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Structural characterization of possible intermediates in vanadium-catalysed sulfide oxidation†

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Reaction between 3-methoxysalicylaldehyde and (*R*,*R*)-1,2-diaminocyclohexane with VO^{2+} as a template yielded the racemic Schiff-base complex $[VO(L^1)]$ $[H_2L^1$ = *N*,*N*′-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine] which is converted into *trans*-$[VCl_2(L^1)]$ with $SOCl_2$. The crystal structures of both have been determined. The former is a tetragonal-pyramidal complex, whereas the structure of the latter is best described as an octahedron distorted towards a trigonal prism. The complex $[VO(acac)_2]$ (acac = acetylacetonate) reacted with $HN(CH_2CH_2OH)_2$ in the presence of oxygen to yield $[VO(acac)\{PhN(CH_2CH_2O)_2\}]$, the crystal structure of which reveals a co-ordination geometry in-between tetragonal-pyramidal and octahedral (provided by a weak vanadium-to-nitrogen bonding interaction). Aeration of a reaction mixture consisting of $[VO(acac)_2]$ and the Schiff base (H_2L^2) formed between $H_2NCH_2CH_2OH$ and *o*-hydroxynaphthaldehyde afforded $[\{VO(L^2)\}_2O]$ having a bent and slightly asymmetric oxo-bridge, and an additional weak bridging interaction between one of the V–O (ethanolate) centres and the second vanadium centre (crystal structure). In solution, the inequivalency of the two vanadium centres is offset. The reactivity of the complexes towards Me_2SO and/or PhSMe has been studied by EPR and ^{51}V NMR spectroscopy.

Vanadium compounds such as oxides, (hetero)polyvanadates, alkoxides, acetylacetonate and other co-ordination compounds have been employed as effective catalysts in hydrogenation and dehydrogenation/oxidation catalysis of organic and inorganic substrates.[1] Related biological functions have been established: vanadate and vanadyl may act as mediators in nicotineamide adenine dinucleotide phosphate-driven redox processes,[2] and vanadate has been shown to be in the active centre of haloperoxidases from several groups of primitive organisms.[3] Moreover, a role of vanadate as an oxidant of thiol groups has been inferred from the inhibition of glycolysis by glyceraldehyde 3-phosphate dehydrogenase.[4]

More recently, vanadium-(III) and -(IV) co-ordination compounds containing chiral ligands have been shown to catalyse enantioselectively the oxidation of organic sulfides to sulfoxides (and sulfones, in some cases) by hydrogen peroxide[5] or organic hydroperoxides.[6,7] The catalyst systems that have been employed were either oxovanadium complexes of Schiff bases[6,7] such as the double Schiff bases derived from salicylaldehydes and 1,2-diaminocyclohexane (*cf.* **1** in Fig. 1),[6] or mixtures of $[VO(acac)_2]$ [acac = acetylacetonate(1 −)] and Schiff bases containing chiral ethanolamines as amine constituent (see **2** in Fig. 1 for a plausible structure of a catalytically active intermediate). We have now structurally characterized the $V^{IV}O$ complex **1** in addition to a sequential product, the dichloro complex **3**, and two vanadium(V) complexes related to **2**, *viz.* $[VO(acac)\{PhN(CH_2CH_2O)_2\}]$ **4** and $[\{VO(L^2)\}_2O]$ **5** (H_2L^2 = Schiff base derived from *o*-hydroxynaphthaldehyde and 2-aminoethanol). While a variety of well characterized Schiff-base complexes of vanadium exists,[7,11] those with ethanolamines as amine constituents are scarce.[8] This also applies to vanadium complexes of $H_2NCH_2CH_2OH$ and $HN(CH_2CH_2OH)_2$. A structure for the 1 : 1 complex formed between the latter and vanadate in water has been proposed mainly on the basis of NMR spectroscopic evidence (**6** in Fig. 1),[9] and supported by crystal structures of $N(CH_2CHROH)_3$ complexes (*e.g.* **7** in Fig. 1, R = Me).[10]

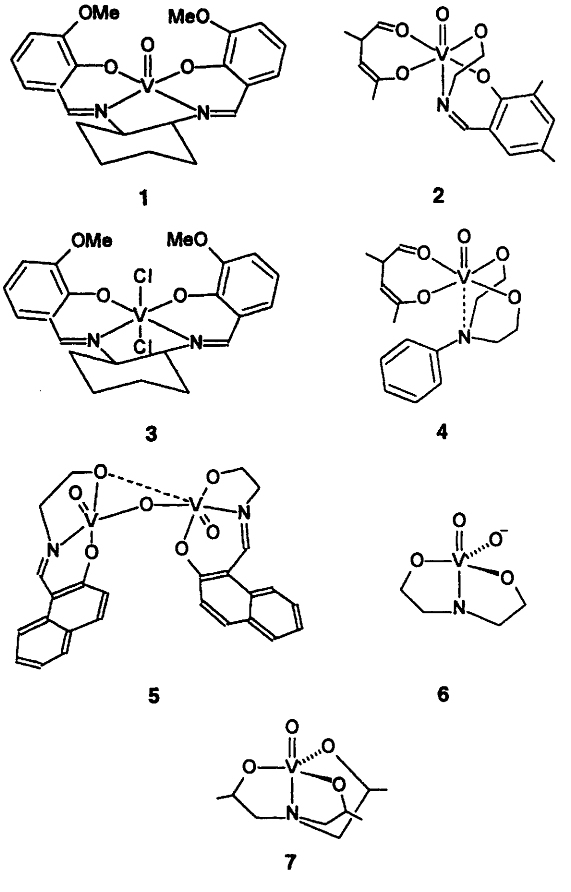

Fig. 1 Structures **1** and **2** proposed for vanadium complexes exhibiting catalytic activity in the oxidation of organic sulfides;[5,6] **1**, its precursor **3**, and the ethanolamine complexes **4** and **5** have been structurally characterized (this work). See also ref. 8 for a complex closely related to **5**. Structure **6** is that suggested in solution for the complex formed between V^V and $HN(CH_2CH_2OH)_2$,[9] and **7** is the solid-state structure for the corresponding complex with $N(CH_2CHROH)_3$[10]

