Reactivity of Oximes and Amide Oximes Towards Oxo-vanadium Compounds

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The reactions of salicylaldoxime and salicylamide oxime with $[VO(acac)_2]$ yield several unusual compounds, including $[V_3O_3(OR)_5(OC_6H_4CH{=}NO)_2]$ (R = Me, Et), $[VO_2\{OC_6H_4CX{=}NOC(Me){=}NH\}]$ (X = H, NH_2) and $[VO(OR)\{OC_6H_4CH{=}NCHC_6H_4OC(O)(Me)CHCOMe\}]$ where the tetradentate ligand results from the coupling of acetylacetone with salicylaldimine and salicylaldehyde.

While the coordination chemistry of polyoxomolybdates has now reached a stage of maturation, that of polyoxovanadates is just beginning to emerge.[1] One reason for this difference is that many organic ligands undergo transformation upon reaction with oxo-vanadium complexes. Nevertheless, a lot of oxo-vanadium complexes with alkoxo,[2] organophosphonate,[3a] organoarsonate[3b] and carboxylate[4] ligands have now been characterized. We have recently investigated the reactions of oximes[5] and amide oximes[6] with oxo-molybdenum complexes. These studies have now been extended to oxo-compounds of vanadium(IV) and vanadium(V). Although oxo-vanadium complexes with simple† amide oximes do exist,‡ the development of their chemistry has been so far hampered by the easy deoxygenation of amide oximes into amidines. Thus we turned to functionalized† oximes and amide oximes. We report here some reactions of salicylaldoxime and salicylamide oxime with $[VO(acac)_2]$.

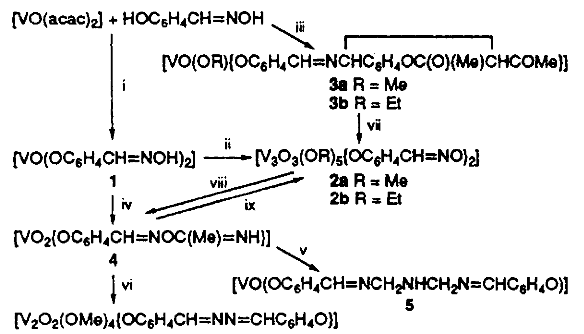
At room temp. the reaction of salicylaldoxime with $[VO(acac)_2]$ in MeOH yields the already reported[7,8] complex $[VO(OC_6H_4CH{=}NOH)_2]$ **1**, isolated in 25% yield as a green powder, and a brown solution from which red–brown crystals of $[V_3O_3(OMe)_5(OC_6H_4CH{=}NO)_2]$ **2a** were recovered after 5 days standing. Prior heating to reflux results in the formation of $[VO(OMe)\{OC_6H_4CH{=}NCHC_6H_4OC(O)(Me)CHCOMe\}]$ **3a**, isolated as red–brown crystals in 70% yield. The ethoxo derivative **3b** has been similarly obtained in EtOH. Attempts to recrystallize **1** from refluxing MeCN gave $[VO_2\{OC_6H_4CH{=}NOC(Me){=}NH\}]$ **4**. The complex $[VO\{OC_6H_4C(NH_2){=}NOH\}_2]$ **1′**, obtained by reaction of salicylamide oxime with $[VO(acac)_2]$ in MeOH, similarly gave $[VO_2\{OC_6H_4C(NH_2){=}NOC(Me){=}NH\}]$ **4′** in refluxing MeCN. Some reactions of **4** are presented in Scheme 1. In other respects, **2a** can be recovered in *ca.* 20% yield by reaction of **3a** with $NH_2OH{\cdot}HCl$ in refluxing MeOH.

