Inorganica Chimica Acta 420 (2014) 103–111

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Synthesis, characterization of dinuclear vanadium(III) hydroquinonate–iminodiacetate complexes

Chryssoula Drouza [a,*], Manolis Vlasiou [b], Anastasios D. Keramidas [b,*]

[a] Department of Agricultural Sciences, Biotechnology and Food Science, Cyprus University of Technology, Lemesos 3036, Cyprus
[b] Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

ARTICLE INFO

Article history:
Available online 8 January 2014
Recent Advances in Vanadium Chemistry
Special Issue

Keywords:
Vanadium
Hydroquinone
Crystal structure
EPR
Electrochemistry
Iminodiacetic acid

ABSTRACT

A new V^{III} complex (**1**) of 2,5-bis[N,N-bis(carboxymethyl)aminomethyl]hydroquinone ($bicah^{6-}$) was synthesized by reaction of H_6bicah with two equivalents of VCl_3 and six equivalents of base in aqueous solution. Crystallographic characterization shows the neutral complex to have a dinuclear hydroquinonate bridged structure. The octahedral environment of vanadium is occupied by the four (N, O, O, O) donor atoms in each binding site of the ligand and two H_2O oxygen atoms. Addition of 2,2-bipyridine (bipy) in the reaction mixture resulted in the synthesis of a new dinuclear V^{III}-μ-$bicah^{6-}$ complex (**2**) containing a bipy chelated to each vanadium center. The structure of **1** was compared with the respective dinuclear structures of the $bicah^{6-}$ complexes with $V^{IV}O^{2+}$ (**3**) and $V^{V}O_2^{+}$ (**4**). Strong hydrogen bonds between the free, the ligated to vanadium water molecules and the carboxylate and hydroquinonate oxygen atoms result in supramolecular 3D structures by self-assembly of the dinuclear units. These structures are controlled by synthesis conditions and vanadium ion coordination environment. The cyclic voltammogram of **1** showed a reversible $V^{IV} + e^- \leftrightharpoons V^{III}$ process at 0.48 V versus NHE. The EPR spectra of **3** gave a broad peak indicating magnetic interactions between the uncoupled electrons of the two vanadium centers through the hydroquinone bridge. In acidic pHs bellow 2.0, EPR data reveal protonation of the hydroquinonate oxygen and hydrolysis of the complex. The relation of these results with the reduction of V^{IV} and stabilization of V^{III} ions is discussed.

1. Introduction

Vanadium(III) (V^{III}) chemistry has attracted much attention of the scientists in recent years [1–3] because of the presence of V^{III} in marine fanworm *pseudopotamilla occelata* [4] and in *ascidians* [5], the antidiabetic [6–9] and anticancer [10–12] properties of V^{III} complexes as well as the magnetic properties of V^{III} clusters [13–17] and the C–H activation catalytic properties [18–20].

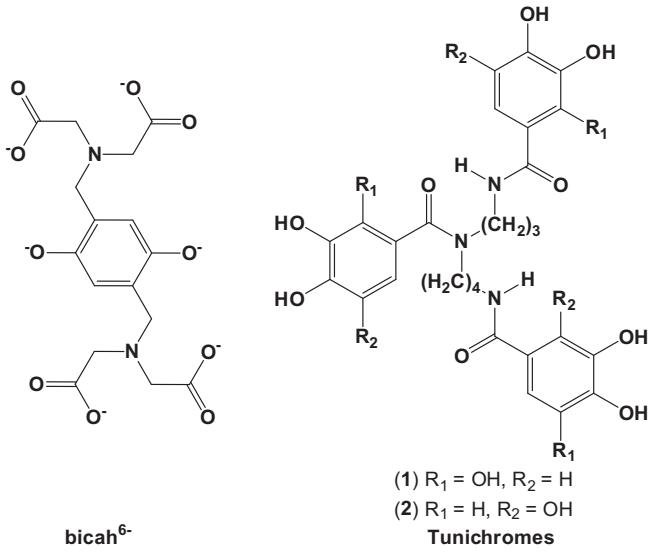
V^{III} is readily oxidized under aerobic conditions to VO^{2+} and thus, the aqueous chemistry of V^{III} has been investigated far less than the corresponding aqueous chemistry of vanadium(IV) (V^{IV}) and vanadium(V) (V^{V}) ions. Despite of the redox instability of V^{III}, marine organisms are able to take up vanadium from the sea water as vanadate, then reduce V^{V} to V^{IV} and finally stabilize vanadium as V^{III} at highly acidic conditions (pH ~ 2) [21–25]. The mechanism for the reduction of V^{IV} to V^{III} is still under debate. This reduction process might proceed via a V^{IV}, more likely via a non-oxo V^{IV} intermediate species, probably formed because of the weakening of the V^{IV}=O bond in the strongly acidic environment of the *ascidians*' blood cells. Spontaneous reduction of V^{IV} model complexes supports this mechanism [26–28]. Tunichromes (Scheme 1), a group of phenol-rich organic molecules, present in high concentrations in the blood cells of *ascidians*, may play a role in the reduction of V^{IV} to V^{III}. In addition, aminocarboxylate donor atoms have been suggested to provide an environment in proteins suitable for the stabilization of V^{III} [21,23,29,30].

