Vanadium(IV/V) Complexes Containing $[VO]^{2+}$, $[VO]^{3+}$, $[VO_2]^+$ and $[VO(O_2)]^+$ Cores with Ligands Derived from 2-Acetylpyridine and *S*-Benzyl- or *S*-Methyldithiocarbazate

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Vanadium complexes containing $[VO]^{2+}$, $[VO]^{3+}$, $[VO_2]^+$ and $[VO(O_2)]^+$ cores with ligands (LH) derived from 2-acetylpyridine and *S*-benzyldithiocarbazate (Hacpy-sbdt, **I**) or *S*-methyldithiocarbazate (Hacpy-smdt, **II**) are introduced. The dioxovanadium(V) complexes $[VO_2L]$ [HL = **I** (**2**), **II** (**5**)] were isolated from the reaction between LH and $[VO(acac)_2]$ in the presence of air and KOH in dry methanol. Treatment of **II** with aerated $[VO(acac)_2]$ in *wet* methanol yielded the malonato complex [VO(acpy-smdt)mal] (**6**), with the malonate ligand originating from acetylacetonate. Under anaerobic reaction conditions, LH replaced one of the acac(1−) ligands to yield the oxovanadium(IV) complexes [VO(acac)L] [HL = **I** (**1**), **II** (**4**)]. Treatment of these complexes with H_2O_2, catechol or benzhydroxamic acid gave rise to oxo(peroxo)vanadium complexes $[VO(O_2)L]$ [HL = **I** (**3**), **II** (**7**)], catecholato complexes [VOL(cat)] [HL = **I** (**8**), **II** (**9**)] or benzhydroxamato complexes [VOL(bha)] [HL = **I** (**10**), **II** (**11**)]. Compounds **3** and **7** were capable of transferring an oxo group to PPh_3. In the presence of L-ascorbic acid under aerobic conditions, **8** and **11** were converted into **2** and **5**, possibly through intermediate reduction. Acidification of **2** with HCl in methanol afforded a hydroxo(oxo) complex. The crystal and molecular structures of **2** and **6** were determined, confirming the *NNS* (enethiolate) binding mode of L^-, and the bidentate coordination of the malonate ligand in **6**. The geometrical arrangement of the ligand set in **2** is intermediate between a trigonal bipyramid and a tetragonal pyramid.

Introduction

The coordination chemistry of oxovanadium(IV), oxovanadium(V) and dioxovanadium(V) has acquired new interest as these complexes can serve as good models for vanadium-containing biomolecules.[1−3] Potential therapeutic applications,[4−6] studies on the metabolism and detoxification of vanadium compounds under physiological conditions,[7] and the stability and speciation of vanadium complexes in biofluids[8] have further influenced the study of the coordination chemistry of vanadium. In this context, vanadium complexes containing thiofunctional ligands have received less attention.[9−11] Complexes with *OS* coordination [such as bis(1-oxy-2-pyridinethiolato)oxovanadium(IV)] have been found to be orally active insulin mimetic agents in the treatment of diabetic model animals.[12] In addition, coordination of a sulfur atom to the vanadium centre has been well established in vanadium nitrogenase found in nitrogen-fixing bacteria of the genus *Azotobacter*.[13,14] Vanadium complexes that model parts of the structure of the enzyme have been designed (cf. ref.[9]). Vanadium−sulfur coordination is also of interest for the inhibition of phosphatases (interaction between the vanadium centre and the active site cysteinate)[15,16] and the enantioselective oxidation of prochiral thioethers to sulfoxide by vanadate-dependent haloperoxidases.[17,18]

Unless bulky groups are attached to the ligand to provide sufficient steric hindrance, interaction between monobasic tridentate ligands and $[VO(acac)_2]$ under aerobic conditions generally produces dimeric, pseudo-octahedral complexes with the $[VO_2]_2$ core.[19−22] In the current work, we have employed less bulky ligands (cf. Scheme 1) with an *NNS* donor set, which stabilise monomeric dioxovanadium(V) ($[VO_2]^+$) complexes with the vanadium centre in a tetragonal-pyramidal array, strongly distorted towards a trigonal bipyramid. Other complexes, with $[VO]^{2+}$, $[VO]^{3+}$ and $[VO(O_2)]^+$ cores, have also been prepared. The hitherto unknown coordination of malonate to oxovanadium(V) has been achieved by the unprecedented preparation of the complex [VO(acpy-smdt)mal] by oxidative removal of the methyl groups from one of the acetylacetonates in $[VO(acac)_2]$ in the presence of the supporting *NNS* ligand. In all cases reported here, the ligands coordinate from their thioenolate form; cf. refs.[23−31] for other examples of stable oxo- and dioxovanadium(V) complexes with this coordination mode. Apart from their interesting coordination beha-

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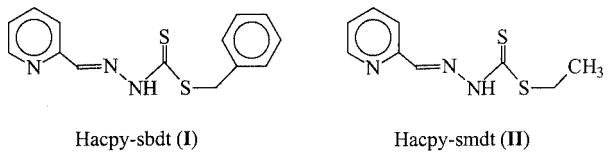
viour, our motivation to use these particular ligands (**I** and **II**, Scheme 1) also arises from the recently assessed antiamoebic activity of their ruthenium(II) and palladium(II) complexes against *Entamoeba histolytica* (strain HK-9).[32,33]

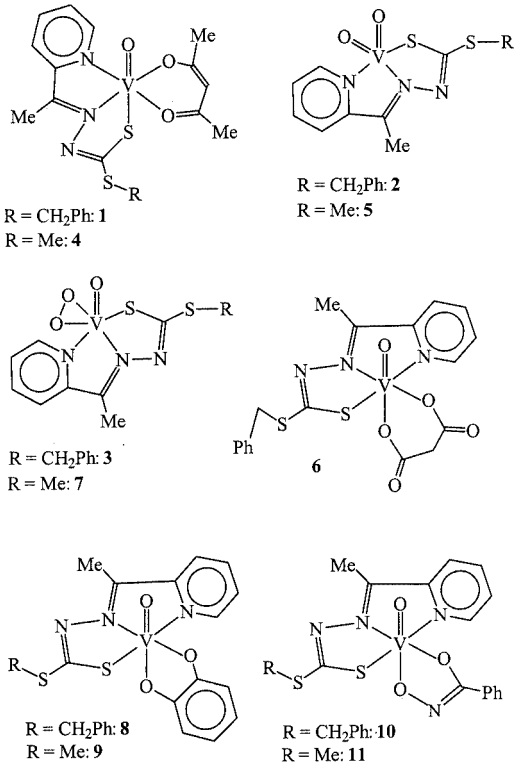


Scheme 1

Results and Discussion

Synthesis, Reactivity and Solid-State Characteristics

Direct treatment of the ligands Hacpy-sbdt (**I**) and Hacpy-smdt (**II**) (Scheme 1) with methanolic solutions of $[VO(acac)_2]$ in equimolar amounts under anaerobic conditions provided the oxovanadium(IV) complexes [VO(acac)L] [**1** and **4**, Scheme 2, Equation (1)].



Scheme 2

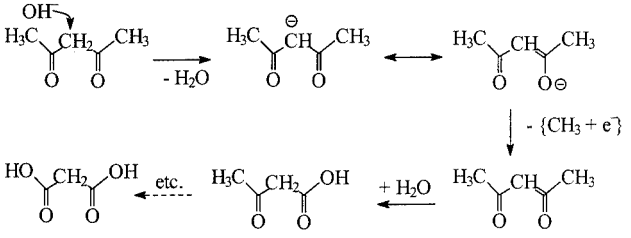
Solutions of $[VO(acac)_2]$ in organic solvents undergo rather slow oxidation under aerobic conditions.[34] In methanolic KOH, however, oxidation occurred within 8−10 h, possibly to a complex of composition $K[VO_2(acac)_2]$ [Equation (2a)]. Treatment of **I** or **II** with this species, generated in situ, under aerobic conditions yielded the monomeric pentacoordinated dioxovanadium(V) complexes **2** and **5**, respectively [Scheme 2, Equation (2b)]. A pentacoordinated vanadium(V) complexes with the dioxo groupe may have either tetragonal-pyramidal or trigonal-bipyramidal coordination geometry. The former tend to dimerise through oxo bridges to produce pseudo-octahedral coordination environments.[19] With bulky substituents on the ligand, the formation of tetragonal-pyramidal species, and thus dimerisation, can be circumvented, and trigonal-bipyramidal species can be stabilised.[20−22] The procedure employed here, refraining from bulky substituents, directly provided monomeric, square-pyramidal complexes.

