Activation of Metal-bound Salicylaldoximes

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Neutral, bis-complexes of oxovanadium(IV) with salicylaldoximes and salicylketoximes react with a range of nitriles to afford a novel organic ligand type; the prototypical reaction product [$V^VO_2\{C_6H_4(O)CH{=}N{-}OC(Me){=}NH\}$] is characterised by single crystal X-ray diffraction and spectroscopic studies.

Salicylaldoxime and various of its substituted derivatives are important as analytical reagents,[1] extractants in hydrometallurgy[2] and corrosion inhibitors.[3] These applications magnify the challenges of understanding the chemistry of the complexes of these ligands. First row d-transition elements in the II oxidation state form stable bis-chelates with salicylaldoxime (saloxH) of general formula M(salox)$_2$ and the copper[4] and nickel[5] systems are notable examples. Salicylaldoxime complexes of these metals are stable in solution in a wide range of organic solvents. However, the blue bis-complex of salicylaldoxime with oxovanadium(IV) has been reported[6] to show instability in organic solvents over a period of several hours, as evidenced by dramatic colour changes. We have investigated the nature of this reaction in a range of nitriles with both aldoximes and ketoximes as ligands to VO^{2+} and shown that the reaction involves the net addition of the oxime-OH group across the nitrile C≡N bond to form a novel tridentate chelate.

The addition of an ethanolic solution of aldoxime or ketoxime to an aqueous solution of vanadyl sulphate in 2:1 molar ratio affords a blue or blue–purple solid of composition VO(oxyoxime)$_2$.† When, for example, [VO(salox)$_2$] is dissolved in MeCN there is a gradual darkening of the solution to an intense brown, whereupon a yellow microcrystalline product **1** is precipitated. This product does not have an appreciable

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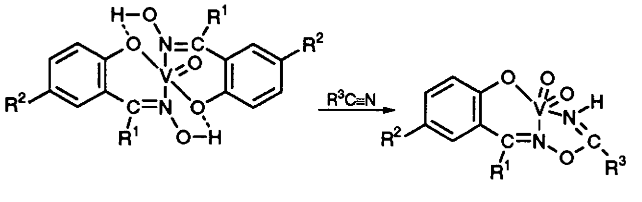
† An X-ray crystallographic study of [VO(oxyoxime)$_2$] for which R^1 = Me and R^2 = H (see Table 1) has established that the compound is composed of five-coordinate, monomeric, square-based pyramidal molecules. These studies will be reported in detail elsewhere.

Table 1 Yields[a] of the reactions of the oxovanadium(IV) aldoxime and ketoxime complexes with nitriles



R¹	R²	R³	Yield (%)[a]
H	H	Me	64
Me	H	Me	<5
Et	H	Me	*b*
H	H	Ph	90
Me	H	Ph	48
Et	H	Ph	24
H	H	p-NO$_2$-C$_6$H$_4$	60
Me	H	p-NO$_2$-C$_6$H$_4$	<5
Et	H	p-NO$_2$-C$_6$H$_4$	*b*
H	H	p-Me-C$_6$H$_4$	<5
H	H	MeCOCH$_2$	<5
H	Cl	Me	17
H	Cl	Ph	61
H	Bu^t	Me	*b*
H	Bu^t	Ph	24

[a] Yield (%) based on vanadium conversion after 48 h at ambient temperature. The yields quoted are for the nitrile as the solvent; the yields were reduced when the reaction was performed in CH$_2$Cl$_2$ solution; there was no appreciable variation in yield when the reactions were performed under anaerobic vs. aerobic or anhydrous vs. hydrous conditions. [b] No product was detected, either as a precipitate or spectroscopically.

solubility in MeCN nor other common organic solvents and crystals suitable for X-ray crystallography‡ were grown directly from the reaction medium.

