2]\text{Cl}_3\cdot 9\text{H}_2\text{O} (3)\).  

|     | bond distances (Å) |     | bond angles (º) |     |
|-----|--------------------|-----|----------------|-----|
| 1   | V1–O2 2.143(2)     | O5–C1 1.501(3) |
|     | V1–O1 1.935(2)     | O5–C5 1.340(3) |
|     | V1–O3 1.615(2)     | O4–C2 1.229(3) |
|     | V1–N3 2.126(2)     | O6–C5 1.213(4) |
|     | V1–N2 2.045(2)     | C2–C1 1.551(3) |
|     | V1–N1 2.134(2)     | C1–C3 1.501(4) |
|     | O2–C2 1.275(3)     | C5–C4 1.464(4) |
|     | O1–C1 1.348(3)     | C4–C3 1.332(4) |
|     |                   | C4–C6 1.498(4) |
|     | O1–V1–O2 77.27(7)  | O3–V1–N2 101.11(9) |
|     | O1–V1–N3 97.96(8)  | O3–V1–N1 94.87(9) |
|     | O1–V1–N2 160.15(8) | N3–V1–O2 84.08(7) |
|     | O1–V1–N1 104.28(9) | N3–V1–N1 151.96(8) |
|     | O3–V1–O2 175.42(8) | N2–V1–O2 83.14(7) |
|     | O3–V1–O1 98.57(9)  | N2–V1–N3 76.67(8) |
|     | O3–V1–N3 98.50(9)  | N2–V1–N1 76.64(9) |
|     |                   | N1–V1–O2 84.40(8) |
| 2   | V1–O1w 2.206(2)    | V1–N2 2.109(2) |
|     | V1–O1 1.864(2)     | V1–N3 2.141(2) |
|     | V1–O3 1.598(2)     | V1–N1 2.140(2) |
|     | V1–O2 1.859(2)     | O1–O2 1.423(2) |
|     | O1–V1–O1w 85.14(7) | O2–V1–O1w 84.31(7) |
|     | O1–V1–N2 150.45(8) | O2–V1–O1 44.95(7) |
|     | O1–V1–N3 160.15(8) | O2–V1–O2 150.26(7) |
|     | O1–V1–N1 104.28(9) | O2–V1–N3 82.05(7) |
|     | O3–V1–O1w 170.65(8) | O2–V1–N1 126.30(8) |
|     | O3–V1–O1 103.45(8) | N2–V1–O1w 75.86(7) |
|     | O3–V1–O2 104.33(8) | N2–V1–N3 74.53(7) |
|     | O3–V1–N2 94.79(8)  | N2–V1–N1 74.15(7) |
|     | O3–V1–N3 92.28(8)  | N3–V1–O1w 85.32(7) |
|     | O3–V1–N1 92.85(8)  | N1–V1–O1w 84.64(7) |
|       | N1–V1–N3  | 148.57(8) |
|-------|-----------|-----------|
| V1–O3 | 1.794(4)  | V2–O3     | 1.817(4) |
| V1–O1 | 1.596(4)  | V2–O2w    | 2.108(4) |
| V1–O1w| 2.069(4)  | V2–O2     | 1.602(4) |
| V1–N1 | 2.099(5)  | V2–N4     | 2.103(5) |
| V1–N2 | 2.146(5)  | V2–N5     | 2.183(4) |
| V1–N3 | 2.116(5)  | V2–N6     | 2.106(5) |
| O3–V1–O1w| 165.2(2)  | O3–V2–O2w| 169.5(2) |
| O3–V1–N1 | 91.0(2)    | O3–V2–N4 | 91.0(2)  |
| O3–V1–N2 | 86.0(2)    | O3–V2–N5 | 93.7(2)  |
| O3–V1–N3 | 90.8(2)    | O3–V2–N6 | 90.2(2)  |
| O1–V1–O3 | 104.1(2)   | O2W–V2–N5| 75.8(2)  |
| O1–V1–O1w| 90.7(2)    | O2–V2–O3 | 101.4(2) |
| O1–V1–N1 | 103.8(2)   | O2–V2–O2w| 89.1(2)  |
| O1–V1–N2 | 169.9(2)   | O2–V2–N4 | 105.8(2) |
| O1–V1–N3 | 105.5(2)   | O2–V2–N5 | 164.9(2) |
| O1W–V1–N1| 86.6(2)    | O2–V2–N6 | 106.2(2) |
| O1W–V1–N2| 79.3(2)    | N4–V2–O2w| 85.3(2)  |
| O1W–V1–N3| 83.9(2)    | N4–V2–N5 | 73.3(2)  |
| N1–V1–N2 | 74.6(2)    | N4–V2–N6 | 147.1(2) |
| N1–V1–N3 | 149.2(2)   | N6–V2–O2w| 87.6(2)  |
| N3–V1–N2 | 74.9(2)    | N6–V2–N5 | 73.8(2)  |
| V1–O3–V2 |           |           | 177.7(2) |

