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Unexpected reduction of vanadium(IV) to vanadium(III) in the presence of the chelate ligands 2,2′-bipyridine (bpy) and 1,8-hydroxyquinoline (Hquin)

Manolis J. Manos,[a] Anastasios J. Tasiopoulos,[a] Catherine Raptopoulou,[b] Aris Terzis,[b] J. Derek Woollins,[c] Alexandra M. Z. Slawin,[c] Anastasios D. Keramidas[d] and Themistoklis A. Kabanos *[a]

[a] *Department of Chemistry, Section of Inorganic and Analytical Chemistry, University of Ioannina, 45110 Ioannina, Greece. E-mail: tkampano@cc.uoi.gr*
[b] *NCPS Demokritos, Institute of Material Science, Agia Paraskevi 15310, Attiki, Greece*
[c] *Department of Chemistry, University of St. Andrews, St. Andrews, Fife, UK KY16 9ST*
[d] *Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus*

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The structures, NMR spectra and electrochemical properties of the vanadium(III) compounds, *cis*-[$V^{III}Cl_2$(acac)(bpy)] and [V^{III}(quin)$_3$]·2CH_3OH, formed from [$V^{IV}Cl_2$(acac)$_2$]·0.25CH_2Cl_2 (Hacac = pentane-2,4-dione) and [$V^{IV}OCl_2$(thf)$_2$] with bpy and Hquin respectively are described as well as the structure of the catecholate dioxovanadium(V) dimer [Et_3NH]$_2$[VO_2(μ-dtbc)]$_2$ (H_2dtbc = 3,5-di-*tert*-butylcatechol).

Vanadium is accumulated as vanadium(III) in certain species of tunicates (ascidians) at levels up to 10^6 times that present in their marine environment.[1,2] Although the existence of vanadium in blood cells of ascidians was discovered about 90 years ago,[3] many questions remain unanswered. One of these questions is related to the mechanism of reduction of vanadium(V), which is present in sea water, to vanadium(III) in the blood cells of tunicates. A successive one-electron reduction *via* vanadium(IV) would be a more favourable pathway for the *in vivo* reduction system utilized by ascidians than the one-step two-electron reduction of vanadium(V).[4] Vanadium(V) can be easily reduced to vanadium(IV) by a number of biological reducing agents, such as ascorbate,[5] cysteine,[6] glutathione,[7] NADPH,[8] *etc.*

A literature survey revealed, surprisingly, the reduction, without heat or catalyst, of only two vanadium(IV) compounds to the vanadium(III) species. Namely compound [$V^{IV}O$(acac)$_2$] is reduced by H_2dtbc to [V^{III}(dtbsq)$_3$][9] (Hdtbsq = 3,5-di-*tert*-butylsemiquinone) and by pyrogallol (1,2,3-trihydroxybenzene) to a pyrogallol-bridged V^{III} dimer, {(acac)$_4V_2^{III}$[μ-OC_6H_3-(OH)$_2$]$_2$},[10] and the compound [$V^{IV}O$(salen)] [H_2salen = bis(salicylidene)ethylenediamine] disproportionates, in the presence of acid, to a vanadium(III) species and to [V^VO-(salen)]$^+$,[11] but as yet only the pyrogallol-bridged vanadium(III) derivative has been structurally characterized.

Herein we describe the synthesis, structural and physicochemical characterization of the products of reduction of [$V^{IV}Cl_2$(acac)$_2$]·0.25CH_2Cl_2[12a] and [$V^{IV}OCl_2$(thf)$_2$][12b] by bpy and Hquin respectively, in very high yields (60–80%), namely: *cis*-[$V^{III}Cl_2$(acac)(bpy)] and [V^{III}(quin)$_3$]·2CH_3OH. The crystallographic characterization of the first dioxo–catecholate–vanadium(V) compound, [Et_3NH]$_2$[V^VO_2(μ-dtbc)]$_2$, which resulted from the oxidation of an acetonitrile solution containing *cis*-[$V^{III}Cl_2$(acac)(bpy)] (1 mmol), H_2dtbc (1 mmol) and Et_3N (2 mmol), is also reported.