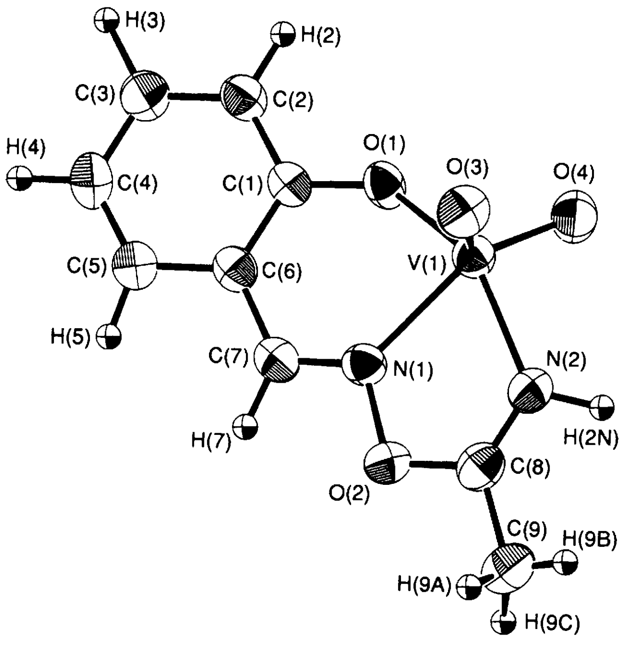


Fig. 1 Structure of [VO$_2${C$_6$H$_4$(O)CH=N–OC(Me)=NH}}, **1**. Selected dimensions: V(1)–O(1) 1.901(4), V(1)–O(3) 1.600(4), V(1)–O(4) 1.629(4), V(1)–N(1) 2.152(5), V(1)–N(2) 2.063(5), O(1)–C(1) 1.333(6), O(2)–N(1) 1.438(6), O(2)–C(8) 1.352(7), N(1)–C(7) 1.298(7), N(2)–C(8) 1.255(8), N(2)–H(2N) 1.020(5), C(7)–H(7) 1.029(6), C(9)–H(9A) 0.919(7), C(9)–H(9B) 0.856(7) Å, O(1)–V(1)–O(3) 104.3(2), O(1)–V(1)–O(4) 98.9(2), O(1)–V(1)–N(1) 80.1(2), O(1)—V(1)–N(2) 146.9(2), O(3)–V(1)–O(4) 109.2(2), O(3)–V(1)–N(1) 108.3(2), O(3)—V(1)–N2 99.9(2), O(4)–V(1)–N(1) 141.5(2), O(4)–V(1)–N(2) 94.0(2), N(1)–V(1)–N(2) 71.0(2), V(1)–N(1)–O(2) 117.7(3), V(1)–N(1)–C(7) 132.5(4), O(2)–N(1)–C(7) 109.8(4), V(1)–N(2)–C(8) 122.8(4), O(2)–C(8)–N(2) 119.7(6), O(2)–C(8)–C(9) 110.4(6), N(2)–C(8)–C(9) 129.9(6), V(1)–N(2)–H(2N) 127.0(4), C(8)–N(2)–H(2N) 109.4(5), N(1)–C(7)–H(7) 111.6(5), C(6)–C(7)–H(7) 127.5(6), C(8)–C(9)–H(9A) 107.2(6), C(8)–C(9)–H(9B) 103.8(7), H(9A)–C(9)–H(9B) 105.5(8)°.

A representation of the molecular structure of **1**, [VO$_2${C$_6$H$_4$(O)CH=NOC(Me)=NH}], is shown in Fig. 1. The molecule comprises a monomeric *cis*-dioxovanadium(V) centre bound by the novel tridentate chelate which presents an {ON$_2$} donor set to the metal. The overall coordination at the vanadium corresponds to a distorted square pyramidal geometry with V(1)–O(3) defining the principal axis. There is an intramolecular hydrogen bond between O(4) and the N(2)-H group [O(4)···N(2) = 2.870(6) Å] and the low solubility of the compound is, in part, attributed to the intermolecular hydrogen bonding between O(3) and the C(7)H(7) group [O(3)···C(7) = 2.949(7) Å]. The structure of **1** may be compared with [VO$_2${HOC$_6$H$_3$(O)CH=N–NH–C(SMe)=NH}], **2**,[7] formed by the reaction of NH$_4$VO$_3$ and 2,4-dihydroxybenzaldehyde *S*-methylthiosemicarbazone in concentrated aqueous ammonia, precipitation and subsequent protonation in aqueous ethanol. The molecular structure of **1** and **2** are closely related, with O(2) substituted by NH and the Me group replaced by an SMe group, and the two molecules involve remarkably similar dimensions for corresponding interatomic distances and interbond angles.

The {VO$_2$}$^+$ group of **1** involves the dimensions: V(1)–O(3) = 1.600(4) Å; V(1)–O(4) = 1.629(4) Å; and O(3)–V(1)–O(4) = 109.2(2)°, values which are typical of this moiety.[8] The assignment of the oxidation state V^V is also consistent with the absence of an ESR signal, the diamagnetism of solid **1**, and the

