Dioxo- and Oxovanadium(V) Complexes of Biomimetic Hydrazone *ONO* Donor Ligands: Synthesis, Characterisation, and Reactivity

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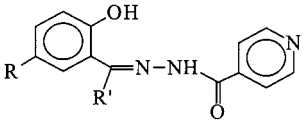
The dioxovanadium(V) complexes M[VO_2(L)*solv*] (**2**, **5**, **6**) have been isolated along with dimeric, oxo-bridged monooxovanadium complexes with the formula [{VOL}$_2$μ-O] (**1**, **4**), and characterised by their spectral and thermogravimetric properties and reactivity patterns. H_2L is the hydrazone H_2{(R-sal)-iNH} [sal derives from salicylaldehyde (R = H) or *p*-Cl-salicylaldehyde (R = Cl)] or H_2hap-iNH, where hap is the *o*-hydroxyacetophenone moiety, and iNH stands for isonicotinic acid hydrazide. In the isolated potassium (M = K) complexes **2a**, **5** and **6**, *solv* is a water molecule, which was exchanged for methanol or DMSO in the respective solutions as shown by ^{51}V NMR. Treatment of the dimeric (**1** and **4**) or anionic complexes (**2a** and **5**) with H_2O_2 yielded (unstable) oxoperoxovanadium complexes K[$VO(O_2)$L] (**7**, **8**). Acidification of **1** and **4** afforded oxohydroxo complexes. When compound **2a** is dissolved in methanol, it is partly deoxygenated to form [VO(OMe)(HOMe)L] (**9**), the crystal and molecular structures of which have been determined, confirming the *ONO* binding mode of L in its enolate form.

Introduction

The coordination chemistry of vanadium with multidentate ligands has achieved a special status in the last decade because of its catalytic[1,2] and medicinal[3−5] input. Structural and/or functional models for vanadate-dependent haloperoxidases, for vanadium nitrogenases and other biologically active vanadium compounds have further stimulated vanadium coordination chemistry.[6,7] The active site structures of the vanadate-dependent haloperoxidases have been revealed by X-ray diffraction studies. Accordingly, the vanadate ion is distorted towards a trigonal pyramid, thus providing a fifth coordination site which is occupied by N^{ε} of a histidine, covalently linking the vanadate ion to the protein.[8−10] These enzymes lose their activity upon reduction or removal of vanadium; re-oxidation or reconstitution with vanadate fully restores their activity,[11] demonstrating that V^V (VO^{3+} or VO_2^+) is essential for catalytic activity. Various types of oxovanadium(V) complexes such as [VO(OR)(HOR)L],[12−16] [VO(OR)L][17,18] [{VOL}$_2$μ-O],[19−22] [VOL(DD)],[23−30] [VO_2L][29,31−42] [H_2L is an *ONO* (hydrazone, azo or Schiff base) ligand, and DD a monobasic, bidentate *OO* or *ON* donor], [VO_2-(picolinate)$_2$]$^-$,[43] and [VO_2(nitrilotriacetate)]$^{2-}$[44] have been studied in this context.

Dioxovanadium(V) complexes are commonly synthesised by the reaction of (i) vanadates with *ONO*-functional ligands in aqueous solution,[33−38] or (ii) [VO(acac)$_2$] (acacH = acetylacetone) or $VOSO_4$ with the ligands in non-aqueous or mixed solvent media followed by oxidation with O_2.[37−40] Pecoraro et al. have prepared dioxovanadium(V) complexes by the reaction of [$VO(OEt)_3$] with appropriate ligands[41] or by oxidation of oxovanadium(IV) complexes with KNO_2 in H_2O/MeOH.[42] The present series of dioxovanadium complexes containing *ONO*-functional ligands[37−42,45] is comparatively limited. We present here the preparation and characterisation of VO_2^+ complexes of *N*-isonicotinamidosalicylaldimines (aroylhydrazones; Scheme 1). These ligands possess five potential donor sites, three of which are used, namely the phenolate and enolate oxygen atoms, and the imine nitrogen atom originating from the condensation of the hydrazine and salicylaldehyde. Coordination compounds of aroylhydrazones have been reported to act as inhibitors of enzymes,[46a] and antifungal/antibacterial agents.[46b] Spectral and structural aspects, reactivity patterns of the compounds, and the crystal structure of a deoxygenation product are reported.



R' = H, R = H: **H_2sal-iNH**
R' = H, R = Cl: **H_2Clsal-iNH**
R' = Me, R = H: **H_2hap-iNH**

Scheme 1

Results and Discussion

Synthesis and Solid-State Characteristics of Dioxovanadium Complexes

Structures of the dioxovanadium complexes **2**, **5** and **6**, based on spectroscopic data, thermogravimetric studies, elemental analyses and the X-ray diffraction analysis of **9** (the deoxygenation product of **5**) are shown in Scheme 2. The structures are formulated for the solid samples isolated as described in the Exp. Sect. As shown by ^{51}V NMR spectro-

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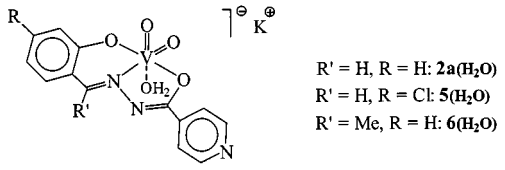
scopy (see below), the water ligand is possibly replaced by a solvent molecule in methanol and DMSO.



R' = H, R = H: **2a(H_2O)**
R' = H, R = Cl: **5(H_2O)**
R' = Me, R = H: **6(H_2O)**

Scheme 2

A solution of potassium vanadate(V), generated in situ by dissolving V_2O_5 in aqueous KOH, reacts with the potassium salt of the ligands H_2Rsal-iNH (Scheme 1) at pH = 7.5 to give two types of vanadium(V) complexes, namely the neutral, oxo-bridged dimeric monooxovanadium complexes [{VO(Rsal-iNH}$_2$μ-O] (**1**: R = H; **4**: R = Cl), and potassium salts of the anionic dioxovanadium complexes K[VO_2(Rsal-iNH)H_2O)] [**2a(H_2O)**: R = H; **5(H_2O)**: R = Cl]. Using $NH_4[VO_3]$ and the sodium salt of the ligands results in the formation of the corresponding ammonium salts NH_4[VO_2(Rsal-iNH)H_2O)] [**2b(H_2O)**: R = H] along with the dimers. The final pH value of the reaction mixture plays an important role in that a decrease (to pH = 6.5) increases the yield of the dimeric complex. Neutral dimeric and anionic complexes can be separated by fractional crystallisation from methanol, where the dimers crystallise first. The ligand H_2hap-iNH only yields the dioxovanadium complex K[VO_2(hap-iNH)H_2O] [**6(H_2O)**]. Complex **1** was also synthesised by allowing equimolar amounts of [$VO(acac)_2$] and H_2sal-iNH to react in acetone, followed by aerial oxidation [Equations (1) and (2)].

$$[VO(acac)_2] + H_2\text{sal-iNH} \rightarrow \underset{\mathbf{3}}{[VO(\text{sal-iNH})]} + 2\text{acacH} \quad (1)$$

$$2\underset{\mathbf{3}}{[VO(\text{sal-iNH})]} + 1/2O_2 \rightarrow \underset{\mathbf{1}}{[\{VO(\text{sal-iNH})\}_2\mu\text{-O}]} \quad (2)$$

The intermediate complex **3** can be isolated as a stable solid. Furthermore, **1** is obtained from the reaction of $VO(OEt)_3$ with H_2sal-iNH in absolute ethanol under aerobic conditions. The most probable reaction pathways for this reaction are given by Equations (3) and (4), based on the analogy of the formation of the dimeric complex [{VO(sal-L-pheala)}$_2$μ-O] (H_2sal-L-pheala = *N*-salicylidene-L-phenylalaninato) by exposure of CH_2Cl_2 solutions of [VO(OMe)(MeOH)(sal-L-pheala)] to air.[21] The underlying reaction is probably an exchange of OR by OH (from moisture), followed by condensation to form the dimeric compound.

$$VO(OEt)_3 + H_2\text{sal-iNH} \xrightarrow{\text{EtOH}} [VO(OEt)(EtOH)(\text{sal-iNH})] \quad (3)$$

$$[VO(OEt)(EtOH)(\text{sal-iNH})] \xrightarrow{(H_2O)} [\{VO(\text{sal-iNH})\}_2\mu\text{-O}] \quad (4)$$

The brown, dimeric complexes **1** and **4** are poorly soluble in methanol, ethanol, DMF and DMSO, while the yellow to yellow-orange dioxo complexes **2, 5** and **6** are soluble in all these solvents.

