

Supporting Information

Formations of mixed-valence oxovanadium^{V,IV} citrates and homocitrate with N-heterocycle chelated ligand

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- Fig. S1. Calculated and experimental XRD patterns of complexes **1** and **2**. a and d are the calculated patterns of **1** and **2**, b is the experimental pattern of complex **1**, and c is the XRD pattern of the product from **1**.
- Fig. S2. The ORTEP plot of $[\text{VO}_2(\text{phen})_2]_2[\text{V}_2\text{O}_4(\text{R,S-H}_2\text{homocit})_2] \cdot 4\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_5\text{OH}$ (**4**) at the 30% probability level.
- Fig. S3. Crystal of $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})] \cdot 5\text{H}_2\text{O}$ (**1**), left: before exposal; right, after exposal on UV light 100 W for 20 mins.
- Fig. S4. XPS spectra of $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})] \cdot 5\text{H}_2\text{O}$ (**1**) and $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})_2(\text{phen})_3\text{O}_3\text{V}_2] \cdot 12\text{H}_2\text{O}$ (**2**).
- Fig. S5. X-Band EPR spectra of citrate vanadate(IV/V) at 100 K, 150 K, 200 K and 250 K, a) $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})] \cdot 5\text{H}_2\text{O}$ (**1**); b) $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})_2(\text{phen})_3\text{O}_3\text{V}_2] \cdot 12\text{H}_2\text{O}$ (**2**)
- Fig. S6. ^{13}C NMR spectra of homocitrate $\text{Na}_3(\text{Hhomocit}) \cdot \text{H}_2\text{O}$ (**5**) in D_2O .

Fig. S7. ^{13}C NMR spectra of homocitric acid γ -lactone in D_2O .

Fig. S8. IR spectra of $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})]\cdot 5\text{H}_2\text{O}$ (**1**) and $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})_2(\text{phen})_3\text{O}_3\text{V}_2]\cdot 12\text{H}_2\text{O}$ (**2**) in the range of $400 \sim 4000 \text{ cm}^{-1}$.

Fig. S9. IR spectra of $[\text{V}_2\text{O}_3(\text{phen})_3(\text{H}_2\text{homocit})]\text{Cl}\cdot 6\text{H}_2\text{O}$ (**3**) in the range of $400 \sim 4000 \text{ cm}^{-1}$.

TABLE S1. Selected bond distances ($\text{\AA}$) and angles ($^\circ$) for $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})]\cdot 5\text{H}_2\text{O}$ (**1**), $[\text{V}_2\text{O}_3(\text{phen})_3(\text{Hcit})_2(\text{phen})_3\text{O}_3\text{V}_2]\cdot 12\text{H}_2\text{O}$ (**2**), and $[\text{V}_2\text{O}_3(\text{phen})_3(\text{R,S-H}_2\text{homocit})]\text{Cl}\cdot 6\text{H}_2\text{O}$ (**3**)

TABLE S2. Selected bond distances ($\text{\AA}$) and angles ($^\circ$) for $[\text{VO}_2(\text{phen})_2]_2[\text{V}_2\text{O}_4(\text{R,S-H}_2\text{homocit})_2]\cdot 4\text{H}_2\text{O}\cdot 2\text{C}_2\text{H}_5\text{OH}$ (**4**)