$$\underset{\mathbf{1,4}}{[VO(acac)_2]} + HL \rightarrow \underset{\mathbf{1,4}}{[VO(acac)L]} + Hacac \quad (1)$$

$$2[VO(acac)_2] + 2KOH + \tfrac{1}{2}O_2 \rightarrow \text{“}2K[VO_2(acac)_2]\text{”} + H_2O \quad (2a)$$

$$K[VO_2(acac)_2] + HL \rightarrow \underset{\mathbf{2,5}}{[VO_2L]} + Hacac + Kacac \quad (2b)$$

On addition of a few drops of water to solutions of $[VO(acac)_2]$ in methanol plus KOH, followed by addition of Hacpy-smdt in the presence of air, the malonato(oxo)vanadium(V) complex **6** was obtained. This unprecedented formation of malonate from acetylacetonate was apparently a consequence of oxidative removal of the methyl groups from acetylacetone, activated by coordination, and catalysed by OH^-, as depicted in Scheme 3. The malonic acid thus formed ultimately reacted with the oxidised vanadium species in the presence of Hacpy-smdt to give **6**.



Scheme 3

Complexes **1**, **2**, **4** and **5** served as good starting materials for the preparation of other oxovanadium(V) complexes. For example, **1** and **4** were oxidised in the presence of the strong oxidant H_2O_2 to give the corresponding oxo(peroxo)vanadium(V) complexes, as shown by Equations (3) and (4).

$$\underset{\mathbf{1}}{2[VO(acac)(acpy\text{-}sbdt)]} + 3H_2O_2 \rightarrow \underset{\mathbf{3}}{2[VO(O_2)(acpy\text{-}sbdt)]} + 2Hacac + 2H_2O \quad (3)$$

$$\underset{\mathbf{4}}{2[VO(acac)(acpy\text{-}smdt)]} + 3H_2O_2 \rightarrow \underset{\mathbf{7}}{2[VO(O_2)(acpy\text{-}smdt)]} + 2Hacac + 2H_2O \quad (4)$$

These complexes could also be prepared from the corresponding dioxo species as shown for **3** by Equation (5).

$$\underset{\mathbf{2}}{[VO_2(acpy\text{-}sbdt)]} + H_2O_2 \rightarrow \underset{\mathbf{3}}{[VO(O_2)(acpy\text{-}sbdt)]} + H_2O \quad (5)$$

Treatment of catechol or benzhydroxamic acid with **1** and **4** under aerobic conditions resulted in the formation of the mixed chelate oxovanadium(V) complexes **8**, **9**, **10** and **11**, as represented by the general Equations (6) and (7). For proposed structures, cf. Scheme 2.

$$2[VO(acac)L] + 2H_2cat + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2[VO(cat)L] + 2Hacac + H_2O \quad (LH = \mathbf{I}: \mathbf{8}; LH = \mathbf{II}: \mathbf{9}) \quad (6)$$

$$2[VO(acac)L] + 2H_2bha + \tfrac{1}{2}O_2 + 2H^+ \rightarrow 2[V^{V}OL(bha)] + 2Hacac + H_2O \quad (LH = \mathbf{I}: \mathbf{10}; LH = \mathbf{II}: \mathbf{11}) \quad (7)$$

Analytical and IR spectroscopic data of the complexes are included in the Exp. Sect. All complexes were fairly soluble in CH_3CN, DMF and DMSO; peroxo complexes were sparingly soluble in CH_3CN only. Complexes **1** and **4** were paramagnetic with magnetic moments of $\mu = 2.10$ and 2.16 BM, respectively, while all other complexes were diamagnetic, as to be expected for $3d^0$ systems.

Thermogravimetric Studies

The mixed-ligand complexes **1**, **4** and **8**−**11** lost about 1−3% weight (due to residual water of crystallisation) between 80 and 135 °C. The weight loss in the temperature range 195−225 °C corresponded to the loss of acac, cat or bha, minus one oxygen atom, thus giving rise to the formation of dioxo intermediates as shown by Equation (8) for **1** and **4**.

$$[V^{IV}O(acac)L] \rightarrow [V^{V}O_2L] + \{acac - O\} \quad (8)$$

The peroxo complexes **3** and **7** lost some weight (about 3%) below 150 °C. The main decomposition process took place above 180 °C, and corresponded to the simultaneous loss of an oxygen atom plus part of the ligand, possibly forming $[VO_2L']$ and $[VOL']$ intermediates, where L′ is a fragment of L. The dioxo complexes **2** and **5** decomposed in three major steps. Between 190 and 330 °C the weight loss corresponded to $SCH_2C_6H_5$ (in **2**) or SCH_3 (in **5**), followed by a second step between 330 and 500 °C corresponding to the loss of the SCN group. On further heating, the remaining residue decomposed to yield V_2O_5 as the end product. The final residue always weighed a little more than expected, probably due to incomplete oxidation of the end-product.

Structure Descriptions

The molecular structure of $[VO_2(acpy\text{-}sbdt)]$ (**2**) together with the atom-numbering scheme is shown in Figure 1, with selected bond lengths and angles in Table 1. The geometry of this neutral, five-coordinated mononuclear complex can be described either in terms of a trigonal bipyramid, distorted towards a tetragonal pyramid, or in terms of a tetragonal pyramid, distorted towards a trigonal bipyramid. The τ value, which is 0 for ideal tetragonal and 1 for ideal trigonal arrangements, amounts to $\tau = (N1-V-S1 - O2-V-N2)/60 = 0.47$. This is significantly more than in the related thiohydrazone complex [VO(OEt)(*ONS*)], in which $\tau = 0.27$.[31] The two alternative views are depicted in Scheme 4. In both views, the distortion comes about from the steric requirements resulting from the small bite angles of the bicyclic structure constituted by the two five-membered chelate rings.

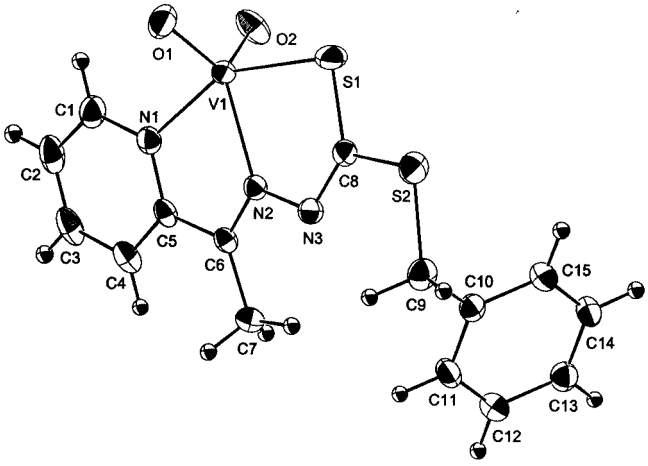
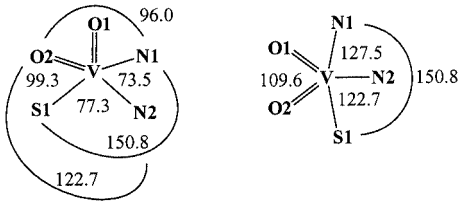


Figure 1. ORTEP plot (30% probability level) of $[VO_2(acpy\text{-}sbdt)]$ (**2**) with atom-numbering scheme

Table 1. Bond lengths [Å] and bond angles [°] for $VO_2(acpy\text{-}sbdt)$ (**2**)

