Models for Vanadate-Dependent Haloperoxidases: Vanadium Complexes with *O_4N*-Donor Sets☆

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Reaction of vanadyl sulfate with the Schiff base H_2L^1 derived from *o*-vanillin and glycine leads to $[V^{IV}O(H_2O)L^1]$ (**1**), treatment of which with acetyl chloride affords *cis*-$[V^{IV}Cl_2L^1]$ (**2**). Reaction of $[VO(acac)_2]$ with the Schiff base H_2L^2 derived from *o*-hydroxynaphthaldehyde and *o*-hydroxyaniline under aerobic conditions yields $[\{V^VO(L^2)\}_2\mu\text{-}O]$ (**3**), which undergoes methanolysis in excess methanol to form $[V^VO(MeOH)(OMe)L^2]$ (**5a**). Complex **5a** is also obtained via $[V^VOCl(L^2)]$ (**4**) and MeOH. On treatment of **3** with an equimolar amount of ethanol, $[V^VO(OEt)L^2]$ (**5b**) is obtained. With the chiral tertiary bis(ethanol)amine (*S*)- or (*R*)-$(HOCH_2CH_2)_2NCH(Ph)Me$, H_2L^3, $[VO(acac)_2]$ loses only one acetylacetonate(1−) ligand, and the complexes (*S*)- and (*R*)-$[V^VO(acac)L^3]$ (**6a**) are formed. As is evident for the corresponding reaction with $(HOCH_2CH_2)_2NPh$, H_2L^4, which affords $[V^VO(acac)L^4]$ (**6b**), the substitution is a second-order process (rate constant $0.013\ M^{-1}\ h^{-1}$). **5a** · MeOH, **5b**, (*R*)-**6a**, and (*S*)-**6a** have been structurally characterized by single crystal X-ray diffraction analysis. The molecular connectivities have also been established for **1** · H_2O. All of the structurally characterized complexes contain an O^*O_3N donor set (O^* denotes a doubly-bonded oxo group) and thus model the coordination environment of the active site in vanadate-dependent haloperoxidases. This model character is particularly pronounced in **5b**, the coordination geometry of which is half-way to trigonal-bipyramidal. **5a** and **6a** contain, in addition to the O^*O_3N set, a labile V−O or V−N bond, respectively, which may mimic substrate binding to the active centre. **6a** is also of relevance to the enantioselective peroxide oxidation of sulfides to sulfoxides by catalyst systems containing vanadium and H_2L^3.

Introduction

Vanadate-dependent haloperoxidases[1] catalyze the halogenation of organic substrates in the presence of inorganic halide (X^-) by peroxide via an X^+ intermediate (probably hypohalous acid)[2]. A recent X-ray structure investigation of the 60 kDa chloroperoxidase from the fungus *Curvularia inaequalis* has revealed a vanadium(V) centre in a trigonal-bipyramidal environment with three oxo/hydroxide ligands in the plane, one of the axial positions occupied by the N_ε of the imidazole moiety of histidine, and the other one by azide[3]. In the native enzyme, this latter position is probably occupied by O^{2-}, HO^-, or H_2O. The same coordination environment appears also to be present in a bromo/iodoperoxidase (a 120 kDa homodimer) from the marine brown alga *Ascophyllum nodosum*[4]. Reduction of the native V^V to the inactive V^{IV} form is accompanied, as evidenced by XANES[5] and EXAFS spectroscopy[6], by a change in the coordination sphere, although nitrogen remains covalently bound to vanadium (see also ESEEM investigations of the V^{IV} enzyme[7]) and the coordination sphere remains dominated by oxygen functionalities, including one doubly-bonded oxo group.

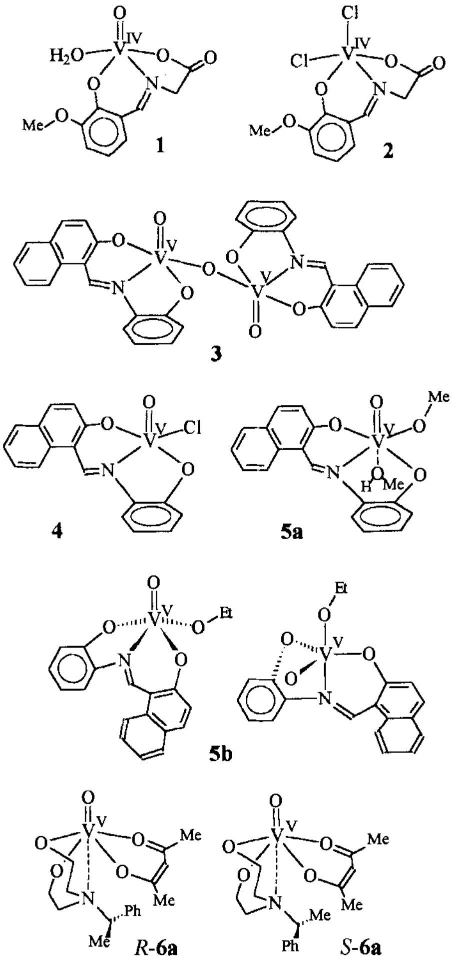
In an extension of former work[8], we have synthesized a number of $V^{IV}O^{2+}$ and V^VO^{3+} complexes containing variable coordination spheres each built up of a tridentate *ONO′* ligand, an oxo group and one or two additional oxygen-functional ligands, viz. H_2O, methanol, alkoxide or acetylacetonate(1−) (acac). Schematic drawings are shown in Figure 1. The *N* of the *ONO′* ligand is either the enamine-*N* of a Schiff base, as in **1** to **5**, or a tertiary amino-*N*, as in **6**. The oxygen functions of the *ONO′* ligands are variously two phenolate-*O*'s (**2** to **5**), two alkoxide-*O*'s (**6**), or a phenolate- plus a carboxylate-*O* (**1**). Similar complexes have been shown to catalyze the peroxide oxidation of halide to form hypohalous acid[2,9], or of organic sulfides to form sulfoxides[8a,10]. When chiral complexes are used, the latter reaction becomes enantioselective.