As shown by, inter alia, thermogravimetric analysis, **2**, **5** and **6** contain one molecule of water. Thermogravimetric data are collated in Table 1. The dioxo complexes lose water in the temperature range 90−200 °C, indicative of covalently, though not particularly strongly bonded water. This is expected if the water is coordinated in the *trans* position to one of the doubly bonded oxygen atoms (cf. Scheme 2). The remaining anhydrous complexes **2a**, **5** and **6** decompose at higher temperatures (loss of the ligand less one oxygen atom) to form potassium metavanadate $K[VO_3]$. The decomposition pattern is different for the anhydrous ammonium salt **2b**: Between 205 and 330 °C, a weight loss of 7.5% corresponding to the loss of NH_3 and H_2O occurs, possibly by the reaction sequence represented by Equations (5) and (6).

$$NH_4[VO_2(\text{sal-iNH})] \rightarrow H[VO_2(\text{sal-iNH})] + NH_3 \quad (5)$$

$$2H[VO_2(\text{sal-iNH})] \rightarrow [\{VO(\text{sal-iNH})\}_2\mu\text{-O}] + H_2O \quad (6)$$

On further heating, [{VO(sal-iNH)}$_2$μ-O] decomposes to yield V_2O_5 as the final product. The decomposition pattern of **4** is interesting because it undergoes elimination of oxy-

Table 1. Thermogravimetric analyses

Compound	Temperature range (°C)	% Weight loss obs. (calcd.)	Group lost	(Expected) residue	% Residue obs. (calcd.)
2a	100-200	5.2 (4.8)	H_2O	K[VO_2(sal-iNH)]	
	350-750	59.0 (58.8)	L − 1O	K[VO_3]	35.8 (36.4)
2b	110-185	5.0 (5.0)	H_2O	NH_4[VO_2(sal-iNH)]	
	205-330[a]	7.5 (7.3)	NH_3 + 1/2H_2O	1/2[V_2O_3(sal-iNH)$_2$]	
	340-600	63.0 (62.3)	L − 1O	V_2O_5	24.5 (25.4)
4	160-225	2.5 (2.3)	1/2O_2	2[VO(Clsal-iNH)]	
	255-730	71.5 (71.4)	2L − 3O	V_2O_5	26.0 (26.0)
5	90-185	4.5 (4.4)	H_2O	K[VO_2(Clsal-iNH)]	
	63.0 (62.3)		L − 1O	K[VO_3]	33.5 (33.4)
6	4.5 (4.6)		H_2O	K[VO_2(hap-iNH)]	
	61.0 (60.3)		L − 1O	K[VO_3]	34.5 (35.1)

[a] See text for additional details.

gen by the rupture of the μ-$O(VO)_2$ fragment with the concomitant thermally induced reduction of V^V to V^{IV} and the formation of **3** [Equation (7)].

$$\underset{\mathbf{1}}{[\{VO(sal\text{-}iNH)\}_2\mu\text{-}O]} \rightarrow 2\underset{\mathbf{3}}{[VO(sal\text{-}iNH)]} + 1/2O_2 \quad (7)$$

The poor stability of **3** did not allow for its isolation, in contrast to the corresponding Mo and W systems, where the intermediately formed species have been isolated and characterised.[47]

The IR spectra of the ligands exhibit bands in the regions 1678−1680 and 3100−3180 cm^{-1} due to ν(C=O) and ν(NH) stretches, respectively. These bands disappear on complexation, indicating the transformation of the carbonyl moiety owing to enolisation and consequent replacement of H by the metal ion. A new band appearing in the 1210−1250 cm^{-1} region was assigned to the ν(C−O) (enolato) mode. The ν(C=N) (azomethine) stretch of the ligands appears at 1609−1629 cm^{-1}, and this band is shifted to a lower wavenumber by 10−15 cm^{-1} in the complexes, thereby indicating the coordination of the azomethine nitrogen atom. In the dimeric complexes **1** and **4**, this band is doubled, suggesting a nonequivalence of the two halves of the molecule, e.g. because of an asymmetric bridge. A ligand band at 900−1000 cm^{-1} due to the ν(N−N) stretch undergoes a 10−40 cm^{-1} shift to a higher wavenumber upon complexation. The high frequency shift of the ν(N−N) band is expected because of diminished repulsion between the lone pairs of adjacent nitrogen atoms.[48] A broad band for the ligands at approximately 2800 cm^{-1} was assigned to intramolecular hydrogen bonds involving the phenolic OH group; the absence of this band in the dioxo complexes indicates the deprotonation of the phenol and subsequent coordination of the oxygen atom to the metal centre. However, the presence of a broad band at approximately 3400 cm^{-1} is possibly due to coordinated water in these complexes. The dimeric complexes exhibit weak combination bands covering the region 2300−2700 cm^{-1}. This again suggests extensive intermolecular hydrogen bonding in the complexes.

All dioxovanadium(V) complexes exhibit two sharp bands in the 900−950 cm^{-1} region, indicative of the *cis*-$\{VO_2\}^+$ structural unit. In the dimeric complexes, two sharp bands arise at ca. 960 cm^{-1}, assigned to ν(V=O), and a broad band is observed at ca. 860 cm^{-1} due to ν[V−(μ-O)−V]. The presence of two ν(V=O) in the dimers **1** and **4** supports the nonequivalence of the two oxo-bridged halves[22] already noted above.

Solution Studies

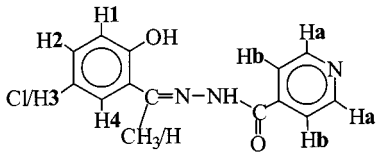
The electronic absorption spectra of all the ligands and complexes were recorded in methanol, and the absorption maxima with their extinction coefficients (wherever possible) are listed in Table 2. The UV spectra of the ligands exhibit three spectral bands at 214.5−219.5, 284−289.5 and 330−342 nm. The most probable assignments for these bands are $\Phi \rightarrow \Phi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. A weak shoulder associated with the second band, due to hydrogen bonding and association, is absent in the dioxo complexes. This indicates that the hydrogen bonds are broken after complex formation. In dimeric complexes, however, this band is still present, therefore indicating the existence of hydrogen bonding in solution as well. Other intra-ligand bands are still present in the complexes, with significant shifts in the band positions towards lower wavelengths. Dioxovanadium(V) complexes have a $3d^0$ configuration, and d−d bands are therefore not expected. All the complexes display an intense to medium electronic spectral band in the visible region at 403−410 nm. This was assigned to a ligand-to-metal charge-transfer (LMCT) transition from the phenolate oxygen atom to an empty d-orbital of the vanadium atom.

Table 2. Electron absorption spectra

Compound	λ_{max}/nm (ε/$M^{-1}cm^{-1}$)
H_2sal-iNH	333(16240), 289(18800), 214(25930)
$[\{VO(sal\text{-}iNH)\}_2\mu\text{-}O]$, **1**	402.5, 322, 279(sh), 226
$K[VO_2(sal\text{-}iNH)H_2O]$, **2a**	403.5(3746), 321(6245), 277(6790), 225(13890)
$NH_4[VO_2(sal\text{-}iNH)H_2O]$, **2b**	402.5(3000), 323(5070), 280(5410), 229(10140)
H_2Clsal-iNH	342.5(8025), 289.5(10475), 219.5(14875)
$[\{VO(Clsal\text{-}iNH)\}_2\mu\text{-}O]$, **4**	408.5, 321.5, 277(sh), 237
$K[VO_2(Clsal\text{-}iNH)H_2O]$, **5**	410.5(6100), 316.5(9600), 279(10085), 235(20730)
H_2hap-iNH	330(4860), 284.5(6350), 215(11960)
$K[VO_2(hap\text{-}iNH)H_2O]$, **6**	387(6200), 310(9500), 279(10800), 228(21900)
$K[VO(O_2)(sal\text{-}iNH)H_2O]$, **7**	412, 321, 222
$K[VO(O_2)(Clsal\text{-}iNH)H_2O]$, **8**	410, 322, 225

Further evidence for the coordination mode of the ligands was obtained from the ^1H and ^{13}C NMR spectra. The relevant spectral data are collected in Tables 3 and 4. They confirm the IR and UV/Vis evidence. A significant downfield shift of the azomethine (−CH=N−) proton signal in the complexes relative to the corresponding free ligands demonstrates the coordination of the azomethine nitrogen atom. In the ^1H NMR spectrum of the complexes, the absence of the ligand signals arising from the phenolic −OH and the hydrazone −NH protons in the δ = 11.08−13.19 region further indicates that bonding occurs through the phenolate and enolate groups. The methyl protons of H_2hap-iNH resonate at δ = 3.36, and this signal