The mononuclear olive-green compound *cis*-[$V^{III}Cl_2$-(acac)(bpy)]† was prepared by adding solid bpy (1.6 mmol) into a suspension of [$V^{IV}Cl_2$(acac)$_2$]·0.25CH_2Cl_2[12a] (1.6 mmol) in acetonitrile (10 ml), while the mononuclear brown compound [V^{III}(quin)$_3$]·2CH_3OH† was prepared by adding solid [$VOCl_2$(thf)$_2$][12b] (3.5 mmol) into a methyl alcohol (5 ml) solution containing Hquin (10.5 mmol) and Et_3N (17.5 mmol). Vapour diffusion of diethyl ether, at 4 °C, into an acetonitrile solution containing *cis*-[$V^{III}Cl_2$(acac)(bpy)] (1 mmol), H_2dtbc (1 mmol) and Et_3N (2 mmol) resulted in the formation of deep-red crystals of [Et_3NH]$_2$[VO_2(μ-dtbc)]$_2$.† Oxidation of [V^{III}(quin)$_3$]·2CH_3OH in CH_2Cl_2 with $AgSbF_6$ gave [V^{IV}(quin)$_3$]SbF_6† in 80% yield.

An ORTEP[13] structural plot for *cis*-[VCl_2(acac)(bpy)]·CH_3COCH_3‡ is presented in Fig. 1A. The coordination environment about the vanadium atom is distorted octahedral, involving the oxygen atoms from acac$^-$, two *cis*-chlorines and the nitrogen atoms from bpy. The V–Cl(1) bond length [2.333(3) Å] is substantially longer (*ca.* 0.1 Å) than the V–Cl(2) bond length [2.233(3) Å] as a consequence of the strong *trans* influence of the carbonyl oxygen O(2). The V–Cl(2) bond length constitutes the shortest V–Cl distance so far reported for octahedral vanadium(III) species.[14,15] The bond lengths to N(1) [2.142(6) Å] and N(2) [2.140(5) Å], the pyridine nitrogens, as well as the length of the V^{III}–O bonds to the pentane-2,4-dionate ligand (average V^{III}–O distance 1.973 Å) are in the usual range.[14–17]

Compound [Et_3NH]$_2$[V^VO_2(μ-dtbc)]$_2$‡ is a non-centrosymmetric dimer (Fig. 1B). Each metal has a distorted square pyramidal geometry with two *cis* terminally bonded oxo groups occupying two sites. Adjacent vanadium atoms are bridged by the oxygen atoms of two catecholate ligands. The bridging catecholate ligands are chelated to one metal and bridge to the second. The mean C–O and C–C bond distances of 1.36 and 1.37 Å respectively are indicative of catecholate coordination.[9,18] The central vanadium atom in [V^{III}(quin)$_3$]·0.5CH_3OH‡ (Fig. 1C) is octahedrally coordinated by a meridional arrangement of three N and three O atoms. The molecular structure of [V^{III}(quin)$_3$]·0.5CH_3OH is very similar to its isostructural Cr^{III},[19a] Mn^{III}[19b] and Fe^{III}[19c] analogues. The *d*(V–N) of the two *trans*-nitrogens, N(1)/N(11), is ≈2.12 Å, while the *d*(V–O) of the two *trans*-oxygens O(18)/O(28) is ≈1.95 Å. The bond length to N(21) [2.164(2) Å] is substantially longer than the V–N(1/11) bond distances as a consequence of the strong *trans*-influence of the phenolate oxygen O(8), which has a very short V–O bond distance of 1.918(2) Å.