Bond	Length	Bond	Angle
V(1)−O(1)	1.6148(13)	O(1)−V(1)−O(2)	109.58(8)
V(1)−O(2)	1.6152(13)	O(1)−V(1)−N(1)	97.97(6)
V(1)−N(1)	2.1038(14)	O(2)−V(1)−N(1)	95.98(6)
V(1)−N(2)	2.1454(14)	O(1)−V(1)−N(2)	127.49(6)
V(1)−S(1)	2.3852(5)	O(2)−V(1)−N(2)	122.70(7)
S(1)−C(8)	1.7273(17)	N(1)−V(1)−N(2)	73.47(5)
S(2)−C(8)	1.7406(16)	O(1)−V(1)−S(1)	100.15(5)
S(2)−C(9)	1.8113(19)	O(2)−V(1)−S(1)	99.25(5)
N(1)−C(1)	1.338(2)	N(1)−V(1)−S(1)	150.79(4)
N(1)−C(5)	1.350(2)	N(2)−V(1)−S(1)	77.32(3)
N(2)−C(6)	1.2991(19)	C(8)−S(1)−V(1)	98.61(5)
N(2)−N(3)	1.3904(17)	C(8)−S(2)−C(9)	103.22(8)
N(3)−C(8)	1.294(2)	C(1)−N(1)−C(5)	119.69(16)
		C(1)−N(1)−V(1)	122.07(13)
		C(5)−N(1)−V(1)	117.75(10)
		C(6)−N(2)−N(3)	115.40(13)
		C(6)−N(2)−V(1)	119.42(10)
		N(3)−N(2)−V(1)	125.07(10)
		N(3)−C(8)−S(1)	126.62(13)
		N(3)−C(8)−S(2)	119.95(13)
		S(1)−C(8)−S(2)	113.42(9)
		C(10)−C(9)−S(2)	115.12(12)



Scheme 4

The N_2SO_2 coordination in **2** is supplied by the pyridine nitrogen, the imine nitrogen and the thiolate sulfur atom of the monobasic tridentate ligand acpy-sbdt(1−), and by the two oxo groups. If viewed as a tetragonal pyramid, O1 is at the apex, while the three ligand functions and O2 form the tetragonal plane. If viewed as a trigonal bipyramid, N1 and S1 are in axial positions (N1−V−S1 = 150.8°), with the remaining ligand function (N2) plus the two doubly bonded oxygen atoms in the trigonal plane. This arrangement is similar to that reported for other $[VO_2L]$ compounds in which LH is a Schiff base derived from 2-hydroxy-1-naphthaldehyde and 8-aminoquinoline (Hsal-amq)[21] or *N*-anisoyl-*N′*(picolinylidene)hydrazine (Hpic-anh).[22] The V=O distance of 1.615(1) Å (for both oxo groups) is typical of V=O groups not involved in hydrogen bonding and other weak intermolecular contacts.[35] Furthermore, the bond lengths *d*(V1−N1) [2.1038(14) Å], *d*(V1−N2) [2.1454(14) Å] and *d*(V1−S1) [2.3852(5) Å] are in agreement with literature values for aromatic ring and imine nitrogen atoms[36] and for thioamide sulfur atoms coordinating to the vanadium centre.[29−31] The bond lengths *d*(N2−N3) [1.3904(17) Å], *d*(N3−C8) [1.294(2) Å] and *d*(S1−C8) [1.7273(17) Å] are consistent with the enethiolate mode of coordination.

For the structures of the closely related complex **5** and the peroxo complexes **3** and **7**, we assume a ligand arrangement corresponding to that in **2**; cf. Scheme 2.

The ORTEP drawing of $[VO(acpy\text{-}smdt)\{CH_2(COO)_2\}]$ (**6**) along with its atom-labelling scheme is presented in Figure 2, with selected structure parameters in Table 2. The coordination environment around vanadium is distorted octahedral, with malonate(2−) in axial/equatorial and the tridentate acpy-smdt(1−) in equatorial positions. The second axial position is occupied by the oxo group. The vanadium atom is displaced from the equatorial plane defined by N1, N2, S1 and O2 by 0.2415(9) Å towards the oxo ion O1. At 176.79(8)°, the O=V−O(malonate) axis is almost linear. Because of the strong *trans* influence of the oxo group, *d*(V−O3) [2.1387(17) Å] is significantly elongated with respect to the second, equatorial V−carboxylate bond, *d*(V−O2) = 1.9933(18) Å. Such elongation has previously been observed in other complexes with similar structures.[37−40] Bond lengths *d*(V1−N1) [2.125(2) Å] and *d*(V1−N2) [2.068(2) Å] are well within the common range.[37] The range of V−S bond length generally reported in the literature for oxovanadium(V) complexes of ligands derived from *S*-benzyldithiocarbazate is 2.343−2.365 Å.[29−31] The bond length *d*(V1−S1) = 2.4364(7) Å found here is somewhat longer. The distances *d*(N3−C8) [1.306(3) Å] and *d*(S1−C8) [1.736(3) Å] again support thioenolisation in the coordinated ligand. The bite angles in the two five-membered rings formed by the tridentate ligand are 75.77(7)° (N1−V1−N2) and 79.70(6)° (S1−V1−N2), and thus compare with the bite angles in **2**. The two "open" angles N1−V1−O2 and S1−V1−O2 amount to 95.43(8) and 106.05(6)°, respectively.

From the structural evidence provided for **6**, with the bidentate, dianionic malonato ligand occupying an axial and an equatorial position, the structures for other mixed-ligand complexes containing dianionic oxygen-functional ligands, [VO(cat)L] (**8** and **9**) and [VO(bha)L] (**10** and **11**) have been formulated accordingly in Scheme 2. For the complexes [VO(acac)L] (**1** and **4**), an axial coordination of the sulfur atom has been assumed on the basis of EPR results (see below).

IR Spectra

IR spectra of the ligands exhibited two bands at 3175 and 1064 cm^{-1} (in Hacpy-sbdt, **I**) and at 3150 and 1062 cm^{-1} (in Hacpy-smdt, **II**) due to ν(NH) and ν(C=S) stretches. The presence of both bands in the ligands was indicative of their thionic nature [−NHC(=S)− functionality] in the solid state. Absence of these bands in the spectra of the complexes indicates that the tautomeric enethiol form of the ligand [−N=C(SH)− functionality] is the preferred one on coordination to vanadium. A strong ligand band in the 1579−1600 cm^{-1} region was assigned to the ν(C=N) azomethine stretch, and this band underwent a shift to higher wave numbers by 5−42 cm^{-1} on complexation, indicating the participation of the azomethine nitrogen atom in coordination.[32,33] A sharp band appearing at ca. 1020 cm^{-1} was within the 990−1050 cm^{-1} range commonly observed for monodentate coordination of the >N−N< residue, though this band could not be located unequivocally in the ligands.[41] The band due to the coordinated pyridine nitrogen atom could not be assigned because of the strong absorption of ν(C=N) in this region. The coordination of the pyridine nitrogen atom has, however, been confirmed by single-crystal X-ray studies of, for example, $[VO_2(pic\text{-}anh)]_2$,[16] and in the complexes **2** and **6** reported here.

All of the monooxo complexes displayed one sharp band in the 945−967 cm^{-1} region, due to the ν(V=O) mode, while the dioxo compounds **2** and **5** showed two sharp bands at 930−939 and 947 cm^{-1}, corresponding to the $\nu_{sym}(O=V=O)$ and $\nu_{antisym}(O=V=O)$ modes. The existence of two sharp bands in the dioxo complexes suggested a *cis*-VO_2 arrangement, as verified by the structure results of **2**. The peroxo complexes **3** and **7** showed three IR-active vibrational modes associated with the peroxo moiety at ca. 928, 775 and 620 cm^{-1} and assigned to the O−O intrastretch (ν_1), the antisymmetric $V(O_2)$ stretch (ν_3), and the symmetric $V(O_2)$ stretch (ν_2), respectively.[42] These bands confirmed the η^2-coordination of the peroxo group.