Table 3. ^{1}H chemical shifts; see numbering scheme below



Compound[a,b]	-OH	-NH	-CH=N-	H_a	H_b	H4	H2	H1, H3
H_2sal-iNH	12.30	11.08	8.67(s)	8.79(d)	7.84(d)	7.59(d)	7.31(td)	6.94(d), 6.90(d)
[{VO(sal-iNH)}$_2\mu$-O], **1**			9.04(s)	8.77(br)	8.00(d)	7.65(d)	7.42(t)	ca. 6.88(m)
($\Delta\delta$)			(0.37)	(-0.02)	(0.16)	(0.06)	(0.11)	(-0.04)
K[VO_2(sal-iNH)H_2O], **2a**			9.05(s)	8.68(br)	7.86(d)	7.59(d)	7.37(t)	6.81(d)
($\Delta\delta$)			(0.38)	(-0.09)	(0.02)	(0)	(0.06)	(-0.11)
H_2Clsal-iNH	12.36	11.11	8.65(s)	8.79(d)	7.83(d)	7.65(dd)	7.32(td)	6.95(d)
[{VO(Clsal-iNH)}$_2\mu$-O], **4**			9.05(s)	8.80(br)	8.06(br)	7.76(br)	7.42(d)	6.95(d)
($\Delta\delta$)			0.40	(0.01)	(0.23)	(0.11)	(0.10)	(0)
K[VO_2(Clsal-iNH)H_2O], **5**			9.05(s)	8.68(br)	7.87(br)	7.58(br)	7.37(br)	6.80(d)
($\Delta\delta$)			(0.40)	(0.11)	(0.04)	(-0.07)	(0.05)	(-0.15)
H_2hap-iNH[c]	13.19	11.59	-	8.81(d)	7.84(d)	7.65(dd)	7.32(td)	6.89, 6.92(d)
K[VO_2(hap-iNH)H_2O][d], **6**				8.68(d)	7.90(d)	7.78(d)	7.32(t)	6.80(d), 6.83(d)
($\Delta\delta$)			-	(-0.13)	(0.06)	(0.13)	(0)	(-0.09) (-0.21)

[a] Letters given in parentheses indicate the signal structure: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, br = broad (unresolved). – [b] ($\Delta\delta$) = δ(complex) – δ(ligand). – [c] Methyl proton signals at δ = 3.36. – [d] Methyl proton signals at δ = 3.14 and 3.16.

appears as two independent signals of equal intensity at δ = 3.14 and 3.16 for complex **6**. Aromatic protons appear in the expected regions in spectra of the ligands as well as of the complexes, with slight shifts in their positions. All these data are consistent with what has previously been observed in dioxo molybdenum(VI)[49] and dioxotungsten(VI)[50] complexes with these ligands, and supports their dibasic tridentate *ONO* coordination mode.

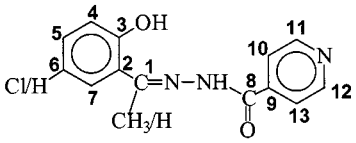
^{13}C NMR spectra (Table 4 and Figure 1) also provide useful diagnostic tools for the elucidation of the structures of the complexes. Assignments were based on the chemical shift and intensity patterns, and on the coordination-induced shifts $\Delta\delta$ = [δ(complex) – δ(free ligand)] of the signals for carbon atoms in the vicinity of the coordinating functions.[51] Large coordination shifts were observed for the carbon atoms bearing the phenolate and enolate oxygen atoms (C3 and C8) and for the azomethine carbon atom (C1). The ^{13}C NMR spectra of the dimeric, neutral complexes are nearly identical to those of the anionic dioxo complexes. The nonequivalence of the two halves of the molecules in solutions of dimers **1** and **4** is reflected in a broadening of the respective resonances. The solubility of the ammonium complex **2b** is too low to obtain high quality spectra. The spectral pattern of **2b** is, however, identical to that of the potassium salts **2a** and **5**. Heating the solutions to improve the solubility, causes slow demetallation of the complexes.

To further characterise the complexes, we recorded ^{51}V NMR spectra; δ(^{51}V) values of specific compounds are presented in the Exp. Sect. Owing to the quadrupole moment (spin 7/2) of the ^{51}V nucleus, the resonances are somewhat broadened; the line widths at half-height are typically approximately 200 Hz, which is still relatively narrow in ^{51}V NMR spectroscopy.[52] The dioxovanadium complexes **2**, **5** and **6** all show one strong resonance between δ = –530 and –550, which is what one would expect for a dioxovanadium complex containing a mixed *O*/*N* donor set.[52,53] For **2** and **5**, there is a distinct solvent dependence: In [D_6]DMSO, the signal appears at δ = –532, in methanol between δ = –539 and –541, and in deuterated methanol (CD_3OD) at δ = –549, hinting at participation of the solvent in coordination. The solvent dependence is less pronounced for **6** (δ = –533 and –538 in [D_6]DMSO and CD_3OD, respectively), which may be explained by steric hindrance imparted by the methyl group on the azomethine carbon atom, preventing effective binding of the solvent to the sixth coordination site. The approximately 10 ppm upfield shift of the signals in deuterated with respect to nondeuterated methanol can be traced back to a deuterium isotope effect $^n\Delta^D$ through two bonds ($DOCD_3$) plus three bonds ($DOCD_3$), [($^2\Delta$ + $3^3\Delta$)^D]: The heavier isotope gives rise to a more pronounced shielding of the metal nucleus as a consequence of a diminished paramagnetic deshielding term in the overall shielding.[52a]

Reactivity Patterns of 1 to 6, and the Structure of 9

cis-Dioxovanadium(V) complexes commonly generate oxomonoperoxo species in solution on treatment with

Table 4. ^{13}C NMR chemical shifts; for atom labelling see scheme below



Compound	C1	C8	C3	C9	C11, C12	C10, C13	C2, C4, C5, C6, C7
H_2sal-iNH	148.94	161.35	157.47	139.99	150.40	131.76	116.45, 118.70, 119.45, 121.52, 129.19
[{VO(sal-iNH)}$_2$μ-O], **1** (Δδ)[a]	156.50 (7.56)	167.20 (5.85)	164.30 (6.83)	141.80	148.00	134.20	116.20, 118.40, 118.80, 122.50, 133.20
K[VO_2(sal-iNH)H_2O], **2a** (Δδ)	157.37 (8.43)	167.82 (6.37)	164.96 (7.49)	140.13	150.04	133.68	116.85, 119.94, 121.55, 132.88
H_2Clsal-iNH	146.49	161.52	156.02	139.92	150.41	131.14	118.28, 120.72, 121.54, 123.10, 127.23
[{VO(Clsal-iNH)}$_2$μ-O], **4** (Δδ)	156.66 (10.17)	168.32 (6.80)	163.94 (7.92)	143.41	148.22	131.14	119.08, 122.54, 123.89, 132.35
K[VO_2(Clsal-iNH)H_2O], **5** (Δδ)	157.38 (10.89)	167.82 (6.30)	164.96 (8.90)	140.09	150.07	133.68	116.85, 119.94, 121.56, 123.89
H_2hap-iNH[b]	159.50	162.98	158.73	140.10	150.15	131.58	117.35, 118.62, 119.42, 122.01, 128.74
K[VO_2(hap-iNH)H_2O][c], **6** (Δδ)	163.90 (4.40)	167.30 (4.32)	161.33 (2.60)	149.26	150.26	133.39	116,52, 120.32, 121.89, 122.56, 130.28

[a] Δδ = δ(complex) − δ(free ligand). − [b] Methyl carbon signal at δ = 14.30. − [c] Methyl carbon signal at δ = 16.95.