The complexes **2b**, **3a** and **4′** have been characterized by X-ray crystallography.¶ The trinuclear complex **2b** displays approximate C_2 symmetry, with the pseudo-axis passing by the V(2) atom (Fig. 1). Each salicylaldoximato(2-) ligand is chelating one vanadium atom, *e.g.* V(1) or V(11), through the phenolate oxygen atom and the nitrogen atom and is bridging the two other vanadium atoms by the oximate oxygen atom. The dimensions of the *cis*-$\{VO(OEt)\}^{2+}$ units are typical of the $\{VO(OR)\}^{2+}$ moiety.[9] The short V–O bonds involving the ethoxo groups indicate some multiple-bond character. Only a few trinuclear vanadium(V) complexes have been previously reported.[10]

The formation of the vanadium(V) complexes **2**–**4** from a vanadium(IV) precursor occurs in the absence as well as in the presence of air. The oxidant could be the ligand itself, as it is well known that oximes and amide oximes[11] can act as oxygen-transfer reagents. The formation of $[VO_2\{OC_6H_4C(NH_2)_2\}(acac)]$ **7** by reaction of $[VO(acac)_2]$ with salicylamide oxime in refluxing methanol provides definitive support for the conversion of amide oximes into amidines in the presence of oxo-vanadium(IV) compounds.[12]

The molecular structure of **4′** is closely related to that of **4**.[8] The complex displays a square pyramidal geometry with one oxo ligand in apical position (Fig. 2). There is an intramolecular hydrogen bond between O(4) and the NH_2 group. The tridentate ligand in **4′** results from the addition of salicylamide oxime on MeCN. Amide oximes themselves can be formed by addition of NH_2OH on RCN,[13] and oxidation of benzamide oxime yields a compound which apparently results from the addition of $PhC(NH_2)NOH$ on PhCN.[14] However, the addition of salicylamide oxime on MeCN as well those of salicylaldoximes and salicylketoximes on nitriles[8] require the presence of vanadium. The reaction can be reversed as shown by the transformation of **4** to **2a** in refluxing methanol.

The complex **3a** displays a highly distorted octahedral geometry (Fig. 3). Bond lengths to the vanadium centre range from 1.577(5) to 2.575(6) Å while *cis*-bond angles range from 69.7(2) to 103.6(3)°. The carbonyl oxygen atom O(4) is only weakly bounded to vanadium.



Scheme 1 *Reagents and conditions*: i and ii, ROH at room temp.; iii and ix, reflux in ROH; iv and viii, reflux in MeCN; v, NH_2OH, reflux in MeOH; vi, $[N_2H_6]Cl_2$, MeOH; vii, $[NH_3OH]Cl$, reflux in MeOH

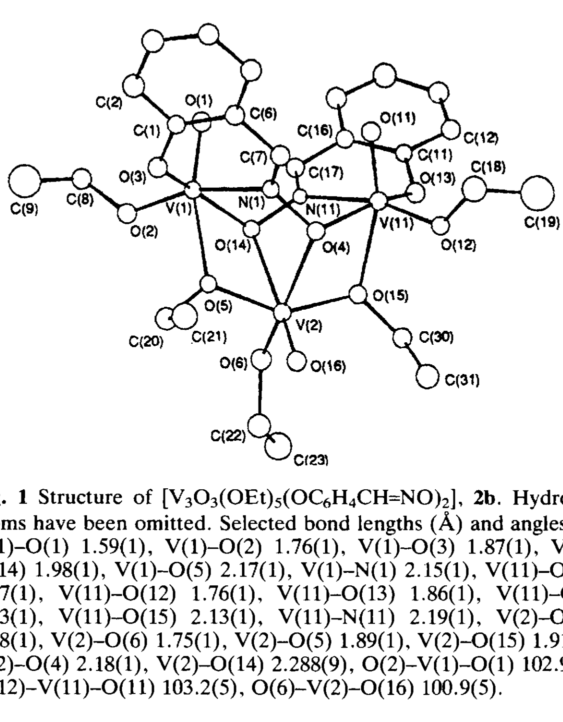


Fig. 1 Structure of $[V_3O_3(OEt)_5(OC_6H_4CH{=}NO)_2]$, **2b**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.59(1), V(1)–O(2) 1.76(1), V(1)–O(3) 1.87(1), V(1)–O(14) 1.98(1), V(1)–O(5) 2.17(1), V(1)–N(1) 2.15(1), V(11)–O(11) 1.57(1), V(11)–O(12) 1.76(1), V(11)–O(13) 1.86(1), V(11)–O(4) 2.03(1), V(11)–O(15) 2.13(1), V(11)–N(11) 2.19(1), V(2)–O(16) 1.58(1), V(2)–O(6) 1.75(1), V(2)–O(5) 1.89(1), V(2)–O(15) 1.91(1), V(2)–O(4) 2.18(1), V(2)–O(14) 2.288(9), O(2)–V(1)–O(1) 102.9(5), O(12)–V(11)–O(11) 103.2(5), O(6)–V(2)–O(16) 100.9(5).