Results and Discussion

Preparation and Properties

The V^{IV} complex **1** was prepared in a one-pot reaction by treating a 1:1 mixture of glycine and *o*-vanillin (which form the Schiff base H_2L^1), dissolved in acetate-buffered oxygen-free water, with vanadyl sulfate, eqn. (1). The presence of water in the coordination sphere (in addition to a water of crystallization) was revealed by an X-ray structure analysis and is consistent with the elemental analysis. The coordination mode of the glycine carboxylate, again revealed by the structure determination, is also evident from the large difference[11] between the symmetric and antisym-

Figure 1. Schematic drawings of the complexes characterized in this work; X-ray structures have been obtained for **1** · H_2O, **5a** · MeOH, **5b**, (*S*)-**6a**, and (*R*)-**6a**; for **5b**, two alternative idealized structural views (tetragonal pyramidal vs. trigonal bipyramidal) are shown; for discussion, see text



metric ν(COO$^-$) absorptions (Table 1), and has been documented in a number of comparable cases where the Schiff base contains an amino acid as the amine component[8c,8f,10c,12]. Conversion of the green, crystalline **1** to the dichloro complex **2** was carried out by treatment with acetyl chloride in dichloromethane according to eqn. (2). Complex **2** lacks the characteristic ν(V=O) (998 cm^{-1}) of its oxo precursor **1**; instead, two ν(V–Cl) absorptions of comparable intensity are observed at 379 and 374 cm^{-1}, indicative of a *cis* orientation of the two chlorines in this complex with the *tri*dentate *ONO′* donor set. This is in contrast to the *trans* orientation found in similar complexes containing a *tetra*dentate *ONNO* set[8a,e]. Since no substantial changes in the IR patterns of the bicyclic V*ONO′* moiety (see Table 1) are apparent, we suggest a structure for **2** directly derived from that of **1** by replacing the oxo and the water ligands by chlorines.

$$H_2L^1 + VO^{2+} + H_2O \rightarrow \underset{\mathbf{1}}{[VO(H_2O)L^1]} + 2H^+ \qquad (1)$$

$$\underset{\mathbf{1}}{[VO(H_2O)L^1]} + 2\,MeCOCl \rightarrow \underset{\mathbf{2}}{[VCl_2L^1]} + 2\,MeCO_2H \qquad (2)$$

Table 1. Compilation of characteristic IR data

Compound	ν(C=N)	ν(CO)	ν(V=O)	ν(V–Cl) [cm^{-1}]
1	1624	1605 [CO_2^-(as)], 1376 [CO_2^-(s)]	998	
2	1621	1586 [CO_2^-(as)], 1379 [CO_2^-(s)]		379, 374
3	1618		989	
4	1618		996	385
5a	1618		993	
5b	1618		992	
6a		1570, 1521 [acac][a]	977	

[a] Compare 1556 and 1530 cm^{-1} for $[VO(acac)_2]$.

For the preparation of the V^V complexes **5**, the Schiff base H_2L^2, derived from 2-hydroxynaphthaldehyde(1) and *o*-hydroxyaniline, was reacted in acetone under aerobic conditions with $[VO(acac)_2]$ [acac = acetylacetonate(1−)] to form the dinuclear complex **3**, which was then converted to **5a** by treatment with excess methanol; eqn. (3a). Alternatively, **5a** may also be generated via the monochlorooxo complex **4**, prepared by the reaction of $VOCl_3$ and H_2L^2 in CH_2Cl_2; eqn. (3b). The HCl generated in the course of the formation of **4** is removed by passing N_2 through the solution. If **3** is dissolved in absolute $CHCl_3$ and treated with an equimolar amount of ethanol, the pentacoordinate complex $[VO(OEt)L^2]$ (**5b**) is obtained. The formation of dinuclear complexes such as **3** has been reported previously[8f,10c]. Characteristic spectroscopic features of **3** are the chemical shift δ(^{51}V) = −531 and the IR band at 735 cm^{-1}, associated with the symmetrically bridged $V_2\mu$-O unit. The black chloro presursor **4** exhibits a δ(^{51}V) = −434, typical of a coordination sphere dominated by *O* functionalities with one chloro ligand also present[13].

$$2\,H_2L^2 + 2[VO(acac)_2] \xrightarrow{(O_2)} \underset{\mathbf{3}}{[\{VOL^2\}_2\mu\text{-}O]} + 4\,Hacac \qquad (3a)$$