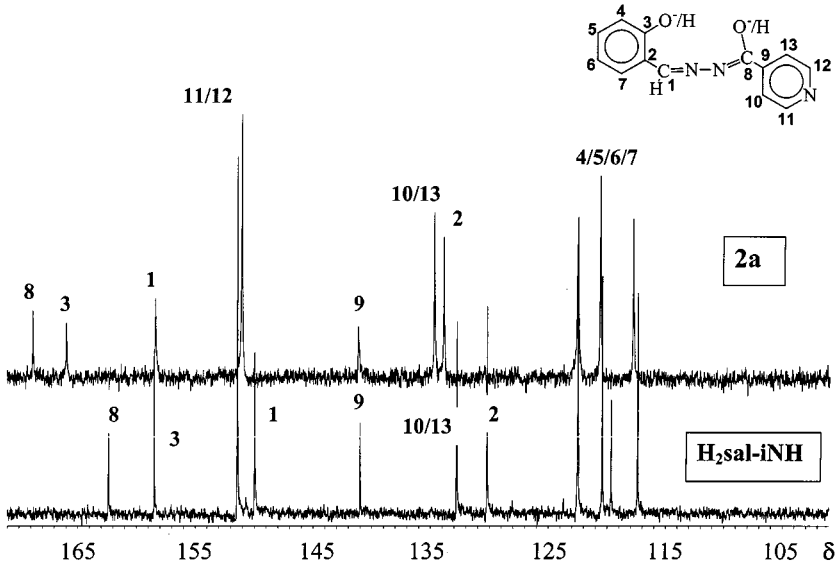


Figure 1. 90.56 MHz $^{13}C\{^1H\}$ NMR spectra of H_2sal-iNH (below) and its dioxovanadium complex **2a** in [D_6]DMSO (above); the inset shows the enol(ate) form of the ligand

H_2O_2,[14,54,55] and a corresponding reaction was also accomplished with **2a** and **5** with 30% H_2O_2 in methanol in an ice bath to yield **7** and **8** [cf. Equations (8) and (9)], which can also be obtained from the dimeric compounds **1** and **4.** The reaction, as monitored by electron absorption spectroscopy (Figure 2), exhibits an increase in intensity and shift of the band at 402.5 nm for **1** to 412 nm for **7**. Correspondingly, the 403.5 nm band of **2a** is shifted to 410 nm. This new band remains constant for several hours at approximately 10 °C. The rate at which peroxo complex formation occurs, seems to be dependent on the amount of H_2O_2 added. In both cases, the bands of the starting products at 322 and 226 nm remain almost unchanged, while the band at 279 nm gradually disappears. A similar spectral pattern was observed for **8**, in which these bands appear at 410, 322 and 225 nm. The relative stability of the peroxo

species at approximately 10 °C in the presence of excess of H_2O_2 enabled us to isolate complexes **7** and **8** (see Exp. Sect.), which showed a UV/Vis spectrum similar to that observed during spectroscopic studies. The peroxo complexes **7** and **8** show three IR-active modes associated with the $\{V(O_2)\}^{2+}$ moiety, namely the symmetric $V(O_2)$ stretch (ν_2) at ca. 580 cm^{-1}, the antisymmetric $V(O_2)$ (ν_3) at ca. 740 cm^{-1}, and the O−O (ν_1) stretch at ca. 895 cm^{-1}, characteristic of η^2-coordination of the peroxo group.[56] In addition, complexes **7** and **8** display the ν(V=O) mode at 950 (**7**) and 954 cm^{-1} (**8**). The isolated peroxo complexes are unstable and lose oxygen even at ambient temperature within a day. The species obtained in this way have spectral patterns (IR as well as electronic) similar to those of the dimers. The overall reaction may thus be represented as shown by the coupled (through **7**) [Equations (8) and (9)].

$$\underset{\mathbf{2a}}{[VO_2(\text{sal-iNH})]^-} + H_2O_2 \leftrightarrows \underset{\mathbf{7}}{[VO(O_2)(\text{sal-iNH})]^-} + H_2O \quad (8)$$

$$2\underset{\mathbf{7}}{[VO(O_2)(\text{sal-iNH})]^-} + 2H^+ \leftrightarrows \underset{\mathbf{1}}{[\{VO(\text{sal-iNH})\}_2\mu\text{-O}]} + H_2O_2 + \tfrac{1}{2}\,O_2 \quad (9)$$

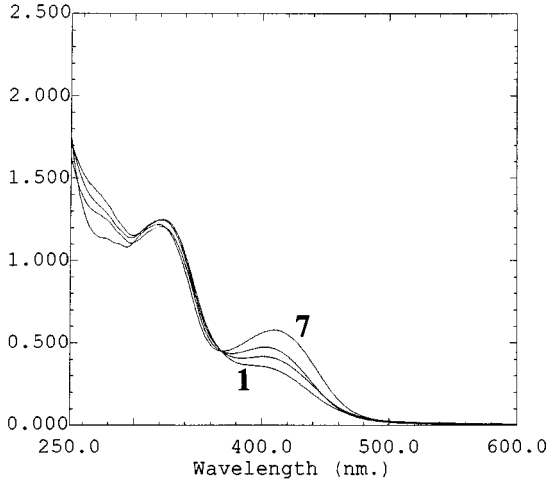


Figure 2. Titration of $[\{VO(\text{sal-iNH})\}_2\mu\text{-O}]$ (**1**) with 30% H_2O_2; the spectra were recorded after the successive addition of 2-drop portions of H_2O_2 to 5 mL of ca. 10^{-4} M solutions of **1** in MeOH

At ambient temperature, the ^{51}V NMR spectrum of **1** after addition of H_2O_2 in CD_3OD showed five resonances at δ = −616, −658, −678, −687 and −692. All these resonances are further upfield than those of the starting products and should indicate the formation of peroxo species.[57] The signal at δ = −692 corresponds to the diperoxovanadate $[VO(O_2)_2OH]^{2-}$, which is formed by partial decomposition of the peroxo complex.[58]

A solution of dimers **1** and **4** in methanol was treated with methanolic KOH at pH ≈ 8.5 and stirred for 1−2 h to provide $K[VO_2L(H_2O)]$-type complexes. The reaction is reversible, i.e. treatment of the monomeric complexes **2a** and **5** with HCl in methanol at pH ≈ 6.5 provides $[\{VOL\}_2\mu\text{-O}]$.

Addition of methanol *saturated* with HCl gas to a methanolic solution of **4** results in a colour change from orange-red to dark red with a gradual shift of the bands at 321.5 and 408.5 nm to 337 and 428 nm, respectively, as illustrated in Figure 3a. A similar behaviour has also been observed for **1**; the bands at 322 and 402.5 nm gradually shifted to 341 and 425 nm on acidification. Based on literature reports[42,59] on similar reactions, the species formed on acidification is most probably $[VO(OH)(\text{Clsal-iNH})H_2O]$. A hydroxooxo complex, viz. $[VO(OH)(HL)]^+$, H_2L = *N*-[(*o*-hydroxyphenyl)methyl]-*N*′-(2-hydroxyethyl)ethylenediamine, has been generated by Pecoraro et al.[33] in solution from the respective dioxovanadium(V) dimer, and the hydroxovanadium(IV) complex $[TpVO(OH)(H_2O)]$ [Tp = tris(pyrazolyl)borate] has recently been structurally characterised.[60] The formation of a hydroxo complex is further corroborated by an upfield shift of the ^{51}V NMR resonance from $\delta(^{51}V) = -533$ for **4** to δ = −554 for the species formed on acidification. The dependence of the ^{51}V shielding on protonation is well documented for vanadates(V)[57] and peroxovanadates.[57a,61] IR and electronic spectra of the compound isolated from the solution under study match well with those of **4**, indicating that on isolation, deprotonation and recovery of the starting material occurs. The reversibility of the reaction is also pertinent in solution (Figure 3b), when the acidified solution is treated with KOH dissolved in methanol. These results are of some interest in the context of the active-site structure and the function of vanadate-dependent haloperoxidases, for which a hydroxo ligand in an apical position has been noted on the basis of X-ray diffraction data[8−10] and proposed as an intermediate on the basis of kinetic studies.[42] Interestingly, no isosbestic points were observed during the progress of the reaction, which indicates complete conversion of $[(VOL)_2\mu\text{-O}]$ into the new species. A further increase in the HCl concentration does not cause changes in the LMCT band positions; excess HCl finally results in decomposition.