Fig. S1

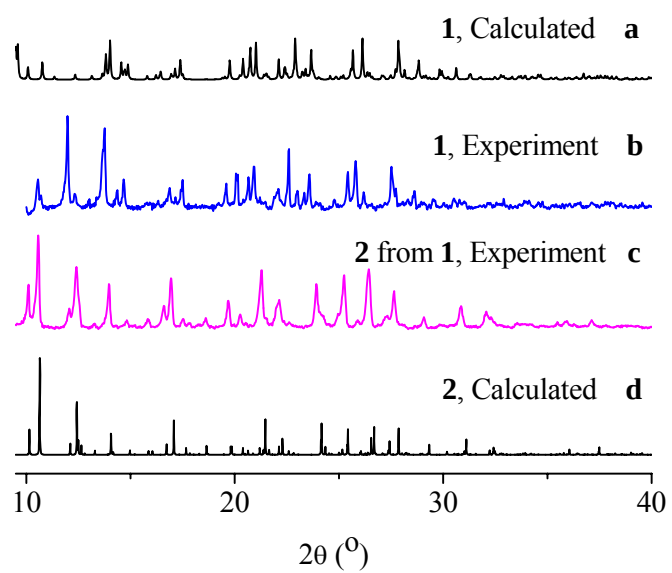


Fig. S2

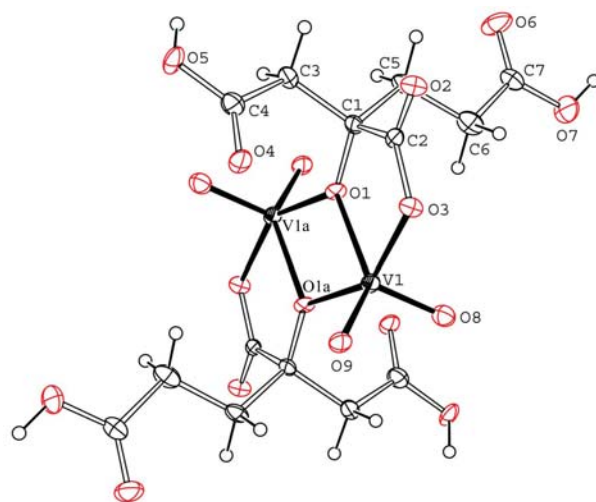
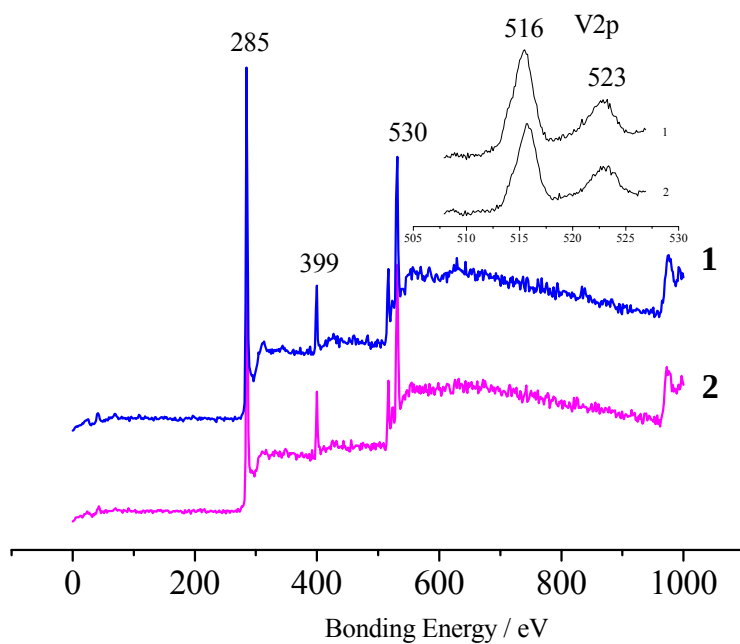


Fig. S3



Fig. S4



	[V ₂ O ₃ (phen) ₃ (Hcit)]·5H ₂ O (1)	[V ₂ O ₃ (phen) ₃ (Hcit) ₂ (phen) ₃ O ₃ V ₂]·12H ₂ O (2)
C1s	285	285
N1s	399	399
O1s	530	530
V2p _{3/2}	516	516
V ⁵⁺ 2p _{3/2}	517.2	
V ⁴⁺ 2p _{3/2}	515.8	
V2p _{1/2}	523	523
V ⁵⁺ 2p _{1/2}	524.5	
V ⁴⁺ 2p _{1/2}	523.2	