The ^1H-NMR spectra of the CD_2Cl_2 solutions of the vanadium(III) complexes *cis*-[$V^{III}Cl_2$(acac)(bpy)] and [V(quin)$_3$]·2CH_3OH (Fig. 2) exhibit broadening and shifting of the resonances, in the range of +60 to −60 ppm, due to the unpaired electron density at the vanadium nucleus. The aromatic protons of both V(III) complexes display an alternative shift pattern, characteristic of contact shifts, resulting from spin delocalization onto the aromatic ligands (bpy or quin$^-$)

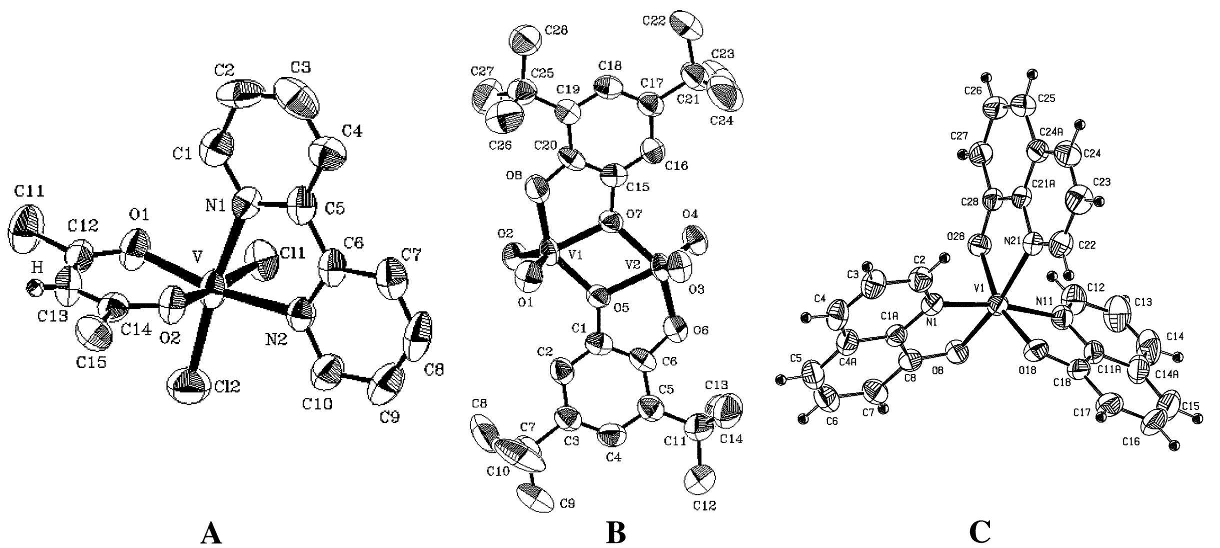

Fig. 1 The single-crystal X-ray structure of *cis*-[$V^{III}Cl_2(acac)(bpy)]\cdot CH_3COCH_3$ (A), $[Et_3NH]_2[VO_2(\mu\text{-}3,5\text{-dtbc})]_2$ (B) and [$V^{III}(quin)_3]\cdot 0.5CH_3OH$ (C). Selected interatomic distances (Å): For *cis*-[$V^{III}Cl_2(acac)(bpy)]\cdot CH_3COCH_3$, V(1)–O(1) 1.964(4), V(1)–O(2) 1.982(4), V(1)–N(2) 2.140(5), V(1)–Cl(1) 2.333(3), V(1)–Cl(2) 2.233(3), V(1)–N(1) 2.142(6). For $[Et_3NH]_2[VO_2(\mu\text{-dtbc})]_2$, V(1)–O(1) 1.591(4), V(1)–O(2) 1.622(4), V(1)–O(8) 1.945(5), V(1)–O(7) 2.010(4), V(1)–O(5) 1.997(4), V(2)–O(4) 1.597(4), V(2)–O(3) 1.636(4), V(2)–O(6) 1.933(4), V(2)–O(7) 1.981(4), V(2)–O(5) 2.032(4). For [$V^{III}(quin)_3]\cdot 0.5CH_3OH$, V(1)–O(8) 1.918(2), V(1)–O(18) 1.952(2), V(1)–O(28) 1.956(2), V(1)–N(1) 2.125(2), V(1)–N(11) 2.115(2), V(1)–N(21) 2.164(2).

