p-Hydroquinone–metal compounds: synthesis and crystal structure of two novel V(V)–p-hydroquinonate and V(IV)–p-semiquinonate species†

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Reaction of the p-hydroquinone derivative H_2Na_4bicah·$4H_2O$ with either V(IV)OSO_4·$3H_2O$ and NaV^VO_3 in equivalent quantities or with NaV^VO_3 yields the tetranuclear V(IV)O^{2+} macrocycle–semiquinonate compound $Na_6\{(V^{IV}O)_4(\mu_2$-$O)_2[\mu_2$-bicas·(-5)-$N,O,O,O]_2\}$·Na_2SO_4·$20H_2O$ (1·Na_2SO_4·$20H_2O$) and the dinuclear cis-V(V)O_2^+–hydroquinone species $Na_4\{(V^VO_2)_2[\mu_2$-bicah(-6)-$N,O,O,O]\}$·$11H_2O$ (2·$11H_2O$) respectively. Compounds 1·Na_2-SO_4·$20H_2O$ and 2·$11H_2O$ were characterized by X-ray structure analysis and ab initio calculations.

p-Hydroquinones along with their oxidation products, p-semiquinones and p-quinones, comprise perhaps the quintessential organic electron and hydrogen transfer systems.[1] For example, 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,[2,3] tissue (collagen and elastin) formation,[3,4] photosynthesis[5] and aerobic (mitochondrial) respiration.[6] 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[7] such as the reduction of vanadium(v), present in sea water, to vanadium(III) in the blood cells of tunicates.[8,9] In marked contrast to the extensive structural chemistry for chelate stabilized o-(hydro/semi)quinone metal compounds,[10] examples of structurally characterized non-polymeric[11] σ-bonded p-hydroquinone–metal compounds are surprisingly rare[12] and there are no examples of σ-bonded p-semiquinone–metal complexes. 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. In this communication, we wish to report the synthesis of the potentially μ-bridging chelate o-disubstituted ligand 2,5-bis[N,N-bis(carboxymethyl)aminomethyl]hydroquinone (H_6bicah) as well as its tetranuclear V(IV)O^{2+} and dinuclear V(V)O_2^+ compounds.

The sodium salt of H_6bicah, Na_4H_2bicah·$4H_2O$, was synthesized by condensing p-hydroquinone with iminodiacetic acid in the presence of formaldehyde (Mannich reaction) in alkaline water/ethyl alcohol solution under argon.‡ Compound 1·Na_2-SO_4·$20H_2O$ was prepared by reacting V(IV)OSO_4·$3H_2O$ (4 mmol) and NaV^VO_3 (4 mmol) with Na_4H_2bicah·$4H_2O$ (4 mmol) in water (5 mL) under argon (pH ≈ 4), followed by vapor

diffusion of methyl alcohol at 4 °C into this solution (yield 45%). Compound 2·$11H_2O$ was prepared by reacting NaVO_3 (2 mmol) with Na_4H_2bicah·$4H_2O$ (1 mmol) in water (5 mL) (pH ≈ 8) under argon followed by vapor diffusion of ethyl alcohol into this solution (yield 60%).

The molecular structures§ of the anions of 1 and 2 are shown in Fig. 1. The anion of 2 (Fig. 1B) contains a bridging (μ-) N,O,O,O ligated p-hydroquinonate(-6) ligand (Scheme 1,a), as is clearly borne out by the observation,[13] that (i) the C–C bonds of the six-membered ring are equidistant at 1.386 ± 0.004 Å and (ii) the C–O bond length at 1.354(6) Å is long and typical for p-hydroquinonates (Scheme 1,a). In contrast, the anion of 1 (Fig. 1A) contains two bridging (μ-) N,O,O,O coordinated p-
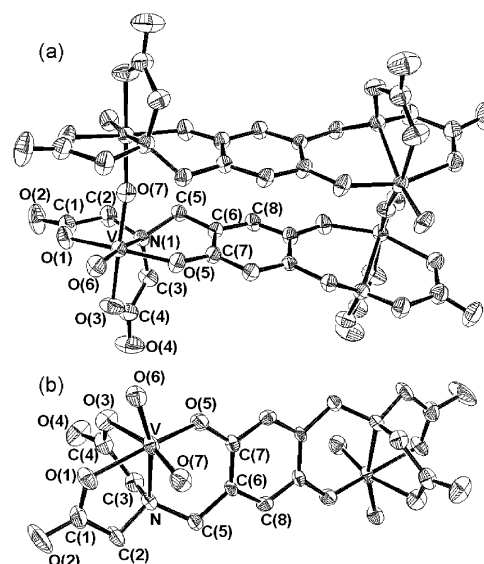
Fig. 1 ORTEP drawing of the anions of (a) 1 and (b) 2 at 50% probability ellipsoids giving atomic numbering. For clarity, hydrogen atoms are omitted. Selected bond lengths (Å) for 1·Na_2SO_4·$20H_2O$ and 2·$11H_2O$ (in square brackets): V–O(1) 2.022(4) [2.019(3)], V–N(1) 2.289(4) [2.280(4)], V–O(3) 2.068(4) [2.209(3)], V–O(5) 1.887(3) [1.864(3)], V–O(6) 1.620(3) [1.652(3)], V–O(7) 1.807(1) [1.620(4)].
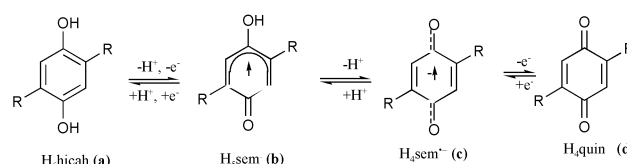
Scheme 1