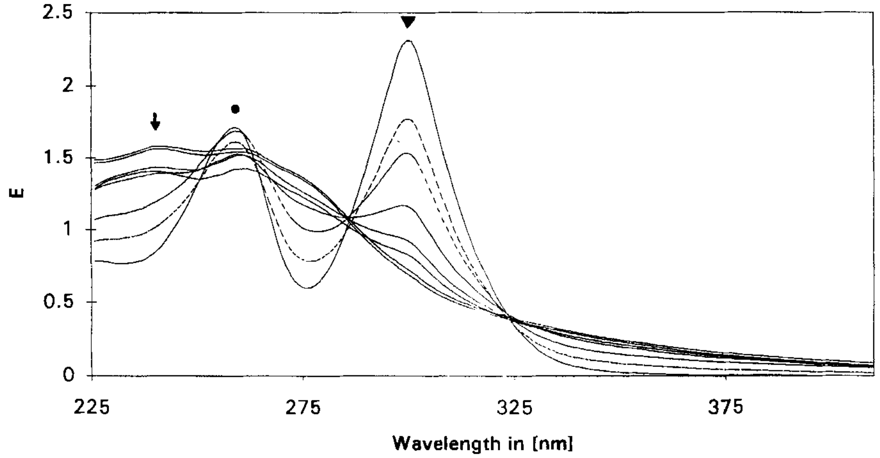
$$\mathbf{3} \xrightarrow{+\,4\,MeOH} \underset{\mathbf{5a}}{2[VO(OMe)L^2(MeOH)]} + H_2O$$

$$H_2L^2 + VOCl_3 \rightarrow \underset{\mathbf{4}}{[VO(Cl)L^2]} + 2\,HCl \qquad (3b)$$

$$\mathbf{4} \xrightarrow{+\,2\,MeOH} \underset{\mathbf{5a}}{[VO(OMe)L^2(MeOH)]} + HCl$$

Reaction between $[VO(acac)_2]$ and optically pure (*R*/*S*)-*N*,*N*-bis(2-hydroxyethyl)phenylethylamine H_2L^3 in acetone under oxygen simultaneously generates products derived from the displacement of one or both of the acac ligands. The minor reaction product arises from the replacement of both acetylacetonates; a dinuclear type **3** complex forms, which was not characterized in detail. On substitution of one acac, orange, hydrolytically unstable (*R*)-**6a** or (*S*)-**6a** is formed; eqn. (4). The reaction is analogous to that between $[VO(acac)_2]$ and *N*,*N*′-diethanolaniline (H_2L^4) which leads to the non-chiral complex $[VO(acac)L^4]$, **6b**[8a]. In the ^{1}H-NMR spectrum, all of the eight protons of the two ethylene backbones in chiral **6a** are represented by distinct eight-line

Figure 2. Electronic absorption spectra for reaction mixtures of $[VO(acac)_2]$ (▼), H_2L^4 (•) (vanishing peaks) and the newly emerging **6b** (↓) after 0, 1, 2, 5, 9, 11, 22 and 28 hours



patterns (doublets of doublets of a doublet; see Experimental Section for details). The kinetics of the replacement reaction have been investigated for the formation of **6b** by means of electronic absorption spectroscopy (see Figure 2): The substitution is a second-order process with a rate constant of 0.013 $\text{M}^{-1}\ \text{h}^{-1}$, and hence is rather slow, which is of significance in terms of the degree of enantioselectivity in the peroxide oxidation of thioether to sulfoxide by the bulk catalyst system $[VO(acac)_2]/H_2L^3$[10a], in which **6a** is thought to be the catalytically active species.

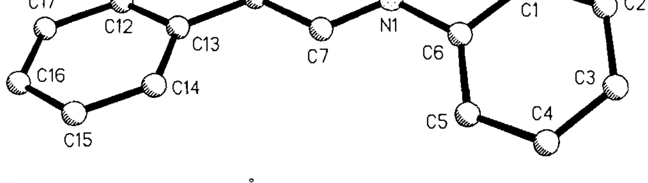
$$H_2L^3 + [VO(acac)_2] \xrightarrow{(O_2)} \underset{\mathbf{6a}}{[VOL^3(acac)]} + Hacac + H^+ \qquad (4)$$

Structure Description

Due to disorder problem (a second molecule representing about 10% of the density is transposed with respect to the former), the crystal structure of **1** · H_2O[14] could be refined to an (*R*) value of only 14.5%. Nonetheless, the molecular connectivities have been established unambiguously, showing that **1** is essentially tetragonal-pyramidal with the oxo group at the apex as illustrated in Figure 1. Vanadium deviates from the plane formed by the Schiff base functions and the oxygen of the coordinated water by 0.57 Å. Both water molecules are involved in hydrogen bonding interactions: There are intramolecular contacts between the aqua ligand and the uncoordinated carboxylate oxygen, and between the coordinated water and the water of crystallization. The distance *d*(O···O) of the "water dimer" thus formed amounts to 2.68 Å. The latter is further weakly hydrogen-bonded to the methoxy, phenoxy, and uncoordinated carboxylate oxygens.