The formation of the neutral, monomeric monooxovanadium complex $[VO(OMe)(HOMe)(\text{Clsal-iNH})]$ (**9**) from the dioxo complex **5** by exposing methanolic solutions to low temperatures for a couple of weeks is of interest in the context of oxovanadium complexes used as oxo-transfer reagents both in catalytic and stoichiometric oxygenation reactions.[62,63] We have not been able to isolate bulk amounts of **9**; the predominant species in the mother liquor remains **5**, suggesting an equilibrium of the kind shown in Equation (10), from which **9** is gradually removed by crystallisation. The presence of small amounts of **9** in solution is also indicated by ^{51}V NMR (minor signal at −543).

$$\underset{\mathbf{5}}{K[VO_2(\text{Clsal-iNH})]} + 2\text{MeOH} \leftrightarrows \underset{\mathbf{9}}{[VO(OMe)(HOMe)(\text{Clsal-iNH})]} + \text{KOH} \quad (10)$$

Figure 4 shows an ORTEP drawing of the molecule, and a section from the unit cell of **9**, and Table 5 contains selected structure parameters. The basic structure is that of a tetragonal pyramid with the doubly bonded oxygen atom in the apex, and the phenolate and enolate oxygen atoms O2 and O3, the methoxide oxygen atom O4 and the imine nitrogen atom N1 in the plane. The vanadium atom devi-

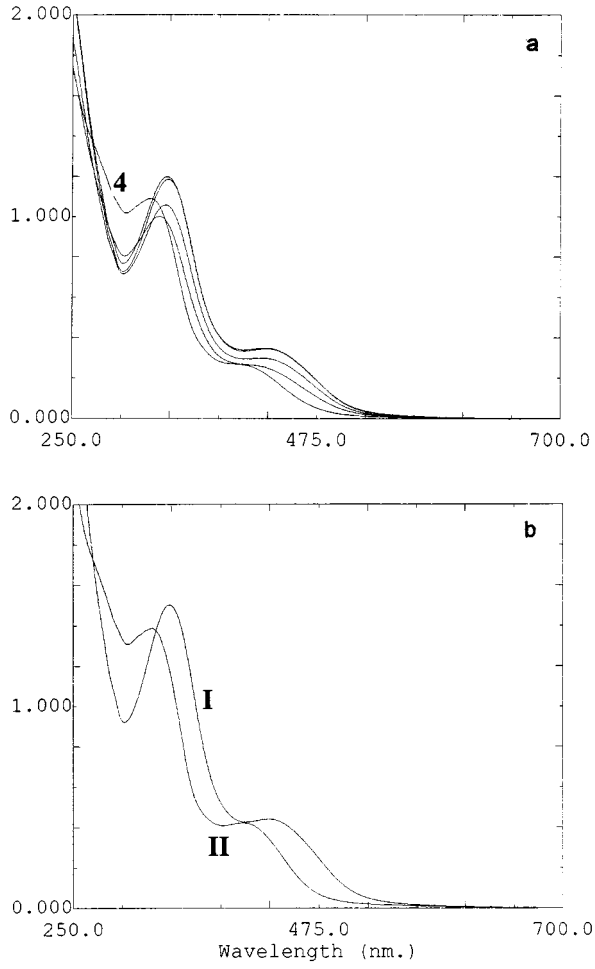


Figure 3. (a): Titration of [{VO(Clsal-iNH}$_2$μ-O] (**4**) with a saturated solution of HCl methanol; the spectra were recorded after the successive addition of 5-drop portions of methanol/HCl to 10 mL of a ca. 10^{-4} M solution of **4**; (b) electronic absorption spectra of **4** in methanol/HCl (I) and at pH ≈ 8.0 after addition of methanolic KOH to this solution (II)

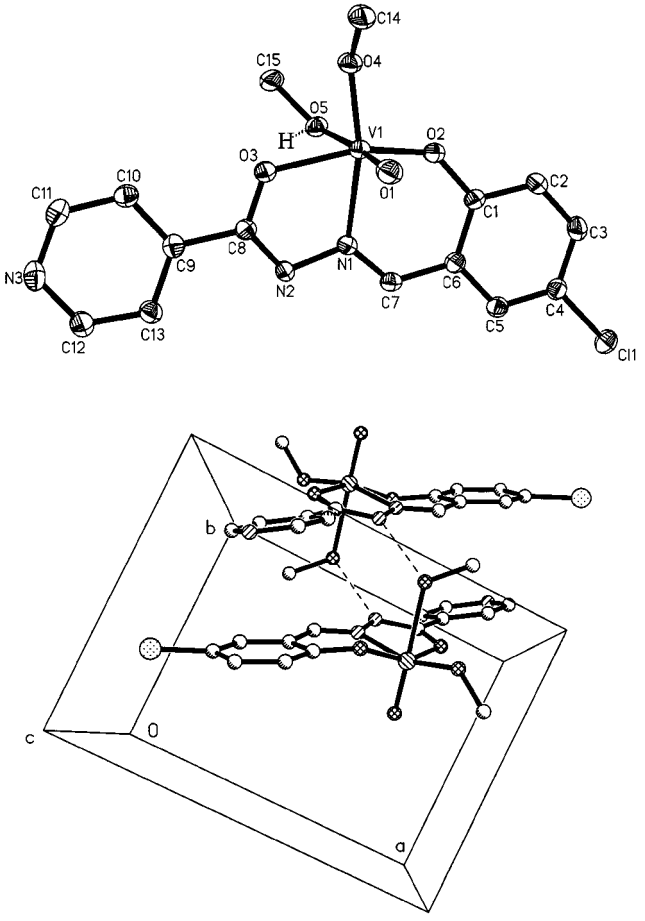


Figure 4. ORTEP plot (at the 50% probability level) of [VO(OMe)-(HOMe)(Clsal-iNH)] (**9**) (top), and a representation of the unit cell showing the interatomic hydrogen bonds (bottom)

Table 5. Selected bond lengths [pm] and bond angles [°] for **9**

V1-O1	1.558(2)	O1-V1-O5	175.84(9)
V1-O2	1.867(2)	O2-V1-O4	101.74(9)
V1-O3	1.971(2)	O3-V1-O4	95.44(9)
V1-O4	1.769(2)	O2-V1-N1	83.33(9)
V1-O5	2.327(2)	O3-V1-N1	74.18(8)
V1-N1	2.130(2)	O1-V1-O3	101.09(10)
O2-C1	1.341(3)	O1-V1-O2	100.13(10)
O3-C8	1.300(3)	O1-V1-O3	97.76(10)
O4-C14	1.426(3)	O2-V1-O5	81.99(9)
O5-C15	1.431(3)	O3-V1-O5	78.97(8)
O5-H5	0.82(4)	O4-V1-O5	81.88(8)
N2···H5	2.052	N1-V1-O5	82.15(8)
Cl1-C4	1.747(3)	V1-N1-N2	116.13(16)
N1-N2	1.402(3)	V1-N1-C7	127.23(17)
N1-C7	1.294(4)	N2-N1-C7	116.4(2)
N2-C8	1.309(3)	N1-N2-C8	108.0(2)

ates from this plane by 0.23 Å. The position *trans* to the oxo group is occupied by a weakly bonded methanol molecule [V−O5 = 2.327(2) Å]. The elongation of this bond is due to the strong *trans* influence of the oxo group and has previously been observed in other complexes containing the {VO(*ONO*)HOR}[12−16,29] or {VO(*ONO*)H_2O}[64] moieties. The other bond lengths *d* are similar to those observed in similar complexes;[12,25,28,29] the distances *d*(O3−C8) [1.300(3) Å] and *d*(N2−C8) [1.309(3) Å] support the enolate mode of coordination. With 175.84(9)°, the O=V−(HOMe) axis is almost linear. In the tetragonal plane, the two "open" angles O2−V−O4 and O3−V−O4 amount to 101.7 and 95.4°, while the bite angles of the tridentate ligand are 74.2° for the 5-membered ring, and 83.3° for the 6-membered ring. The ligand system is practically planar. The only angle that deviates significantly from sp^2 planarity is the angle of 108.0(2)° at the (noncoordinating) N2. This nitrogen atom is involved in intermolecular hydrogen bonding to the proton of the coordinated methanol, as shown in Figure 4, bottom; the N2···H−O5 distance amounts to 2.87 Å.

Conclusion

Oxovanadium(V) complexes show in vitro and in vivo activity in oxidation and oxygen-transfer reactions.[62,65] In the native systems (vanadate-dependent haloperoxidases) which have also been shown to exhibit oxo-transferase activity,[66] vanadium is in an O_4N-coordination environment. Intermediates formed during catalytic turnover, containing protonated {VO_2} [{VO(OH)}, {VO(H_2O)}] and {VO(O_2)}

cores have been postulated.[42,62,67,68] The dioxovanadium compounds described here model the active site in vanadate-dependent haloperoxidases in that they contain an O_4N-donor set (as well as a weakly bonded water molecule), including a doubly bonded oxo group which can be protonated to form a hydroxooxo complex, or replaced by peroxide to form an oxoperoxo complex. Furthermore, the ability of vanadium compounds to transfer oxo groups is modelled by the formation of a structurally characterised monooxo complex [VO(OMe)(HOMe)L] (**9**) by deoxygenation of the dioxo complex K[VO_2L(HOMe)] [**2a(MeOH)**].