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† *Non-SI unit employed:* G = 10^{-4} T.

Results and Discussion

Preparation and solution characteristics

The complexes have been prepared according to equations (1)–(4). The Schiff-base complex 1 is generated in a one-pot reaction

$$\mathrm{VO^{2+}} + \mathrm{(2\text{-}HO)(3\text{-}MeO)C_6H_3CHO} + \mathrm{1,2\text{-}(H_2N)_2C_6H_{10}} \longrightarrow \underset{\mathbf{1}}{[\mathrm{VO(L^1)}]} + \mathrm{2H_2O} + \mathrm{2H^+} \quad (1)$$

$$\mathbf{1} + \mathrm{SOCl_2} \longrightarrow \underset{\mathbf{3}}{trans\text{-}[\mathrm{VCl_2(L^1)}]} + \mathrm{SO_2} \quad (2)$$

$$[\mathrm{VO(acac)_2}] + \mathrm{PhN(CH_2CH_2OH)_2} \xrightarrow{\mathrm{O_2}} \underset{\mathbf{4}}{[\mathrm{VO(acac)\{PhN(CH_2CH_2O)_2\}}]} + \mathrm{Hacac} \quad (3)$$

$$2[\mathrm{VO(acac)_2}] + \mathrm{2H_2L^2} \xrightarrow{\mathrm{O_2}} \underset{\mathbf{5}}{[\mathrm{\{VO(L^2)\}_2O}]} + \mathrm{4Hacac} \quad (4)$$

(1) from vanadyl sulfate, *o*-vanillin and (*R*,*R*)-1,2-diaminocyclohexane in the molar ratio 1 : 2 : 1 in water–ethanol [H_2L^1 = *N*,*N'*-bis(3-methoxysalicylidene)cyclohexane-1,2-diamine];[6] the vanadyl ion acts as a template, as in the generation of other Schiff-base complexes {compare, *e.g.* [$VO(L)(H_2O)$];[11c] L = the dianion of the Schiff-base formed from 2-hydroxynaphthaldehyde and amino acids such as glycine or histidine}. As suggested by the results of the X-ray structure analysis (see below), racemization occurs in the course of the reaction. In solution, 1 may co-ordinate a solvent molecule as a sixth ligand. Treatment of 1 with thionyl chloride in toluene yields the dichloro complex 3 [equation (2)], with the two chloride ligands in *trans* position as in the corresponding salen complexes *trans*-[$V(salen)X_2$] (X = Cl[12a] or I;[13] salen is the double Schiff-base dianion formed between salicylaldehyde and ethane-1,2-diamine), but in contrast to the *cis*-configurated complex *cis*-[$V(nap\text{-}gly)Cl_2$] (nap-gly is the Schiff base derived from *o*-hydroxynaphthaldehyde and glycine).[12a] The *trans* position of the chloride ligands is reflected by a single ν(V–Cl) at 407 cm^{-1} and further documented by the X-ray structure analysis. The reaction between [$VO(acac)_2$] and $PhN(CH_2CH_2OH)_2$ yields the oxovanadium(v) complex 4 [equation (3)] by exchange of one of the acac ligands, combined with an oxidation of V^{IV} to V^V. The oxidant possibly is oxygen, since the reaction does not lead to a defined product under anaerobic conditions. A similar reaction between [$VO(acac)_2$] and 2-(2-hydroxynaphthylmethyleneamino)ethanol (H_2L^2), again with aeration of the reaction medium, results in the complete removal of acetylacetonate and formation of the dinuclear, oxo-bridged complex 5 [equation (4)].

The ^{51}V NMR chemical shifts of the two vanadium(v) complexes 4 (δ −472) and 5 (δ −561) are in the region expected for five- to six-co-ordinated vanadium complexes with a mixed N,O donor set.[14,15] The two vanadium(IV) complexes 1 and 3 exhibit EPR characteristics similar to those of other oxo- and dichloro-Schiff base complexes[12a] (**1**, A_{iso} = 99.6 G, g_{iso} = 1.98; compare A_{iso} = 100 G, g_{iso} = 2.01 in ref. 6. **3**, A_{iso} = 80 G, g_{iso} = 1.9597). Complexes 1 and 4 show ν(V=O) bands at 986 and 983 cm^{-1}, respectively, characteristic of oxovanadium(v) complexes.[6] The corresponding band for 5 is at 988 cm^{-1}. The V–Cl stretch for 3 at 407 cm^{-1} is shifted hypsochromically with respect to other [VCl_2(Schiff base)] complexes (301–382 cm^{-1}).[12a] The cyclovoltammogram of 1, dissolved in MeCN, exhibits a reversible oxidation/reduction (V^V/V^{IV}) step $E_{\frac{1}{2}}$ = +0.392 V, which compares to $E_{\frac{1}{2}}$ = +0.286 V *vs.* saturated calomel electrode (SCE) for the same compound dissolved in Me_2SO.[6] No reversible behaviour was found in the case of 4 (reduction in MeCN at −0.50 V) and 5. The dichloro complex 3 (in CH_2Cl_2) gives rise to a reversible oxidation at $E_{\frac{1}{2}}$ = +1.208 ($V^{IV}\rightarrow V^V$) and a reversible reduction at +0.075 V ($V^{IV}\rightarrow V^{III}$), Fig. 2.

