Stabilisation of an endiolate by co-ordination to vanadium(IV)

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The redox reaction between [$VCl_2(tmeda)_2$] (tmeda = *N,N,N′,N′*-tetramethylenediamine) and benzil yielded the non-oxo V^{IV} benzoin complex [V(tmeda){Ph(O)C=C(O)Ph}$_2$]·thf (C_2 symmetry), the first structurally characterised vanadium–endiolate complex.

V^{II} is a versatile reducing agent which has been used to effectively reduce, *inter alia,* nitrogen to ammonia,[1] protons to hydrogen,[2] bromoalkanes to alkanes[3] or sulfidophenylsulfanylethane to ethylene and thiocatecholate.[4] V^{II} is also the active intermediate in many reductive hydrogenation and C–C coupling reactions carried out in the presence of the catalyst system VCl_n–H^+–Zn.[5–8] In an effort to establish general pathways leading to non-oxo vanadium-(IV) and -(V) complexes, we have now exploited the reducing potential of V^{II}, stabilised in the form of [$VCl_2(tmeda)_2$], to reduce benzil to 1,2-dihydroxyethylene and to concomitantly coordinate this tautomeric form of benzoin to vanadium. The use of [$VCl_2(tmeda)_2$][9] allows the reaction to be carried out in solvents which, unlike water or alcohols, do not straight away provide an oxo group which would otherwise give rise to the formation of the favoured vanadyl [oxovanadium(IV)] moiety. Non-oxo (sometimes also termed 'bare') complexes of high-valent vanadium are of interest in the context of amavadin, a molecular compound of V^{IV} isolated from mushrooms of the genus *Amanita,*[10] and of vanadium nitrogenase, which presumably contains a {V(μ-S)$_3$(his)(homocitrate)} coordination site.[11]

Non-oxo complexes of vanadium in its oxophilic oxidation states +IV and +V are still scarce. Examples include [V(salen)(benzilate)],[12] [V(tben)] [H_4tben = *N,N,N′,N′*-tetrakis(2-hydroxybenzyl)ethylenediamine],[13] and [V(salhan)] [H_2salhan = bis(salicylaldehyde-2-hydroxyanil)].[14] Nor has the chemistry of vanadium complexes containing 1,2-diolates as ligands[15–18] yet been developed to a great extent, although this class of complexes is of some interest with respect to model compounds for the physiologically relevant interaction of vanadium with sugars and sugar derivatives such as nucleotides and nucleosides. One such complex, a dimeric adenosyldioxovanadate, has recently been structurally characterised.[19] In contrast to simple α-hydroxycarbonyl compounds, the equilibrium between enediol and the α-hydroxycarbonyl form may be in favour of the former in the case of sugars. Complexes containing the enediol tautomeric form of an α-diketone bound to a vanadium centre have so far not been described. They are known in the dinuclear systems [$W_2X_6(O_2C_2R_2)_2$] (X = Cl, OR′)[20] and [$Mo_2O_5(O_2C_2Ph_2)_2$].[21] Vanadium coordination to enolate[22a] and ynolate[22b] has also been reported.

[V(tmeda){Ph(O)C=C(O)Ph}$_2$] forms on addition of benzil to [$VCl_2(tmeda)_2$] (molar ratio 1:1) dissolved in refluxing, absolute thf. Black, crystalline material of [V(tmeda){Ph(O)C=C(O)Ph}$_2$]·thf,† suitable for the X-ray structure determination, is obtained as *n*-pentane is allowed to diffuse into the saturated thf solution within a few days. Since the conversion of benzil to benzoin is a two-electron reduction, half of the vanadium is lost in a side-reaction, the nature of which has not yet been revealed. The exclusive formation of the *Z* isomer of the enediol tautomeric form of benzoin hints at a reaction mechanism where benzil is associated with and thus activated by the V^{II} centre prior to reduction. The coordination of bidentate oxo-functional ligands such as β-diketonates[23] and β-diolates[24] to V^{II} has been noted before (*cf.* also ref. 9).

An ORTEP drawing of [V(tmeda){Ph(O)C=C(O)Ph}$_2$]·thf‡ is shown in Fig. 1. The overall geometry is distorted octahedral. V, N1, N1A, O2 and O2A form an approximate plane (deviations: V 0.000, O2 +0.240, O2A −0.240, N1 −0.265, N1A +0.265 Å), O1 and O1A are in the axis, which is slightly bent; the angle O1–O1A amounts to 169.77(8)°. The point symmetry is C_2, with the twofold axis bisecting the angles O2–V–O2A, N1–V–N1A, and the ethylene backbone of the tmeda ligand. Distorted octahedral geometries have also been reported for other non-oxo vanadium complexes,[12–14] while the trigonal-prismatic or distorted trigonal-prismatic arrangements are realised in [V(hazb)$_2$] [H_2hazb = bis(2,2′-dihydroxyazobenzene],[25] and in non-oxo vanadium(IV) complexes containing ONS donor sets.[26] The carbon–carbon bond length [1.369(3) Å] and the bond angles (average 120°) at the carbons forming the benzoin backbone clearly indicate that the enediol form (sp^2 hybridisation at both carbons) prevails. The V–O bond lengths [1.896(1) and 1.922(1) Å] exceed those of V–O(alkoxide) with a sp^3 hybridised carbon of the alkoxo group (typically 1.77–1.81 Å[12,15a,16–18]); they compare to V–O(phenolate) (1.87–1.91 Å) and V–O(enolate)[22a] [1.928(2) Å], and also to the V–O bond lengths to the non-bridging sugar alkoxides in [VO_2(μ-adenosine)$_2$]$^{2-}$ [1.939(2) and 1.916(2) Å];[19] but they are exceeded by V–O(β-diketonate) bond lengths (1.98–2.02 Å).[27]

