# Structural and electron paramagnetic resonance (EPR) characterization of novel vanadium(V/IV) complexes with hydroquinonate-iminodiacetate ligands exhibiting "noninnocent" activity\*

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Abstract: Reaction of KVO3 with 2-[N,N'-(carboxymethyl)aminomethyl]-5-methylhydroquinone ( $H_4$ mecah) in aqueous solution at pH 8.2 results in the isolation of mononuclear  $K_2[V^V(O)_2{Hmecah(-3)}]$ ·2H<sub>2</sub>O complex. On the other hand, reaction with the 2-[N,N'-(carboxymethyl)aminomethyl]-5-tert-butylhydroquinone (H<sub>4</sub>tbutcah) under the same conditions  $K_6[\{V^VO(\mu-O)V^{IV}O\}\{\mu-tbut$ gives tetranuclear mixed-valent complex the bicah(-6)}]<sub>2</sub>·10.5H<sub>2</sub>O (H<sub>6</sub>tbutbicah, 2,2'-({2-[bis(carboxymethyl)amino]-3,6-dihydroxy-4methylbenzyl}azanediyl)diacetic acid). The structures of both complexes were determined by single-crystal X-ray crystallography. The coordination environment of vanadium ions in both complexes is octahedral, with four out of the six positions to be occupied by the two *cis* carboxylate oxygens, one hydroquinonate oxygen, and one amine nitrogen atoms of the ligands' tripod binding sites. The importance of the chelate ring strains in the stabilization of the *p*-semiquinone radical is also discussed. A protonation of the ligated to vanadium(IV) ion hydroquinonate oxygen at low pH was revealed by continuous wave (cw) X-band electron paramagnetic resonance (EPR) and UV-vis spectroscopies.

*Keywords*: electron paramagnetic resonance (EPR); hydroquinone; iminodiacetic; oxovanadium compounds; synthesis; X-ray structure.

## INTRODUCTION

The interaction of the metal ions with redox-active ligands, also referred to as "noninnocent", is of great importance because the interaction plays an essential role in redox biochemical processes. In particular, proton-coupled electron-transfer reactions between transition-metal centers and p-quinone cofactors are vital for all life occurring in key biological processes as diverse as the oxidative maintenance of biological amine levels [1,2], tissue (collagen and elastin) formation [2–4], photosynthesis [2–6], and aerobic (mitochondrial) respiration [7,8]. The interaction of p-hydroquinones with vanadium, in high-oxidation states, presents additional interest due to the participation of vanadium in redox reactions in biological systems [9–15] such as the reduction of vanadium(V), present in sea water, to vanadium(III) in the blood cells of tunicates [16,17].

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In marked contrast to the extensive structural chemistry for chelate-stabilized o-(hydro/semi)quinone metal compounds [18–22], examples of structurally characterized non-polymeric  $\sigma$ -bonded p-hydroquinone/semiquinone–metal compounds are surprisingly rare [23]. This is mainly due to the absence of a chelate coordination site in simple p-(hydro/semi)quinone. A strategy to prepare such species is to synthesize substituted, in the o-position, p-hydroquinones with substituents containing one or more donor atoms, thus enabling the metal atom to form chelate rings [24–26].

Over the last few years, our research team has pursued the synthesis and stabilization of two redox center metal complexes with hydroquinonate/*p*-semiquinonate ligands [25,27–29], which model enzymes exhibiting one inorganic and one organic redox centers in the active site, such as galactose oxidase and copper amine oxidase [30–33]. Our recent work has shown that ligation of dinucleating bis-iminodiacetate-substituted hydroquinone ligand (H<sub>6</sub>bicah, Scheme 1) to vanadyl ion results in stabilization of *p*-semiquinone radicals in acidic aqueous solutions [25,28].



Scheme 1 Drawings of the ligands used in this work.