semiquinonate(−5) π radical ligands (Scheme 1,**c**);[13] the C–O bond length [1.322(5) Å] is shorter than in **2** and longer than the bond length expected for quinone [~ 1.21 Å][12] and this denotes a partial double bond character (Scheme 1,**c**). In addition, the C–C bonds of the six-membered ring, 1.399(7), 1.371(7) and 1.427(7) Å in a long-short-long pattern (Scheme 1,**c**), are expected for *p*-semiquinonates. Although the six-membered ring of the ligated *p*-quinone ligands shows a similar pattern to *p*-semiquinonates; different bond lengths are expected [~ 1.46, ~ 1.33 and ~ 1.46 Å].[12] These data unambiguously define the oxidation levels of the organic ligands in **1** and **2**, which render the central metal ions as V^{IV} (d[1]) and V^{V} (d°) for **1** and **2** respectively. The structure of the anion of **1** contains two $[V_2^{IV}(\mu\text{-bicas})]$ edges linked together with two μ-oxo-bridged ligands to get a twisted rectangular structure. The four vanadium atoms in the anion of **1** are indistinguishable and each of them resides in a distorted octahedral NO_5 coordination environment. The unit cell of **2**·11H_2O contains two discrete molecules of **2**. Each of them has two indistinguishable six-coordinate vanadium atoms bridged with a μ-bicah[−6] ligand. The coordination environments of the vanadium atoms and the bond lengths in **2** are similar to those found in complex **1**, except that the two μ-O^{2-} bridged atoms in **1** have been replaced by two terminal oxo groups *anti* to each other in **2**.

A full geometry optimization of $[V_4O_4(\mu\text{-O})_2(\mu\text{-bicas})_2]^{6-}$ (**1**) and $[(V^VO_2)_2(\mu\text{-bicah})]^{4-}$ (**2**) was carried at the UHF level and HF level under the symmetry constrains of and D_2 and C_i point group respectively, using the effective core potential approximation of Hay and Wadt with a valence double-ζ basis set for the V atom[14] and the STO-3G basis set for all other atoms.[15] There is an overall agreement between the calculated and experimental data in both cases. The optimized structures remain unchanged upon distortion and reoptimization with no symmetry constraints. Bond distances agree within 0.06 Å, while the largest deviation of bond angles appears to be about 7°. The calculated Mulliken and Lowdin atomic spin densities for the four vanadium atoms in **1** found equal to 0.8458 and 0.8345 respectively, confirm further the characterization of all vanadium atoms as V^{IV}. The bond distances within the aromatic rings of **1** were 1.450, 1.369 and 1.454 Å revealing that the organic ligand has a semiquinonate structure (bicas[5−]), whereas those in **2** were almost equal (1.405, 1.412 and 1.408 Å) as expected for a *p*-hydroquinonate. Each of the four highest single occupied molecular orbitals (SOMOs), shown in Fig. S1 (ESI†), is localized on the d orbitals of the four V^{IV} atoms with zero participations from orbitals of the intervening π-system of the bicas[5−·] ligand and a significant participation from a p-orbital of the two oxygen atoms bridging the two parallel slices of the complex. Thus, whereas a magnetic coupling of the two V^{IV} centers is expected due to both the spatial proximity and the high overlap between the orbitals within the oxygen bridge, no exchange interaction is expected through the bridged bicas[5−·] ligand. This is quite in line with the experimentally observed value of the μ_{eff} being 1.9 μ_B at room temperature, indicating that the vanadium(IV) ($S = 1/2$) centers are strongly coupled.