Structural description

The molecular structures of complexes 1 and 3–5, including the atom labelling, are shown in Figs. 3–5. Selected bonding parameters are given in Tables 1–4.

Compound 1 crystallizes with two CH_2Cl_2 of crystallization per molecule in the triclinic space group $P\bar{1}$. The carbon atoms C(31), C(33), C(34) and C(30) of the cyclohexane are

Table 1 Selected bond lengths (Å) and angles (°) for [$VO(L^1)$] **1**

V–O(1)	1.595(5)	O(1)–V–O(2)	110.2(2)
V–O(2)	1.933(5)	O(1)–V–O(4)	108.3(2)
V–O(4)	1.929(5)	O(1)–V–N(1)	103.1(3)
V–N(1)	2.054(6)	O(1)–V–N(2)	108.0(3)
V–N(2)	2.036(6)	O(2)–V–O(4)	86.0(2)
O(2)–C(10)	1.330(8)	O(2)–V–N(1)	86.8(2)
O(4)–C(20)	1.329(8)	O(4)–V–N(2)	88.0(2)
N(1)–C(16)	1.287(9)	N(1)–V–N(2)	78.8(2)
N(2)–C(26)	1.304(9)	C(16)–N(1)–V	124.7(5)
O(3)–C(17)	1.429(9)	C(30)–N(1)–V	109.9(7)
O(5)–C(27)	1.415(9)	C(16)–N(1)–C(30)	121.1(8)

Table 2 Selected bond lengths (Å) and angles (°) for [$VCl_2(L^1)$] **3***

V–Cl(1)	2.370(2)	Cl(1)–V–Cl(2)	175.01(6)
V–Cl(2)	2.364(2)	O(1)–V–O(3)	108.6(2)
V–O(1)	1.816(3)	N(1)–V–N(2)	78.3(2)
V–O(3)	1.801(4)	O(1)–V–N(1)	86.9(2)
V–N(1)	2.084(4)	O(3)–V–N(2)	86.3(2)
V–N(2)	2.085(4)	Cl(1)–V–N(1)	88.86(14)
N(1)–C(16)	1.300(7)	Cl(1)–V–O(1)	91.31(14)
N(2)–C(26)	1.284(7)	Cl(2)–V–O(1)	91.98(14)
		Cl(2)–V–N(1)	87.58(14)

* For one of the two independent molecules [V(1)].

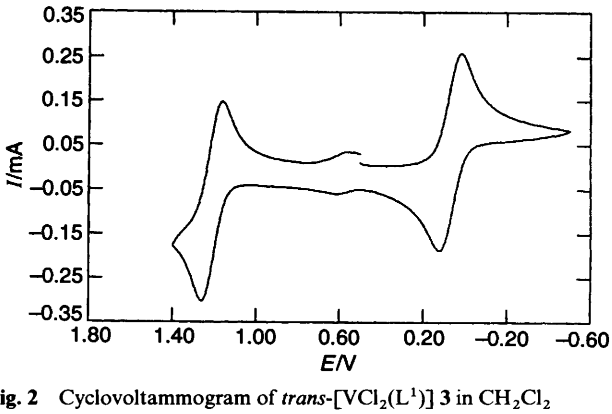


Fig. 2 Cyclovoltammogram of *trans*-[$VCl_2(L^1)$] 3 in CH_2Cl_2

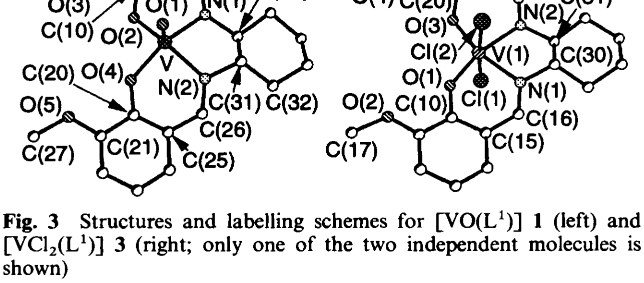


Fig. 3 Structures and labelling schemes for [$VO(L^1)$] 1 (left) and [$VCl_2(L^1)$] 3 (right; only one of the two independent molecules is shown)

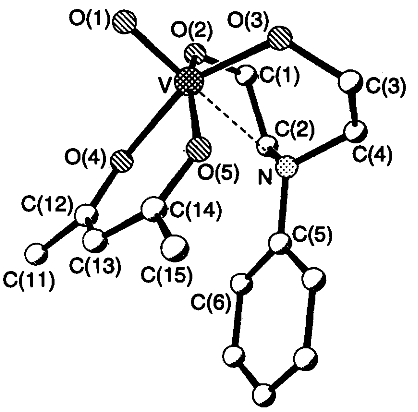


Fig. 4 Structure and labelling scheme for $[\mathrm{VO(acac)\{PhN(CH_2CH_2O)_2\}}]$ **4**