In this work, new iminodiacetate-hydroquinone ligands have been synthesized. Their redox activity, and thus their "noninnocence", is regulated by additional substitution of the hydroquinone ring with methyl (2-[N,N]-(carboxymethyl)aminomethyl]-5-methylhydroquinone, H<sub>4</sub>mecah) or tert-butyl (2-[N,N]-(carboxymethyl)aminomethyl]-5-tert-butylhydroquinone, H<sub>4</sub>tbutcah) groups (Scheme 1). Reaction of these molecules with VO<sub>4</sub><sup>3-</sup> at pH 8.2 shows that only the  $H_4t$  butcah is oxidatively activated by vanadium(V), resulting in further substitution of the ligand with an iminodiacetate group, H<sub>6</sub>tbutbicah (2,2'-({2-[bis(carboxymethyl)amino]-3,6-dihydroxy-4-methylbenzyl}azanediyl)diacetic acid, Scheme 1) and formation of the tetranuclear mixed-valent vanadium(IV/V) complex  $K_6[\{V^VO(\mu-O)V^{IV}O\}]$  $\{\mu$ -tbutbicah(-6)}]<sub>2</sub>·10.5H<sub>2</sub>O, **2**. On the other hand, reaction of VO<sub>4</sub><sup>3-</sup> with H<sub>4</sub>mecah gave the mono-nuclear complex K<sub>2</sub>[V<sup>V</sup>(O)<sub>2</sub>{Hmecah(-3)}]·2H<sub>2</sub>O, **1**. Despite the similarities among bicah<sup>6-</sup> and tbutbicah<sup>6-</sup> (both have the same donor atoms at the two binding sites and form similar rectangularshaped tetranuclear vanadium complexes), tbutbicah<sup>6-</sup> does not stabilize the p-semiquinone radical upon coordination with vanadium(IV). This is attributed to the intra-ring strains originated from the smaller-size  $O_{hydroquinone} \cdots N_{amine}$  chelating ring in *t*butbicah<sup>6-</sup>, five- vs. six-membered rings in bicah6-. Furthermore, electron paramagnetic resonance (EPR) and UV-vis spectroscopies were employed for the investigation of the stability and protonation of the hydroquinonate oxygen, ligated to vanadium(IV), atoms.

#### **RESULTS AND DISCUSSION**

#### Syntheses of compounds 1 and 2

The syntheses of the vanadium(V) and the mixed-valent vanadium(IV/V)-hydroquinonate complexes are summarized in Scheme 2.

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The mononuclear complex 1 was prepared by treatment of  $KVO_3$  aqueous solution with an equivalent amount of the H<sub>4</sub>mecah at pH 8.2. The same conditions were used for the synthesis of the tetranuclear compound 2 from  $KVO_3$  and H<sub>4</sub>tbutcah. However, the yield of the reaction was increased by reacting 2 equiv of  $KVO_3$  with 1 equiv of H<sub>4</sub>tbutcah. During the reaction the ligand is further substituted by an additional iminodiacetate group forming the ligand tbutbicah<sup>6–</sup> (Schemes 1 and 2). A possible mechanism of this condensation reaction is shown in Scheme 3. According to this, the first step should be the formation of a vanadium(V) mononuclear complex similar to 1 followed by reduction of the metal ion to vanadium(IV) and simultaneous oxidation of ligand to semiquinone radical. Then, an iminodiacetic group from another Htbutcah<sup>3–</sup> nucleophilically attacks the semiquinone. The new bifunctional hydroquinonate derivative ligates one additional vanadium(V) and two of these units connect through V<sup>IV</sup>–O–V<sup>V</sup> bridges to form the mixed-valent tetranuclear complex 2. The difference of the



Scheme 2 Synthetic routes leading to the isolation of compounds 1 and 2.



Scheme 3 A possible mechanism for the formation of the bis-iminocarboxylate mixed-valent vanadium(IV/V) complex 2.

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reactivity with vanadate between the  $H_4$  mecah and the  $H_4$  butcah ligands is attributed to their different oxidation potential. The methyl hydroquinone is more difficult to be oxidized from vanadate compared with the *tert*-butyl- one and thus, for this ligand the reaction stops at the formation of the vanadium(V) mononuclear complex **1**. In addition, it is well known that vanadium(IV) stabilizes the *p*-semiquinone radicals [25], further supporting the mechanism of Scheme 3. Aqueous solutions of **1** are stable at alkaline pH (7–8.5) in a similar way to other vanadium(V)-iminodiacetate hydroquinonate complexes [29]. However, complex **2** is stable in a much wider pH range (2–9).

#### Solid-state characterization of complexes 1 and 2

Complexes 1 and 2 were characterized in solid-state by IR spectroscopy and single-crystal X-ray crystallography.

The IR spectra of **1** show two bands, one symmetric and one antisymmetric at 917 and 893 cm<sup>-1</sup> attributed to the V=O bonds of VO<sub>2</sub><sup>+</sup>. The stretching vibration of the V=O bonds of **2** appears as a broad strong peak at 947 cm<sup>-1</sup> and the V<sup>IV</sup>–O–V<sup>V</sup> bridge at 910 cm<sup>-1</sup>. For both **1** and **2**, the carboxylate stretching vibrations appear as two peaks at 1638 and 1420 cm<sup>-1</sup> (one antisymmetric and one symmetric, respectively), indicating coordination of the vanadium atom from the carboxylate oxygen atoms of the iminodiacetate group. A shift of 8 and 34 cm<sup>-1</sup> of the C–O<sub>phenolate/hydroquinonate</sub> stretching vibration to higher energy in the complexes compared to free ligands for **1** and **2**, respectively, supports also coordination of the vanadium ions with the hydroquinonate oxygen atoms.