In summary, the dinuclear V^V–*p*-hydroquinonate and the tetranuclear V^{IV}–*p*-semiquinonate compounds were synthesized by taking advantage of the two *ortho* substituents present in the *p*-hydroquinone moiety and structurally characterized. *Ab initio* theoretical calculations for **1**·Na₂SO₄·20H₂O and **2**·11H₂O are nicely corroborated with the crystallographic data and confirm the semiquinonate and hydroquinonate redox levels of the organic ligand respectively. The isolation of a stable metal-*p*-semiquinonate species is the first one to be reported. In order to understand the reasons for the stability of such an actually unstable species, variable-temperature magnetic measurements and EPR studies are under way.

Notes and references

‡ **1·Na₂SO₄·20H₂O**: The deep blue crystals analysed satisfactorily (C,H,N,Na) as **1**(Na₂SO₄·20H₂O. UV-Vis of **1**·Na₂SO₄·20H₂O [λ(nm),

ε(M⁻¹cm⁻¹)] at pH ~ 4, 856 (8800), 642 (10 300), 195 (70 000) and 294(sh) (10 300). DC cyclic voltammetry, rotating disk voltammetry and coulometry of **1**·Na₂SO₄·20H₂O in H₂O at pH 4.19 gave a reversible and a quasi-reversible one-electron metal centered redox processes at 0.48 ([$V^{IV}_3V^V + e^- \rightleftharpoons V^{IV}_4$]) and 0.10 V ([$V^{IV}_4 + e^- \rightleftharpoons V^{IV}_3V^{III}$]) (*vs.* NHE, normal hydrogen electrode) respectively. Compound **1** does not possess observable NMR spectra (¹H, ¹³C, ⁵¹V).

2·11H₂O: The brown red crystals analyzed satisfactorily (C,H,N,Na) as **2**·12H₂O. UV-Vis of **2**·11H₂O [λ(nm), ε(M⁻¹cm⁻¹)] at pH = 7.00, 396 (with a tail up to 500 nm) (4000), 304 (8000), 243(sh) (15 000). ⁵¹V NMR δ(D₂O, pH = 8.0) 492.¹H NMR δ(D₂O, 0 °C) 6.03 (2H, aromatic), 4.37(2H, broad, Ar-CH₂-N), 3.68 (2H, broad, N-CH₂-COO), 3.47 (2H, broad, Ar-CH₂-N), 3.13 (4H, broad, N-CH₂-COO), 2.75 (2H, broad, N-CH₂-COO). ¹³C{¹H} δ(D₂O, 0 °C) 60.63 (C2,C3), 64.65 (C5), 119.13 (C8), 123.78 (C6), 155.78 (C7), 178.34 (C4), 180.41 (C1) numbering is shown in Fig. 1.
§ Crystal data for $C_{32}H_{68}N_4Na_8O_{50}SV_4$ **1**·Na₂SO₄·20H₂O: M = 1728.76, space group $P4/ncc$, tetragonal, a = 23.307(9), b = 23.307(9), c = 12.233(5) Å, V = 6645(5) Å³, Z = 4, ρ_{calc} = 1.727 g cm⁻³, T = 298 K. 3748 reflections measured, 2924 unique (R_{int} = 0.0131), $R1$ and $wR2$ are 0.0605 and 0.1533 respectively, for 2193 reflections with $I > 2\sigma(I)$.

Crystal data for $C_{16}H_{36}N_2Na_4O_{25}V_2$ **2**·11H₂O: M = 850.31, space group $P\bar{1}$, triclinic, a = 9.664(6), b = 12.009(4), c = 14.629(4) Å, α = 97.69(2), β = 101.01(4), γ = 99.78(4)°, V = 1617.9(12) Å³, Z = 2, ρ_{calc} = 1.745 g cm⁻³, μ = 0.732 mm⁻¹, T = 293 K. 3283 reflections measured, 3039 independent (R_{int} = 0.013), $R1$ = 0.0566, $wR2$ = 0.1724. The positions of the hydrogen atoms of **1** and **2** were calculated from stereochemical considerations and kept fixed isotropic during refinement; the hydrogen atoms for the water molecules were not located.

CCDC reference numbers 136227 (**1**·Na₂SO₄·20H₂O) and 190302 (**2**·11H₂O). See http://www.rsc.org/suppdata/cc/b2/b207330g/ for crystallographic data in CIF or other electronic format.

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