As shown in Fig. 1, oxidovanadium is coordinated by terpyridine and 5-hydroxy-3-methyl-2(5H)-furanone-5-carboxylate, the latter chelates to vanadium through hydroxy and carboxy groups. The VO$^{2+}$ ion in I exists in a distorted octahedral geometry. Three equatorial positions are occupied by three nitrogen atoms of terpyridine ligand, the forth site is occupied by the hydroxy group of hmf2 ligand, and the carboxy group is at one axial position, trans to the terminal oxygen atom. As a kind of γ-butenolide derivative, the 2(5H)-furanone was α-substituted by a methyl group and γ-substituted by hydroxy and carboxy groups.
The red complex 2 contains an η²-peroxo ligand as shown in Fig. 2. The vanadium exists in hepta-coordinated pentagonal-bipyramidal geometry. Five equatorial positions are occupied by three nitrogen atoms of terpydine and two oxygen atoms of peroxide. A water molecule is coordinated to one axial position, trans to the terminal oxygen atom. The peroxide group is on side-on mode and the O–O distance [1.423(2) Å] and V–O distances [1.864(2) Å and 1.859(2) Å] are consistence with those of other peroxo vanadium complexes [16, 17]. It is the rare example of the formation of a peroxo vanadium complex from molecular oxygen [17-20].
a series of hydrogen bonds with free water solvent and chloride ions. The two dimensional water units are shown in Fig. 4.

![Figure 3](image3.png)

**Figure 3.** The ORTEP plot of the cation in [V$_2$O$_3$(terpy)$_2$]Cl$_3$·9H$_2$O (3) at the 30% probability levels, water molecules and chlorides were omitted for clarity.

![Figure 4](image4.png)

**Figure 4.** The hydrogen bonded network of [V$_2$O$_3$(terpy)$_2$]Cl$_3$·9H$_2$O (3) view down from $a$ axis. The carbon atoms from terpy ligands were omitted for clarity.

3.3. IR spectroscopies

FT-infrared spectra of 1-3 show well-resolved strong and sharp absorptions for the coordinated hydroxy furanone carboxylate or terpydine in Fig. 5. For 1, the stretching vibration $\nu$(C=O) of lactone is observed
at 1726 cm⁻¹, and ν(C–O–C) of lactone is observed at 1276 cm⁻¹. The antisymmetric stretching vibration νₐ(COO⁻) is observed at 1648 cm⁻¹, and the corresponding symmetric stretches νₛ(COO⁻) appears at 1368 cm⁻¹. The carboxy absorptions are shifted to lower frequencies with respect to those of free carboxylic acid. The frequency difference Δ[νₐ(COO⁻) - νₛ(COO⁻)] [21] is 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. For 2, typical band corresponding to the peroxide group ν(O–O) is observed at 947 cm⁻¹, and the ν(V–O) vibrations are at 586 and 570 cm⁻¹. For 1–3, the vibrational bands above 2000 cm⁻¹ are assigned to C–H and O–H stretching vibrations. Moreover, the peaks at 945 cm⁻¹ for 1, 964 cm⁻¹ for 2, 963, 947 and 927 cm⁻¹ for 3 are assigned to V=O bonds, which are in consistent with the values observed in other vanadium complexes [22-26].

![Figure 5. The IR spectra of [VO(hmfc)(terpy)]·3.5H₂O (1), [VO(O₂)(terpy)(H₂O)]Cl·H₂O (2) and [V₂O₃(terpy)]Cl₃·9H₂O (3).](image)

3.4. UV-visible spectroscopies

In Fig. 6, solid diffused reflectance UV-visible spectra show the bands at 227, 284, 330 and 358 nm for 1, 235, 285, 323, 358 and 458 nm for 2, 227, 282, 323, 357 and 437 nm for 3 respectively. In these cases, tentative assignments to d-d transitions could be made for the spectral features above 500 nm. The features below 500 nm could be reasonably attributed to charge-transfer bands or π→π bands [27]. The spectrum of 2 exhibits O₂²⁻→V charge transfer band typical for mono-peroxo vanadium complex at λ_max=458 nm, in line with the observations in the literature [28, 29].
3.5. EPR and bond valence calculations