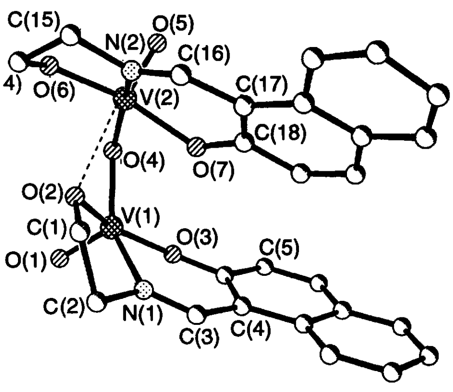


Fig. 5 Structure and labelling scheme for $[\{\mathrm{VO(L^2)}\}_2\mathrm{O}]$ **5**

Table 3 Selected bond lengths (Å) and angles (°) for $[\mathrm{VO(acac)\{PhN(CH_2CH_2O)_2\}}]$ **4**

V–O(1)	1.568(4)	O(2)–V–O(3)	96.8(2)
V–O(2)	1.819(4)	O(4)–V–O(5)	83.5(2)
V–O(3)	1.794(5)	O(2)–V–O(4)	87.8(2)
V–O(4)	1.977(4)	O(3)–V–O(5)	84.8(2)
V–O(5)	1.997(4)	O(1)–V···N	177.1
V···N	2.559	O(1)–V–O(2)	99.9(2)
O(4)–C(12)	1.275(7)	O(1)–V–O(3)	102.9(2)
O(5)–C(14)	1.272(7)	O(1)–V–O(4)	98.9(2)
C(12)–C(13)	1.347(9)	O(1)–V–O(5)	98.3(2)
C(13)–C(14)	1.397(9)		

Table 4 Selected bond lengths (Å) and angles (°) for $[\{\mathrm{VO(L^2)}\}_2\mathrm{O}]$ **5**

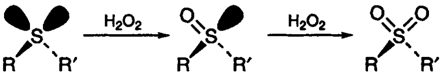
V(1)–O(1)	1.572(12)	V(2)–O(5)	1.584(14)
V(1)–O(2)	1.895(12)	V(2)–O(6)	1.802(12)
		V(2)···O(2)	2.459
V(1)–O(3)	1.833(13)	V(2)–O(7)	1.918(12)
V(1)–O(4)	1.785(12)	V(2)–O(4)	1.820(12)
V(1)–N(1)	2.08(2)	V(2)–N(2)	2.09(2)
N(1)–C(3)	1.26(2)	N(2)–C(16)	1.30(2)
O(3)–C(5)	1.33(2)	O(7)–C(18)	1.31(2)
V(1)–O(4)–V(2)	109.3(6)		
O(1)–V(1)–O(2)	103.0(7)	O(5)–V(2)–O(6)	101.1(7)
O(1)–V(1)–O(3)	101.9(7)	O(5)–V(2)–O(7)	98.9(7)
O(1)–V(1)–O(4)	108.4(7)	O(5)–V(2)–O(4)	103.2(6)
O(1)–V(1)–N(1)	107.1(7)	O(5)–V(2)–N(2)	101.2(7)
O(2)–V(1)–O(4)	85.2(6)	O(6)–V(2)–O(4)	103.1(6)
O(2)–V(1)–N(1)	76.8(6)	O(6)–V(2)–N(2)	78.7(6)
O(3)–V(1)–O(4)	100.1(6)	O(7)–V(2)–O(4)	88.9(6)
N(1)–V(1)–O(4)	142.9(6)	N(2)–V(2)–O(4)	154.7(6)

'disordered' giving rise to an *RR*/*SS* racemate in the crystal. The overall geometry is that of a tetragonal pyramid with the oxo group O(1) at the apex, and without substantial deviations of bond angles and lengths from those commonly observed in related complexes (*cf.* ref. 11). The normal V=O double bond length of 1.595 Å indicates that O(1) is not involved in hydrogen-bonding interactions. The relatively narrow chelate angle N(1)–V–N(2) is a consequence of the steric restrictions imparted by the 1,2-bis(enamine) cyclohexane unit. Vanadium deviates from the tetragonal plane N(1)–N(2)–O(2)–O(4) by 0.596 Å.

Crystals of complex **3** have been isolated in the form of racemic twins (with *RR* and *SS* domains). The compound crystallizes in the monoclinic space group $P2_1$. As already derived from the IR pattern, the two chlorine atoms are in *trans* positions to each other, while the tetradentate ligand forms a plane N(1)–N(2)–O(1)–O(3). Vanadium deviates from this plane by 0.012 Å. The two chlorine atoms are slightly bent off the Cl(1)–V–Cl(2) axis towards the N(1)–N(2) edge of the plane. The bite angle N(1)–V–N(2) [78.3(2)°] is the same as in the oxo precursor **1**. In contrast, O(1)–V–O(3) (*i.e.* phenolate–vanadium–phenolate), 108.6(2)°, is considerably widened with respect to the corresponding angle in **1** [86.0(2)°]. Concomitantly, the bond lengths *d*[V–O(1)] [1.816(3) Å] and *d*[V–O(3)] [1.801(4) Å] are substantially shorter than in **1** [1.933(5) and 1.929(5) Å] and other vanadium complexes containing a V–O (phenolate) bond (usually in the range 1.83–1.91 Å),[11] while the bonding distances to the enamine nitrogens are longer in **3** than in **1**. The overall geometry hence is a distorted (towards a trigonal prism) octahedron. The extent of distortion is comparable to that in *trans*-$[\mathrm{VI_2(salen)}]$,[13] but substantially less distinct than in *trans*-$[\mathrm{VCl_2(salen)}]$.[12a]