The ORTEP structures of complexes 1 and 2 are shown in Figs. 1 and 2. Experimental data and selected interatomic distances and bond angles relevant to the vanadium coordination sphere in 1 and 2 are listed in Tables 1–3. The oxidation state of the metal ions and the ligand was calculated from the bond lengths applying bond valent sums and  $\Delta$  calculations, respectively [25,27].



Fig. 1 ORTEP representation (50 % thermal ellipsoids) of the crystal structure of 1. Hydrogen atoms have been omitted for clarity.



Fig. 2 ORTEP representation (50 % thermal ellipsoids) of the crystal structure of the anion of 2. Hydrogen atoms, potassium counter cations, and water co-crystallized molecules have been omitted for clarity.

Table 1 Experimenta	l data of X-ray diffraction	on study of $1, 2.^{a,b}$
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Compounds	1	2
Empirical formula	C <sub>12</sub> H <sub>16</sub> K <sub>2</sub> NO <sub>10</sub> V	C <sub>10</sub> H <sub>25 25</sub> K <sub>3</sub> N <sub>2</sub> O <sub>18 25</sub> V <sub>2</sub>
Formula weight	463.40	792.84
Crystal system	monoclinic	monoclinic
Space group	P2(1)/n	P2(1)/c
Unit cell dimensions		
a (Å)	8.9751(4)	13.7167(9) Å
<i>b</i> (Å)	6.9164(5)	11.8426(7) Å
<i>c</i> (Å)	28.2058(13)	18.4105(12) Å
$\beta$ (deg)	93.983(4)	103.065(5)
Volume (Å <sup>3</sup> )	1746.66(17)	2913.2(3)
Z, d (g/cm <sup>3</sup> )	4, 1.762	4, 1.808
$\mu$ (mm <sup>-1</sup> )	1.098	1.156 mm <sup>-1</sup>
F(000)	944	1609
$\theta$ range	3.66-31.24	3.46-39.17
Limiting indices	$-12 \le h \le 12$	$-9 \le k \le 9$
	$-39 \le 1 \le 40$	$-19 \le h \le 24$
	$-16 \le k \le 16$	$-32 \le 1 \le 25$
Reflections	26058/5280	41677/12154
collected/unique		
R <sub>int</sub>	0.0357	0.0788
Data/parameters	5280/287	12154/485
Goodness-on-fit (GOF) on $F^2$	1.135	1.102
Final $R [I > 2\sigma(I)]$	R1 = 0.0492	R1 = 0.0961
	wR2 = 0.1049	wR2 = 0.2087
R (all data)	R1 = 0.0564	R1 = 0.2184
	wR2 = 0.1086	wR2 = 0.2541

<sup>a</sup>All structures determined at T = 100 K using Mo K $\alpha$  radiation ( $\lambda = 0.71$  073 Å). <sup>b</sup>Refinement method, full-matrix least-squares on  $F^2$ .

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Parameter	Bond length (Å)	Parameter	Bond length (Å)
V(1)-O(1)	2.205(2)	V(1)–N(1)	2.259(2)
V(1)–O(2)	2.051(2)	K(1)–O(2)	2.985(2)
V(1)–O(3)	1.888(2)	K(1)–O(6)	2.771(2)
V(1)–O(5)	1.659(2)	K(2)–O(6)	2.700(2)
V(1)–O(6)	1.639(2)	K(2)–O(1)	2.737(2)
Parameter	Angle (°)	Parameter	Angle (°)
O(6)-V(1)-O(3)	99.83(8)	O(6)-V(1)-N(1)	161.53(8)
O(5)–V(1)–O(3)	101.68(8)	O(5)-V(1)-N(1)	89.16(8)
O(6)–V(1)–O(2)	92.95(8)	O(3)–V(1)–N(1)	85.39(7)
O(5)–V(1)–O(2)	91.75(8)	O(2)-V(1)-N(1)	77.13(7)
O(3)–V(1)–O(2)	157.80(8)	O(1)-V(1)-N(1)	75.28(7)
O(6)–V(1)–O(1)	87.30(8)	C(4)-O(1)-V(1)	118.4(2)
O(5)–V(1)–O(1)	161.92(9)	C(5)–O(2)–V(1)	119.5(2)
O(3)–V(1)–O(1)	86.43(7)	V(1)-O(6)-K(1)	110.44(8)
O(2)–V(1)–O(1)	76.05(7)	C(1)-N(1)-V(1)	110.4(1)
V(1)–O(1)–K(2)	96.10(7)	C(2)-N(1)-V(1)	104.6(1)
C(7)-O(3)-V(1)	133.4(2)	C(3)-N(1)-V(1)	110.6(2)
V(1)–O(2)–K(1)	91.96(7)	C(7)–O(3)–V(1)	133.4(2)
V(1)-O(6)-K(2)	114.41(9)	V(1)-O(1)-K(2)	96.10(7)

 Table 2 Selected bond lengths and angle parameters for 1.

