Mononuclear *cis*-Dioxovanadium(v) Anionic Complexes $[VO_2L]^-$ {H_2L = [1 + 1] Schiff Base derived from Salicylaldehyde (or Substituted Derivatives) and 2-Amino-2-methylpropan-1-ol}: Synthesis, Structure, Spectroscopy, Electrochemistry and Reactivity Studies†

Gebray Asgedom,[a] Alavattam Sreedhara,[a] Jussi Kivikoski,[b] Jussi Valkonen[b] and Chebrolu P. Rao *,[a]
[a] *Bioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India*
[b] *Department of Chemistry, University of Jyvaskyla, Fin 40351, Jyvaskyla, Finland*

The compounds $[H_3NCMe_2CH_2OH][VO_2L]$ {H_2L = [1 + 1] Schiff base derived from salicylaldehyde (or substituted derivatives) and 2-amino-2-methylpropan-1-ol} have been synthesized in good yields by reaction of the Schiff base (formed *in situ*) and a further equivalent of the amino alcohol with $[VO(acac)_2]$ (Hacac = acetylacetone). The structures of three of the complexes have been solved by single-crystal X-ray studies. All the compounds were also characterized by UV/VIS, FTIR and NMR spectroscopy and by cyclic voltammetry. The three structurally characterized mononuclear complexes contain the *cis*-dioxovanadium(v) moiety and exhibit distorted square-pyramidal geometry at vanadium which is displaced from the equatorial plane by ≈0.5 Å. The crystal and molecular structures of these compounds showed extensive hydrogen bonding between the anionic portion of the complexes and the counter-cations of the amino alcohol which resulted in some unusual metric features of interest to the binding of vanadium in biological systems. Two of the compounds showed the longest V=O distances reported so far for mononuclear *cis*-dioxovanadium(v) complexes. Three of the complexes undergo photoreduction in the solid state which is attributed to their intermolecular interactions in the crystal.

The study of the biochemical role of vanadium has become recently a hot topic of bioinorganic chemistry particularly due to the presence of this element in significant amounts in some organisms and its involvement in both promotory and inhibitory enzymatic processes in biological systems.[1] Tunicates accumulate V^V from the marine environment and store it in their blood cells in the reduced tetra- and tri-valent states.[2] The mushroom, *Amanita muscaria*, accumulates vanadium to produce amavadin.[3] However, the function of vanadium is not yet known in either of these systems. In the enzyme vanadium nitrogenase the metal ion is known to be present as V^{III} and is active in the conversion of acetylene to ethane and hence differs from the role of its counterpart in Mo-nitrogenase.[4] It has also been reported that a product of the reaction of vanadate and peroxide is strongly insulin mimetic.[5] Vanadium(v) has been found to be present as a mononuclear unit in the resting state of haloperoxidase enzymes.[6] Comparison of the extended X-ray absorption fine structure (EXAFS) and other spectral data and some reactivity patterns of both the native protein in oxidation state V^V and its dithionite reduced form in oxidation state V^{IV} with those (including crystal structures) of model molecules has led to some inconclusive and controversial postulations. Among these the presence of a dioxovanadium(v) moiety (VO_2^+) in five- or six-co-ordination can be considered as important in the design of model molecules due to its aqueous reactivity, ability to brominate substrates and absence of ligand-to-metal charge transfer (l.m.c.t.) bands in the visible region as found for the native enzymes.[7] Synthetic reactions between $[VO(acac)_2]$ (Hacac = acetylacetone) and dibasic tridentate ligands have yielded dinuclear structures;[8] however, use of a sterically demanding monobasic tridentate ligand has yielded a mononuclear species with a VN_2O_3 core which is proposed as a model for the transition-state analog-RNAse inhibitor.[9] Involvement of VO_2L^- and VO(OH)L species has also been implicated in solution during substrate bromination based on ^{51}V NMR spectroscopy studies.[10]

Current interest in the biochemistry of vanadium has been spurred by the findings of Cremo *et al.*[11] who demonstrated highly specific photomodifications of polypeptides in the presence of vanadate and UV or visible light. In the photocleavage of proteins at either Ser or Pro residues of the side chains, vanadate is known to undergo one-electron reduction, although the electron donor was not unambiguously assigned.