In contrast to the vanadium(IV) complexes $[\mathrm{VO(L^3)}]$ and $[\{\mathrm{VO(L^3)}\}_2]$ $[\mathrm{H_2L^3}$ = 2-(salicylideneamino)ethanol], where the alcoholic groups are pendant or bridging, respectively,[8] but in analogy to the vanadium(V) complexes **7** (*cf.* Fig. 1)[10] and **5** (see below), the ethanolate in **4** directly co-ordinates to a single vanadium centre. The basic structure is a tetragonal pyramid with the plane spanned by the acetylacetonate and the two alkoxides, and the doubly bonded oxygen at the apex. Vanadium deviates from the plane O(2)–O(3)–O(4)–O(5) by 0.331 Å, *i.e.* to a lesser extent than in **1**. The reason possibly is a long-distance bonding interaction of 2.559 Å between vanadium and the amine nitrogen, which thus completes an octahedral co-ordination sphere. The geometry of **4** hence differs from that reported for **7** (trigonal bipyramidal),[10] and for $[\{\mathrm{VO(L^3)}\}_2]$ (tetragonal pyramidal).[8] The V–O (alkoxide) bond lengths in **4** [1.819(4) and 1.794(5) Å] slightly exceed those commonly found in other alkoxovanadium(V) complexes, *e.g.* 1.763 Å in $[\{\mathrm{VO(cyclo\text{-}C_5H_9O)_3}\}_2]$[16] and 1.759 in $[\mathrm{VO(nap\text{-}ala)(OBu^t)(HOBu^t)}]$ (nap-ala is the Schiff base derived from *o*-hydroxynaphthaldehyde and L-alanine),[11b] but are comparable to the corresponding parameters found in **5** and **7**.

The complex $[\{\mathrm{VO(L^2)}\}_2\mathrm{O}]$ **5** is an asymmetric, oxo-bridged dimer with the two O-bridged oxovanadium groups in the twist configuration with respect to each other. One of the vanadium centres [V(1)] is in a distorted tetragonal-pyramidal environment, while the other [V(2)] is in an approximate six-co-ordinate environment due to the formation of a weak bond (2.459 Å) between it and the alkoxy-oxygen O(2) at V(1). As a consequence, V(2) deviates from the tetragonal plane formed by the strongly bridging oxygen [O(4)], O(alkoxide) [O(6)], O(phenolate) [O(7)] and the enamine nitrogen N(2) by just 0.369 Å, whereas the deviation of V(1) from the plane O(4)–O(2)–O(3)–N(1), 0.490 Å, is about normal for a vanadium centre in a tetragonal-pyramidal co-ordination sphere. Complex **5** resembles $[\{\mathrm{VO(L^4)}\}_2\mathrm{O}]$[8] $[\mathrm{H_2L^4}$ = 1,1-dimethyl-2-(salicylideneamino)ethanol] in structure and most of the bonding parameters. There are, however, a few distinct differences which may be brought about by the sterically more demanding ligand $\mathrm{L^4}$ in the latter. Thus, the torsion angle V(1)=O(1)/V(2)=O(5) amounts to 79.7° in **5**, while it is *ca.* 105° in $[\{\mathrm{VO(L^4)}\}_2\mathrm{O}]$. The V–(μ-O)–V angles [109.3(6) and 103°]



Scheme 1

differ only marginally. In both complexes the bridge is slightly asymmetric [Δd(V–μ-O) = 0.095 Å in **5**, 0.035 Å in the salicylidene complex; with the longer bond directed towards the six-co-ordinated vanadium]. The bonding distance between the six-co-ordinated vanadium centres [V(2) in **5**] and the strongly bonded alkoxide are about equal in **5** and the salicylidene complex (1.802 and 1.805 Å). This is not so for the d[V–O (alkoxide)] bonds at the five-co-ordinated vanadium centres [V(1) in **5**], where the distances are 1.895 Å in **5** and 1.828 Å in [{VO(L^4)}$_2$O].

Complex–substrate interaction

The oxidation of sulfides to sulfoxides (and sulfones) by peroxides (Scheme 1) is a slow process in the absence of vanadium.[6] In the case of PhSMe dissolved in CH$_2$Cl$_2$ it took 3 d for complete conversion and did not proceed beyond the formation of PhS(O)Me. The complex [VO(acac)$_2$] accelerates the reaction. Small amounts of PhS(O)$_2$Me can then be recovered along with PhS(O)Me as the main product. Addition of *catalytic* amounts of [VO(acac)$_2$] and PhN(CH$_2$CH$_2$OH)$_2$, *i.e.* the components constituting complex **4**, further speed up the reaction, and sulfoxide and sulfone are formed in a molar ratio of approximately 7:3 in contact with air or under nitrogen. Additional treatment with oxygen shifted the ratio to 4:5. The sulfide is converted practically completely within 19 or (nitrogen atmosphere) 33 h. Similar results are obtained with catalytic amounts of the isolated complex **4**; in this case the sulfoxide:sulfone ratio was 6:4. These preliminary results support a key role of an active intermediate having molecular connectivities provided by or similar to those of **4** in the catalysis of sulfide oxidation. The effect of such catalysis by the Schiff-base complex **1** has been documented elsewhere.[6,7]