 Table 3 Selected bond lengths and angle parameters for 2.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
V(1)-O(1)	2.191(3)	V(2)–O(6')	1.617(3)
V(1)–O(3)	1.860(3)	V(2)–O(2')	2.028(3)
N(1) - V(1)	2.265(4)	V(2)–O(4)	1.925(3)
V(1)-O(2)#3	2.014(3)	V(2)–O(5)	1.924(3)
O(6)-V(1)#7	1.628(3)	V(2)–O(1')	2.028(3)
V(1)-O(5)#8	1.715(3)	N(1')-V(2)	2.329(4)
Parameter	Angle (°)	Parameter	Angle (°)
O(3)-V(1)-O(1)	85.1(1)	O(4)–V(2)–O(2')	152.2(1)
O(2)#3-V(1)-O(1)	80.8(1)	O(1')-V(2)-O(2')	87.3(1)
O(5)#8-V(1)-O(1)	163.5(1)	O(5)-V(2)-O(1')	163.7(1)
O(6)#8-V(1)-O(1)	87.4(1)	O(6')-V(2)-O(1')	92.7(2)
O(1)-V(1)-N(1)	73.6(1)	O(1')-V(2)-N(1')	76.9(1)
O(3)-V(1)-O(2)#3	158.4(1)	O(4)–V(2)–O(2')	152.2(1)
O(2)#3-V(1)-N(1)	78.6(1)	O(2')-V(2)-N(1')	74.5(1)
O(6)#8-V(1)-O(2)#3	93.9(1)	O(6')–V(2)–O(2')	100.0(2)
O(5)#8-V(1)-O(2)#3	91.5(1)	O(5)–V(2)–O(2')	87.6(1)
O(5)#8-V(1)-O(3)	97.7(1)	O(5)-V(2)-O(4)	89.5(1)
O(6)#8-V(1)-O(3)	101.8(1)	O(6')–V(2)–O(4)	107.5(2)
O(6)#8-V(1)-O(5)#8	107.8(2)	O(6')–V(2)–O(5)	103.4(2)
O(3)–V(1)–N(1)	81.7(1)	O(4)-V(2)-N(1')	77.7(1)
O(5)#8-V(1)-N(1)	90.7(1)	O(5)-V(2)-N(1')	86.8(1)
O(6)#8-V(1)-N(1)	160.3(2)	O(6')-V(2)-N(1')	168.3(2)
C(10)-O(4)-V(2)	119.5(2)	C(7)–O(3)–V(1)	129.7(2)
V(1)#7–O(5)–V(2)	134.9(2)		

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The vanadium atom in **1** has a distorted octahedral geometry and is bonded to a tetradentate Hmecah<sup>3–</sup> ligand by the two carboxylate oxygen atoms, the imine nitrogen atom, and the hydroquinone oxygen atom as well as two oxido groups [O(5) and O(6)]. The two *cis* carboxylate and the hydroquinone oxygen atoms, and the oxido groups [O(5)] define the equatorial plane of the octahedron. The vanadium ions form very long bonds with the amine nitrogen, [V–N(1), 2.259(2) Å] and with the carboxylate oxygen atoms, [V–O(1), 2.205(2) Å] due to the *trans* effect from the strong bonded oxido groups O(6) [V=O(6), 1.639(2) Å] and O(5) [V=O(5), 1.659(2) Å], respectively. The V–O<sub>hydroquinone</sub> exhibits significant double-bond character supported from its short length [1.888(2) Å] and the open C(7)–O(3)–V(1) angle [133.4(2)°].

The tetranuclear complex, **2**, has a rectangular-shaped structure with the long sides [7.803(1) Å, distance between vanadium atoms] defined by two *t*butbicah<sup>6–</sup> ligands, and the short sides [3.362(1) Å, distance between vanadium atoms] by two  $V^V$ –O– $V^{VI}$  bridges (Fig. 3). One interesting feature of this molecule is that the two hydroquinones do not overlay one over the other, which is in contrast to the structures of all the other rectangular-shaped vanadium-hydroquinonate/semiquinonate complexes reported to date [25,28].



**Fig. 3** Ball-and-stick representation of the crystal structure of the anion of **2**, emphasizing the rectangle defined by the  $V^{V}$ –O– $V^{IV}$  and the hydroquinone bridges, (A) side view, (B) top view.