Involvement of vanadate at the catalytic site of ribonuclease-T_1 through *ca.* eleven hydrogen bonds is an interesting crystal feature and needs further study to clarify the role of such a structure in its biological activity.[12]

All this clearly indicates the need for the development of small molecular vanadium analogues to understand more clearly the role of vanadium in its various oxidation states relevant to biological processes. In this context we have developed synthetic methodology to prepare mononuclear anionic dioxovanadium(v) species $[VO_2L^n]^-$ derived from Schiff-base ligands H_2L^1–H_2L^6. We report here the synthesis, spectral and electrochemical studies, structural aspects, photoreduction and the interaction of such complexes with H_2O_2.

Experimental

Methods and Materials.—All experimental methods of characterization, *viz.*, elemental analyses, UV/VIS, FTIR, NMR spectroscopies and electrochemistry, have been reported

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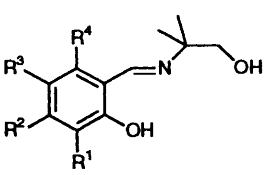
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



	R¹	R²	R³	R⁴
H_2L^1	H	H	H	H
H_2L^2	H	H	—C_4H_4—	
H_2L^3	OMe	H	H	H
H_2L^4	Bu^t	H	Bu^t	H
H_2L^5	H	H	OH	H
H_2L^6	H	H	Br	H

previously.[13] Cyclic voltammetric experiments were carried out using a platinum working electrode and Ag–AgCl reference electrode in the scan speed range 0.05–0.5 V s^{-1} in MeOH with 0.1 mol dm^{-3} NEt_4Br supporting electrolyte. The NMR spectra were recorded in $(CD_3)_2SO$. Salicylaldehyde (Hsal) and 2-amino-2-methylpropan-l-ol (amp) were distilled before use. β-Naphthol, 5-hydroxysalicylaldehyde, 3-methoxysalicylaldehyde, 2,4-di-*tert*-butylphenol, bromine and dimethylformamide (dmf) were used as received. Methanol was distilled from CaH_2 before use. 2-Hydroxy-1-naphthaldehyde, 5-bromosalicylaldehyde, 3,5-di-*tert*-butylsalicylaldehyde and [VO(acac)$_2$] were prepared by routine methods.

Preparation of Complexes.—[Hamp][VO$_2$L^1] **1**. To Hsal (0.37 g, 3 mmol) dissolved in MeOH (5 cm^3) was added amp (0.54 g, 6 mmol) in MeOH (5 cm^3). The reaction mixture was heated for 1 h and cooled to room temperature. To this was added [VO(acac)$_2$] (0.80 g, 3 mmol) in MeOH (15 cm^3) and reflux was continued for 5 h. The solution was then cooled and the solvent was removed *in vacuo*, resulting in a pasty material. Addition of MeCN (10 cm^3) resulted in some white and yellow material and the reaction mixture was left overnight at 4 °C. The yellow material dissolved in hot acetonitrile and the insoluble white material was filtered off. The product **1** was obtained from the acetonitrile fraction and was recrystallized again from acetonitrile to give pure **1** in 61% yield (Found: C, 48.95; H, 7.00; N, 7.50; V, 13.90. Calc. for $C_{15}H_{25}N_2O_5V$: C, 49.45; H, 6.90; N, 7.70; V, 14.00%); NMR ^{1}H, δ 8.59 (imine), 7.6–7.8 (br, NH_3^+), 6.62–7.44 (Ph), 5.47 (br, OH), 3.86 (CH_2), 1.25 (CH_3) and 1.16 (CH_3); ^{13}C, δ 166, 162, 134, 122, 120, 115.5, 79.3, 67.5, 65.5, 54, 26 and 22. IR, $\tilde{\nu}$/cm^{-1}: 3365 (OH), 3050–2800 (NH_3^+), 1635 (C=N), 947 and 872 (V=O).

[Hamp][VO$_2$L^2] **2**. To 2-hydroxy-1-naphthaldehyde (0.52 g, 3 mmol) dissolved in MeOH (10 cm^3) was added amp (0.54 g, 6 mmol) in MeOH (5 cm^3). The reaction mixture was heated for 1 h and cooled to room temperature. To this was added [VO(acac)$_2$] (0.80 g, 3 mmol) in MeOH (15 cm^3) and reflux was continued for 5 h. The reaction mixture was cooled and concentrated to give a yellow precipitate. This was recrystallized twice from methanol to give pure yellow crystals of **2** in 41% yield (Found: C, 54.60; H, 6.50; N, 6.75; V, 11.90. Calc. for $C_{19}H_{27}N_2O_5V$: C, 55.05; H, 6.55; N, 6.75; V, 12.30%). NMR: ^{1}H, δ 9.33 (imine), 6.93–8.26 (Ph), 7.62–7.68 (br, NH_3^+), 5.5 (br, OH), 3.82 (CH_2), 1.25 (CH_3) and 1.16 (CH_3); ^{13}C, δ 166.7, 156.7, 134.6, 129.1, 128.3, 127.8, 126.6, 124.1, 122.6, 120.1, 111.4, 79.5, 67.1, 54.6, 25.8 and 22.8. IR, $\tilde{\nu}$/cm^{-1}: 3365 (OH), 3050–2800 (NH_3^+), 1624 (C=N), 933 and 877 (V=O).