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‡ *Crystal data* for C$_9$H$_9$N$_2$O$_4$V: M = 260.12, monoclinic $P2_1/c$, Z = 4, a = 7.2918(9), b = 15.562(1), c = 9.3988(6) Å, β = 105.935(6)°, V = 1025.5(1) Å^3, D_c = 1.685 g cm^{-3}, $F(000)$ = 528, μ = 82.28 cm^{-1} for Cu-Kα radiation (λ = 1.54178 Å), crystal size 0.070 × 0.250 × 0.300 mm. Rigaku AFC5R diffractometer, T = 297 K, cell parameters from 2θ values of 23 reflections with $75.7 < 2\theta < 79.9°$, $2\theta_{max}$ = 119.9°. An empirical absorption correction was applied using the program DIFABS, which resulted in transmission factors ranging from 0.76 to 1.43. The data were corrected for Lorentz and polarization effects. 1733 reflections were collected of which 1597 were unique (R_{int} 0.023). The intensities of three representative reflections, which were measured after every 150 reflections, showed no significant change. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in successive difference maps and fixed in these positions. For all except C(9)-H, their isotropic temperature factors were allowed to refine. The temperature factor for H(9)C was fixed at B 10 Å^2. The hydrogen atom N(2)-H was also located by difference Fourier. The final cycle of full-matrix least squares refinement was based on 1119 observed reflections [$I > 3.00\sigma(I)$] and 153 variable parameters and converged (largest parameter shift was <0.01 times its e.s.d.) with unweighted and weighted agreement factors of: $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.052$, $R_w = [(\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2)]^{\frac{1}{2}} = 0.063$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.44 and −0.32 e Å^{-3}, respectively.

Anomalous dispersion effects were included in F_c. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Molecular structure diagrams were produced using PLUTO and ORTEP. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

observation of ^{51}V (78.9 MHz) and ^{13}C (75 MHz) solid state NMR spectra.§

Spectroscopy thus demonstrates that the present reaction is quite general but the extent depends on the nature of both the oxime and the nitrile (Table 1). The mechanism of the reaction is likely to involve initial coordination of the nitrile to the oxovanadium(IV) centre, prior to oxidation and the loss of a salicylaldoxime (or ketoxime) ligand. The reaction to form the tridentate chelate can be considered to occur *via* addition of the oxime-OH group across the C≡N bond. This reaction with nitriles is optimal for salicylaldoxime with benzonitrile, since addition of electron-withdrawing or -donating groups onto the aromatic nitrile ring, or change to an alkyl nitrile, decreased the yield of the corresponding $\{VO_2\}^+$ complex. The systematic variation in R^1 or R^2 shows that an increase in electron donation also decreases the yield, *e.g.* for R^2, H > Cl > Bu^t. The greater yields for R^1 = Me compared with Et imply that a steric effect is also operating.

We have no evidence that the novel ligand type in **1** is produced from a direct combination of the nitrile with the aldoxime or ketoxime, nor upon the dissolution of other metal bis-complexes in a nitrile.

The oxidation of oxovanadium(IV) to dioxovanadium(V) in the presence of organic bases has been reported previously. Thus, oxo-bis(3-hydroxy-1,3-diphenyltriazine)vanadium(IV) reacts with various basic media such as pyridine, α-picoline or aniline to produce the dioxovanadium(V) complex [VO$_2$TX], where TH is a molecule of the ligand and X is a molecule of the base.[9] A related observation has been reported for oxohydroxo-bis(quinaldinato)vanadium(V), $[VO(OH)Q_2]\cdot 2H_2O$, which on heating with pyridine forms [VO$_2$Q].[10] One aspect of the reaction to produce **1** has been reported recently[11] for the Pt^{IV} mediated redox coupling of propan-2-one oximes to produce $[Pt(N(=O)CMe_2ONCMe_2)Cl_2]$. Here, the oxime oxygen atom appears to be activated to attack an unsaturated carbon atom, but the metal is reduced by two electrons. Despite the diverse applications of salicylaldoxime and its derivatives, which generally appear to rely upon the stability of the resultant metal complex, this work has demonstrated that the oxime functionality can be chemically activated by binding to a metal (VO^{2+}) centre.

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§ A single ^{51}V resonance was observed at δ −604 (linewidth 947 Hz) *vs.* VOCl$_3$. The nine chemically distinct carbon atoms were resolved in the ^{13}C NMR spectrum; the Me group at δ 18 and eight other resonances in the range δ 115–174. The ^{1}H NMR spectrum was recorded for **1** in $(CD_3)_2SO$, despite the limited solubility: δ 2.1 s (3H, CH_3); 6.8–7.1 m (2H), 7.3—7.9 m (2H, C_6H_4); 9.55 s (1H, $C_{oxime}H$); 10.5–11.0 s br (1H, $N_{imine}H$). The IR spectrum includes absorptions at (cm^{-1}): 917 *vs.* and 956 *vs.* $\nu(O{=}V{=}O)$; 1534 m $\nu(C{=}N_{oxime})$; 1508 s $\nu(C{=}N_{imine})$. Positive ion FAB mass spectrometry gave *m/z* values for the parent ion and several identifiable fragments.