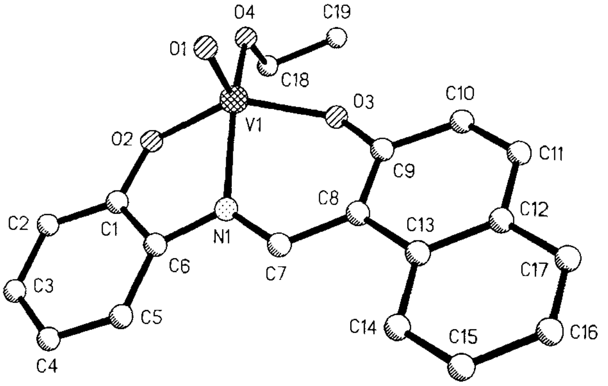
The complexes **5a** · MeOH (Figure 3) and **5b** (Figure 4) are closely related to each other in that they both contain an alkoxo ligand (O4) in an approximate *trans* position to the enamine *N* of the Schiff base, and a relatively long *d*(V−N) of 2.151(2) (**5a**) and 2.135(2) Å (**5b**). The angles O4−V−N are 167.57(7)° in the case of **5a**, and 156.99(8)° in the case of **5b**, which is indicative of a substantial difference in structure: The pentacoordinate **5b** does not simply derive from the hexacoordinate, essentially octahedral **5a** by removal of the bound alcohol [*d*(V−O5) = 2.131(2) Å]. As a consequence, **5b** exhibits a strong deviation from tetragonal-pyramidal towards trigonal-bipyramidal geometry. This is illustrated by the two limiting structures shown for **5b** in Figure 1: Based on a tetragonal-pyramidal geometry with the oxo group forming the top of the pyramid, vanadium deviates from the best plane (deviations in Å) N1(−0.11)−O2(0.11)−O3(0.10)−O4(−0.10) by −0.49 Å (i.e. towards O1). In contrast, based on a trigonal-bipyramidal arrangement with N and the methoxide-O (O4) axially oriented, the deviation of V from the trigonal plane formed by the remaining three oxygens (O1, O2, O3) is 0.19 Å towards O4. The angles in this plane amount to 108.75(9) (O1−V−O2), 107.59(9) (O1−V−O3), and 139.94(8)° (O2−V−O3).

Figure 3. SCHAKAL drawing and numbering scheme for **5a** (the methanol of crystallization has been omitted)[a]



[a] Selected bond lengths [Å] and angles [°]: V−O1 1.600(2), V−O2 1.944(2), V−O3 1.882(2),V−O4 1.793(2), V−O5 2.131(2), V−N 2.151(2), N−C7 1.308(3); O1−V−O2 102.19(8), O1−V−O3 99.2(8), O1−V−O4 100.49(8), O1−V−O5 175.47(7), O1−V−N 90.45(8), O3−V−N 82.41(7), O3−V−N 77.63(7), O2−V−O4 94.16(7), O3−V−O4 101.43(7).

Figure 4. SCHAKAL drawings and numbering schemes for **5b**[a]



[a] Selected bond lengths [Å] and angles [°]: V−O1 1.957(2), V−O2 1.892(2), V−O3 1.865(2), V−O4 1.788(2), V−N 2.135(2), N−C7 1.312(3); O1−V−O2 108.75(9), O1−V−O3 107.59(9), O1−V−O4 106.34(9), O1−V−N 96.43(8), O2−V−N 77.94(8), O3−V−N 81.82(8), O4−V−N 156.99(8), O2−V−O3 139.94(8), O2−V−O4 91.42(8), O3−V−O4 94.13(8).

Another noteworthy feature of **5a** is the bond length of the bond formed between vanadium and the coordinated methanol, viz. d(V−O5) = 2.131(2) Å. Although a relatively weak V−O single bond (cf. Table 2) as a consequence of the *trans* effect exerted by O^{2-}, it is much stronger than in the related alkoxo complexes [VO(OR)(*ONO*)(ROH)], where R = *s*Bu and H*ONO*H = the Schiff base formed from *o*-hydroxynaphthaldehyde and alanine [d(V−OHR) = 2.328(8)][8c], or R = Me and H*ONO*H = the Schiff base formed from salicylaldehyde and alanine [d(V−OHR) = 2.384(4) Å][10c]. Nonetheless, the vanadium centre in **5a** is significantly displaced (by 0.28 Å towards the oxo ligand) from the plane spanned by O2(−0.102), O3(−0.094), O4(0.092), and N(0.103). Other bond lengths in **5a**, including the comparatively short single bond d(V−O4) = 1.793(2) Å typical for V−alkoxide moieties[8c,10c,12b,15], are comparable to those of the related Schiff base complexes mentioned above. The coordinated methanol MeO(5)H(50) in **5a** is further linked to the methanol of crystallization MeO(6)H(60) by a hydrogen bonding interaction: There is a close contact between H50 and O6 (1.947 Å), leading to d(O5···O6) = 2.687 Å. H60 is connected to the phenolate oxygen O2 [d(H60−O2) = 2.056, d(O6···O2) = 2.819 Å].