[Hamp][VO$_2$L^3] **3**. To 3-methoxysalicylaldehyde (0.46 g, 3 mmol) dissolved in MeOH (10 cm^3) was added amp (0.54 g, 6 mmol) dissolved in MeOH (5 cm^3). The mixture was heated for 1 h and cooled to room temperature. To this solution was added [VO(acac)$_2$] (0.80 g, 3 mmol) in MeOH (15 cm^3) and it was gently refluxed for 5 h. The mixture was filtered to discard a small amount of green residue. The filtrate was dried *in vacuo* to give a pasty material. Addition of acetonitrile gave both yellow and white products and pure **3** was separated in 43% yield in the same manner as for **1** (Found: C, 48.80; H, 6.85; N, 7.25; V, 12.50. Calc. for $C_{16}H_{27}N_2O_6V$: C, 48.75; H, 6.90; N, 7.10; V, 12.90%). NMR: ^{1}H, δ 8.59 (imine), 7.76 (br, NH_3^+), 6.56–7.07 (Ph), 5.52 (br, OH), 3.86 (CH_2), 3.73 (OCH_3), 1.25 (CH_3) and 1.18 (CH_3); ^{13}C, δ 162, 156.9, 150.5, 125.3, 121.4, 115.5, 114.9, 79.5, 67, 65.76, 65.7, 56, 54.6, 25.6 and 22.8. IR, $\tilde{\nu}$/cm^{-1}: 3216, 3170 (OH), 3050–2800 (NH_3^+), 1630 (C=N), 952 and 850 (V=O).

[Hamp][VO$_2$L^4] **4**. Compound **4** (43% yield) was synthesized and purified adopting the procedure used for **3** (Found: C, 57.60; H, 8.55; N, 5.55; V, 10.65. Calc. for $C_{23}H_{41}N_2O_5V$: C, 57.95; H, 8.65; N, 5.90; V, 10.70%). NMR: ^{1}H, δ 8.6 (imine), 7.6 (br, NH_3^+), 7.29 (Ph), 5.5 (br, OH), 3.83 (CH_2), 1.35, 1.26 and 1.17 (CH_3); ^{13}C, δ 163, 138.7, 136.72, 127.62, 127.38, 120.67, 79.2, 67.5, 65.4, 54.34, 35.31, 34.13, 31.88, 30, 25.75 and 23.1. IR, $\tilde{\nu}$/cm^{-1}: 3173 (OH), 3050–2800 (NH_3^+), 1625 (C=N), 960 and 850 (V=O).

[Hamp][VO$_2$L^5] **5**. Compound **5** (45% yield) was synthesized and recrystallized adopting the procedure used for **1** (Found: C, 47.80; H, 6.85; N, 7.60; V, 13.10. Calc. for $C_{15}H_{25}N_2O_6V$: C, 47.35; H, 6.60; N, 7.35; V, 13.40%). NMR: ^{1}H, δ 8.40 (imine), 6.15–7.23 (Ph), 5.5 (br, OH), 3.82 (CH_2), 1.22 and 1.10 (CH_3); ^{13}C, δ 167.7, 163.6, 161.2, 135.1, 114.9, 106.1, 105.1, 79.4, 67.2, 65.7, 54.6, 25.8 and 22.9. IR, $\tilde{\nu}$/cm^{-1}: 3212, 3146 (OH), 3050–2800 (NH_3^+), 1630 (C=N), 930 and 875 (V=O).