Each vanadium ion exhibits a distorted octahedral environment with two *cis* carboxylate and a phenolate oxygen atom and the bridging oxido group to define the equatorial plane, whereas the oxo and the amine nitrogen atom occupy the axial positions. The V<sup>VI</sup>–O–V<sup>V</sup> bridges are asymmetric  $[d(V^V-O) = 1.715(3)$  Å and  $d(V^{IV}-O) = 1.924(4)$  Å] and the V<sup>VI</sup>–O–V<sup>V</sup> angle bend  $[134.9(2)^{\circ}]$ , indicating that the spins are localized [34-41]. The V<sup>V</sup>–O<sub>hydroquinone</sub> bond length [1.860(3) Å] is significantly shorter than the respective V<sup>IV</sup>–O<sub>hydroquinone</sub> distance [1.925(3) Å]. In addition, the V(1)–O(3)–C(7)  $[129.7^{\circ}]$  is larger than the V(2)–O(4)–C(10) angle  $[119.5(2)^{\circ}]$ , revealing the stronger bonding of the vanadium(V) than the vanadium(IV) with the hydroquinonate oxygen. Although the donor atoms at the two binding positions of *t*butbicah<sup>6–</sup> ligands are the same, they provide a different coordination environment to the vanadium ions because of the different size of the O<sub>hydroquinone</sub>…N<sub>amine</sub> chelate ring, five- vs. six-membered chelate rings. The tripod binding site containing the five-membered O<sub>hydroquinone</sub>…N<sub>amine</sub> chelate ring prefers to bind the vanadium(IV), and the six-membered vanadium(V) ions (Scheme 4). These differences have been attributed to steric intra-ring interactions arising from the different V–O<sub>hydroquinone</sub> bond distances and the V–O<sub>hydroquinone</sub>–C angles dependent on the oxidation state of the vanadium atoms.

In addition, the nonstabilization of a *p*-semiquinonate radical in complex **2** is attributed to the  $O_{hydroquinone} \cdots N_{amine}$  five-membered ring. The vanadium(IV) exhibits stronger affinity for the semiquinonate than the hydroquinonate oxygen donor atom and thus, the  $d(V^{IV}-O_{semiquinone})$  are similar to  $d(V^V-O_{hydroquinone})$  and the  $V^{IV}-O_{semiquinone}-C$  angles tend to be larger than the  $V^V-O_{hydroquinone}-C$ 



 $\begin{array}{l} \label{eq:scheme 4} \textbf{Scheme 4} Drawings of the structures of 2 and the bicah^{6-} mixed-valent semiquinonate complex $$ [\{V^{IV}O(O)V^{IV}O\}_2\{bicah\}\}^{5-}$ [25], showing the tripod binding site preference to ligate $V^{IV}$-$O_{semiquinonate}$ or $V^V$-$O_{hydroquinonate}$ (six-membered ring) vs. the $V^{IV}$-$O_{hydroquinonate}$ (five-membered ring). } \end{array}$ 

angles [23]. Apparently, the intra-ring sterics in the five-membered  $O_{hydroquinone} \cdots N_{amine}$  ring do not favor the formation of the *p*-semiquinonate radical. In this concept, the 2,5-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]hydroquinone (H<sub>6</sub>bicah) ligand containing six-membered rings in both binding sites stabilizes the *p*-semiquinonate radical through ligation with vanadium(IV) ions (Scheme 4) [25].

The highly negative charged anions, **1** and **2**, attract strongly the positive ions. The oxido group [O(5)] and the carboxylate oxygen atoms form extensive dipole-ionic bonds with the K<sup>+</sup> counterions and the co-crystallized water molecules. The result is the creation of polymeric dipole-ionic-bonded supramolecular 2D and 3D structures by self-assembly of the mononuclear or tetranuclear anions and the K<sup>+</sup> counterions. Complex **1** forms 2D layers, parallel to the plane defined by the axes *a* and *b*, each one constructed from K<sup>+</sup> ions covered from both sides of the layer from the anions of the complex connected together with strong K<sup>+</sup>···O bonds (Fig. 4). Some of the stronger bonds include the K(1)–O(6) [2.771(2) Å], K(2)–O(6) [2.700(2) Å], K(1)–O(12) [2.688(2) Å], K(2)–O(11) [2.714(2) Å], and K(2)–O(1) [2.737(2) Å].



**Fig. 4** Ball-and-stick representation of the crystal structure of **1**, viewed along the *b*-axis, showing two 2D layers; each one is consisted from mononuclear vanadium(IV) anions connected through dipole–ionic interactions with potassium counter cations and water molecules.

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Complex 2 also exhibits a similar layered structure along the bc plane. However, the K<sup>+</sup> layers are bridged together through dipole–ionic bonds with the carboxylate oxygen and the oxido groups of both sides of the tetranuclear units resulting in a 3D layered network (Fig. 5).



**Fig. 5** Ball-and-stick representation of the crystal structure of 2, viewed along the *b*-axis, showing the layers of the tetranuclear vanadium(IV/V) anions connected through dipole–ionic interactions with K<sup>+</sup> counter cations – water layers.