In order to provide evidence that complexes of the kind described here have available binding sites for peroxide, sulfide and/or sulfoxide, CH$_2$Cl$_2$ solutions of **1** (V^{IV}), **4** and **5** (both V^{V}) were treated with these substrates and investigated by EPR and ^{51}V NMR spectroscopy, respectively. The conversion into the peroxo complexes on addition of H$_2$O$_2$ is immediately visible by a change to brick-red. The δ(^{51}V) for the peroxo derivative of **4**, −534 (**4**, δ −472), further indicates that the oxo group is replaced by a peroxo group, a commonly observed feature for vanadium complexes containing, *inter alia*, amine ligands.[17] Addition of PhSMe to **4** resulted in a relatively small downfield shift in the ^{51}V NMR spectrum (δ −465.0 as compared to −472.1 for **4**). In contrast, addition of Me$_2$SO shifts the signal upfield to δ −496.8. These results can be interpreted in terms of weak (PhSMe) and relatively strong interaction (Me$_2$SO) of the substrates with the complex. The signal for the dinuclear vanadium(v) Schiff-base complex **5** (δ −560.6) experiences a downfield shift to δ −536.7 on addition of PhSMe, indicative of effective co-ordination of the thioether, containing a soft co-ordination site.[18] A less dramatic effect is observed on addition of Me$_2$SO (δ −557.1). This small shift difference might be interpreted in terms of a solvent effect. Distinct changes in the EPR parameters of **1** ($g_{\parallel}$ = 1.95, $g_{\perp}$ = 1.99; $A_{\parallel}$ = 176.4 G, $A_{\perp}$ = 62.5 G) in the presence of substrates were observed in the case of Me$_2$SO. The spectrum shows rhombic distortions at 100 K; the main variation is in $A_{\parallel}$ (= 172.3, $A_{\perp}$ = 56.2 and 60.8 G; $g_{\parallel}$ = 1.96, $g_{\perp}$ = 1.99 and 1.98), which conforms with an interaction of Me$_2$SO with the vanadium centre along the preferential (V=O) axis and probably indicates the formation of an octahedral complex of composition **1**·OSMe$_2$ with the Me$_2$SO opposite the oxo group.

Conclusion

Complexes **4** and **5** contain five-co-ordinated, tetragonal-pyramidal vanadium centres with a strongly bonded oxo group at the apex and the opposing site occupied by a weakly bound amine-N or alkoxide-O. The d(V–N) and d(V–O) exceed those noted for bond elongations originating from the *trans* effect imparted by the oxo group by *ca.* 0.3 Å. A weak vanadium-to-ligand bonding interaction and hence an easily available co-ordination site, or an open co-ordination site as in **1**, or V(1) of **5**, along with the variability of geometric arrangements (tetragonal pyramidal *vs.* octahedral, tetragonal *vs.* distortions towards trigonal bipyramidal, and octahedral *vs.* distortions towards trigonal prismatic) are preconditions for catalytic activity. A potential substrate, *e.g.* organic sulfide and/or peroxide as in the case of the catalytically induced oxidation of sulfide to sulfoxide, may well be activated by an intermediate co-ordination to the vacant or easily accessible site at the vanadium centre(s). Peroxo complexes of vanadium with supporting oligodentate ON ligand sets are well known and their efficiency in alkane and aromate oxidation catalysis has been noted.[1,17,19] Kinetic data for the interaction of V^{IV} with inorganic and organic hydroperoxides are available.[20] The co-ordination of inorganic and organic sulfides to vanadium has also been noted,[21] and is documented here by the formation of a sulfide adduct with complex **5**.

Whether the catalytic oxidation is accompanied by a change in the vanadium oxidation state between v and iv (and iii) remains open. The reversibility of the electrochemical oxidation of complex **1** suggests such a change, as does the existence of mixed-valence V^{V}V^{IV} Schiff-base complexes such as [{VO(sal-ser)}$_2$O] (sal-ser is the Schiff base derived from salicylaldehyde and L-serine) with a bent V–O–V bridge[22] as in **5**. The irreversibility of the reduction in the case of complexes **4** and **5** does not support such an assumption.

Experimental

Operations, if not mentioned otherwise, were carried out in water-free solvents and in an inert-gas atmosphere to prevent hydrolysis. To prevent photoinduced decomposition, the samples were protected from direct light. The following compounds were obtained from commercial sources (Merck, Serva, Fluka): VO(SO)$_4$·5H$_2$O, [VO(acac)$_2$], SOCl$_2$, (*R*,*R*)-1,2-diaminocyclohexane, PhN(CH$_2$CH$_2$OH)$_2$, vanillin, H$_2$NCH$_2$CH$_2$OH and 2-hydroxynaphthalene-1-carbaldehyde. The complex [VO(L^1)] **1** was prepared from vanillin and 1,2-diaminocyclohexane according to a literature procedure.[7]