In the case of **6a**, it was possible to structurally characterize both enantiomers (cf. Figure 5). To a first approximation, **6a** is tetragonal-pyramidal with the vanadium centre displaced by 0.28 Å from the plane spanned by the acac (O2, O3) and ethanolate oxygens (O4, O5). As in the previously reported case of the corresponding diethanolaniline (H_2L^4) complex [VO(acac)L^4] (**6b**)[8a], there is, however, a non-negligible bonding interaction between the amino nitrogen and the vanadium [d(V···N) = 2.528 Å], occupying a sixth position in a very distorted octahedron. The angle N−V−O1 amounts to 172.5°. Comparison with the V−N bond lengths of the trigonal-bipyramidal triethanolamine (H_3tea) complex [VO(tea)] [d(V−N) = 2.276(7) Å[16]] and the octahedral amine-alcoholate complex [VO(*ONN′O*$_2$)], with *N′* an amino nitrogen *trans* to the O^{2-} ligand [d(V−N′) = 2.309(3) Å[17]], shows that the V−N distance in **6a** is beyond what one might expect to be attributable to the *trans* effect of the oxo group. V−N bond lengths to tertiary amine nitrogens in oxovanadium(V) complexes where there is no *trans* effect induced by an oxygen functionality, may be as long as 2.21 Å as in [$VO_2(N_2N'_2)$]$^+$ [$N_2N'_2$ is a bis(amine)-bis(pyridine) tetradentate ligand][18]. Apart from the labile sixth coordination site in compound **6a**, the rather large bite angle O4−V−O5 of 101.78(7)° for the bis(ethoxide) moiety, as compared to 82.7−85.5° for all of the other angles in the tetragonal plane, is noteworthy. This relatively large angle (compare e.g. 96.8(2)° in **6b**) is associated with relatively long V−O(alkoxide) bond lengths of 1.820(3) and 1.835(2) Å [compare 1.794(5) and 1.819(4) Å in **6b**].

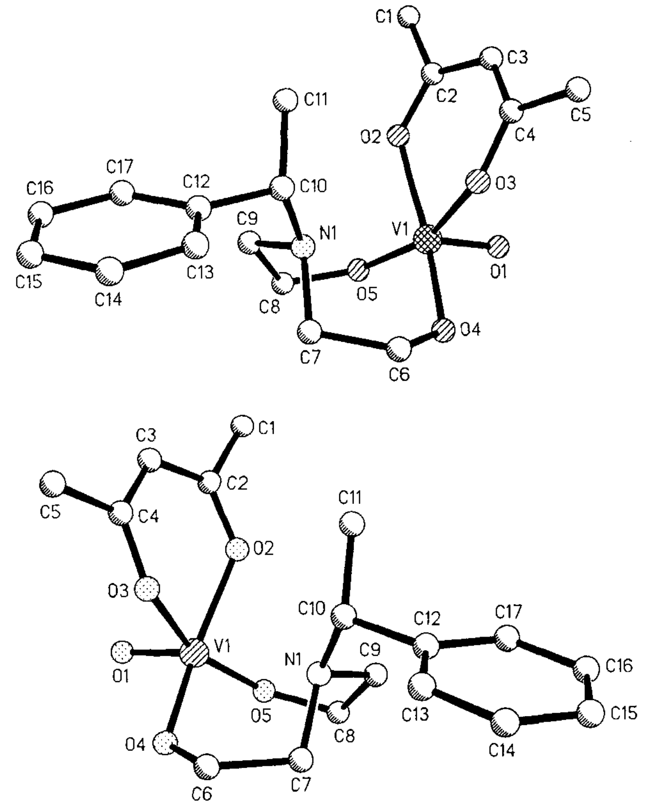
Table 2. Crystal structure analyses

	5b	**5a**·MeOH	(*R*)-**6a**	(*S*)-**6a**
empirical formula	$C_{19}H_{16}NO_4V$	$C_{20}H_{22}NO_6V$	$C_{17}H_{24}NO_5V$	$C_{17}H_{24}NO_5V$
molecular mass	373.27	423.33	373.31	373.31
crystal system	monoclinic	triclinic	orthorhombic	orthorhombic
space group	*P*2(1)/*n*	$P\bar{1}$	*P*2(1)2(1)2(1)	*P*2(1)2(1)2(1)
a [Å]	8.403(2)	7.338(1)	7.841(2)	7.8550(10)
b [Å]	14.054(3)	10.619(2)	11.911(2)	11.902(5)
c [Å]	13.903(3)	12.633(3)	18.656(4)	18.654(10)
α [°]		82.93(3)		
β [°]	99.92(3)	79.41(3)		
γ [°]		85.81(3)		
V [Å^3]	1617.3(6)	959.0(3)	1742.4(7)	1744.0(12)
Z	4	2	4	4
ρ_{calc} [g cm^{-3}]	1.533	1.466	1.423	1.422
F(000)	768	440	784	784
μ(Mo-K_α) [mm^{-1}]	0.64	0.55	0.59	0.60
cryst. dim. [mm]	0.4, 0.5, 0.6	0.4, 0.5, 0.6	0.2, 0.2, 0.5	0.2, 0.3, 0.3
hkl-range	$-2>h>10$, $-2<k<16$, $-16<l<16$	$-2<h<7$, $-13<k<13$, $-16<l<16$	$-2<h<10$, $-2<k<15$, $-2<l<24$	$-1<h<8$, $-1<k<12$, $-1<l<20$
θ range [°]	2.65 to 25.07	2.40 to 27.56	2.77 to 27.55	2.77 to 22.54
measured reflections	4711	5287	3502	1906
independent reflections	2860	3864	2912	1690
R_{int}	0.0265	0.0197	0.0224	0.0300
refined parameters	227	264	220	220
Goodness of fit	1.045	1.031	1.095	1.049
R for refl. with $I>2\sigma(I_o)$: *R*1 (*wR*2)	0.0369 (0.0821)	0.0393 (0.0976)	0.0279 (0.0714)	0.0361 (0.0842)
R, all data: *R*1 (*wR*2)	0.0596 (0.0906)	0.0491 (0.1039)	0.0298 (0.0728)	0.0426 (0.0842)
ρ_{fin} (max/min) [e Å^{-3}]	0.344/−0.269	0.384/−0.561	0.305/−0.369	0.259/−0.318
Flack parameter			0.00(2)	−0.03(4)