#### EPR characterization in aqueous solution

The continuous wave (cw) X-EPR spectrum of **2** shows the presence of two different environments around vanadium ion that are reversibly interconverted to each other by varying the pH (Fig. 6). These two different environments have been identified, at high pH, to be that found in the crystal structure consisting of the two carboxylate  $[-C(O)O^-]$ , the hydroquinonate  $[HQO^-]$ , and the bridging oxygen atoms  $[-O_-]$ , and at low pH to the same environment having the hydroquinonate oxygen atom protonated [HQOH]. The hydroquinone oxygen atom [O(4)] is more accessible to protonation than the rest of the



**Fig. 6** Cw X-Band EPR spectra of frozen (130 K) aqueous solutions of **2** (1.6 mM) at various pH from 2.0 up to 8.9.

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donors [42,43] and exhibits higher basicity from [O(3)] as this is evident from the crystallographic data. The cw X-EPR experimental and the simulated spectra of frozen aqueous solutions of **2** at pH 2.0 and 8.9 are shown in Fig. 7. Each of the anisotropic spectra are consisted from 16 lines, indicating that the complex is valence-localized, which is in accordance with the 0.21 Å difference of the bridging oxygen–vanadium bond lengths in the  $V_2O_3^{3+}$  core [44]. The best fitting of the experimental spectra with the simulation gave at pH = 2.0  $g_{\perp} = 1.978$ ,  $g_{\parallel} = 1.936$ ,  $A_{\perp} = -69.7 \times 10^{-4}$  cm<sup>-1</sup> and  $A_{\parallel} = -178.8 \times 10^{-4}$  cm<sup>-1</sup> and for the spectra at pH = 8.9  $g_{\perp} = 1.976$ ,  $g_{\parallel} = 1.939$ ,  $A_{\perp} = -57.7 \times 10^{-4}$  cm<sup>-1</sup>, and  $A_{\parallel} = -168.7 \times 10^{-4}$  cm<sup>-1</sup>. The p $K_a$  values (7.7 ± 0.2 and 3.2 ± 0.2) of the two successive protononation steps of **2** were calculated from the UV–vis spectra in pH range 2.4–8.9 (Fig. 8).

The additivity relationship [45] allows the prediction of the hyperfine coupling constant  $A_{\parallel}$ , which is correlated to the number and types of ligands present in the equatorial plane. As this has been reviewed by Pecoraro [46], the hyperfine coupling constant also depends on the degree of the geometric distortion. From the donor atoms of the current study the contribution of the hydroquinone oxygen atom is not known. However, it may be considered that HQO<sup>-</sup> contributes similarly to the phenolate oxygen (38.  $6 \times 10^{-4} \text{ cm}^{-1}$ ) or the OH<sup>-</sup> (38.7  $\times 10^{-4} \text{ cm}^{-1}$ ) and the HQOH similar to H<sub>2</sub>O (45.7  $\times 10^{-4} \text{ cm}^{-1}$ ). The contribution of -O- is more difficult to be predicted because the various model compounds exhibit different V-O<sub>bridged</sub> bond strength and electron spin delocalization. For example, making the above considerations, a 44.7  $\times 10^{-4} \text{ cm}^{-1}$  contribution has been calculated for the -O- in complex 2 at pH 8.9. Other complexes containing spin-localized {V<sub>2</sub>O<sub>3</sub>}<sup>3+</sup> cores gave for the -O- even higher contributions up to  $\sim 53 \times 10^{-4} \text{ cm}^{-1}$  [37].

However, the  $10 \times 10^{-4}$  cm<sup>-1</sup> change of  $A_{\parallel}$  upon protonation of the HQO<sup>-</sup> is close to the  $A_{\parallel}$  change observed for the conversion of the OH<sup>-</sup> ligand to H<sub>2</sub>O (~7 × 10<sup>-4</sup> cm<sup>-1</sup>), considering that the –O– contributes the same in both low and high pH coordination environments.



**Fig. 7** Cw X-Band EPR spectra of frozen (130 K) aqueous solutions of **2** (1.6 mM) at pH 2.0 and 8.9 (solid black lines) and simulated spectra (red dashed lines). The parameters used for the spectra simulation are: at pH = 2.0  $g_{\perp}$  = 1.978,  $g_{\parallel}$  = 1.936,  $A_{\perp}$  = -69.7 × 10<sup>-4</sup> cm<sup>-1</sup>,  $A_{\parallel}$  = -178.8 × 10<sup>-4</sup> cm<sup>-1</sup> and at pH = 8.9  $g_{\perp}$  = 1.976,  $g_{\parallel}$  = 1.939,  $A_{\perp}$  = -57.7 × 10<sup>-4</sup> cm<sup>-1</sup>,  $A_{\parallel}$  = -168.7 × 10<sup>-4</sup> cm<sup>-1</sup>.