Fig. S5

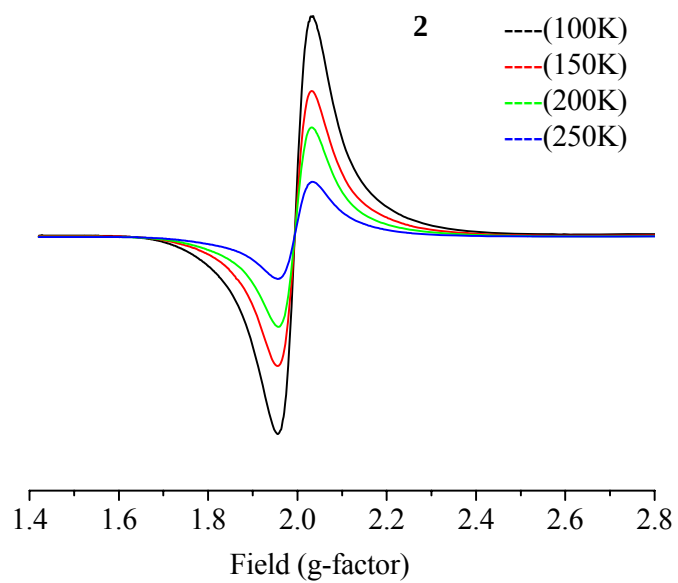
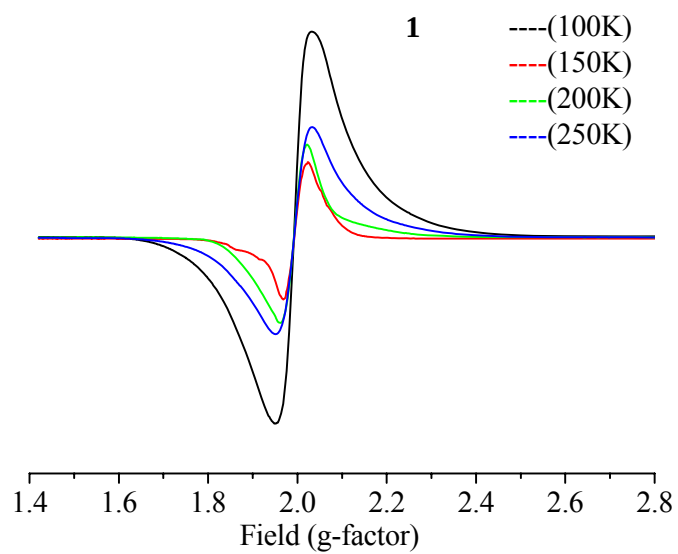