Experimental Section

General Remarks: V_2O_5, NH_4VO_3, salicylaldehyde (sal), isonicotinic acid hydrazide (iNH) and *o*-hydroxyacetophenone (hap) were purchased from Loba Chemie, India. 5-Chlorosalicylaldehyde was prepared according to a literature procedure.[69] H_2sal-iNH,[70a] H_2Clsal-iNH,[70a] H_2hap-iNH[70b] (cf. Scheme 1) and [VO(acac)$_2$][71] were prepared as described previously. − Elemental analyses were carried out by the Central Drug Research Institute, Lucknow, India. − IR spectra were recorded as KBr pellets with a Perkin−Elmer model 1600 FT-IR. − UV/Vis spectra (in methanol) were recorded with a UV-1601 PC UV/Vis spectrophotometer. − ^{1}H NMR spectra were obtained with a Bruker 200 MHz spectrometer, ^{13}C and ^{51}V NMR spectra with a Bruker AM 360 spectrometer at 90.56 and 94.73 MHz, respectively, in rotating 10-mm diameter vials with the common parameter settings. All δ(^{51}V) values are quoted relative to $VOCl_3$ as external standard. − Thermogravimetric analyses of the complexes were carried out on a simple manually operated thermobalance constructed in our laboratory. The instrument was calibrated using crystallised $CuSO_4 \cdot 5H_2O$. Samples were run under a dynamic air atmosphere, with a heating rate of 3 to 5 °C min^{-1}.

Crystal Structure Determination: Data were collected with a Syntex $P2_1$ diffractometer in the 2θ-scan mode using a graphite monochromator and Cu-K_α radiation. Crystal data and details of the data collection and refinement are collated in Table 6. The program systems SHELXS 86 and SHELXL 93 were used throughout.[72] The methanolic hydrogen atom (H5O on O5) was found explicitly; all other hydrogen atoms were placed into calculated positions and included with common thermal parameters in the last cycles of refinement. An absorption correction (DIFABS) was carried out. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data centre as supplementary publication no. CCDC-148428. Copies of the data can be obtained free of charge on application to CCDC,12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.)+ 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 6. Crystal data and structure refinement for [VO(OMe)(HOMe)(Clsal-iNH)] (**9**)

Empirical formula	$C_{15}H_{15}ClN_3O$ V
Molecular mass, g mol^{-1}	403.69
Temperature, K	173(2) K
Wavelength, Å	1.54178
Crystal system, space group	monoclinic, *P*2(1)/*c*
Unit cell dimensions,	
a, Å	10.730(2)
b, Å	7.9047(13
c, Å	19.902(4)
β, °	105.188(16)
Cell volume, Å^3	1629.2(5)
Z	4
Calculated density, g cm^{-3}	1.646
Absorption coefficient, mm^{-1}	6.908
F(000)	824
Crystal size, mm	0.50 × 0.40 × 0.40
θ range for data collection, °	4.27–76.42
Index ranges	$-13 \le h \le 4, -3 \le k \le 9, -24 \le l \le 25$
Reflections collected/unique	3626/3401 [*R*(int) = 0.0285]
Data/restraints/parameters	3401/0/247
Goodness-of-fit	1.032
Final *R* indices [$I > 2\sigma(I_0)$]	*R*1 = 0.0465, *wR*2 = 0.1266
R indices (all data)	*R*1 = 0.0576, *wR*2 = 0.1346
Extinction coefficient	0.0024(3)
Largest diff. peak and hole, eÅ^{-3}	0.871 and –0.935

Preparation of Complexes: For thermogravimetric analyses and UV/Vis, ^{1}H and ^{13}C NMR spectroscopic data, cf. Tables 1−4 in the Discussion; IR and ^{51}V NMR spectroscopic data are included in the Exp. Sect.

[{VO(sal-iNH)}$_2$μ-O] (1), K[VO_2(sal-iNH)H_2O] (2a) and [VO(sal-iNH)] (3): Vanadium(V) oxide (0.50 g, 5 mmol) was dissolved in aqueous KOH (0.30 g, 5 mmol in 10 mL) and stirred for 2 h. The resulting solution was filtered. A filtered solution of H_2sal-iNH (1.20 g, 5 mmol), dissolved in aqueous KOH (0.60 g, 10 mmol in 20 mL), was added to the above solution with stirring, and the pH value of the reaction mixture was slowly adjusted to 7.5 with HCl (4 M). After 2 h of stirring, the precipitated orange solid was filtered, washed with cold water followed by acetone, and dried. On recrystallisation from methanol (ca. 40 mL), **1** precipitated as a brown solid, which was filtered off and dried in vacuo over silica gel. After reducing the volume of the filtrate to ca. 10 mL and keeping it at ca. 10 °C, yellow crystalline **2a** separated within 2−4 d. This was filtered off, washed with acetone and dried as above. Yield of **1**: 256 mg (15%); **2a**: 820 mg (40%). − **Data for 1:** $C_{26}H_{18}N_6O_7V_2$ (628.4): calcd. C 49.69, H 2.87, N 13.38; found C 49.79, H 3.12, N 13.11. − IR (KBr): $\tilde{\nu}_{max}$ = 1635 cm^{-1}, 1605 (C=N), 1212 (C−O, enolic), 1045(N−N), 970, 955(V=O), 864 [V-(μ-O)−V], 477, 461, 406(V−O, V−N). − ^{51}V NMR: δ = −541 ([D$_6$]DMSO), −549 and a minor signal at −541 (CD_3OD/CH_3OH). − **Data for 2a:** $C_{13}H_{11}KN_3O_5V$ (379.3) calcd. C 41.17, H 2.90, N 11.08; found C 41.00, H 3.13, N 10.86. − IR (KBr): $\tilde{\nu}_{max}$ = 1603 (C=N) cm^{-1}, 1213 (C−O, enolic), 1025 (N−N), 928, 907 (sym and asym VO_2), 595, 405 (V−O, V−N). − ^{51}V NMR: δ = −532 ([D$_6$]DMSO), −541 and minor signal at −549 (CH_3OH/CD_3OD).

Alternative Preparation of 1: A solution of H_2sal-iNH (1.20 g, 5 mmol) in acetone (20 mL) was added with stirring to an equimolar amount of [VO(acac)$_2$], dissolved in acetone (10 mL), and the resulting yellowish green suspension was heated at reflux in a water bath for 4 h. After cooling to room temperature, a green precipitate of [VO(sal-iNH)] (**3**) was filtered off, washed with acetone and dried. Compound **3** was suspended in acetone (30 mL), and air was slowly passed through the suspension at ca. 40 °C for ca. 20 h with occasional shaking, or until the yellowish green suspension had completely disappeared and crystalline orange-red solid **1** separated instead. This was filtered, washed with acetone, recrystallised from methanol and dried. Yield (based on [VO(acac)$_2$]) 60%. For the preparation of **1**, it is not necessary to isolate intermediate **3**. − **Data for 3:** $C_{13}H_9N_3O_4V$ (322.2): calcd. C 50.99, H 2.94, N 13.73; found C 50.68, H 3.08, N 13.60. − IR (KBr): $\tilde{\nu}_{max}$ = 1606(C=N) cm^{-1}, 994(V=O). − Complex **1** was also prepared in almost the same yield from the reaction of VO(OEt)$_3$ and H_2sal-iNH in absolute ethanol under aerobic conditions: A solution of H_2sal-iNH (1.20 g, 5 mmol) in absolute ethanol (20 mL) was added to VO(OEt)$_3$ (equiv. to 5 mmol, prepared[41] in situ) in absolute ethanol (10 mL), and the reaction mixture was heated at reflux for

6 h. After reducing the volume to ca. 10 mL, the flask was kept open to air at room temp., yielding orange-red **1** within 24 h. This was filtered, washed with ethanol and dried in vacuo.