Conclusion

The reaction of "free" vanadyl (in the form of vanadyl sulfate in acetate-buffered, aqueous solutions, where the main species present is [$VO(H_2O)_4OH$]$^+$), or of "bound" vanadyl (in the form of [$VO(acac)_2$]) with suitable bis-chelating *ONO′*(2−) donor sets leads to coordination com-

Figure 5. SCHAKAL drawing and numbering scheme for (*R*/*S*)-**6a**[a]



[a] Selected bond lengths [Å] and angles [°]: V–O1 1.5998(14), V–O2 2.003(2), V–O3 2.021(2), V–O4 1.8347(14), V–O5 1.820(2), V···N 2.526; O1–V–O2 99.02(8), O1–V–O3 96.62(7), O1–V–O4 98.09(7), O1–V–O5 99.49(8), O2–V–O3 82.69(6), O2–V–O4 85.22(7), O3–V–O5 85.45(7), O4–V–O5 101.78(7), O1–V···N 172.7.

pounds of VO^{2+} or – if oxygen is present – VO^{3+} containing the coordinated *ONO* ligand in addition to a co-ligand. Suitable donor sets are provided by either bis(ethanol)amine, or by Schiff bases based on an aromatic *o*-hydroxyaldehyde and an amine containing an *O*′-functionality such as carboxylate or a second phenolate. While bis(ethanol)amines preferentially replace only one acac(1–) in $[VO(acac)_2]$ to form the complexes **6**, the Schiff bases substitute both acetylacetonates and form the complexes **3**, **5a**, and **5b** (cf. Figure 1). Free vanadyl also adds the Schiff base, leaving one water molecule in its coordination sphere (the V^{IV} complex **1**). In all cases, X-ray structure analyses reveal an essentially *tetragonal-pyramidal* coordination environment with the oxo group at the apex, but with distinct deviations from this geometry: **5b** may also be described as a distorted trigonal prism, hence coming close to being a structural model for vanadate-dependent haloperoxidases from the seaweed *Ascophyllum nodosum* and the fungus *Curvularia inaequalis*, for which this geometry in an O_4N donor set (*N* stemming from histidine and one of the oxygens being an oxo group) has been established[3,4]. The chiral complexes **6a** supplement an approximate octahedral coordination by a weak bonding interaction of 2.53 Å to the amine nitrogen *trans* to the oxo group. Similarly, in the case of **5a**, a methanol occupies this position, although a somewhat stronger bond of 2.13 Å is formed. A sixth position as provided by an "open" coordination site as in **1** and **5b**, or an easily accessible coordination site as in **5a** and **6a**, is essential where these complexes (or appropriate precursor mixtures thereof) are employed as catalysts in the (enantioselective) oxidation of thioethers to sulfoxides by peroxide[10a], and the availability of such a coordination site may also be a precondition for the enzymatic peroxide oxidation of inorganic halides by vanadate-dependent haloperoxidases[19]. This general view is supported by preliminary results on the potential of **6a** and **6b** in catalytically conducted peroxide oxidation of thioethers and sulfoxides, and by the outcome of a kinetic study of the formation of **6b** from $[VO(acac)_2]$ and H_2L^4, according to which the reaction follows an associative mechanism, i.e. the rate-limiting step is the coordination of L^4 to the open site in tetragonal-pyramidal $[VO(1,3\text{-diketonate})_2]$ complexes[20]. Finally, compounds such as $[VCl_2L^1]$ (**2**) and $[VO(Cl)L^2]$ (**4**), obtained by chlorination of **1** or by direct reaction between $VOCl_3$ and H_2L_2 (**4**), are potent precursors in consecutive reactions involving, inter alia, salt metathesis[8d,e].

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Experimental Section

Unless mentioned otherwise, experiments were carried out under nitrogen. Solvents were deoxygenated and saturated with nitrogen by passing N_2 through the purified solvent. Starting materials were obtained from commercial sources {$[VO(acac)_2]$, $VOSO_4 \cdot 5\,H_2O$, *o*-vanillin, acetyl chloride, *o*-hydroxaniline, 2-hydroxynaphthalenecarbaldehyde(1)} or prepared according to literature procedures {**6b**[8a], (*R*)-(+)- and (*S*)-(–)-(α-methylbenzyl)bis(2-hydroxyethyl)amine (H_2L^3)[21]}. – IR: Perkin-Elmer FT-IR spectrometer 1720 (4000–400 cm^{-1}), Perkin-Elmer FIR spectrometer 1700 XFT (500–200 cm^{-1}). The spectra were obtained using KBr pellets. Characteristic IR bands are collated in Table 1. – NMR: Bruker AM 360 with the usual measuring parameters for ^1H and ^{13}C. ^{51}V-NMR spectra were measured at 94.73 MHz in 10 mm diameter vials and referenced against neat $VOCl_3$ at sweep widths of 125 kHz (time domain 8200 K), a pulse angle of 60°, no relaxation delay, and with a line broadening factor of 30 Hz.