[Hamp][VO$_2$L^6] **6**. This was synthesized and purified following the procedure used for **1**, giving a pure product in 47% yield (Found: C, 40.60; H, 5.55; N, 6.30; V, 11.05. Calc. for $C_{15}H_{24}BrN_2O_5V$: C, 40.65; H, 5.45; N, 6.30; V, 11.50%). NMR: ^{1}H, δ 8.6 (imine), 7.73 (br, NH_3^+), 7.69–6.61 (Ph), 5.48 (br, OH), 3.89 (CH_2), 1.26 and 1.19 (CH_3); ^{13}C, δ 165.2, 161.4, 136.0, 135.2, 123.3, 122.9, 105.7, 79.6, 67.1, 66.0, 54.7, 25.7 and 22.8. IR, $\tilde{\nu}$/cm^{-1}: 3365 (OH), 3050–2800 (NH_3^+), 1635 (C=N), 933 and 870 (V=O).

[(VOL^1)$_2$O] **7**. To H_2L^1 (3 mmol, 0.576 g) in MeOH (10 cm^3) was added [VO(acac)$_2$] (3 mmol, 0.8019 g) in MeOH (15 cm^3). The solution was heated for 5 h, cooled and concentrated to give a pasty material which was dissolved in acetonitrile. This solution was kept for a week to give red crystals of **7** in 60% yield and yellow crystals of **1** in 8% yield. Complex **7** was also prepared in almost the same yield from the reaction of [VO(OEt)$_3$] with H_2L^1 in ethanol (Found: C, 49.70; H, 4.95; N, 5.00; V, 18.75. Calc. for $C_{22}H_{26}N_2O_7V_2$: C, 49.65; H, 4.90; N, 5.25; V, 19.15%).

[{VO$_2$(H$_2$NCMe$_2$CH$_2$O)}$_2$] **8**. To amp (5 mmol, 0.48 cm^3) in MeOH (10 cm^3) was added [VO(acac)$_2$] (5 mmol, 1.335 g) in MeOH (25 cm^3). The solution was refluxed for 24 h to give a white product which was filtered off. On cooling and concentrating the filtrate another crop of the product was collected. After thoroughly washing with methanol complex **8** was obtained in 55% yield (Found: C, 27.60; H, 5.95; N, 7.95; V, 30.30. Calc. for $C_8H_{20}N_2O_6V_2$: C, 28.10; H, 5.90; N, 8.20; V, 29.80%). This compound was also isolated in low yields (< 10%) in the formation of **1**–**6**. NMR: ^{1}H, δ 4.82 (NH_2), 3.58 (CH_2) and 1.33 (CH_3); ^{13}C, δ 84.56 and 24.59. IR, $\tilde{\nu}$/cm^{-1}: 3200 and 3100 (NH_2), 950 and 930 (V=O).

X-Ray Crystallography.—Data were collected for complexes **1**, **2** and **3** on an Enraf-Nonius CAD4 diffractometer at ambient temperature in the ω–2θ scan mode using Mo-Kα radiation. The structures were solved using SHELXS 86,[14] refined with CRYSTALS[15a] and diagrams generated using ORTEP.[15b] The hydrogen atoms bonded to C were placed geometrically (C–H 1.00 Å) whereas Fourier-difference syntheses were used to locate the H atoms associated with the O and N atoms. Other details of data collection and refinement are provided in Table 1.

Table 1 Summary of crystallographic data and parameters for complexes **1**–**3**

Complex	**1**	**2**	**3**
Formula	$C_{15}H_{25}N_2O_5V$	$C_{19}H_{27}N_2O_5V$	$C_{16}H_{27}N_2O_6V$
M_w	362.32	414.37	394.34
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
Cell constants			
a/Å	6.404(1)	6.465(4)	7.907(1)
b/Å	10.256(2)	10.425(8)	20.609(4)
c/Å	13.511(2)	14.784(9)	12.346(3)
α/°	98.50(1)	90.58(6)	—
β/°	95.23(1)	96.57(7)	104.33(1)
γ/°	92.98(1)	95.13(7)	—
U/Å^3	872.1(2)	986(1)	1949.2(7)
Z	2	2	4
D_c/g cm^{-3}	1.39	1.396	1.343
$F(000)$	384	436	960
μ/cm^{-1}	5.73	5.16	5.22
2θ range/°	2–25	2–25	2–27
Total reflections	3024	3574	5282
Unique reflections	3024	3251	4237
	1416 [$I > 3\sigma(I)$]	1477 [$I > 3\sigma(I)$]	3440 [$I > 2\sigma(I)$]
Parameters	208	244	226
R	0.036	0.057	0.033
R'*	0.037	0.058	0.034

* $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, where a Chebychev waiting scheme was employed.