Infrared spectra in the range 4000–400 cm^{-1} were obtained in Nujol or KBr on a Perkin-Elmer 1700 X FT, FIR spectra (400–50 cm^{-1}) in KBr on a Perkin-Elmer 1720, and NMR spectra on a Bruker AM 360 spectrometer in CDCl$_3$. The ^{51}V NMR spectra were measured at 94.73 MHz in 10 mm diameter vials and referenced against VOCl$_3$. Measuring parameters: sweep width 125 kHz, time domain 8200 K, pulse angle 60°, line-broadening factor 30 Hz, no relaxation delay. The EPR spectra were recorded in 0.05 mol dm^{-3} solutions in CH$_2$Cl$_2$ on a Bruker ESP 300 E spectrometer at 9.78 GHz and a microwave power of 5 mW. Cyclic voltammetry was carried out with an EG&G Princeton Applied Research potentiostat 273 A with a three-electrode arrangement (platinum bead, platinum-wire working electrode, saturated calomel electrode SCE) for *ca.* 1 mmol dm^{-3} solutions in acetonitrile or CH$_2$Cl$_2$ and with 0.2 mol dm^{-3} tetrabutylammonium hexafluorophosphate as supporting electrolyte. Potentials were referenced against the ferrocene–ferrocenium couple employed as an external standard, and are quoted relative to the SCE.

The samples for testing the catalytic activity of complex **4** comprised CH$_2$Cl$_2$ (2 cm^3), PhSMe (0.12 cm^3, 1 mmol), **4** (3.4 mg, 0.01 mmol) or [VO(acac)$_2$] (2.6 mg, 0.01 mmol)

Table 5 Crystal data and refinement parameters for complexes **1**·2CH_2Cl_2, **3**·2MeCN, **4** and **5**

	1·2CH_2Cl_2	**3**·2MeCN	**4**	**5**
Empirical formula	$C_{24}H_{28}Cl_2N_2O_5V$	$C_{26}H_{30}Cl_2N_4O_4V$	$C_{15}H_{20}NO_5V$	$C_{26}H_{22}N_2O_7V_2$
M	617.22	584.38	345.26	576.34
T/K	173(2)	153(2)	293(2)	173(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P\bar{1}$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a/pm	855.2(4)	950.3(2)	839.1(4)	1214.2(3)
b/pm	1293.1(8)	1913.3(6)	1267.1(11)	1242.6(4)
c/pm	1418.0(6)	1505.7(8)	1510.9(12)	1528.8(3)
α/°	64.54(4)			
β/°	75.70(4)	97.12(2)		
γ/°	78.25(4)			
U/nm^3	1.3634(12)	2.717(2)	1.606(2)	2.3066(10)
Z	2	4	4	4
D_c/g cm^{-3}	1.503	1.429	1.428	1.660
μ/mm^{-1}	7.0	0.6	0.6	7.3
F(000)	634	1212	720	1176
Crystal dimensions/mm	0.4 × 0.2 × 0.1	0.4 × 0.3 × 0.2	0.8 × 0.2 × 0.2	0.1 × 0.15 × 0.3
θ Range/°	3.51–76.47	2.41–25.05	2.70–22.49	4.49–76.36
hkl Range	0–10, −15 to 16, −17 to 17	−2 to 11, −2 to 22, −17 to 17	−2 to 9, −2 to 13, −2 to 16	−15 to 15, 0–19, 0 to −15
Measured reflections	6178	7587	2297	5279
Independent reflections	5713	5588	1775	4836
R_{int}	0.0824	0.0213	0.0264	0.1259
Refined parameters	372	677	202	335
Final $R1$ ($wR2$) [$I > 2\sigma(I)$]	0.0968(0.2410)	0.0388(0.0829)	0.0448(0.0956)	0.1249(0.2636)
all data	0.1390(0.2750)	0.0526(0.0885)	0.0596(0.1025)	0.2952(0.3770)
Goodness of fit	1.126	1.032	1.069	1.038
Maximum, minimum residual electron density/e nm^{-3}	1316, −1029	325, −406	230, −186	797, −758

+$PhN(CH_2CH_2OH)_2$ (2.7 mg, 0.01 mmol) and 30% aqueous H_2O_2 (0.0337 cm^3, 1.1 mmol). The solutions were kept in air or under nitrogen and stirred vigorously in order to provide intimate contact between the two phases. To analyse the product spectrum the organic phase was collected and filtered through neutral Al_2O_3 to remove the vanadium component. The organic residue was chromatographed on a Varian Star 3400 C_x apparatus using a DB 5 non-polar capillary column.

Preparation of complexes

***trans*-[$VCl_2(L^1)$] 3.** Complex **3** was prepared in analogy to [VCl_2(salen)]:[12a,b] [$VO(L^1)$] **1** (0.89 g, 2 mmol) was suspended in toluene (70 cm^3), $SOCl_2$ (0.40 cm^3, 0.52 mmol) was added and the reaction mixture refluxed for 1 h. After cooling to room temperature the black residue of **3** was filtered off, washed with toluene until the filtrate remained colourless, and dried in high vacuum to yield a black, air-sensitive, powdery solid, which was soluble in CH_2Cl_2 and MeCN. Yield: 80% (Found: C, 52.25; H, 4.70; N, 5.80. $C_{22}H_{24}Cl_2N_2O_4V$ requires C, 52.6; H, 4.80; N, 5.60%). $\tilde{\nu}_{max}$/cm^{-1} (KBr) 407. g_{iso} (CH_2Cl_2) 1.9597, A_{iso}/G 80. $E_{\frac{1}{2}}$/V (CH_2Cl_2, SCE) +0.075 and +1.208. Crystals suitable for X-ray crystallography were obtained from a saturated, dark green solution in acetonitrile.