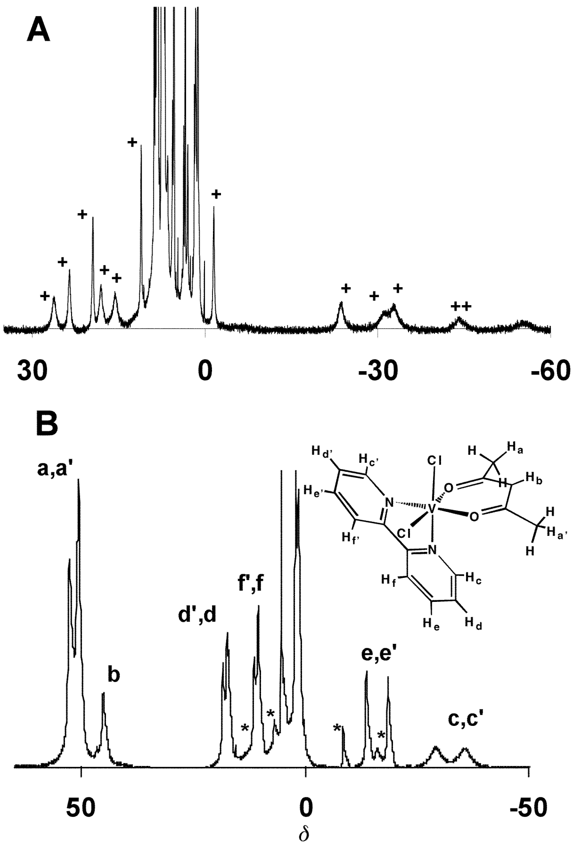

Fig. 2 300 MHz ^{1}H-NMR spectra of [$V^{III}(quin)_3]\cdot 2CH_3OH$ (A) in CD_2Cl_2 (the peaks corresponding to the ligated quin$^-$ are marked with a plus sign) and of [$V^{III}Cl_2(acac)(bpy)$] (B) in CD_2Cl_2 (the peaks marked with an asterisk are from a decomposition product).

via a π-delocalization pathway.[16,20] Excluding signals from the CD_2Cl_2, the co-crystallized CH_3OH and peaks from the free ligand (aromatic region ≈ 8 ppm) due to some decomposition of the compound in solution, complex [$V(quin)_3]\cdot 2CH_3OH$ gave 12 peaks corresponding to the coordinated quin$^-$ ligand. The assignment of the ^{1}H-NMR peaks of *cis*-[$V^{III}Cl_2(acac)(bpy)$] was performed by taking into account the peaks' integration and data from NMR studies of other V(III)–bpy derivatives.[16] In addition, this compound gave satisfactory 2D COSY and EXSY ^{1}H-NMR spectra, thus allowing confident assignments of the proton resonances. More specifically, the ^{1}H-NMR spectrum of *cis*-[$V^{III}Cl_2(acac)(bpy)$] shows eight peaks of positive and negative shift assigned to the bpy ligand and three additional signals at 52.60, 50.60 and 45.00 ppm assigned to the two methyl groups and the methylene proton of the coordinated acac$^-$ ligand.