Solution Studies

NMR and EPR Studies

The typical ^1H NMR chemical shifts of the ligands and complexes are shown in Table 3. The Schiff bases each exhibited a signal due to the NH proton at δ = 9.90−9.95, indicating their presence as their thionic tautomers. The absence of this signal in the complexes further supported the thioenolisation of the thione group and consequent replacement of H by the metal ion. A downfield shift of the signal for the methyl protons of the acetylpyridine residue from

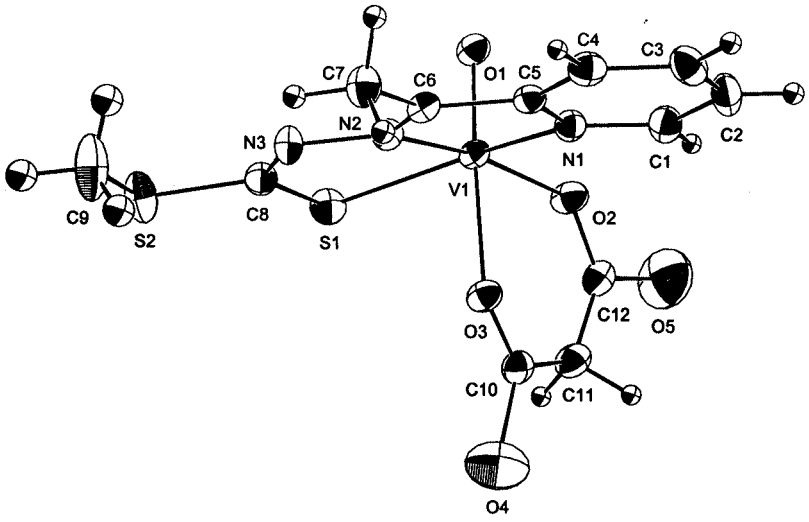


Figure 2. ORTEP plot (30% probability level) of [VO(acpy-smdt)$CH_2(COO)_2$] (**6**) with atom-numbering scheme

Table 2. Bond lengths [Å] and angles [°] for [VO(acpy-smdt)$CH_2(COO)_2$] (**6**)

Bond	Length	Bond	Angle
V(1)−O(1)	1.6132(17)	O(1)−V(1)−O(2)	93.83(8)
V(1)−O(2)	1.9933(18)	O(1)−V(1)−N(2)	99.19(8)
V(1)−N(1)	2.125(2)	O(2)−V(1)−N(2)	164.96(8)
V(1)−N(2)	2.086(2)	O(1)−V(1)−N(1)	96.25(8)
V(1)−O(3)	2.1386(17)	O(2)−V(1)−N(1)	95.43(8)
V(1)−S(1)	2.4364(7)	N(2)−V(1)−N(1)	75.77(7)
S(1)−C(8)	1.736(3)	O(1)−V(1)−O(3)	176.79(8)
S(2)−C(8)	1.743(2)	O(2)−V(1)−O(3)	83.45(7)
S(2)−C(9)	1.807(4)	N(2)−V(1)−O(3)	83.29(7)
O(3)−C(10)	1.264(3)	N(1)−V(1)−O(3)	82.35(7)
O(2)−C(12)	1.287(3)	O(1)−V(1)−S(1)	97.87(7)
O(5)−C(12)	1.513(4)	O(2)−V(1)−S(1)	106.05(6)
O(4)−C(10)	1.516(3)	N(2)−V(1)−S(1)	79.70(6)
N(1)−C(1)	1.336(3)	N(1)−V(1)−S(1)	153.32(6)
N(1)−C(5)	1.360(3)	O(3)−V(1)−S(1)	84.54(5)
N(3)−C(8)	1.306(3)	C(8)−S(1)−V(1)	94.95(8)
N(3)−N(2)	1.386(3)	C(8)−S(2)−C(9)	101.78(14)
N(2)−C(6)	1.299(3)	C(10)−O(3)−V(1)	128.08(15)
C(12)−C(11)	1.379(3)	C(12)−O(2)−V(1)	132.48(16)
C(10)−C(11)	1.406(3)	C(1)−N(1)−C(5)	119.0(2)
C(1)−C(2)	1.389(4)	C(1)−N(1)−V(1)	125.82(17)
C(2)−C(3)	1.379(4)	C(5)−N(1)−V(1)	114.96(14)
		C(6)−N(2)−V(1)	119.56(15)
		N(3)−N(2)−V(1)	124.19(15)

δ = 2.55−2.60 in the ligand to δ = 2.73−2.79 in the complex indicated coordination of the azomethine nitrogen atom. The aromatic protons of the coordinated catecholate groups (in **8** and **9**) resonated as two multiplets between δ = 6.59 and δ = 6.72, while the aromatic protons of the benzylhydroxamate groups (in **10** and **11**) appeared along with other aromatic protons (Table 3). Signals due to the methyl protons of the *S*-methyldithiocarbazate and methylene protons of the *S*-benzyldithiocarbazate residue all appeared well within the expected ranges and did not shift significantly with respect to those of the free ligands. Complexes **8**, **9**, **10** and **11** exhibited two signals both for the methyl and for the methylene protons. One set of signals corresponded to the complexes of composition [VO(cat/bha)L], while the other set belonged to the dioxo complexes $[VO_2L]$, which formed by slow decomposition in the DMSO solvent (see also below).

The ^{13}C NMR spectra of the dioxo complexes and ligands (Table 4) provided a useful diagnostic tool for the elucidation of the structures of the complexes. Assignments were based on the chemical shift and intensity patterns, and on the coordination-induced shift δΔ = δ(complex) − δ(free ligand) of the signals for the carbon atoms in the vicinity of the coordinating atoms.[43] A large coordination shift was observed for the signal of the carbon atom (C7) bearing the enethiolate sulfur atom, and for the azomethine carbon atom (C1). Even the methyl carbon signals associated with the azomethine group experienced some downfield shift.

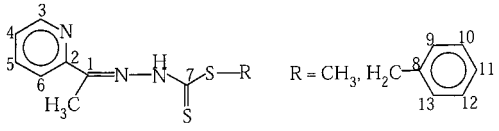
To characterise the compounds further in solution, ^{51}V NMR spectra of **2**, **5**, **6**, **8**, **9**, **10** and **11** were also recorded; for data see Table 5. The resonances were somewhat broadened as a consequence of the nuclear quadrupole moment of the spin 7/2 nucleus ^{51}V; line widths at half height were approximately 200 Hz, which is still considered narrow in ^{51}V NMR spectroscopy.[44−46] Each dioxo complex showed one strong resonance at δ = −444.0 (**2**) or −442.5 (**5**). The ^{51}V nucleus was thus less shielded than commonly observed with dioxovanadium(V) complexes with a mixed *ON* donor set; the chemical shifts, however, were well within the range expected for coordination of a soft (thio) function in addition to *O* and *N*.[31,48−50] The catecholato complexes **8** and **9** displayed two resonances: the lowfield signals at δ = +368.4 (**9**) and +373.7 (**8**) (peak 1) were indicative of catecholate coordination and thus belonged to the mixed-ligand complexes [VO(cat)L], while the signal at δ = −434.0 (peak 2) corresponded to the decomposition product $[VO_2L]$. Similarly, the hydroxamate complexes **10** and **11** each exhibited a lowfield resonance at δ = +135.6 (**11**) or +143.0 (**10**) along with a signal in the upfield region

Table 3. ^{1}H NMR spectroscopic data of ligands and complexes

Compound[a]	NH	CH_2	CH_3	Aromatic
Hacpy-sbdt	9.95 (s, 1 H)	4.57 (s, 2 H)	2.55 (s, 3 H)	7.30 (m, 2 H), 7.44 (m, 1 H), 7.59 (d, 1 H), 7.67 (dt, 1 H), 7.90 (td, 1 H), 8.14 (d, 1 H), 8.58 (d, 1 H), 8.77 (d, 1 H)
[VO_2(acpy-sbdt)] (**2**)		4.49 (s, 2 H)	2.73 (s, 3 H)	7.36 (m, 3 H), 7.45 (d, 2 H), 7.79 (t, 1 H), 8.32 (m, 2 H), 8.74 (d, 1 H)
[$VO(O_2)$(acpy-sbdt)] (**3**)		3.38 (s, 2 H)	2.06 (s, 3 H)	7.89 (t, 3 H), 8.09 (d, 2 H), 8.38 (t, 2 H), 9.60 (d, 3 H)
[VO(acpy-sbdt)cat] (**8**)		4.46, 4.48 (s, 2 H)	2.57, 2.79 (s 3 H)	6.59 (m, 2 H), 6.71 (m, 2 H), 7.32 (m, 2 H), 7.43 (d, 2 H), 7.75 (q, 1 H), 8.09 (d, 1 H), 8.31 (bd, 1 H), 8.83 (s, 1 H)
[VO(acpy-sbdt)bha] (**10**)		4.47, 4.49 (s, 2 H)	2.73, 2.76 (s, 3 H)	7.3 (m, 4 H), 7.45 (m, 4 H), 7.77 (q, 1 H), 7.84 (d, 1 H), 8.03 (d, 1 H), 8.15 (d, 1 H), 8.35 (m, 2 H)
Hacpy-smdt	9.90 (s, 1 H)		2.25 (s, 3 H), 2.60 (s, 3 H)	6.94 (d, 1 H), 7.10 (d, 1 H), 7.32 (m, 1 H),7.5 (d,1 H)
[VO_2(acpy-smdt)] (**5**)			2.62, 2.73 (s,3 H)	7.78 (m, 1 H), 8.30 (d, 1 H), 8.37 (m, 1 H), 8.73 (m, 1 H)
[$VO(O_2)$(acpy-sbdt)] (**7**)			2.48 (s,3 H), 2.50 (s,3 H)	7.89 (t, 1 H), 8.09 (d, 1 H), 8.35 (dt, 1 H), 9.60 (d, 1 H)
[VO(acpy-smdt)cat] (**9**)			2.61, 2.63 (s, 3 H), 2.74, 2.78 (s,3 H)	6.60 (m, 2 H), 6.72 (m, 2 H), 7.77 (m, 1 H), 8.12 (d, 1 H), 8.33 (m, 1 H), 8.82 (s, 1 H)
[VO(acpy-smdt)bha] (**11**)			2.62, 2.63 (s, 3 H), 2.72, 2.74 (s, 3 H)	7.47 (m, 4 H), 7.78 (m, 1 H), 7.84 (d, 1 H), 8.05 (d, 1 H), 8.16 (d, 1 H), 8.39 (d, 1 H)

[a] Letters given in parentheses indicate the signal structure: s = singlet, d = doublet, t = triplet, td = triplet of doublets, m = multiplet, b = broad (not resolved).