Table 2 Fractional atomic coordinates with estimated standard deviations in parentheses for complex **1**

Atom	*x*	*y*	*z*
V	0.174 2(1)	0.304 25(7)	0.335 06(6)
O(7)	−0.045 9(4)	0.183 0(3)	0.262 6(2)
O(14)	0.373 8(4)	0.449 3(3)	0.341 4(2)
O(51)	0.291 1(4)	0.213 4(3)	0.408 0(2)
O(52)	0.008 5(4)	0.398 1(3)	0.397 7(2)
O(100)	1.016 1(5)	0.364 1(3)	0.690 6(3)
N(9)	0.302 8(5)	0.266 3(3)	0.192 6(2)
N(100)	0.691 8(5)	0.334 6(3)	0.522 2(3)
C(1)	0.140 8(8)	0.047 0(5)	0.146 3(4)
C(2)	−0.026 3(8)	0.068 6(4)	0.205 4(3)
C(3)	−0.182 5(9)	−0.034 8(5)	0.201 3(4)
C(4)	−0.160(1)	−0.155 8(6)	0.145 4(5)
C(5)	0.010(1)	−0.177 9(6)	0.090 5(5)
C(6)	0.155(1)	−0.076 8(5)	0.090 6(4)
C(8)	0.286 4(8)	0.154 4(5)	0.137 2(3)
C(10)	0.442 8(6)	0.376 8(4)	0.172 1(3)
C(11)	0.618 0(8)	0.337 3(6)	0.106 6(4)
C(12)	0.303 7(8)	0.471 7(5)	0.124 8(4)
C(13)	0.535 9(7)	0.439 0(5)	0.277 0(3)
C(100)	0.765 4(6)	0.219 0(4)	0.568 8(3)
C(101)	0.993 6(7)	0.254 8(5)	0.614 3(4)
C(102)	0.621 6(7)	0.197 3(5)	0.648 9(4)
C(103)	0.758 1(7)	0.100 3(4)	0.486 9(4)

Table 3 Fractional atomic coordinates with estimated standard deviations in parentheses for complex **2**

Atom	*x*	*y*	*z*
V	0.174 6(2)	0.330 4(1)	0.357 01(9)
O(7)	−0.058 1(7)	0.221 5(5)	0.294 7(3)
O(14)	0.373 6(7)	0.474 8(5)	0.355 9(3)
O(51)	0.291 2(8)	0.231 6(5)	0.425 1(3)
O(52)	0.012 9(7)	0.413 4(5)	0.412 1(4)
O(100)	1.016 6(9)	0.343 8(6)	0.680 0(5)
N(9)	0.289 0(8)	0.309 1(5)	0.227 4(4)
N(100)	0.698 1(8)	0.331 0(5)	0.524 8(4)
C(1)	0.100(1)	0.101 2(7)	0.186 2(5)
C(2)	−0.056(1)	0.118 8(7)	0.242 5(5)
C(3)	−0.230(1)	0.026 2(7)	0.239 9(5)
C(4)	−0.240(1)	−0.082 2(8)	0.188 9(6)
C(5)	−0.083(1)	−0.107 7(7)	0.134 1(5)
C(6)	0.094(1)	−0.015 3(7)	0.131 2(5)
C(8)	0.254(1)	0.209 4(7)	0.176 1(5)
C(10)	0.430(1)	0.421 6(6)	0.204 4(5)
C(11)	0.601(1)	0.388 2(8)	0.145 5(6)
C(12)	0.299(1)	0.517 1(7)	0.155 5(5)
C(13)	0.529(1)	0.471 9(7)	0.296 8(5)
C(15)	−0.089(2)	−0.223 3(8)	0.080 7(6)
C(16)	0.063(2)	−0.244 7(8)	0.028 4(6)
C(17)	0.233(1)	−0.153 3(8)	0.026 3(6)
C(18)	0.248(1)	−0.041 8(8)	0.077 1(6)
C(100)	0.769(1)	0.213 5(7)	0.571 9(5)
C(101)	0.994(1)	0.246 1(8)	0.614 3(6)
C(102)	0.625(1)	0.177 5(8)	0.643 5(6)
C(103)	0.764(1)	0.107 2(7)	0.500 6(6)