The redox-properties of [$V(quin)_3]\cdot 2CH_3OH$ in CH_3CN and in the non-coordinating solvents CH_2Cl_2 and CH_3NO_2 have been studied by DC-cyclic voltammetry (CV) and polarographic techniques.[21] In acetonitrile,[22] the compound displays two reversible one-electron redox processes[21] at 0.03 and −1.90 V assigned to oxidation and reduction of vanadium(III) respectively [eqns. (1) and (2)], while in CH_2Cl_2 and CH_3NO_2 the

$$[V^{IV}(quin)_3]^+ + e^- \rightleftharpoons [V^{III}(quin)_3] \quad E_{1/2} = 0.03\ \text{V}\ vs.\ \text{Fc}^+/\text{Fc} \quad (1)$$

$$[V^{III}(quin)_3] + e^- \rightleftharpoons [V^{II}(quin)_3]^- \quad E_{1/2} = -1.90\ \text{V}\ vs.\ \text{Fc}^+/\text{Fc} \quad (2)$$

redox process at ≈−1.9 V is not reversible presumably because the base line current increases sharply at ≈−2.0 V due to the solvent reduction.

CV examination of *cis*-[$V^{III}Cl_2(acac)(bpy)$] in CH_3CN revealed a reversible one-electron redox process at 1.16 V assigned to the oxidation of V^{III} to V^{IV}.

In conclusion, we have shown that the reduction of both oxo and non-oxovanadium(IV) complexes to vanadium(III) species occurs quite easily in the presence of the chelate ligands Hquin and bpy respectively, almost quantitatively, with neither heat nor catalyst. Thus, the chelation of $V^{IV}/V^{IV}O^{2+}$ species must be taken into consideration in the elucidation of the reduction pathway to vanadium(III) in the vanadocytes of ascidians. Efforts to understand the mechanism of reduction of $V^{IV}/V^{IV}O^{2+}$ species in the presence of bpy or Hquin respectively are underway, as well as efforts to test the ability of other nitrogeneous chelate ligands to reduce vanadium(IV) to vanadium(III).

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Notes and references

† The compounds analysed satisfactorily (C, H, N, V) as *cis*-[$V^{III}Cl_2$(acac)(bpy)], [V^{III}(quin)$_3$]·2CH_3OH, [$Et_3NH]_2[VO_2$(μ-dtbc)]$_2$ and [V^{IV}(quin)$_3$]SbF_6, namely: Anal. calc. for [$V^{III}Cl_2$(acac)(bpy)] ($C_{15}H_{15}Cl_2N_2O_2V$): C, 47.77; H, 4.01; N, 7.43; V, 13.51. Found: C, 47.50; H, 4.04; N, 7.38; V, 13.45%. Anal. calc. for [V^{III}(quin)$_3$]·2CH_3OH ($C_{29}H_{26}N_3O_5V$): C, 63.62; H, 4.79; N, 7.68; V, 9.30. Found: C, 63.54; H, 4.49; N, 7.85; V, 9.45%. Anal. calc. for [$Et_3NH][VO_2$(μ-dtbc)]$_2$ ($C_{40}H_{72}N_2O_8V_2$): C, 59.25; H, 8.95; N, 3.45; V, 12.56. Found: C, 59.10; H, 8.75; N, 3.65; V, 12.62%. [V^{IV}(quin)$_3$]SbF_6 ($C_{27}H_{18}F_6N_3O_3SbV$): C, 45.10; H, 2.52; N, 5.84; V, 7.08. Found: C, 45.15; H, 2.75; N, 5.70; V, 6.85%. The μ_{eff} is 2.70 and 2.65 μ_B for the *cis*-[$V^{III}Cl_2$(acac)(bpy)] and [V^{III}(quin)$_2$]·2CH_3OH respectively and 1.60 μ_B for [V^{IV}(quin)$_3$]-SbF_6. Electronic spectra in CH_2Cl_2, λ_{max}, nm (ε_M/M^{-1} cm^{-1}): *cis*-[VCl_2(acac)(bpy)], 431 (sh) (600), 299 (16783), 241 (13648), 222 (14754); [V^{III}(quin)$_3$]·2CH_3OH, 415 (11170), 217 (48500), 257 (81300); [V^{IV}(quin)$_3$]SbF_6, 598 (1850), 372 (4900), 307 (6560), 244 (106600), 219 (47600).