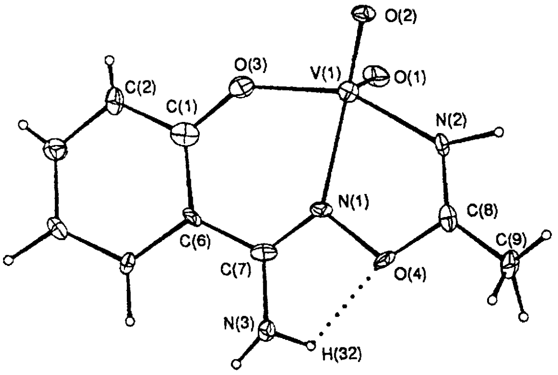


Fig. 2 Structure of $[VO_2\{OC_6H_4C(NH_2){=}NOC(Me){=}NH\}]$, **4′**. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.62(1), V(1)–O(2) 1.647(9), V(1)–O(3) 1.89(1), V(1)–N(2) 2.02(1), V(1)–N(1) 2.11(1), C(6)–C(7) 1.45(2), C(7)–N(3) 1.35(2), C(7)–N(1) 1.30(2), N(1)–O(4) 1.47(1), O(4)–C(8) 1.35(2), C(8)–N(2) 1.30(2), O(1)–V(1)–O(2) 109.2(5), O(1)–V(1)–O(3) 103.6(5), O(2)–V(1)–O(3) 100.5(5), N(1)–V(1)–O(1) 114.0(5), N(1)–V(1)–O(2) 135.5(5), N(1)–V(1)–O(3) 79.8(5), N(2)–V(1)–O(1) 98.8(5), N(2)–V(1)–O(2) 91.3(5), N(2)–V(1)–O(3) 149.5(5), N(1)–V(1)–N(2) 72.2(5).

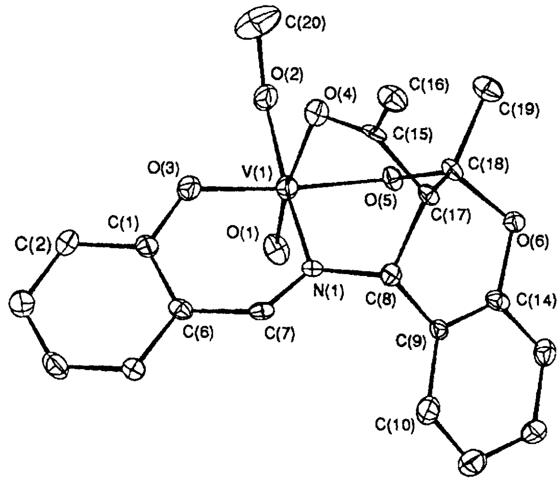


Fig. 3 Structure of $[VO(OMe)\{OC_6H_4CH{=}NCHC_6H_4O{-}C(O)(Me)CHCOMe\}]$, **3a**. Hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (°): V(1)–O(1) 1.577(5), V(1)–O(2) 1.750(6), V(1)–O(5) 1.850(5), V(1)–O(3) 1.877(5), V(1)–N(1) 2.143(6), V(1)–O(4) 2.575(6), C(7)–N(1) 1.294(9), N(1)–C(8) 1.464(8), C(8)–C(17) 1.540(9), C(17)–C(18) 1.54(1), C(17)–C(15) 1.51(1), C(15)–C(16) 1.49(1), C(15)–O(4) 1.221(8), C(18)–C(19) 1.51(1), C(18)–O(5) 1.367(8), O(1)–V(1)–O(2) 103.6(3), N(1)–C(8) C(17) 111.1(5), N(1)–C(8)–C(9) 111.6(6), C(9)–C(8)–C(17) 110.4(9), C(8)–C(17)–C(15) 111.7(6), C(8)–C(17)–C(18) 107.5(6), C(15)–C(17)–C(18) 110.5(6), C(17)–C(18)–O(6) 107.9(6), C(17)–C(18)–C(19) 112.9(6), C(17)–C(18)–O(5) 110.1(6), O(5)–C(18)–C(19) 112.9(6), O(5)–C(18)–O(6) 108.4(6), O(6)–C(18)–C(19) 104.1(6), C(17)–C(15)–C(16) 118.9(7), C(17)–C(15)–O(4) 120.6(7), C(16)–C(15)–O(4) 120.5(8).