Atomic coordinates for all non-hydrogen atoms of structures **1**, **2** and **3** are given in Tables 2–4 respectively. Important bond lengths and bond angles are given in Table 5 and hydrogen-bonding parameters in Table 6.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Dibasic tridentate ligands often do not satisfy the co-ordination requirements for the vanadyl moiety in monomeric species and hence generally dimeric complexes are obtained. When salts of V^V or V^{IV} in aerobic condition are treated with such ligands, both mono- or dioxo-vanadium complexes are possible products. For instance in the reaction of H_2L^1 with V^{IV} a in 1 : 1 ratio an asymmetric dimer $[(VOL^1)_2O]$ was obtained as the stable product.[8b] On the other hand monobasic tridentate ligands favour formation of neutral mononuclear dioxovanadium(v) complexes provided dimerization is prevented on steric grounds.[9] In this work a synthetic procedure was developed to obtain mononuclear complexes in good yields using Hsal (or related species) and amp in a 1 : 2 ratio. The excess amine acts as a base and subsequently is utilized as a counter cation to stabilize the anionic form of the complex. The excess amine was also found to compete with the Schiff-base ligand for complexation with vanadium and hence the side-product

Table 4 Fractional atomic coordinates with estimated standard deviations in parentheses for complex **3**

Atom	*x*	*y*	*z*
V	0.499 34(3)	0.343 90(1)	0.940 11(2)
O(7)	0.379 2(2)	0.368 99(6)	0.790 58(9)
O(14)	0.483 0(2)	0.315 66(6)	1.083 06(9)
O(15)	0.357 4(2)	0.387 2(1)	0.578 2(1)
O(51)	0.673 9(2)	0.387 12(7)	0.964 9(1)
O(52)	0.541 4(2)	0.270 44(6)	0.898 5(1)
O(100)	0.742 9(2)	0.328 73(7)	0.498 0(1)
N(9)	0.313 8(2)	0.411 34(6)	0.982 3(1)
N(100)	0.623 7(2)	0.292 52(7)	0.686 8(1)
C(1)	0.252 1(2)	0.472 21(8)	0.810 1(1)
C(2)	0.314 5(2)	0.425 06(9)	0.748 7(1)
C(3)	0.299 9(2)	0.437 0(1)	0.633 3(1)
C(4)	0.233 3(3)	0.494 9(1)	0.586 3(2)
C(5)	0.174 6(3)	0.541 8(1)	0.648 7(2)
C(6)	0.181 3(2)	0.530 76(9)	0.758 9(2)
C(8)	0.246 7(2)	0.460 47(7)	0.924 3(1)
C(10)	0.283 8(2)	0.400 54(8)	1.095 5(1)
C(11)	0.267 3(3)	0.463 02(9)	1.158 6(1)
C(12)	0.121 5(3)	0.358 4(1)	1.080 4(2)
C(13)	0.445 6(2)	0.363 18(9)	1.155 5(1)
C(16)	0.328 0(4)	0.391 1(2)	0.460 5(2)
C(100)	0.812 3(2)	0.307 73(9)	0.697 8(1)
C(101)	0.853 1(3)	0.293 7(1)	0.585 7(2)
C(102)	0.838 6(4)	0.379 0(1)	0.728 3(2)
C(103)	0.920 3(3)	0.263 4(2)	0.786 3(2)

Table 5 Selected bond distances (Å) and bond angles (°) for complexes **1**, **2** and **3**

	1	**2**	**3**
V–O(7)	1.921(3)	1.938(4)	1.926(1)
V–O(14)	1.895(3)	1.893(4)	1.893(1)
V–O(51)	1.614(3)	1.621(5)	1.607(1)
V–O(52)	1.675(3)	1.688(5)	1.659(1)
V–N(9)	2.157(3)	2.147(6)	2.175(1)
O(7)–C(2)	1.325(5)	1.316(8)	1.317(2)
N(9)–C(8)	1.268(5)	1.269(8)	1.277(2)
N(9)–C(10)	1.481(5)	1.487(8)	1.491(2)
O(14)–C(13)	1.416(5)	1.405(8)	1.406(2)
O(7)–V–O(14)	150.9(1)	149.2(2)	147.7(1)
O(7)–V–O(51)	102.0(1)	102.9(2)	103.3(1)
O(14)–V–O(51)	102.5(1)	104.0(3)	104.3(1)
O(7)–V–O(52)	93.8(1)	91.8(2)	92.2(1)
O(14)–V–O(52)	92.3(1)	92.7(2)	94.2(1)
O(51)–V–O(52)	110.1(1)	110.6(3)	109.7(1)
O(7)–V–N(9)	81.0(1)	80.7(2)	81.7(1)
O(14)–V–N(9)	76.9(1)	77.4(2)	76.6(1)
O(51)–V–N(9)	106.9(1)	106.6(2)	101.5(1)
O(52)–V–N(9)	142.9(1)	142.7(2)	148.9(1)

$[\{VO_2(H_2NCMe_2CH_2O)\}_2]$ **8** was also isolated in low yields from the synthetic reactions.