Table 4. ^{13}C NMR spectroscopic data



Compounds[a]	CH_3/S−CH_3	CH_2	C1	C2/C3	C6	C4/C5	C7	C8−C13
Hacpy-smdt	13.7, 17.6		144.9	142.2	129.0	127.3, 127.8	200.6	
[VO_2(acpy-smdt)] (**5**)	14.8, 18.2		166.8	153.1, 155.1	143.3	126.5, 127.7	184.7	
δΔ[b]	1.1		21.9				−15.9	
Hacpy-sbdt	13.7	38.6	154.4	149.2, 152.6	120.8	137.1, 137.2	199.2	125.1−129.6
[VO_2(acpy-sbdt)] (**2**)	15.5	38.3	167.7	154.3	143.5	137.6	189.8	127.1−129.4
δΔ[b]	2.2		18.3				−9.4	

[a] For atom labelling see scheme above. Assignments of the aromatic carbon atoms 4−6 and 8−13 are preliminary. [b] δΔ = [δ(complex) − δ(free ligand)].

at δ = −430 and −434, again due to dioxo species [VO_2L] formed by decomposition. An additional decomposition band at δ = −508 indicated either an oxo- or a dioxovanadium(V) complex with only *O*/*N* coordinating functions. The substantial downfield shift of the ^{51}V resonances (peak 1) in the catecholate and benzhydoxamate complexes has been reported previously and traced back to strong ligand-to-metal charge transfer (LMCT);[47] cf. also the UV/Vis spectra. The downfield shift of peak 2 (the resonance corresponding to the decomposition product) by ca. 10 ppm with respect to solutions containing authentic **2** or **5** is a medium effect, imparted by the presence of catechol in the solution in contact with [VO^2L].

Room-temp. EPR spectra of the two vanadium(IV) (d^1) complexes [VO(acac)L] (**1** and **4**) in DMSO provided a g_0 value of 1.965, and a comparatively large hyperfine coup-

Table 5. ^{51}V NMR chemical shifts

Complex	Chemical shifts	
	Peak 1	Peak 2[a]
$[VO_2$(acpy-sbdt)] (**2**)	−444.0	
$[VO_2$(acpy-smdt)] (**5**)	−442.5	
[VO(acpy-smdt)mal] (**6**)	−432.4	
[VO(acpy-sbdt)cat] (**8**)	373.7	−434.3
[VO(acpy-smdt)cat] (**9**)	368.4	−434.1
[VO(acpy-sbdt)bha] (**10**)	143.0	−429.5, −508.3
[VO(acpy-smdt)bha] (**11**)	135.6	−433.3, −508.4

[a] Corresponds to decomposition product(s); cf. text.

ling constant $A_0 = 93 \cdot 10^{-4}$ cm^{-1}. For the anisotropic spectrum at 97 K, the following parameters were obtained: $g_{zz} = 1.938$, $g_{xy} = 1.978$; $A_{zz} = 178.5$, $A_{xy} = 50.3 \cdot 10^{-4}$ cm^{-1}. These values were essentially in the expected range.[48] The large A_{zz} component accounts for the diminished delocalisation of electron density into the ligand system, which may be a consequence of steric strains in the bicyclic chelate structure, and of a weak bonding contribution in the axial position, provided by coordination of the thio function subjected to the *trans* influence of the oxo group.

Electronic Absorption Spectra

The UV/Vis spectroscopic data of the ligands and complexes recorded in acetonitrile are presented in Table 6. All of the complexes displayed a medium to intense electronic spectral band at $\lambda = 410.5-416$ nm, attributable to LMCT arising from the N_2S^- ligand. Coordinated benzhydroxamate and catecholate induce strong charge transfer to the metal centre in complexes with high-valent metal ions. Thus, a strong band at $\lambda = 565$ nm for **10** and **11**, and two intense bands at $\lambda \approx 500$ and 766 nm for **8** and **9** were assigned to LMCT originating from lone-pair p orbitals on the hydroxamato[49] and catecholato oxygen atoms,[50] respectively, into an empty d orbital of the vanadium ion. As vanadium(V) complexes are d^0 systems, d−d bands were not expected in these complexes. In the oxovanadium(IV) complexes **1** and **4**, however, a weak band at $\lambda \approx 590$ nm was probably due to a d−d transition, as this band slowly disappeared on oxidation of **1** and **4** to the corresponding peroxo complexes by H_2O_2 (vide infra). Other spectral features of the complexes (intraligand bands in the UV region) were nearly identical to those of the free ligands.

Stability and Reactivity Studies

The stabilities of the complexes **8**, **9**, **10** and **11** were studied in various solvents. Complexes **9**, **10** and **11** were stable in solvents such as CH_2Cl_2, MeOH and CH_3CN, while they slowly decomposed in DMF and DMSO. A rather slow loss of coordinated catechol followed by conversion into the respective dioxo species has been noticed in dry solvents, while addition of few drops of water facilitated this conversion, as observed by electronic absorption spectroscopy (Figure 3). Addition of 1 drop of water to 5 mL of a ca.10^{-4} M solution of [VO(acpy-sbdt)cat] (**8**) in DMSO caused the gradual loss of the LMCT bands belonging to coordinated catecholate, which disappeared within 8 h. Complexes **10** and **11** gave comparable results. Similar observations have also been noted for [VO(sal-amq)cat].[21] The suggested reaction is formulated in Equation (9).

$$[VOL(cat)] + H_2O \rightarrow [VO_2L] + H_2cat \quad (9)$$

Oxovanadium(V) complexes generally undergo redox reactions with reducing agents such as L-ascorbic acid, cysteine and cysteine derivatives.[51,52] A model redox reaction with L-ascorbic acid was carried out for complexes **8** and **11**. In a typical reaction, 9 mL of a 10^{-4} M solution of **8** or **11** was treated with 1 mL of a 10^{-1} M solution of L-ascorbic acid in acetonitrile, and the reaction was monitored by electron absorption spectroscopy (Figure 4). The absorption bands at $\lambda = 765.5$ and 501.5 nm for complex **8** slowly disappeared. The band at $\lambda = 410.5$ shifted to $\lambda = 415$ nm with a marginal reduction in intensity, while the band at $\lambda = 338$ nm underwent a blue shift to appear at $\lambda = 331$ nm with a marginal increase in intensity. An additional new band appeared at $\lambda = 277$ nm. For complex **11** (not shown), the bands at $\lambda = 564.5$ and 257 nm slowly disappeared. The band at $\lambda = 411.5$ nm remained unchanged, while the band at $\lambda = 338$ nm shifted to $\lambda = 331$ nm with a slight increase in intensity. As L-ascorbic acid has reducing properties, reduction of **8** and **11** might be anticipated along with the removal of coordinated catecholate/benzhydroxamate. However, the match of the spectral features with those of solutions of **2** and **5**, with only minor deviations in the UV region, indicated that the reduced species was rapidly reoxidised to the dioxo complex $[VO_2L]$, and not to the original mixed ligand compound. The slight deviations in the UV were probably due to factors arising from the presence of uncoordinated catecholate or hydroxamate. L-Ascorbic acid was thus simply involved in electron transfer, without formation of any long-lived complex with **8** or **11**.