The formation of the novel tetradentate ligand in complexes **3**|| is a remarkable template reaction, which apparently involves the coupling of 1 mol of acetylacetone with 1 mol of salicylaldimine and 1 mol of salicylaldehyde. The formation of salicylaldimine from salicylaldoxime has already been mentioned; although there is no direct evidence for hydrolysis of salicylaldoxime into salicylaldehyde, such a reaction is substantiated by the formation of **3** from $[VO(acac)_2]$ and salicylaldoxime and that of **5** from **4**.

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Footnotes

† Simple oximes and amide oximes are ligands without any additional donor set, *e.g.* acetone oxime and acetamide oxime, whereas functionalized oximes and amide oximes have an additional function in α or β of the oxime or amide oxime function.

‡ $[VO_2\{MeC(NH)NHO\}\{MeC(NH_2)NHO\}]\cdot H_2O$ is readily obtained by mixing $VOSO_4\cdot 5H_2O$ and acetamide oxime in water and allowing the solution to stand at room temp.

§ All compounds gave satisfactory analyses.

¶ *Crystal data*: Determination of cell constants and data collection were carried out at room temp. on a Nonius CAD4F (**2b** and **3a**) or Philips PW100 diffractometer (**4′**) using graphite monochromated Mo-Kα radiation. The data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the program DIFABS. The structures were solved by direct methods. The non-hydrogen atoms were refined either isotropically (**2b**) or anisotropically (**3a** and **4′**); hydrogen atoms were located on successive difference Fourier maps and fixed in these positions. All calculations were performed with CRYSTALS. **2b**: $C_{24}H_{35}N_2O_{12}V_3$, $M = 696.37$, triclinic $P\bar{1}$, $a = 10.237(3)$, $b = 12.824(3)$, $c = 13.531(3)$ Å, $\alpha = 114.26(2)$, $\beta = 102.95(2)$, $\gamma = 94.76(2)°$, $V = 1547(2)$ Å^3, $Z = 2$, $D_c = 1.50$ g cm^{-3}. 1120 observed reflections [$I > 3\sigma(I)$; $2\theta_{max} = 40°$]; $R = 0.049$, $R_w = 0.055$ with $w = 1$.

3a: $C_{20}H_{20}NO_6V$, $M = 421.32$, orthorhombic, $Pbna$, $a = 11.631(3)$, $b = 15.913(2)$, $c = 20.623(3)$ Å, $V = 3817(1)$ Å^3, $Z = 8$, $D_c = 1.47$ g cm^{-3}. 1159 observed reflections [$I > 3\sigma(I)$; $2\theta_{max} = 50°$]; $R = 0.041$, $R_w = 0.042$ with $w = 1$.

4′; $C_9H_{10}N_3O_4V$, $M = 275.14$, monoclinic, $C2/c$, $a = 10.317(1)$, $b = 9.826(1)$, $c = 20.310(9)$ Å, $\beta = 90.55(3)°$ $V = 2059(1)$ Å^3, $Z = 8$, $D_c = 1.78$ g cm^{-3}. 597 observed reflections [$I > 3\sigma(I)$; $2\theta_{max} = 40°$]; $R = 0.070$, $R_w = 0.074$ with $w = 1$.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

|| An X-ray crystallographic study of **3b** has confirmed that both complexes **3a** and **3b** contain the same ligand and that their molecular structures are closely related.

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