Description of the Structures.—The dioxovanadium(v) complexes, **1**–**3** contain the discrete complex anion, $[VO_2L]^-$ ($L = L^1, L^2$ or L^3), and a counter cation of the amino alcohol, [Hamp$^+$, $(H_3N^+)CMe_2CH_2OH)$], in their molecular structures. The molecular structures of **1** and **2** are similar and differ from that of **3**. The structures of complexes **1** and **3** are shown in Fig. 1. The complex anions are mononuclear and possess a five-co-ordinated VNO_4 core containing the interesting *cis* dioxovanadium(v) moiety. The geometry around vanadium can be best described as distorted square-pyramidal with O(51) at the apex. The vanadium atom is displaced from the mean plane passing through the four basal atoms, O(7), N(9), O(14) and O(52), by *ca.* 0.5 Å towards O(51). The V=O(51) vector is almost perpendicular to this plane and is tilted only by an angle of 0.8° for **1** and **2** and by *ca.* 2° for **3**. Important bond lengths and bond angles of the core geometries are given in Table 5.

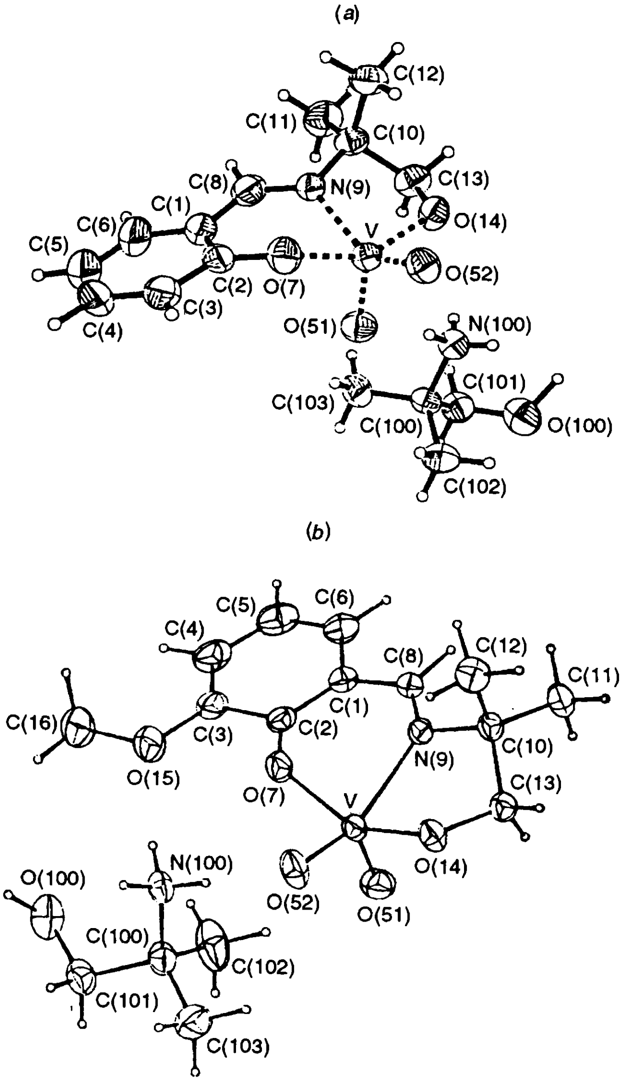


Fig. 1 Molecular structures of **1** (*a*) and **3** (*b*) showing 50% probability level thermal ellipsoids using ORTEP for all non-hydrogen atoms. Small circles indicate hydrogen positions

In the crystal lattices of **1**–**3**, all the anions and the cations are interconnected through four hydrogen-bonds per molecule (Table 6) although the hydrogen-bonding network differs between **1** and **2** and that of **3**. The N–H bonds of the cations act as the hydrogen-bond donors, while the deprotonated alkoxo oxygen $[-HC{=}NC(Me)_2CH_2O^-]$ acts as an acceptor in all the complexes. Interestingly, while the V=O(51) and V=O(52) oxygens show involvement in the intermolecular hydrogen bonding for **1** and **2**, only V=O(52) (basal) shows hydrogen bonding in **3**. However a distinct hydrogen bond is observed in **3** involving the oxygen of the 3-OMe substituent of the phenyl ring. The absence of hydrogen bonds of apical V=O(51) in **3** results in a considerable change in the hydrogen-bonded network in the crystal structure of **3** relative to that of **1** and **2**. This probably results from the orientational differences of the cation with respect to the anion in the structures of **1** and **2** as compared to that in **3** (Fig. 1). Of the four hydrogen-bonds per vanadium complex, one is involved in intra- and three are involved in inter-molecular hydrogen-bonds in complexes **1** and **2**, while two intra- and two inter-molecular hydrogen bonds occur in **3**. The arrangement of two columns of anions intervened by two columns of cations results in the formation of a channel along the *a*-axis through the formation of a spiral