[VO(H₂O){N-(2-oxido-3-methoxysalicylidene)-Gly-O⁻}] $\cdot$ *H₂O* (**1** $\cdot$ H_2O): Glycine (3.75 g, 0.05 mmol) and sodium acetate (8.2 g, 0.1 mol), dissolved in 100 ml of water, were treated with a solution of *o*-vanillin (7.61 g, 0.05 mol) in 125 ml of ethanol. To this mixture was slowly added $VOSO_4 \cdot 5\,H_2O$ (10.80 g, 0.0427 mmol) dissolved in 40 ml of water. After stirring for 30 min, a small amount of a green precipitate had formed, which was filtered off and discarded. The filtrate was stored at room temperture overnight, and thereafter for two days at 2°C to afford **1a** $\cdot$ H_2O as a green, finecrystalline powder including a few larger crystals which were used for the X-ray analysis. The air-stable compound is insoluble in water, acetone, and diethyl ether, but moderately soluble in acetonitrile and dichloromethane. – Yield 7.44 g (51%). – $C_{10}H_{13}No_7V$ (309.15): calcd. C 38.85, H 4.24, N 4.53; found C 38.36, H 3.89, N 4.50.

Table 3. Synopsis of bonding parameters (in Å and °, respectively)[a]

	1	**5a**	**5b**	(*R*)-**6**
V=O	1.577	1.597	1.600	1.600
V–N	2.057	2.135	2.151	2.526
V–O (phenoxy)	1.923	1.892, 1.865	1.944, 1.882	
other V–O	2.009 (carboxylate) 2.033 (water)	178.8 (alkoxy) 2.131 (alcohol)	1.793 (alkoxy)	1.835, 1.820 (alkoxy) 2.003, 2.021 (enolate)
C=N	1.294	1.312	1.308	
bite angles	87.0 78.9	77.94 81.82	82.41 77.63	101.78 82.69
dev. of V from tetragonal plane	0.493	0.281	0.49	0.278

[a] Standard deviations for bond lengths are (2)−(3) in the case of **5** and **6**, and (7)−(9) in the case of **1** in the last digit.

cis-[VCl_2{N-(2-oxido-3-methoxysalicylidene)-Gly-O$^-$}] (**2**): To a suspension of **1** · H_2O (230 mg, 0.75 mmol) in 70 ml of absolute CH_2Cl_2 was added acetyl chloride (0.212 ml, 3.0 mmol). The mixture was refluxed on a 50 °C water bath for 1.5 hours. After cooling to room temperature and standing overnight, the solution was filtered, the filtrate was treated with an equal volume of absolute pentane and allowed to stand at −15 °C for two days. The dark-blue precipitate of **2** thus formed was filtered off, washed with pentane until the washings were colourless (ca. three 25 ml portions of pentane were needed), and the remainder was dried under high vacuum. − Yield 180 mg (74%). − $C_{10}H_9Cl_2NO_4V$ (328.13): calcd. C 36.50, H 2.76, N 4.26; found C 36.33, H 2.96, N 4.43.

[VO{2-(2'-oxynaphthalidene-1'-imino)-1-oxybenzene}]$_2$μ-O (**3**), *[VO(OMe)(HOMe){2-(2'-oxynaphthalidene-1'-imino)-1-oxybenzene}]* (**5a** · MeOH), *and [VO(OEt){2-(2'-oxynaphthalidene-1'-imino)-1-oxybenzene}]* (**5b**): [$VO(acac)_2$] (500 mg, 1.89 mmol) and the Schiff base H_2L^2 (498 mg, 1.89 mmol), prepared from equimolar amounts of *o*-hydroxyaniline and 2-hydroxynaphthalenecarbaldehyde(1) in acetone, were dissolved in 50 ml of acetone and stirred for 2 days with exposure to air, to afford brown **3**. The brown precipitate was filtered off, washed with acetone and dried in vacuo. − Yield 1.24 g (98%). − ^1H NMR ($CDCl_3$): δ = 9.92 (s, HC=N). − ^{51}V NMR (CD_3Cl): −531.

Compound **3** (500 mg, 0.74 mmol) was dissolved in 50 ml MeOH, the solution was refluxed for 8 hours and then stored at −20 °C for one week. Black-red crystals of **5a** · MeOH, suitable for an X-ray analysis were thus obtained. The crystals were filtered off, washed with cold pentane and dried in a stream of N_2. − Yield 228 mg (97%). − $C_{20}H_{19}NO_6V$ (423.33): calcd. C 56.75, H 4.52, N 3.31; found C 56.55, H 4.73, N 3.30. − ^1H NMR ($CDCl_3$): δ = 5.34 (s, OCH_3), 7.05−8.36 (m, aromatic H), 10.21 (s, HC=N). − ^{51}V NMR ($CDCl_3$): δ = −524.

Compound **3** (50 mg, 0.074 mmol) was dissolved in 50 ml of absolute chloroform, treated with ethanol (4.3 µl, 0.074 mmol) and the mixture was refluxed for 8 hours. After storage for one week at −20 °C, dark-red to black crystals of **5b**, suitable for an X-ray analysis, were isolated by filtration. The crystals were washed with cold pentane and dried in a stream of N_2. Yield 25 mg (87%). − ^1H NMR ($CDCl_3$): δ = 1.71 (t, ^3J = 7.0 Hz, CH_3), 5.59 (dq, ^2J = 10.8, ^3J = 6.8 Hz, OCH_2), 7.03−8.32 (m, aromatic H), 10.06 (s, HC=N). − ^{51}V NMR ($CDCl_3$): −530.

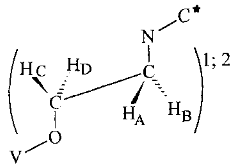
5a and **5b** are readily soluble in THF and in chlorinated hydrocarbons. They are susceptible to hydrolysis, although they are more stable than vanadate esters.