$NH_4[VO_2(sal\text{-}iNH)H_2O]$ (2b): $NH_4[VO_3]$ (0.59 g, 5 mmol) was dissolved in water (10 mL) by heating in a water bath. This solution was added to a filtered solution of H_2sal-iNH (1.20 g, 5 mmol), dissolved in aqueous NaOH (0.40 g, 10 mmol), with stirring, and the pH value was adjusted to 7.5 with HCl (4 M). After 2 h, stirring was stopped, and the orange solid, which had separated, was filtered off, washed with water, followed by acetone, and dried. The crude mass was dissolved by heating in a minimum amount of methanol, and filtered. On standing overnight at ambient temperature, brown solid **1** precipitated. This was filtered off and dried in vacuo. After reducing the filtrate to ca. 10 mL, it was kept at 10 °C for a few days, whereupon yellow crystals of **2b** separated. These were filtered off and dried in vacuo at ambient temperature. Yield of **1**: 317 mg (20%); **2b**: 808 mg (45%). − **Data for 2b:** $C_{13}H_{13}N_4O_5V$ (356.2): calcd. C 43.82, H 3.65, N 15.73; found C 43.61, H 3.83, N 15.56. − IR (KBr): $\tilde{\nu}_{max}$ = 1605 cm^{-1} (C=N), 1225 (C−O, enolic), 1063 (N−N), 946, 927 (sym and asym VO_2), 477, 463, 420 (V−O, V−N).

$[\{VO(Clsal\text{-}iNH)\}_2\mu\text{-}O]$ (4) and $K[VO_2(Clsal\text{-}iNH)H_2O]$ (5): Complexes **4** (25% yield) and **5** (40% yield) were prepared analogously to **1** and **2a**, replacing H_2sal-iNH with H_2Clsal-iNH. − **Data for 4:** $C_{26}H_{16}Cl_2N_6O_7V_2$ (646.30): calcd. C 44.77, H 2.30, N 12.05; found C 44.47, H 2.51, N 11.83. − IR (KBr): $\tilde{\nu}_{max}$ = 1625 cm^{-1}, 1602 (C=N), 1288 (C−O, enolic), 1087 (N−N), 952 (V=O), 846 [V−(μ-O)−V], 462, 427 (V−O, V−N). − ^{51}V NMR: δ = −539 ([D_6]DMSO), −548 and a minor signal at −543 (CD_3OD/CH_3OH). − **Data for 5:** $C_{13}H_{10}ClKN_3O_5V$ (413.7): calcd. C 37.73, H 2.42, N 10.16; found C 37.85, H 2.61, N 10.04. − IR (KBr): $\tilde{\nu}$ = 1607 cm^{-1} (C=N), 1288 (C−O, enolic), 1038 (N−N), 938, 904 (sym and asym VO_2), 462, 416 (V−O, V−N). − ^{51}V NMR: δ = −532 ([D_6]DMSO), −541 (CH_3OH/CD_3OD).

$K[VO_2(hap\text{-}iNH)H_2O]$ (6): The potassium salt of the ligand H_2hap-iNH was prepared in situ by treating H_2hap-iNH (1.27 g, 5 mmol) with KOH (0.60 g, 10 mmol) in water (15 mL). This solution was added dropwise to stirred aqueous potassium vanadate (5 mmol, prepared from V_2O_5 and KOH). The pH value of the reaction mixture was adjusted to 7.5 by slow addition of HCl (4 M). After 2 h, the yellow solid, which had separated, was filtered off, washed with acetone and dried in vacuo. Yield 1080 mg (55%). $-C_{14}H_{13}KN_3O_5V$ (393.3): calcd. C 42.75, H 3.30, N 10.68; found C 42.55, H, 3.63, N 10.74. − IR (KBr): $\tilde{\nu}_{max}$ = 1587 cm^{-1} (C=N), 1248 (C−O, enolic), 1058 (N−N), 943, 907 (sym and asym VO_2), 473 (V−O, V−N). − ^{51}V NMR: δ = −533 ([D_6]DMSO), −538 and a minor signal at −547 (CH_3OH/CD_3OD).

$K[VO(O_2)(sal\text{-}iNH)H_2O]$ (7) and $K[VO(O_2)(Clsal\text{-}iNH)H_2O]$ (8): $K[VO_2(sal\text{-}iNH)\cdot H_2O]$ (**2a**, 0.150 g) was dissolved in methanol (10 mL) and the clear, yellow solution was cooled with ice. H_2O_2 (30%, 4 mL) was added dropwise to the stirred solution. The resulting orange-red solution was stirred for 2 h, and the red solid **7**, which separated was filtered off, washed with cold methanol and dried in vacuo. Additional, impure peroxo complex **7** was obtained from the filtrate on cooling it overnight to 5 °C. Complex **8** was prepared similarly, using $K[VO_2(Clsal\text{-}iNH)\cdot H_2O]$ (**5**, 0.150 g) and H_2O_2 (30%, 4 mL). Satisfactory elemental analyses were not obtained owing to the instability of the peroxo complexes. Further characteristics are discussed in the text.

[VO(OMe)(HOMe)(Clsal-iNH)] (9): Crystals of **9** suitable for X-ray analysis were grown in a saturated solution of **5** in methanol, standing at 4 °C for a few weeks.

Acknowledgments

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[1] A. Butler, M. J. Clague, G. E. Meister, *Chem Rev.* **1994**, *94*, 625.
[2] C. Slebodnick, B. J. Hamestra, V. L. Pecoraro, *Struct. Bond. (Berlin)* **1997**, *89*, 51.
[3] C. Djordjevic, G. L. Wampler, *J. Inorg. Biochem.* **1985**, *25*, 51.
[4] J. H. McNeil, V. G. Yuen, H. R. Hoveyda, C. Orvig, *J. Med. Chem.* **1992**, *35*, 1489.
[5] K. H. Thompson, J. H. McNeil, C. Orvig, *Inorg. Chem.* **1999**, *38*, 2288.
[6] [6a] D. Rehder, *Bioinorganic Chemistry: Transition Metals in Biology and Their Coordination Chemistry*, (Ed.: A. X. Trautwein), Wiley-VCH, Weinheim, **1997**, chapter D6. − [6b] D. Rehder, *Metal Ions in Biological Systems; Vanadium and Its Role in Life* (Eds.: H. Sigel, A. Sigel), Marcel Dekker Inc., New York, **1995**, chapter 1.
[7] D. Rehder, *Coord. Chem. Rev.* **1999**, *182*, 297
[8] M. Weyand, H.-J. Hecht, M. Kieß, M.-F. Liaud, H. Vilter, D. Schomburg, *J. Mol. Biol.* **1999**, *293*, 595.
[9] A. Messerschmidt, L. Prade, R. Wever, *Biol. Chem.* **1997**, *378*, 309.
[10] S. Macedo-Ribeiro, W. Hemrika, R. Renirie, R. Wever, A. Messerschmidt, *J. Biol. Inorg. Chem.* **1999**, *4*, 209.
[11] A. Butler, C. J. Carrano, *Coord. Chem. Rev.* **1991**, *109*, 61
[12] K. Nakajima, M. Kojima, K. Toriumi, K. Saito, J. Fujita, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 760.
[13] V. Vergopoulos, W. Priebsch, M. Fritzsche, D. Rehder, *Inorg. Chem.* **1993**, *32*, 1844.
[14] M. J. Clague, N. L. Keder, A. Butler, *Inorg. Chem.* **1993**, *32*, 4754.
[15] H. Schmidt, D. Rehder, *Inorg. Chim. Acta* **1998**, *267*, 229.
[16] R. Fulwood, H. Schmidt, D. Rehder, *J. Chem. Soc., Chem. Commun.* **1995**, 1443.
[17] M. Bashirpoor, H. Schmidt, C. Schulzke, D. Rehder, *Chem. Ber./Receuil* **1997**, *130*, 651.
[18] W. Wang, F.-L. Zeng, X. Wang, M.-Y. Tan, *Polyhedron* **1996**, *15*, 1699.
[19] C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies, V. L. Pecoraro, *Inorg. Chem.* **1990**, *29*, 944.
[20] J. Costa Pessoa, J. A. L. Silva, A. L. Vieira, L. Vilas. Boas, P. O'Brien, P. Thornton, *J. Chem. Soc., Dalton Trans.* **1992**, 1745.
[21] S. Mondal, P. Ghosh, A. Chakravorty, *Inorg. Chem.* **1997**, *36*, 59.
[22] [22a] H. Schmidt, M. Bashirpoor, D. Rehder, *J. Chem. Soc., Dalton. Trans.* **1996**, 3865. − [22b] C. Grüning, H. Schmidt, D. Rehder, *Inorg. Chem. Commun.* **1999**, *2*, 57.
[23] [23a] J. Chakravarty, S. Dutta, S. K. Chandra, P. Basu, A. Chakravorty, *Inorg. Chem.* **1993**, *32*, 4249. − [23b] S. Dutta, P. Basu, A. Chakravorty, *Inorg. Chem.* **1993**, *32*, 5343.
[24] J. Chakravarty, S. Dutta, A. Day, A. Chakravorty, *J. Chem. Soc., Dalton. Trans.* **1994**, 557.
[25] [25a] S. Mondal, S. P. Rath, S. Dutta, A. Chakravorty, *J. Chem. Soc., Dalton. Trans.* **1996**, 99. − [25b] S. Mondal, S. P. Rath, K. K. Rajak, A. Chakravorty, *Inorg. Chem.* **1998**, *37*, 1713.
[26] S.-X. Liu, S. Gao, *Polyhedron* **1998**, *17*, 81.
[27] S. Gao, Z.-Q. Weng, S.-X. Liu, *Polyhedron* **1998**, *17*, 3595.
[28] S.-X. Liu, S. Gao, *Inorg. Chim. Acta* **1998**, *282*, 149.
[29] K. K. Rajak, S. P. Rath, S. Mondal, A. Chakravorty, *Indian J. Chem.* **1999**, *38A*, 405.
[30] S. Bhattacharya, T. Ghosh, K. R. Sur, *J. Indian Chem. Soc.* **2000**, *77*, 59.
[31] C. Djordjevic, M. Lee, E. Sinn, *Inorg. Chem.* **1989**, *28*, 719.