Treatment of complexes **1** and **4** with H_2O_2 around 0 °C yielded the oxo(peroxo)vanadium(V) complexes **3** and **7** (cf. Exp. Sect.). These reactions, involving dropwise addition of 30% H_2O_2 to 10 mL of ca. 10^{-4} M solutions of **1** or **4** in acetonitrile at ca. 10 ° C, were also monitored by electron absorption spectroscopy. The spectral changes during the reaction are shown in Figure 5 for complex **4**. In each case, the band appearing at $\lambda = 410.5$ nm slowly disappeared, while a red shift to $\lambda = 350.5$ nm was observed for the band at $\lambda = 338.5$ nm of **1**, with a corresponding red shift for the band at $\lambda = 336.5$ nm to $\lambda = 345.5$ nm in the case of **4**. The features of the final spectra were similar to those of the corresponding isolated peroxo complexes **3** and **7**.

The peroxo complexes underwent oxygen transfer with PPh_3 in CH_3CN to give the corresponding dioxovanadium(V) complexes **2** and **5**. During the reaction, PPh_3 possibly inserts directly into one of the metal−peroxo bonds, followed by the transfer of an oxo group from the peroxo

Table 6. Electronic spectroscopic data of ligands and complexes

Compound	λ_{max} [nm]
Hacpy-sbdt	218(9561), 290(4154), 322(11069)
[VO(acac)(acpy-sbdt)] (**1**)	338.5(15278), 407(9320), 590(35)
[VO_2(acpy-sbdt)] (**2**)	207.5(33737), 255(15760), 295(7866), 345.5(10939), 416(7776)
[$VO(O_2)$(acpy-sbdt)] (**3**)	268.5, 336, 446
[VO(acpy-sbdt)cat] (**8**)	336(17755), 411.5(10447), 501(8407), 766(6682)
[VO(acpy-sbdt)bha] (**10**)	211(47630), 340(14529), 410.5(8962), 565(6180)
Hacpy-smdt	216(6806), 285(4167), 331(14331).
[VO(acac)(acpy-smdt)] (**4**)	248(10487), 277(7408), 336.5(9149), 411(5554), 586(48)
[VO_2(acpy-smdt)] (**5**)	208.5(52865), 252.5(31278), 299(17497), 343(23197), 416(17325)
[$VO(O_2)$(acpy-smdt)] (**7**)	270, 334, 433
[VO(acpy-smdt)cat] (**9**)	207(37628), 337(13846), 413(9126), 499.5(6278), 765.5(5017)
[VO(acpy-smdt)bha] (**11**)	208(42090), 256(23362), 337(18650), 412(12129), 565(8324)

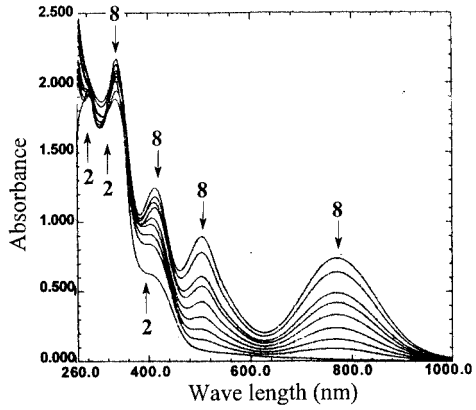


Figure 3. Decomposition of [VO(acpy-sbdt)cat] (**8**) in 5 mL of DMSO after addition of one drop of water, as a function of time

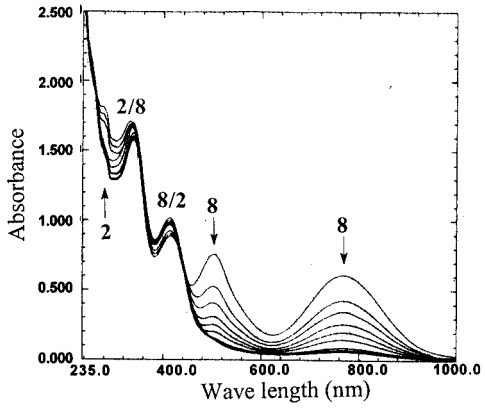


Figure 4. Absorption spectra of a ca. 10^{-4} M solution of [VO(acpy-sbdt)cat] (**8**) in CH_3CN in the presence of L-ascorbic acid (ca. 1:2 molar ratio) as a function of time, over periods of 120 min

ligand to PPh_3. The reaction mechanism in depicted in Scheme 5.

Addition of acetonitrile saturated with HCl gas to an acetonitrile solution of [VO_2(acpy-sbdt)] (**2**) resulted in a colour change from orange-red to dark red, with a reduction in intensity of the bands at λ = 416 and 251.5 nm and a shift of the band at λ = 343 nm to λ = 350.5 nm (Figure 6). An increase in the concentration of the original solution of **2** and addition of HCl/acetonitrile generated a new band at

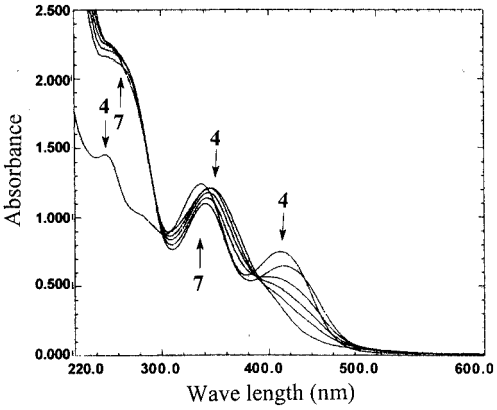
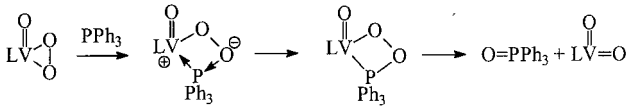


Figure 5. Titration of [VO(acac)(acpy-smdt)] (**4**) with 30% H_2O_2; spectra were recorded after successive addition of 2 drops H_2O_2 to 5 mL of ca. 10^{-4} M solution of the complex in CH_3CN



Scheme 5

λ = 585 nm. We preliminarily interpret these results in terms of the formation, on acidification, of a hydroxo complex of composition $[VO(OH)(acpy\text{-}sbdt)]^+$, similar to the hydroxo(oxo) complex $[VO(OH)(LH)]^+$, where LH_2 = *N*-[{(*o*-hydroxyphenyl)methyl}-*N*′-(2-hydroxyethyl)ethylenediamine][53] or *N*-salicylidene-*N*′-(2-hydroxyethyl)ethylenediamine,[54] generated in a similar manner from the respective dioxyvanadium(V) dimer. {See also [VO(OH)Tp(H_2O)] [Tp = tris(3,5-diisopropyl-1-pyrazolyl)borate][55] and [VO(OH)(8-oxyquinolinato)$_2$][56] for other characterised oxo-hydroxovanadium complexes.} On allowing the above solution to stand overnight, or on addition of KOH dissolved in acetonitrile, the solution reacquired its original character; the reaction was hence reversible and gave the spectrum of **2**. The reversibility of such reactions is an important observation in the context of the vanadate-dependent haloperoxidases, for which a hydroxo group in an apical position has been confirmed by X-ray diffraction analysis.[57]