The investigation of the interaction of vanadium ions with phenol redox active ligands, also referred to as "noninnocent", provide important information for the better understanding of the mechanisms of these redox processes in biological systems [31–40]. *p*-hydroquinones are key molecules in several redox biological processes and recently it has been shown that the oxidation state of vanadium in complexes with hydroquinone derivatives can be controlled by the pH or the temperature [41,42].

Here in, we report the first examples of crystallographically characterized dinuclear V^{III} hydroquinonate complexes. Up to now only one example of a V^{III}-hydroquinonate polymeric compound has been reported in the literature [43,44]. With this work a series of dinuclear complexes of vanadium in oxidation states III (**1**, **2**), IV (**3**) and V (**4**) with the ligand 2,5-bis[N,N-bis(carboxymethyl)aminomethyl]hydroquinone ($bicah^{6-}$) (Scheme 1) is completed. Direct comparison of the crystal structures of these

* Corresponding authors. Tel.: +357 22892764; fax: +357 22895454.
E-mail addresses: chryssoula.drouza@cut.ac.cy (C. Drouza), akeramid@ucy.ac.cy (A.D. Keramidas).

0020-1693/$ - see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ica.2013.12.033



Scheme 1. Drawing of the ligand bicah^{6-} and of tunichromes.

compounds provide an insight of the vanadium-hydroquinone bonding versus the vanadium oxidation states. The iminodiacetate chelate group has been selected to stabilize the V^{III}-hydroquinone coordination and the oxidation of V^{III} to V^{IV} from the air as well as to mimic the environment around the metal ion in vanadium reductase in *ascidians* [21]. In order to correlate the activity of the proteins with the properties of the model compounds the redox properties of V^{III} and the respective VO^{2+}–μ-bicah^{6-} complexes in acidic aqueous solutions were investigated by cyclic voltammetry. In addition, the EPR investigation of a stepwise acidified solution of **3** revealed protonation of the hydroquinonate oxygen and hydrolysis of the complex. Finally, the role of the synthesis conditions and the co-ligands in the formation of defined 3D hydrogen bonded structures of the V^{III} dinuclear complexes has been explored.

2. Experimental

Reagent grade hydroquinone, iminodiacetic acid, 2,2′-bipyridine (bipy), $VO(SO_4)\cdot 4.5H_2O$, Na_2CO_3, guanidinium carbonate ($Guan_2CO_3$) and VCl_3 were purchased from Aldrich. All chemicals were used without further purification. $VOCl_2$ and 2,5-bis[N,N-bis(carboxymethyl)aminomethyl]hydroquinone (H_6bicah) were synthesized as previously described by Drouza et.al [42,45]. UV spectra were recorded on a Schimadzu UV-1601 Spectrophotometer. Microanalyses for C, H, and N were performed by a Euro–Vector EA3000 CHN elemental analyzer. Magnetic measurements were carried out on an MK1 MB magnetic susceptibility balance. All synthesis, compound handling and solution measurements were performed under an Ar atmosphere.

2.1. Synthesis of $[V^{III}_2(\mu\text{-bicah})_2(H_2O)_4]\cdot 13H_2O$ (**1a**)

H_6bicah (0.57 g, 1.3 mmol) was dissolved in 10 mL H_2O with the addition of Et_3N (0.80 g, 7.9 mmol). The solution was heated to boil under continuous bubbling with Ar for 5 min. Then the heating was stopped and solid VCl_3 (0.41 g, 2.6 mmol) was added. The solution turned to brown (pH ~ 2.6) and kept at 4 °C for three days. A brown crystalline precipitate was formed. The solid was filtered off and dried. The yield was 0.51 g (55%). *Anal.* Calc. for $C_{16}H_{48}N_2O_{27}V_2$: C, 23.95; H, 6.03; N, 3.49. Found: C, 23.87; H, 6.11; N, 3.42%. IR (KBr) 3248 (s, υ(O–$H_{free\ H2O}$)), 3073 (s, υ(O–$H_{ligated\ H2O}$)), 2973, 2937, 2924 (w, υ(C–H)), 1606 (vs υ(C=O)), 1479 (s), 1457 (m), 1447 (m), 1431 (s), 1415 (m), 1384 (s), 1356 (s), 1332 (s), 1260 (m), 1221 (m), 1199 (m, υ($C_{hydroquinone}$–O)), 1165 (m), 1110 (m), 1081 (w), 1019 (m), 957 (m), 948 (w), 942 (m), 912 (m), 897 (m), 865 (s), 802 (s), 743 (m), 726 (m), 677 (s), 614 (m), 567 (s), 551 (s), 499(m), 450 (w), 404 (m). ^{1}H NMR δ (H_2O) (ppm): 8.24 (s, 2H, H53). Single crystals suitable for single crystal X-ray analysis was obtained following the same procedure for 6-fold diluted solutions.