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Fig. 8 UV-vis spectra of 2 (0.35 mM) in 0.1 M KCl aqueous solution at pH 2.43-8.85.

#### CONCLUSIONS

One vanadium(V) mononuclear complex and a tetranuclear mixed-valent vanadium(IV/V) complex have been synthesized by reacting NaVO<sub>3</sub> with the tripod hydroquinone-iminodiacetate ligands H<sub>4</sub>mecah and H<sub>4</sub>tbutcah. The crystallographic characterization of the complexes reveals that the *tert*-butyl- ligand has been further substituted by an iminodiacetate group resulting in the bifunctional *t*butbicah<sup>-6</sup>. EPR spectra at different pH show that the tetranuclear complex is stable at a pH range 2–8.9, and the hydroquinonate oxygen atoms which ligate the vanadium(IV) ions are reversibly protonated at low pH. In contrast to other reported binucleating ligands exhibiting the same donor atoms, this molecule does not stabilize the semiquinone oxidation state by ligating vanadium(IV). This has been attributed to intra-ring strains originated from the smaller-size O<sub>hydroquinone</sub>····N<sub>amine</sub> chelating ring, five- vs. six-membered.

#### **EXPERIMENTAL SECTION**

#### Physical measurements

Fourier transform-infrared (FT-IR) transmission spectra of the compounds, pressed in KBr pellets, were acquired on a Shimadzu IRprestige-21 spectrophotometer model. Microanalyses for C, H, and N were performed by a Euro-Vector EA3000 CHN elemental analyzer. NMR spectra were recorded on a 300 MHz Avance Bruker spectrophotometer. The cw X-band EPR spectra of compound **2** were measured on an ELEXSYS E500 Bruker spectrometer at resonance frequency ~9.5 GHz and modulation frequency 100 MHz. Frozen aqueous solutions of **2** were measured at 130 K. The resonance frequency was accurately measured with solid DPPH (g = 2.0036). The optimization of the spin Hamiltonian parameters and EPR data simulation was performed by using the software package easyspin 4.0.0 [47].

The  $pK_a$  values of the two protonation steps of **2** were determined by UV–vis spectrophotometric titration and estimated according to the model proposed by the computational program PSQUAD [48]. The data were fitted assuming the following two equilibriums 1, 2.

$$[\{V^{V}O(\mu-O)V^{IV}O\}\{\mu-t butbicah(-6)\}]_{2}^{6-} + H^{+} \rightleftharpoons$$

$$H[\{V^{V}O(\mu-O)V^{IV}O\}\{\mu-t butbicah(-6)\}]_{2}^{5-}$$
(1)

$$H[\{V^{V}O(\mu-O)V^{IV}O\}\{\mu-tbutbicah(-6)\}]_{2}^{5-} + H^{+} \rightleftharpoons$$

$$H_{2}[\{V^{V}O(\mu-O)V^{IV}O\}\{\mu-tbutbicah(-6)\}]_{2}^{4-}$$
(2)

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All potentiometric titrations were performed three times in the pH range 2.4–8.9. The single-crystal X-ray intensity data for all compounds were measured employing an XCalibur III 4-cycle diffractometer, equipped with a CCD camera detector, using a monochromatized Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation at 100 K. In all cases, analytical absorption corrections were applied. The structures were solved by direct methods using the program SHELX-97 and refined on  $F^2$  by a full-matrix least-squares procedure with anisotropic displacement parameters for all the non-hydrogen atoms based on all data minimizing w $R = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w|F_o|^2]^{1/2}$ ,  $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ , and GOF =  $[\Sigma [w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$ ,  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$  [49,50]. A summary of the relevant crystallographic data and the final refinement details are given in Table 1. The positions of hydrogen atoms were calculated from stereochemical considerations and kept fixed isotropic during refinement or found in DF map and refined with isotropic thermal parameters.

### Synthesis of 2-[N,N'-(carboxymethyl)aminomethyl]-5-methylhydroquinone, H₄mecah

Iminodiacetic acid (5.00 g, 37.5 mmol), paraformaldehyde (1.24 g, 41.3 mmol), and NaOH (3.00 g, 75.0 mmol) were dissolved in a mixture of  $H_2O$  (5 mL) and  $CH_3OH$  (2 mL) under Ar atmosphere. A solution of methylhydroquinone (4.66 g, 37.5) in methanol (9 mL) was added to the above solution under continued Ar flow. The resulting orange solution was stirred for 24 h resulting in the precipitation of a light-pink precipitate. Acetone (10 mL) was added to the above mixture. The solid was collected by filtration and redissolved in  $H_2O$  (10 mL) under Ar atmosphere, and the pH was adjusted at ~4 by addition of HCl (6 M). The mixture was cooled at 4 °C overnight resulting in the formation of a light-pink precipitate. The solid was recrystallized by warm  $H_2O$  (25 mL, 45 °C). The off-pink crystalline solid was isolated by filtration and dried under vacuum yielding 6.5 g (64 %) of product. Elemental analysis calc'd. (%) for  $C_{12}H_{15}NO_6$  (269.25): C 53.53, H 5.62, N 5.20; found: C 53.22, H 5.73, N 5.11. <sup>1</sup>H NMR  $\delta(D_2O)$ : 6.68 (2H, s), 4.29 (2H, s), 3.69 (4H, s), 2.05 (3H, s).