[VO(acac){$PhN(CH_2CH_2O)_2$}] 4. The complex [$VO(acac)_2$] (1.000 g, 3.77 mmol) and $PhN(CH_2CH_2OH)_2$ (0.752 mg, 4.14 mmol) were dissolved in acetone (100 cm^3). On bubbling dry oxygen through the solution *via* a filter plate the originally green solution gradually turned red-brown. After 8 h of reaction the solution was layered with pentane to yield orange-red crystal needles suitable for the X-ray analysis. They were filtered off and dried *in vacuo*. Yield: 72%. M.p. 125 °C (Found: C, 52.05; H, 5.85; N, 4.30. $C_{15}H_{20}NO_5V$ requires C, 52.2; H, 5.85; N, 4.05%). δ_H($CDCl_3$, $SiMe_4$) 1.89 (6 H, s, CH_3), 3.21 and 3.78 (4 H, m, NCH_2), 4.81 and 5.09 (4 H, m, H_2CO), 5.08 (1 H, s, =CH–), 6.84 [2 H, d, ^3J(HH) 8.1, *o*-CH], 6.91 [1 H, t, ^3J(HH) 7.3, *p*-CH], 7.15 [2 H, dd, ^3J(HH) 8.7 and 7.4 Hz, *m*-CH]. δ_C($CDCl_3$, $SiMe_4$) 26.23 (CH_3), 55.80 (NCH_2), 76.95 (H_2CO), 102.53 (=CH–), 116.30 (*o*-CH), 121.55 (*p*-CH), 128.35 (*m*-CH), 150.23 (C_{ipso}) and 190.88 (C=O); δ_V($CDCl_3$, $VOCl_3$) −472. $\tilde{\nu}_{max}$/cm^{-1} (KBr) 983 (V=O). λ_{max}/nm (MeCN) 235.4 (ε 30 600 dm^3 mol^{-1} cm^{-1}). Cyclic voltammetry (MeCN, SCE): irreversible reduction at −0.50 V.

[{$VO(L^2)$}$_2$O] 5. The complex [$VO(acac)_2$] (500 mg, 1.88 mmol) and the Schiff base (445 mg, 2.07 mmol) (prepared from $H_2NCH_2CH_2OH$ and *o*-hydroxynaphthaldehyde in EtOH) were dissolved in acetone (100 cm^3) and refluxed for 24 h. From time to time a stream of O_2 was passed through the solution. Complex **5** precipitated as a black-green, crystalline solid upon concentration of the solution to 50 cm^3. The residue was filtered off, washed with two portions (5 cm^3) of acetone and dried. Yield 75% (Found: C, 53.8; H, 3.85; N, 4.85. $C_{26}H_{22}N_2O_7V_2$ requires C, 54.2; H, 3.85; N, 4.85%). δ_H($CDCl_3$, $SiMe_4$) 3.86 (4 H, m, NCH_2), 4.69 (4 H, m, H_2CO), 7.20–8.24 (12 H, naphthalene) and 9.25 (2 H, s, =CH–). δ_V($CDCl_3$, $VOCl_3$) −561. $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1623 (C=N) and 988 (V=O). Complex **5** also formed when a CH_2Cl_2 solution of [$VOCl(L^3)$] (from $VOCl_3$ and H_2L^3) is treated with NH_3. Crystals suitable for the structure analysis were obtained by allowing a saturated $CHCl_3$ solution of **5** to stand at room temperature for 2 weeks.

Crystallography

X-Ray data were collected on a Hilger & Watts (complexes **3**, **4**) or CAD 4 diffractometer (**1**, **5**)* in the θ–2θ scan mode, using a graphite monochromator, and Mo-Kα (λ = 71.073 pm, **3** and **4**) or Cu-Kα (λ = 154.178 pm, **1** and **5**) radiation, respectively.

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* *Note added at proof.* Refinement of the crystallographic data set for complex **1** in the chiral space group $P1$ lead to an improved view of this compound. The unit cell contains two independent molecules. There is only one enantiomer present, *i.e.* the diaminocyclohexane moiety of L^1 is in the *RR* configuration (as in the starting material). R ($wR2$) for reflections with $I > \sigma(I)$ 0.0757 (0.1776), for all data 0.1238 (0.2205); goodness of fit 1.061; maximum and minimum residual electron density/e nm^{-3} 1153 and −974; absolute structure parameter −0.09(2).

Crystal data and details of the data collection and refinement are collated in Table 5. The program systems SHELXS 86 and SHELXL 93 were used throughout.[23] Hydrogen atoms were placed in calculated positions and included with common isotropic thermal parameters in the last cycles of the refinement (based on F^2). For **1** and **5** empirical absorption corrections using ψ scans have been applied. In the case of $\mathbf{1}\cdot 2CH_2Cl_2$ the cyclohexane carbon atoms C(30), C(31), C(33) and C(34) were treated with a 1 : 1 disorder model. One of the chlorine atoms [Cl(4)] of one of the methylene chlorides of crystallization was treated with a 0.8 : 0.2 disorder model. Compound **3** crystallized as a racemic twin. The Flack factor before the twin refinement was 0.36. The relatively poor quality of the structure analysis of **5** (conventional *R* value 0.125) is a consequence of non-optimum scattering; the connectivities in the molecule have nonetheless been unambiguously established.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/158.

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