Fig. S6

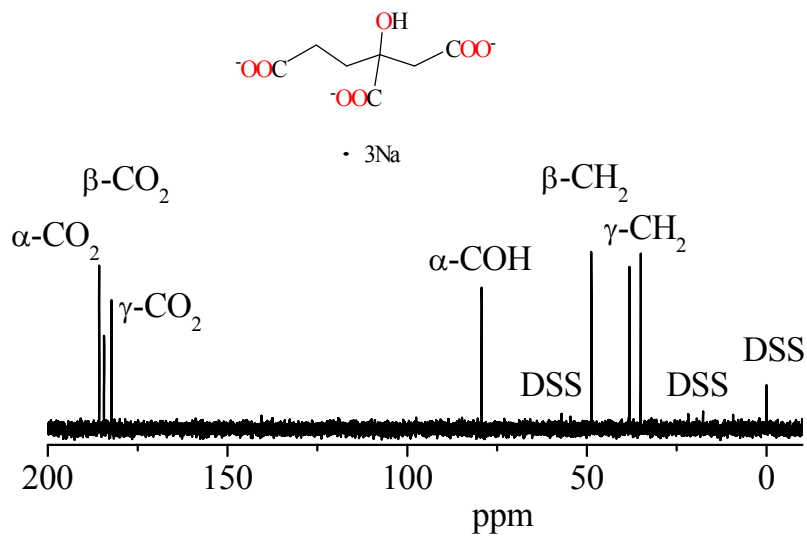


Fig. S7

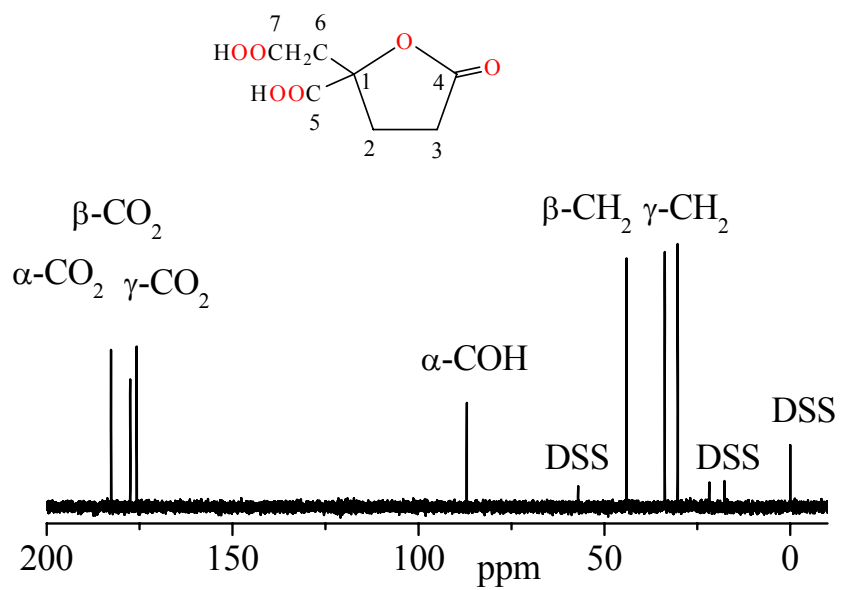


Fig. S8

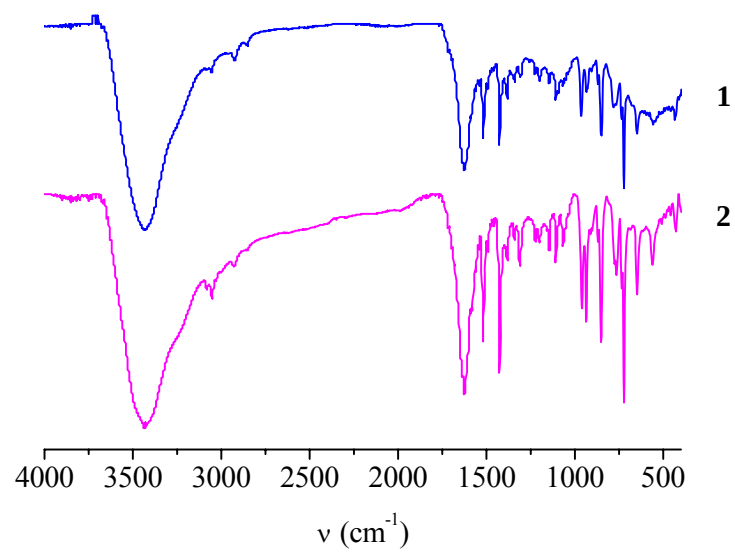


Fig. S9

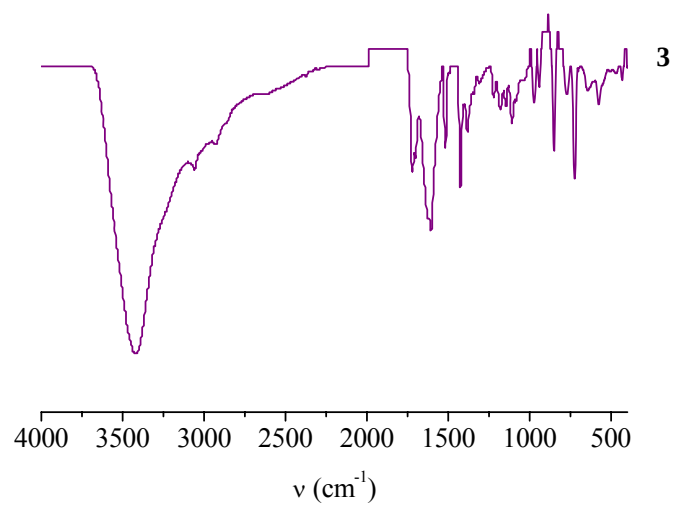


TABLE S1 Selected Bond Distances (Å) and Angles (°) for [V₂O₃(phen)₃(Hcit)]·5H₂O (**1**), [V₂O₃(phen)₃(Hcit)₂(phen)₃O₃V₂]·12H₂O (**2**), and [V₂O₃(phen)₃(*R,S*-H₂homocit)]Cl·6H₂O (**3**)