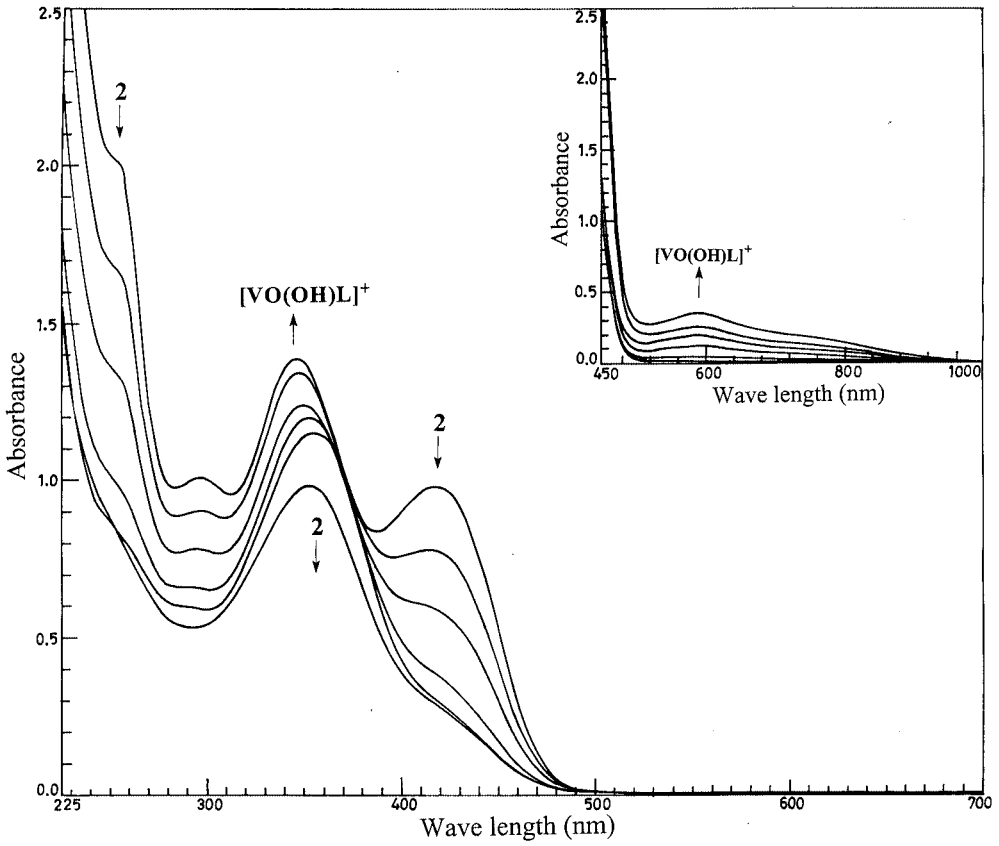


Figure 6. Titration of $[VO_2(acpy\text{-}sbdt)]$ (**2**) with a saturated solution of HCl in CH_3CN; spectra were recorded after the addition of 3 drops of CH_3CN/HCl to 10 mL of a ca. 10^{-4} M CH_3CN solution of **2**

Conclusion

The preparation and characterisation of monomeric dioxovanadium(V) complexes with a structure between a square-pyramidal and a trigonal-bipyramidal ligand arrangement is described, together with octahedral monooxovanadium complexes. A tridentate N_2S^- ligand system derived from acetylpyridine and dithiocarbazine, acpy-sbdt and acpy-smdt, was used. These complexes model part of the structure of vanadium nitrogenase and the active site of vanadate-dependent haloperoxidases. The model includes intermediate species with $[VO(OH)]^{2+}$ and $[VO(O_2)]^+$ cores, as postulated for catalytic turnover by the peroxidases, and which have been generated and characterised in this work. Additional reactions − such as the reversibility of the formation of a hydroxo(oxo) complex from a dioxo complex, the transfer of a peroxo oxygen atom from the (oxo)peroxo complex to triphenylphosphane, and the role of water or ascorbic acid in the conversion of monooxo- to dioxovanadium(V) complexes − are of interest from the perspective of vanadium speciation under physiological conditions, the mechanism by which vanadate-dependent haloperoxidases catalyse oxo transfer to halide and thioethers, and also a possible general role of vanadium in oxotransferases. The oxidative conversion of acetylacetonate in $[VO(acac)_2]$ to malonate, and concomitant oxidation of V^{IV} to V^V under mild basic conditions and in the presence of Hacpy-sbdt afforded the complex [VO(acpy-sbdt)malonate], underlining the versatile reaction patterns accompanying this interesting ligand system.

Experimental Section

Materials and Methods: V_2O_5 (Loba Chemie, India), methyl iodide (Spectrochem, India), benzhydroxamic acid (Merck, Germany), catechol (s. d. fine chemicals, India), acetylacetone and 2-acetylpyridine (Aldrich, U.S.A.) were used as obtained. Other reagents and solvents used were of AR grade. *S*-Benzyldithiocarbazate,[58] *S*-methyldithiocarbazate [59] and $[VO(acac)_2]$ [60] were prepared according to methods reported in the literature. The Schiff bases Hacpy-sbdt (**I**) and Hacpy-smdt (**II**) (cf. Scheme 1) were prepared as reported in a previous paper.[32,33] Elemental analyses were carried out by The Central Drug Research Institute, Lucknow, India. UV/Vis spectra were recorded in acetonitrile and methanol with a UV-1601 PC UV/Vis spectrophotometer. IR spectra were recorded as KBr pellets with a Perkin−Elmer model 1600 FT-IR spectrometer. EPR spectra of the paramagnetic complexes were measured with a Bruker ESP 300E spectrometer at ca. 9.6 GHz (X-band) in ca. 2 mM DMSO solution. Magnetic susceptibilities of oxovanadium(IV) complexes were measured by the Scientific Instrumentation Centre of the Indian Institute of Technology, Roorkee. ^1H 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 $[D_6]$DMSO with the usual parameter settings. The $\delta(^{51}V)$ values have been referenced and are

quoted relative to $VOCl_3$. Thermogravimetric analyses of the complexes were carried out on a simple, manually operated thermobalance as described by us previously. Crystal Structure Determinations: Data were collected with a Siemens/Bruker SMART Apex CCD diffractometer with a graphite monochromator and Mo-K_α radiation (λ = 0.71073 Å) at 153(2) K. Hydrogen atoms were placed in calculated positions and included in the last cycles of refinement. Crystal data and details of the data collection and refinement are collected in Table 7. The programme systems SHELXS 86 and SHELXL 93 were used throughout.[61] CCDC-177111 (**2**) and -177112 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Preparation of Complexes

[VO(acac)(acpy-sbdt)] (1): [VO(acac)$_2$] (0.53 g, 2 mmol) was added to a stirred solution of Hacpy-sbdt (0.60 g, 2 mmol) in 20 mL of dry methanol, and the resulting mixture was refluxed for 4 h. On cooling the reaction flask to ambient temperature, a dark green solid separated and was filtered off, washed with methanol and dried in vacuo to give 0.84 g (90%) of **1**. $C_{20}H_{21}N_3O_3S_2V$ (466.47): calcd. C 51.50, H 4.51, N 9.01; found C 51.42, H 4.54, N 9.20. IR: $\tilde{\nu}$ = 1586 (C=N, C=C), 1022 (N−N), 947 (V=O), 440, 410 cm^{-1} (V−O, V−N).

[VO$_2$(acpy-sbdt)] (2): [VO(acac)$_2$] (0.53 g, 2 mmol) was dissolved in 40 mL of dry methanol, and KOH (0.11 g, 2 mmol) was added. The resulting solution was stirred for 2 h and then left for ca. 10 h in air. The solution slowly changed to red-brown. A solution of Hacpy-sbdt (0.60 g, 2 mmol) in 15 mL of methanol was added slowly, and the mixture was stirred magnetically for 4 h. A lustrous yellow solid separated; it was filtered off, washed with methanol and dried in vacuo to give **2**. Yield 0.42 g (55%). X-ray quality single crystals were grown by slow concentration of an acetonitrile solution of the complex in air. $C_{15}H_{14}N_3O_2S_2V$ (383.36): calcd. C 47.0, H 3.66, N 10.96; found C 47.0, H 3.54, N 10.83. IR: $\tilde{\nu}$ = 1600, 1580, 1557 (C=N, C=C), 1019 (N−N), 947, 939 (O=V=O sym and antisym), 461, 422 cm^{-1} (V−O, V−N).

[VO(O$_2$)(acpy-sbdt)] (3). Method A: Compound **2** (0.192 g, 0.5 mmol) was dissolved in 30 mL of acetonitrile while heating on a water bath, and filtered. The filtrate was treated with H_2O_2 (30%, 4 mL) while stirring and maintaining the reaction mixture at 10 °C. The colour changed from yellow to dark red. After 4 h, the solution was refrigerated (ca. 10 °C) overnight, whereupon orange-red crystalline **3** separated. The product was filtered off and dried in vacuo at ambient temperature. Yield: 70 mg (35%). $C_{15}H_{14}N_3O_3S_2V$ (399.36): calcd. C 45.11, H 3.51, N 10.53; found C 45.20, H 3.63, N 10.68. IR: $\tilde{\nu}$ = 1632, 1580, 1569 (C=N, C=C), 1023 (N−N), 951 (V=O), 929 (O−O), 777 (VO_2 antisym), 617 (VO_2 sym), 435, 414 cm^{-1} (V−O, V−N). **Method B:** Compound **1** (0.466 g, 1 mmol) was dissolved in 60 mL of acetonitrile, and H_2O_2 (30%, 8 mL) was added while stirring. The reaction mixture was stirred for 4 h at 10 °C and then left overnight at the same temp. The orange-red crystals that had separated were filtered and dried in vacuo. Yield: 0.16 g (40%). IR and electronic spectroscopic data matched well with **3** prepared according to method A.