2.2. Synthesis of $[V^{III}_2(\mu\text{-bicah})_2(H_2O)_4]\cdot H_2O$ (**1b**)

H_6bicah (0.20 g, 0.46 mmol) was dissolved in 5 mL H_2O with the addition of Na_2CO_3 (0.15 g, 1.4 mmol). The solution was heated to boil under continuous bubbling with Ar for 5 min. Then the heating was stopped and solid VCl_3 (0.15 g, 0.95 mmol) was added. The solution turned to brown. Acetone (5 mL) was layered over the solution and kept at 4 °C for three days. Brown crystals suitable for single crystal X-ray analysis were formed. The crystals were filtered off and dried under vacuum. The yield was 0.10 g (37%). *Anal.* Calc. for $C_{16}H_{24}N_2O_{15}V_2$: C, 32.78; H, 4.13; N, 4.78. Found: C, 32.51; H, 4.30; N, 4.62%.

2.3. Synthesis of $[V^{III}_2(\mu\text{-bicah})_2(bipy)_2]\cdot 4H_2O$ (**2**)

H_6bicah (0.20 g, 0.46 mmol) was dissolved in 5 mL H_2O with the addition of Na_2CO_3 (0.15 g, 1.4 mmol). The solution was heated to boil under continuous bubbling with Ar for 5 min. Then the heating was stopped and solid VCl_3 (0.15 g, 0.95 mmol) was added. Then bipy (0.15 g, 0.96 mmol) dissolved in acetone (1 mL) was added and the brown solution was turned to red. The solution was kept at 4 °C for two days. Red crystals suitable for single crystal X-ray analysis were precipitated out. The crystals were filtered off and dried under vacuum. The yield was 0.25 g (62%). IR (KBr) 3232 (s, υ(O–$H_{free\ H2O}$)), 3080 (s, υ(O–$H_{ligated\ H2O}$)), 3080, 2989, 2924 (w, υ(C–H)), 1658 (vs υ(C=O)), 1600 (s, υ(C–C)), 1473 (s), 1441 (s), 1421 (s), 1383 (s), 1341 (s), 1311 (s), 1215 (m), 1195 (m, υ($C_{hydroquinone}$–O), 1161 (w), 1049 (w), 1016 (w), 1011 (w), 969 (w), 930 (m), 902 (m), 884 (m), 862 (s), 794 (m), 763 (s), 733 (s), 668 (m), 621 (m), 539 (s), 495(m), 411 (m). *Anal.* Calc. for $C_{36}H_{38}N_6O_{14}V_2$: C, 49.10; H, 4.35; N, 9.54. Found: C, 49.02; H, 4.38; N, 9.49%.

2.4. Synthesis of $Guan_2[V^{IV}_2O_2(\mu\text{-bicah})_2(H_2O)_2]\cdot 7H_2O$ (**3**)

H_6bicah (0.20 g, 0.46 mmol) was dissolved in 5 mL H_2O with the addition of $Guan_2CO_3$ (0.08 g, 0.46 mmol). The solution was heated to boil under continuous bubbling with Ar for 5 min. Then the heating was stopped, the solution was cooled at room temperature and $VOCl_2$ (1.3 mL of 0.75 M freshly prepared acetonitrile solution, 0.98 mmol) was added. The pH of the deep blue-green solution was adjusted to 2.4 using 1 M HCl. Ethanol (5 mL) was added, and the solution was kept at −18 °C for four days. A blue-green precipitate was formed. The solid was filtered off washed with ethanol and dried under vacuum. The yield was 0.22 g (59%)%). IR (KBr) 3400 (s, brm υ(O–$H_{free\ H2O}$, N–H)), 3173 (s, υ(O–$H_{ligated\ H2O}$)), 2950, 2917 (w, υ(C–H)), 1606 (vs υ(C=O)), 1496 (w), 1383 (s), 1318 (m), 1257 (w), 1202 (m, υ($C_{hydroquinone}$–O), 1128 (m), 1041 (w), 1014 (w), 959 (vs υ(V=O)), 904 (s), 858 (w), 781 (w), 732 (m), 714 (m), 610 (m), 561 (s), 481(s). *Anal.* Calc. for **1**, $C_{18}H_{44}N_8O_{21}V_2$: C, 26.68; H, 5.47; N, 13.83, Found: C, 26.57; H, 5.44; N, 13.70%.

2.5. X-ray crystallography

Crystal structure refinement data of **1a**, **1b** and **2** are provided in Table 1. The intensity data for all the complexes were collected on a XCalibur SuperNova 4-cycle diffractometer, equipped with a CCD