‡ Crystal data: Crystals of *cis*-[$V^{III}Cl_2$(acac)(bpy)]·CH_3COCH_3 suitable for single-crystal X-ray structure analysis were obtained by vapour diffusion of diethyl ether into an acetone solution of [$V^{III}Cl_2$(acac)-(bpy)]. $C_{18}H_{21}Cl_2N_2O_3V$, M_r = 435.21, monoclinic, space group $P2_1/n$; a = 12.616(2), b = 12.451(2), c = 14.337(3) Å, β = 115.699(6)°, V = 2029.3(7) Å^3, Z = 4; ρ_{calc} = 1.424 g cm^{-3}, T = 298(2) K. Of the 3921 reflections measured, 3766 symmetry-independent reflections were used to solve the structure. Based on all these data and 279 refined parameters $R1$ = 0.0690 (all data), $wR2$ = 0.1840 and goodness-of-fit on F^2 is 1.100.

For [$Et_3NH]_2[VO_2$(μ-dtbc)]$_2$: $C_{40}H_{72}N_2O_8V_2$, M_r = 810.88, triclinic, space group $P\bar{1}$, a = 14.915(15), b = 15.029(14), c = 11.091(12) Å, α = 90.15, β = 99.02(4); γ = 107.11(3), V = 2343.7(41) Å^3, Z = 2, ρ_{calc} = 1.149 g cm^{-3}, T = 293(2) K. Of the 6829 reflections measured 6451 symmetry-independent reflections were used to solve the structure. Based on all these data and 517 refined parameters $R1$ = 0.0910 (all data), $wR2$ = 0.2328 and goodness-of-fit on F^2 is 1.067.

Crystals of [V^{III}(quin)$_3$]·0.5CH_3OH suitable for X-ray structure analysis were obtained by vapour diffusion of diethyl ether into a methyl alcohol solution of [V^{III}(quin)$_3$]·2CH_3OH: $C_{27.5}H_{20}N_3O_{3.50}V$, M_r = 499.40, monoclinic, space group $P2_1/n$, a = 10.9438(10), b = 13.4026(13), c = 16.912(2) Å, β = 97.921(2)°, V = 2456.9(4) Å^3, Z = 4, ρ_{calc} = 1.350 g cm^{-3}, T = 298(2) K. Of the 10461 reflections measured 3515 symmetry-independent reflections were used to solve the structure. Based on all these data and 328 refined parameters $R1$ = 0.0573 (all data), $wR2$ = 0.1708 and goodness-of-fit on F^2 is 0.916. CCDC reference numbers 156232–156234. See http://www.rsc.org/suppdata/dt/b1/b102095l/ for crystallographic data in CIF or other electronic format.

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21 Platinum disk and dropping mercury electrodes were employed as working electrodes for the cyclic voltammetric and polarographic studies, respectively. A platinum wire was used as an auxiliary electrode, while a silver–silver chloride electrode (saturated with tetrabutylammonium tetrafluoroborate) was used as a reference electrode. The supporting electrolyte was tetrabutylammonium tetrafluoroborate 0.1 M and all solutions were 10^{-3}–10^{-4} M in complex. Values for the reduction potentials ($E_{\frac{1}{2}}$) and the number of electrons involved in the reversible process were obtained from the intercept and the slope of the plot of $\ln[(i_d - i)/i]$ *vs.* potential (E) respectively, according to the Heyrovsky–Ilkovic equation, where i_d is the diffuse current and η the number of electrons involved in the redox process.

$$E = E_{\frac{1}{2}} + (RT/\eta F)\{\ln[(i_d - i)/i]\}$$

All potentials reported in this paper are relative to ferrocene which was used as a secondary internal reference by first measuring against [V^{IV}(cat)(bzac)$_2$] (Hbzac = 1-phenyl-1,3-butanedione) which was then employed as the internal reference. Compound [V^{IV}(cat)-(bzac)$_2$] was prepared according to reference 12(*a*).

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