Theoretical bond valence calculations [30, 31] give the valences 4.259 for 1, 5.098 for 2 and 4.652, 4.479 for 3 respectively, which indicate that V sites are in +4 oxidation state in 1, +5 oxidation state in 2, and a mixed valence +5 and +4 oxidation states in 3. The assignments are supported by EPR experiment recorded in the solid state at 90 K. As shown in Fig. 7 and 8, the EPR spectra of 1 and 3 exhibit bands centred on $g=1.99$ and $g=1.98$ respectively, which are consistent with a $3d^1$ metal centre $V^{4+}$. The spectrum of 3 exhibit some hyperfine structures while 1 only shows one broad band without any resolved hyperfine structures determined by the $^{51}$V nuclear spin ($I=7/2, S=1/2$) [32]. The missing of hyperfine structures is presumably determined by strong spin-spin interactions and spin-orbit coupling interactions.
3.6. Thermogravimetric analysis

To characterize the thermal stability of 1 and 2, thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a heating rate of 10°C/min. As shown in Fig. 9, 1 lost 8.0% of mass from 35 to 72°C, corresponding to the release of lattice water molecules. An obvious weight loss (about 44.0%) was observed from 197°C to 550°C, indicating the decomposition of organic components. In Fig. 10, the 8.2% of weight losses of 2 from 35 to 115°C was assigned to the loss of gest water molecules. The peroxide composition decomposed at 228°C, followed by the decomposition of terpyridine ligand at 423°C. The remaining residue was approximately corresponding to the ultimate product V$_2$O$_5$.

![Figure 8](image_url)

**Figure 8.** EPR spectrum of solid [V$_2$O$_3$(terpy)$_2$]Cl$_3$·9H$_2$O (3) at 90 K.

![Figure 9](image_url)

**Figure 9.** TGA curves of polycrystalline sample of [VO(hmfc)(terpy)]·3.5H$_2$O (1).
Figure 10. TGA curves of polycrystalline sample of [VO(O_2)(terpy)(H_2O)]Cl·H_2O (2).

3.7. Proposed mechanism

The proposed mechanism for the formation of hmfc is shown in scheme 2, which includes dioxygen activation and condensation reaction. V^{IV}-superoxido species was generally proposed to be the first step in dioxygen activation, which was formed via an inner sphere one-electron transfer [16, 19]. The transient superoxido species abstracts an H atom from solvent to give a hydrogen peroxo species, and deprotonation yields the final V^{IV}-peroxo complex [16, 19]. Except the analogous dioxygen activation mechanism described here, the free-radical chain oxidation initiated by the superoxide radical was also proposed. It seems to be the most appropriate explanation for the formation of 5-hydroxy-3-methyl-2(5H)-furanone-5-carboxylate through intermolecular condensation of lactic acid [33]. Based on the mechanism proposed, vanadyl complex was oxidized to peroxo vanadium complex, generating free-radical of lactic acid. This would explain the low yield of 1 and the coprecipitation of 2. Moreover, the peroxo group in 2 is stable for the isolation that will not involve in catalytic cycle.

![Scheme 2. The proposed mechanism for the formation of hmfc ligand.](image-url)

4. Conclusions

In summary, we have isolated 5-hydroxy-3-methyl-2(5H)-furanone-5-carboxylate in a vanadyl terpyridine complexes [V^{IV}O(hmfc)(terpy)]·3.5H_2O (1). Peroxo vanadium complex
[V\(^5\)O\(_2\)(terpy)(H\(_2\)O)]Cl:H\(_2\)O (2) and mixed-valence vanadium complex [V\(_2\)O\(_5\)(terpy)\(_2\)]Cl\(_2\):9H\(_2\)O (3) were also obtained for the process. Structural analysis reveals that 2(5\(H\))-furanone ligand in 1 possesses an \(\alpha\)-substituted methyl group and a \(\gamma\)-substituted hydroxy and carboxy groups. The stable peroxide 2 formed easily via air oxidation was precipitated from the same reaction system in a wide pH range. The dinuclear vanadium terpyridine complex 3 was isolated under strong acid condition, which indicated that the strong acid condition was not suitable for coordination and cyclization of lactic acid. The mechanism for the formation of hmfc was proposed based on the three complexes. The lactate was abstracted an H atom by peroxy vanadium species. Lactic acids with free radicals condensate for the formation of hmfc ligand. And the resulting hydroperoxido vanadium species transform to a stable peroxy complex.

**Accession Codes**
CCDC 1875844–1875846 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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