The +IV state of vanadium has further been established by EPR spectroscopy and cyclic voltammetry.§ The CV exhibits a reversible one-electron reduction step ($V^{IV} \leftrightarrows V^{III}$) at $E_{1/2}$ = −1.080 V, and an irreversible oxidation ($V^{IV} \rightarrow V^{V}$) at +0.27 V *vs.* SCE. The EPR parameters (g_0 = 1.962 , A_0 = 89.0 G; in thf) compare to those commonly found for V^{IV} complexes with a coordination environment dominated by oxygen functionali-

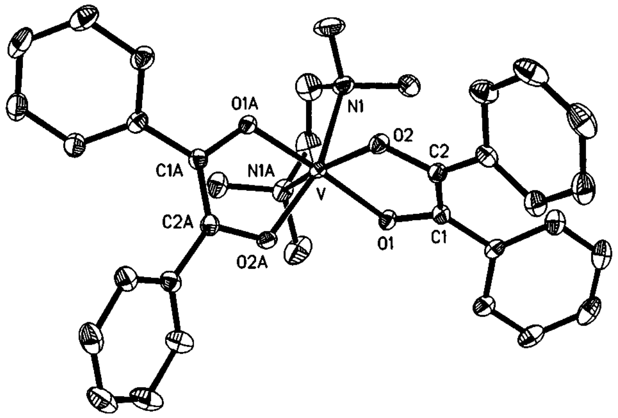

Fig. 1 ORTEP drawing, showing the 50% probability ellipsoids, and numbering scheme for [V(tmeda){Ph(O)C=C(O)Ph}$_2$]. Selected bond distances (Å) and bond angles (°): V–N1 2.204(2), V–O1 1.896(2), V–O2 1.921(2), C1–C2 1.369(3), O1–C1 1.342(2), O2–C2 1.354(2), C1–C10 1.474(3), C2–C20 1.472(3); N1–V–N1A 80.35(11), O1–V–O2 79.19(6), O1–V–O1A 169.80(9), O2–V–O2A 108.93(9), N1–V–O1 100.29(7), N1–V–O2 87.10(7) O1–C1–C2 113.3(2), O1–C1–C10 116.4(2), C2–C1–C10 130.3(2).

ties.[28] The BVS analysis, using the parameters provided by Carrano *et al*.,[29] leads to a valence state for vanadium of 3.9.

We are presently expanding this novel route to non-oxo V^{IV} complexes by redox-interaction between a low-valent vanadium centre and a 'pre-ligand' system that serves as the oxidising agent and, in its reduced form, a ligand to the oxidised vanadium.

Notes and References

† [V(tmeda){Ph(O)C=C(O)Ph}$_2$]·thf was prepared in 44% yield. A satisfactory microanalysis was obtained. The ν(C=O) bands are at 1610 and 1588 cm^{-1} (KBr pellet).

‡ *Crystal data* for [V(tmeda){Ph(O)C=C(O)Ph}$_2$]·thf, $C_{38}H_{44}N_2O_5V$, M = 659.69, orthorhombic, space group *Pccn*, a=27.887(10), b = 8.916(2), c = 14.154(6) Å, Z = 4, V = 3519(2) Å^3, D_c = 1.245 g cm^{-3}, μ = 2.71 mm^{-1}, an absorption correction (DIFABS) was applied. Data were collected at 173(2) K on an Enraf Nonius CAD4 diffractometer (Cu-Kα irradiation, λ = 1.541 78 Å, graphite monochromator) in the 2θ scan mode, θ = 3.17–76.35°. Measured reflections 3716, independent reflections 3680 (R_{int} = 0.0152); refined parameters 234. The solution of the structure (SHELXS 97) and refinement (SHELXL 97) converged to a conventional [*i.e.* based on the $I > 2\sigma(I_0)$ criterion] $R1$ = 0.0454 and $wR2$ = 0.1284. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were calculated into ideal positions and included in the final FMLS refinement. Maximum and minimum residual electron densities were 0.540 and −0.637 e Å^{-3}. Only one half of the structure, including one complete enediolate ligand, is crystallographically unique. The thf of crystallisation was treated with a 1:1 disorder model, as required by the crystallographic C_2 axis (symmetry transformation $-x + 1, -y, -z + 1$). CCDC 182/955.

§ X-Band EPR spectra (Bruker ESP 300E) were obtained at 9.74 GHz in *ca.* 1 mM solutions. CV measurements (Princeton Applied Research potentiostat 273A; working electrode: Pt foil, counter electrode: Pt wire) were carried out in *ca.* 1 mM DMF solution with 0.2 M TBAP as conductance salt. The potentials are referenced against SCE. The same crystalline material used for the X-ray structure determination was employed for the EPR and CV studies.

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