[VO(acac)(acpy-smdt)] (4): Complex **4** was prepared in 85% yield by the procedure described for **1**. $C_{14}H_{17}N_3O_3S_2V$ (390.37): calcd. C 43.07, H 4.36, N 10.77; found C 43.13, H 4.47, N 10.91. IR: $\tilde{\nu}$ = 1588 (C=N, C=C), 1021 (N−N), 951 (V=O), 440, 409 cm^{-1} (V−O, V−N).

Table 7. Crystal data and structure refinement parameters for [VO$_2$(acpy-sbdt)] (**2**) and [VO(acpy-smdt)malonate] (**6**)

	2	**6**
Empirical formula	$C_{15}H_{14}N_3O_2S_2V$	$C_{12}H_{12}N_3O_5S_2V$
Formula mass	383.35	393.31
Temperature [K]	153(2)	153(2)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/n$
Unit cell dimensions		
a [Å], α [°]	7.8794(2), 90	8.2949(3), 90
b [Å], β [°]	25.7527(7), 99.2860(10)	19.6498(7), 102.72(10)
c [Å], γ [°]	8.0071(2), 90	10.7717(4), 90
Cell volume [Å^3]	1603.47(7)	1727.61(11)
Z	4	4
Calculated density [g/cm^3]	1.588	1.525
Absorption coefficient [mm^{-1}]	0.890	0.848
F(000)	784	800
Crystal size [mm]	0.2 × 0.3 × 0.65	0.8 × 0.4 × 0.2
θ range for data collection [°]	2.62 to 32.57	2.20 to 32.50
Limiting indices	$-11 \le h \le 11$, $-32 \le k \le 38$, $-11 \le l \le 12$	$-12 \le h \le 12$, $-29 \le k \le 28$, $-15 \le l \le 16$
Reflections collected/unique	23468/5629	24869/5933
R_{int}	0.0346	0.0418
Max./min. transmission	1.0/0.7924	1.0/0.7935
Data/restraints/parameters	5629/0/208	5933/0/208
Goodness of fit on F^2	0.990	1.072
R indices [$I > 2\sigma(I_0)$]: R_1/wR_2	0.0417/0.1095	0.0581/0.1764
R indices (all data): R_1/wR_2	0.0554/0.1143	0.0664/0.1827
Largest diff. peak/hole(e Å^{-3})	0.732/−0.502	0.885/−1.176

$[VO_2$(acpy-smdt)] (5): An oxidized red-brown methanolic solution of $[VO(acca)_2]$ (0.53 g, 2 mmol) was produced as described for complex **2**. A solution of Hacpy-smdt (0.23 g, 2 mmol), dissolved in 15 mL of methanol, was added with stirring. Workup was carried out as described for **2**. Yield: 0.31 g (50%). $C_9H_{10}N_3O_2S_2V$ (307.26): calcd. C 35.18, H 3.26, N 13.68; found C 35.36, H 3.31, N 13.70. IR: $\tilde{\nu}$ = 1583, 1561 (C=N, C=C), 1033(N−N), 947, 930 (O=V=O sym and antisym), 461, 424 cm^{-1} (V−O, V−N).

[VO(acpy-smdt)malonate] (6): $[VO(acac)_2]$ (0.53 g, 2 mmol) was dissolved in 30 mL of methanol, and two drops of water and KOH (0.11 g, 2 mmol) were added. The resulting solution was stirred for 2 h and then left for ca. 10 h in air. The solution slowly changed to red-brown with the deposition of some white solid on the wall of the flask. A solution of Hacpy-smdt (0.23 g, 2 mmol) in 15 mL of methanol was added, and the mixture was stirred for 2 h. A light green product that gradually precipitated was redissolved by heating the reaction mixture on a water bath, and the mixture was then left in air at ambient temperature. Over ca. 5 h, a light red solid precipitated and was filtered off, washed with methanol and dried. The product was recrystallised from hot acetonitrile. Orange crystals were obtained within 2−3 d on slow evaporation of the solvent in air. Yield: 0.24 g (30%). The elemental analysis showed that the bulk product was a mixture of **6** and **4**. The S/N ratio was reproduced correctly, indicating that the ligand had remained intact.

$[VO(O_2)$(acpy-smdt)] (7): Complex **7** was prepared from **4** and from **5** with H_2O_2 as described for **3**, in ca. 50% yield. $C_9H_{10}N_3O_3S_2V$ (323.26): calcd. C 33.44, H 3.09, N 13.0; found C 33.52, H 3.24, 13.0. IR: $\tilde{\nu}$ = 1628, 1580 (C=N, C=C), 950 (V=O), 928 (O−O), 775 (VO_2 antisym), 620 (VO_2 sym), 435, 410 cm^{-1} (V−O, V−N).

[VO(acpy-sbdt)cat] (8): Compound **1** (0.47 g, 1 mmol) was dissolved in hot methanol (40 mL). After the mixture had cooled to room temp., catechol (0.11 g, 1 mmol) was added and the reaction mixture was stirred for 6 h. The volume of the solvent was reduced to ca. 10 mL and the mixture was kept in the refrigerator overnight, whereupon brown-black solid **7** separated. This was filtered off, washed with cold methanol and dried in vacuo at ambient temp. Yield: 0.19 g (40%). $C_{21}H_{18}N_3O_3S_2V$ (475.45): calcd. C 53.05, H 3.79, N 8.84; found C 53.19, H 3.83, N 8.82. IR: $\tilde{\nu}$ = 1600, 1576 (C=N, C=C), 1020 (N−N), 950 (V=O), 460, 414 cm^{-1} (V−O, V−N).

[VO(acpy-smdt)cat] (9): Complex **9** was prepared analogously to **8** in 52% yield, by replacing **1** with **4**. $C_{15}H_{14}N_3O_3S_2V$ (399.36): calcd. C 45.11, H 3.51, N 10.52; found C 45.38, H 3.56, N 10.47. IR: $\tilde{\nu}$ = 1600, 1577 (C=N, C=C), 1030 (N−N), 950 (V=O), 460, 441, 415 cm^{-1} (V−O, V−N).

[VO(acpy-sbdt)bha] (10): Compound **1** (0.47 g, 1 mmol) was dissolved in 40 mL of hot methanol, and after the reaction flask had cooled to room temp., benzohydroxamic acid (0.137 g, 1 mmol) was added. The resulting reaction mixture was stirred for 6 h. After reduction of the volume to ca. 10 mL, the solution was kept at 10 °C overnight, during which brown solid **10** separated. This was filtered off, washed with methanol, and dried in vacuo. Yield: 0.19 g (38%). $C_{22}H_{20}N_4O_3S_2V$ (503.49): calcd. C 52.48, H 3.97, N 11.13; found C 52.53, H 4.11, N 11.05. IR: $\tilde{\nu}$ = 1600, 1580 (C=N, C=C), 1031 (N−N), 967 (V=O), 473, 420 cm^{-1} (V−O, V−N).

[VO(acpy-smdt)bha] (11): Compound **11** was prepared in 42% yield analogously to **10**, by replacing **1** by **4**. $C_{16}H_{16}N_4O_3S_2V$ (427.39): calcd. C 44.96, H 3.76, N 13.11; found C 45.0, H 3.91, N 13.23. IR: $\tilde{\nu}$ = 1585, 1562 (C=N, C=C), 1025 (N−N), 963 (V=O), 463, 414 cm^{-1} (V−O, V−N).

Treatment of 3 and 7 with PPh_3: PPh_3 (0.195 g, 0.75 mmol) was added to a suspension of **3** or **7** (0.05 mmol) in 15 mL of hot CH_3CN, and the reaction mixture was refluxed on an oil bath for 4 h, during which the complex slowly dissolved. After reduction of the solvent volume to ca. 10 mL, the heating was discontinued, and the flask was kept at ca. 10 °C overnight, whereupon a crystalline solid separated out within 5−6 h. This was filtered off and dried in vacuo. Yield 45%. Analytical and spectroscopic data of the complexes thus obtained matched well with **2** and **5**, respectively

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