[VOCl{2-(2'-oxynaphthalidene-1'-imino)-1-oxybenzene}] (**4**), *and* **5a**: To a suspension of the Schiff base H_2L^2 (2.0 g, 7.6 mmol) in 100 ml of absolute CH_2Cl_2, a solution of $VOCl_3$ (1.3 ml, 7.6 mmol) in 40 ml of CH_2Cl_2 was added dropwise over a period of 2 hours. To remove HCl, N_2 was passed over the solution. The reaction mixture progressively darkened, turning from orange to brown and eventually to black. After stirring for a further two hours, the product (**4**) was filtered off, washed with three 15-ml portions of pentane and 50 ml of CH_2Cl_2, and dried in vacuo. Product **4** was found to be very susceptible to hydrolysis. − Yield 2.6 g (94%). − $C_{17}H_{11}Cl_2O_2NV$ (379.65) calcd. C 54.65, H 3.15, N 3.98; found C 54.90, H 3.12, N 4.08. − ^1H NMR ([D_8]THF): δ = 6.77−8.57 (m, aromatic H), 10.04 (s, HC=N). − ^{51}V NMR ($CDCl_3$): δ = −434.

5a was obtained by dissolving **4** (50 mg, 0.13 mmol) in 20 ml of methanol at room temperature and storing the resulting solution at −20 °C for one week. The black crystals of **5a** were filtered off and dried in a stream of N_2. Yield 14 mg (28%). According to the spectroscopic characteristics and elemental analysis, the product was identical to that obtained by methanolysis of **3** (see above).

[VO(acac){N,N-bis(2-oxyethyl)methylbenzylamine}] {(*S*)-**6a** and (*R*)-**6a**}: [$VO(acac)_2$] (1.0 g, 3.77 mmol) and (*R*)- or (*S*)-H_2L^3 (0.87 g, 4.15 mmol) were dissolved in 100 ml of absolute acetone. Upon passing O_2 through the solution for 2 days, the original green colour gradually changed to red-brown. The reaction mixture was then concentrated to half of its volume, filtered, and the filtrate was allowed to stand for one week at 0 °C. Orange moisture-sensitive crystals of (*R*)-**6a** or (*S*)-**6a** of crystallographic quality separated during this time. They were filtered off and dried in vacuo. − Yield 1.22 g (87%). − $C_{17}H_{24}NO_5$ (373.31): calcd. C 54.68, H 6.48, N 3.75; found C 54.49, H 6.52, N 3.83. − ^1H NMR (CD_3CN) (data for the ethylene protons verified by simulation, see Scheme 1 for labelling): δ = 1.30 [d, *J* = 7.1 Hz, H_3C-CH(Ph)], 2.26 (s, H_3C−C=CH), 2.61 (H^1_A)/2.10 (H^1_B)/4.80 (H^1_C)/4.56 (H^1_D)//2.72 (H^2_A)/2.35 (H^2_B)/4.74 (H^2_C)/4.40 (H^2_D) [$J(AB)^1$ = 13.0, $J(CD)^1$ = 12.9, $J(AC)^1$ = $J(BD)^1$ = 6.2, $J(AD)^1$ = $J(BC)^1$ = 4.8; $J(AB)^2$ = 13.6, $J(CD)^2$ = 12.9, $J(AC)^2$ = $J(BD)^2$ = 6.4, $J(AD)^2$ = $J(BC)^2$ = 4.1 Hz], 3.74 [q, H_3C-C*H*(Ph)], 6.05 (s, H_3C-C=C*H*), 7.36−7.46 (m, Ph). − ^{13}C NMR (CD_3CN): δ = 17.1 (CH_3), 26.0 (H_3*C*-C=CH), 55.7 (NCH_2), 62.1 (CH), 77.0 (H_2CO), 103.2 (H_3C-C=*C*H), 128.2/128.7/141.0 (Ph), 191.0 (H_3C-*C*=CH). − ^{51}V NMR (CD_3CN): δ = −465.

Scheme 1



Crystal-Structure Determinations: The data were collected on a Hilger & Watts (**5a**, **5b**, **6a**) or Syntex $P2_1$ (**1**) diffractometer in the 2Θ scan mode using a graphite monochromator and Mo-$K_α$ radiation (λ = 71.073 pm). Crystal data and details of the data collection and refinement are collated in Table 2. The program systems SHELXS 86 and SHELXL 93 were used throughout[22]. Hydrogen atoms were placed in calculated positions and included with common isotropic thermal parameters in the last cycles of refinement (based on F^2). Absorption corrections were not carried out. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100263. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

☆ Dedicated to Prof. Dr. *R. Nast* on the occasion of his 85th birthday.

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[14] **1**·H_2O crystallizes in the monoclinic space group $P2(1)/c$ with the following cell parameters: a = 7.587(2), b = 17.722(4), c = 10.174 Å, β = 110.57(3)°, V = 1280.7(5) Å, Z = 4.3719 reflections were measured, 2266 of which were unique. Full-matrix least-squares refinement based on 173 parameters gave a final R value for reflections with $I < 2\sigma(I_o)$ of 0.1453 (goodness of fit: 1.166). Maximum and minimum residual electron densities amounted to 2.304 and −0.635 e Å^3. Selected bonding parameters are given in Table 3.

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