# Synthesis of 2-[N,N'-(carboxymethyl)aminomethyl]-5-*tert*-butylhydroquinone, H<sub>4</sub>*t*butcah

Iminodiacetic acid (5.00g, 37.5 mmol), paraformaldehyde (1.24 g, 41.3 mmol) and NaOH (3.00 g, 75.0 mmol) were dissolved in a mixture of  $H_2O$  (5 mL) and  $CH_3OH$  (2 mL) under Ar atmosphere. A solution of *tert*-butylhydroquinone (6.24 g, 37.5 mmol) in methanol (9 mL) was added to the above solution under continued Ar flow. The resulting orange solution was stirred for 24 h resulting in the precipitation of a light-pink precipitate. Acetone (10 mL) was added to the above mixture. The solid was collected by filtration and redissolved in  $H_2O$  (10 mL) under Ar atmosphere and the pH was adjusted at ~4 by addition of HCl (6 M). The solution was evaporated under vacuum. The yellowish oily residue was treated with acetone (30 mL) at 4 °C resulting a light-pink solid. The solid was recrystallized by warm  $H_2O$  (25 mL, 45 °C). The off-pink crystalline solid was isolated by filtration and dried under vacuum yielding 6.0 g (51 %) of product. Elemental analysis calc'd. (%) for  $C_{15}H_{21}NO_6 \cdot H_2O$  (329.35): C 54.70, H 7.04, N 4.25; found: C 54.49, H 7.11, N 4.21. <sup>1</sup>H NMR  $\delta(D_2O)$ : 6.80 (1H, s), 6.67 (1H, s), 4.29 (2H, s), 3.73 (4H, s), 1.22 (9H, s).

# Synthesis of K<sub>2</sub>[V<sup>V</sup>(O)<sub>2</sub>{Hmecah(-3)}]·2H<sub>2</sub>O, 1

 $H_4$ mecah (0.39 g, 1.4 mmol) was dissolved in  $H_2O$  (5 mL) by the dropwise addition of KOH (3 M, aqueous solution) until pH was ~3.5. Aqueous solution of KVO<sub>3</sub> (0.10 g, 0.72 mmol in 2.6 mL  $H_2O$ ) was added resulting in a dark orange–brown solution (pH ~ 7). The pH was adjusted at 8.2 by the addition of KOH (3 M, aqueous solution). The solution was filtered and ethanol was layered over the filtrate. During the slow solvent diffusion, brown single crystals suitable for X-ray analysis were developed between the layers. The crystals were isolated by filtration. The yield was 0.20 g (31%). Elemental

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analysis calc'd. (%) for  $C_{12}H_{12}NO_8K_2V\cdot 2H_2O$  (463.39): C 31.10, H 3.48, N 3.02; found: C 30.98, H 3.52, N 2.99. <sup>1</sup>H NMR  $\delta(D_2O)$ : 6.80 (1H, s), 6.67 (1H, s), 4.29 (2H, s), 3.73 (4H, s), 1.22 (9H, s).

# Synthesis of $K_{6}[\{V^{V}O(\mu-O)V^{IV}O\}\{\mu-tbutbicah(-6)\}]_{2}$ , 10.5H<sub>2</sub>O, 2

 $H_4$ *t*butcah (0.44 g, 1.4 mmol) was dissolved in  $H_2O$  (5 mL) by the dropwise addition of KOH (3 M, aqueous solution) until pH was ~4.0. Aqueous solution of KVO<sub>3</sub> (0.200 g, 1.45 mmol in 5.3 mL  $H_2O$ ) was added resulting in a dark orange–brown solution (pH ~ 8). The pH was adjusted at 8.2 with the addition of KOH (3 M, aqueous solution). The solution was filtered, and ethanol was layered over the filtrate. During the slow solvent diffusion, brown single crystals suitable for X-ray analysis were developed between the layers. The crystals were isolated by filtration. The yield was 0.18 g (16 %). Elemental analysis calc'd. (%) for  $C_{38}H_{39}N_4O_{26}K_6V_4 \cdot 10.5H_2O$  (1595.24): C 28.61, H 3.79, N 3.51; found: C 28.49, H 3.85, N 3.43.

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