1			
V(1)–O(1)	1.851(4)	V(2)–O(9)	1.597(5)
V(1)–O(2)	2.082(4)	V(2)–O(10)	1.902(4)
V(1)–O(8)	1.617(4)	V(2)–N(3)	2.099(5)
V(1)–O(10)	1.706(4)	V(2)–N(4)	2.320(5)
V(1)–N(1)	2.158(6)	V(2)–N(5)	2.133(5)
V(1)–N(2)	2.315(6)	V(2)–N(6)	2.112(5)
V(1)–O(10)–V(2)	172.2(3)		
O(5)···O(7)	2.45(1)	O(5)···H(1)–O(7)	131(5)
2			
V(1)–O(1)	1.858(1)	V(2)–O(9)	1.607(2)
V(1)–O(2)	2.072(1)	V(2)–O(10)	1.873(1)
V(1)–O(8)	1.613(1)	V(2)–N(3)	2.315(2)
V(1)–O(10)	1.722(1)	V(2)–N(4)	2.113(2)
V(1)–N(1)	2.327(2)	V(2)–N(5)	2.143(2)
V(1)–N(2)	2.164(2)	V(2)–N(6)	2.104(2)
V(1)–O(10)–V(2)	160.3(1)		
O(5a)···O(7)	2.487(2)	O(5a)···H(1)–O(7)	173.8(1)
3			
V(1)–O(1)	1.858(4)	V(2)–O(9)	1.595(4)
V(1)–O(2)	2.085(4)	V(2)–O(10)	1.884(4)
V(1)–O(8)	1.606(4)	V(2)–N(3)	2.106(5)
V(1)–O(10)	1.713(4)	V(2)–N(4)	2.326(5)
V(1)–N(1)	2.176(5)	V(2)–N(5)	2.119(5)
V(1)–N(2)	2.332(5)	V(2)–N(6)	2.107(5)
O(7)···Cl(1)	2.982(5)	O(7)···H1–Cl(1)	175.0(6)

Symmetric transformation for **2**: $a, 1 - x, -y, 1 - z$

TABLE S2. Selected Bond Distances (Å) and Angles (°) for [VO₂(phen)₂]₂[V₂O₄(R,S-H₂homocit)₂]₂·4H₂O·2C₂H₅OH (**4**)

V(1)–O(1)	2.003(5)	V(2)–O(10)	1.572(6)
V(1)–O(1a)	1.932(6)	V(2)–O(11)	1.614(5)
V(1)–O(3)	1.937(5)	V(2)–N(1)	2.258(7)
V(1)–O(8)	1.588(6)	V(2)–N(2)	2.091(6)
V(1)–O(9)	1.624(5)	V(2)–N(3)	2.084(6)
V(1)···V(1a)	3.20(1)	V(2)–N(4)	2.217(7)
O(1)–V(1)–O(1a)	71.2(3)	O(10)–V(2)–O(11)	106.4(3)
O(1)–V(1)–O(3)	77.3(2)	O(10)–V(2)–N(1)	161.4(3)
O(1)–V(1)–O(8)	117.1(3)	O(10)–V(2)–N(2)	94.0(3)
O(1)–V(1)–O(9)	136.6(3)	O(10)–V(2)–N(3)	99.8(3)
O(1a)–V(1)–O(3)	147.3(2)	O(10)–V(2)–N(4)	89.5(3)
O(1a)–V(1)–O(8)	102.0(3)	O(11)–V(2)–N(1)	89.8(3)
O(1a)–V(1)–O(9)	98.9(3)	O(11)–V(2)–N(2)	100.3(3)
O(3)–V(1)–O(8)	99.7(3)	O(11)–V(2)–N(3)	91.7(3)
O(3)–V(1)–O(9)	98.1(3)	O(11)–V(2)–N(4)	160.8(3)
O(8)–V(1)–O(9)	106.3(3)	N(1)–V(2)–N(2)	73.6(3)
V(1)–O(1)–V(1a)	108.8(3)	N(1)–V(2)–N(3)	88.7(3)
		N(1)–V(2)–N(4)	76.7(2)
		N(2)–V(2)–N(3)	158.4(3)
		N(2)–V(2)–N(4)	89.0(2)
		N(3)–V(2)–N(4)	74.7(2)

Symmetric transformation for **4**: $a, -x + 1, -y, -z$