[32] D. C. Crans, P. K. Shin, *J. Am. Chem. Soc.* **1994**, *116*, 1305.
[33] G. J. Colpas, B. J. Hamstra, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1994**, *33*, 4669.
[34] D. C. Crans, A. D. Keramidas, M. Mahroof-Tahir, O. P. Anderson, M. M. Miller, *Inorg. Chem.* **1996**, *35*, 3599.
[35] M. Mahroof-Tahir, A. D. Keramidas, R. B. Goldfarb, O. P. Anderson, M. M. Miller, D. C. Crans, *Inorg. Chem.* **1997**, *36*, 1657.
[36] D. C. Crans, A. D. Keramidas, S. S. Amin, O. P. Anderson, S. M. Miller, *J. Chem. Soc., Dalton Trans.* **1997**, 2799.
[37] V. Vergopoulos, W. Priebsch, M. Fritzsche, D. Rehder, *Inorg. Chem.* **1993**, *32*, 1844.
[38] X. Li, M. S. Lah, V. L. Pecoraro, *Inorg. Chem.* **1988**, *27*, 4657.
[39] [39a] G. Asgedom, S. Sreedhara, J. Kivikoski, J. Valkonen, C. P. Rao, *J. Chem. Soc., Dalton Trans.* **1995**, 2459. – [39b] G. Asgedom, S. Sreedhara, J. Kivikoski, E. Kolehmainen, C. P. Rao, *J. Chem. Soc., Dalton Trans.* **1996**, 93.
[40] N. Julien-Cailhol, E. Rose, J. Vaisserman, D. Rehder, *J. Chem. Soc., Dalton Trans.* **1996**, 2111.
[41] C. A. Root, J. D. Hoeschele, C. R. Cornman, J. W. Kampf, V. L. Pecoraro, *Inorg. Chem.* **1993**, *32*, 3855.
[42] B. J. Hamstra, G. J. Colpas, V. L. Pecoraro, *Inorg. Chem.* **1998**, *37*, 949.
[43] M. Melchior, K. H. Thompson, J. M. Jong, S. J. Rettig, E. Shuter, V. G. Yuen, Y. Zhou, J. H. McNeill, C. Orvig, *Inorg. Chem.* **1999**, *38*, 2288.
[44] M.-H. Lee, N. H. Heo, S. Hayashi, *Polyhedron* **1998**, *17*, 55.
[45] J. A. Bonadies, C. J. Carrano, *J. Am. Chem. Soc.* **1986**, *108*, 4088.
[46] [46a] J. C. Craliz, J. C. Rub, D. Willis, J. Edger, *Nature* **1955**, *34*, 176. – [46b] M. J. M. Campbell, *Coord. Chem. Rev.* **1975**, *15*, 279.
[47] M. R. Maurya, S. A. Bhakare, *J. Chem. Res. (S)* **1996**, 390.
[48] S. P. Perlepes, D. Nicholls, M. R. Harrison, *Inorg. Chim. Acta* **1985**, *102*, 137.
[49] M. R. Maurya, *J. Chem. Res. (S)* **1995**, 248.
[50] M. R. Maurya, C. Gopinathan, *Indian J. Chem.* **1996**, *35A*, 701.
[51] A. D. Keramidas, A. B. Papaioannou, A. Vlahos, T. A. Kabanos, G. Bonas, A. Makriyannis, C. P. Rapropoulou, A. Terzis, *Inorg. Chem.* **1996**, *35*, 357.
[52] [52a] D. Rehder, C. Weidemann, A. Duch, W. Priebsch, *Inorg. Chem.* **1988**, *27*, 584. – [52b] D. Rehder, *Transition Metal Nuclear Magnetic Resonance* (Ed.: P. S. Pregosin), Elsevier, New York, **1991**, p. 1.
[53] O. W. Howarth, *Progr. Magn. Reson. Spectrosc.* **1990**, *22*, 453.
[54] R. Schwendt, P. Svancárek, L. Kuchta, J. Marek, *Polyhedron* **1998**, *17*, 2161.
[55] F. W. B. Einstein, R. J. Batchelor, S. J. Angus-Dunne, A. S. Tracey, *Inorg. Chem.* **1996**, *35*, 1680.
[56] A. D. Westland, F. Haque, J.-M. Bouchard, *Inorg. Chem.* **1980**, *19*, 2255.
[57] [57a] H. Schmidt, I. Andersson, D. Rehder, L. Pettersson, *J. Inorg. Biochem.* **2000**, *80*, 149. – [57b] M. Casný, D. Rehder, H. Schmidt, H. Vilter, V. Conte, *J. Inorg. Biochem.* **2000**, *80*, 157.
[58] The species observed by Rao et al.[39a] in the reaction between H_2O_2 and [HAMP][VO_2(Brsal-amp)] (HAMP is 2-amino-2-methylpropanol, and H_2Brsal-amp is the Schiff base derived from 5-bromosalicylaldehyde and 2-amino-2-methylpropanol) in acetonotrile is probably also $[VO(O_2)_2OH]^{2-}$, since the IR spectrum showed peaks due to the peroxovanadium group only and no indication of the coordination of the ligand.
[59] B. S. Parajon-Costa, A. C. Gonzales-Baro, E. J. Baran, *J. Coord. Chem.* **1999**, *47*, 417.
[60] M. Kosugi, S. Hickichi, M. Akita, Y. Moro-oka, *Inorg. Chem.* **1999**, *38*, 2567.
[61] A. T. Harrison, O. W. Howarth, *J. Chem. Soc., Dalton Trans.* **1985**, 1173.
[62] Y. Zhang, R. H. Holm, *Inorg. Chem.* **1990**, *29*, 911.
[63] T. Hirao, *Chem. Rev.* **1997**, *97*, 2707.
[64] D. Rehder, C. Schulzke, H. Dau, C. Meinke, J. Hanss, M. Epple, *J. Inorg. Biochem.* **2000**, *80*, 115, and references cited therein.
[65] I. W. C. E. Arends, M. P. Birelli, R. A. Sheldon, *Stud. Surf. Catal.* **1997**, *110*, 1031.
[66] [66a] M. A. Andersson, S. G. Allenmark, *Tetrahedron* **1998**, *54*, 15293. – [66b] H. B. ten Brink, A. Tuyman, H. L. Dekker, W. Memrika, Y. Izumi, T. Oshiro, H. E. W. Schoemaker, R. Wever, *Inorg. Chem.* **1998**, *37*, 6780.
[67] A. Butler, A. H. Baldwin, *Struct. Bond.* **1997**, *89*, 109.
[68] V. Conte, F. Di Furia, G. Licini, *Appl. Catal.* **1977**, *157*, 335.
[69] F. J. Welcher, *Organic Analytical Reagents*, van Nostrand Co., New York, **1947**, vol. 3, p. 254.
[70] [70a] K. N. Srivastava, S. Das, R. A. Lal, *Indian J. Chem., A* **1986**, *25*, 85. – [70b] C. P. Prabhakaran, B. G. Nair, *Trans. Met Chem.* **1983**, *8*, 368.
[71] R. A. Rowe, M. M. Jones, *Inorg. Synth.* **1957**, *5*, 113.
[72] [72a] G. M. Sheldrick, *SHELXS 86*, University of Göttingen, **1986**. – [72b] G. M. Sheldrick, *SHELXL 93*, University of Göttingen, **1993**.

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