Table 6 Hydrogen bonds (Å) and angles (°) for complexes **1**–**3**

		1	**2**	**3**
O(14) ··· H(1)–N(100)	O ··· H	1.92(1)	1.80(1)	1.78(1)
	O ··· O	2.742(4)	2.776(7)	2.673(2)
	O ··· H–O	172(1)	164(1)	171(1)
O(51) ··· H(2)–N(100)	O ··· H	2.12(1)	1.98(1)	—
	O ··· O	2.979(4)	2.960(7)	—
	O ··· H–O	169(1)	166(1)	—
O(52) ··· H(3)–N(100)	O ··· H	2.01(1)	1.87(1)	1.98(1)
	O ··· O	2.864(4)	2.855(7)	2.882(2)
	O ··· H–O	172(1)	173(1)	169(1)
O(52) ··· H(1001)–O(100)	O ··· H	1.82(1)	1.88(1)	1.71(1)
	O ··· O	2.872(4)	2.897(8)	2.694(2)
	O ··· H–O	153(1)	150(1)	169(1)
O(15) ··· H(2)–N(100)	O ··· H	—	—	2.03(1)
	O ··· O	—	—	2.939(2)
	O ··· H–O	—	—	166(1)

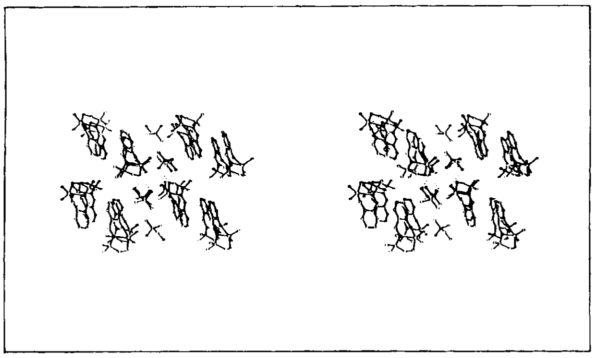


Fig. 2 Stereoview of the crystal structure of **1**, viewed down the *a*-axis

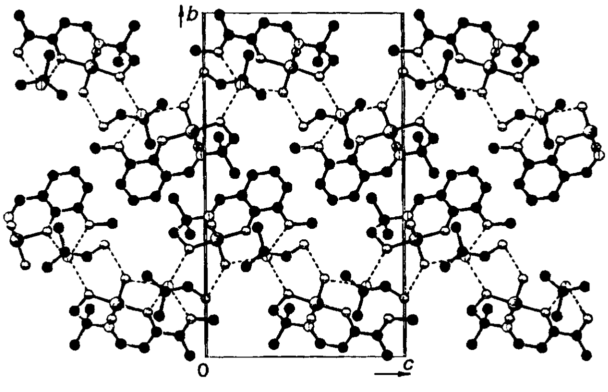


Fig. 3 Packing diagram of the crystal structure of **3**, viewed down the *a*-axis

hydrogen-bonded network extended throughout the crystal lattices of **1** and **2** as revealed by their stereoviews. A typical stereoview is shown for complex **1** in Fig. 2. On the other hand, the crystal structure of **3** exhibits a layer-type hydrogen-bonding in a zigzag fashion (Fig. 3). The observed variation in the lattice networks between **1** and **2**, and that of **3** is expected to be reflected in their solid-state reactivities. No direct interactions are observed between any two VO_2^+ units in the lattice as these are separated through counter cations.

The V–O(14) (alkoxo) bond in compounds **1**–**3** is elongated considerably (*ca.* 1.895 Å) due to hydrogen bonding. While **3** exhibits a V=O(51) distance of 1.607 Å (comparable to non-hydrogen bonded V=O distances[7]) the corresponding bonds in **1** and **2** (1.614 and 1.621 Å) are marginally elongated due to a weak hydrogen bonding. Involvement of O(52) in two moderately strong hydrogen bonds results in a large lengthening of V=O(52), 1.675, 1.688 and 1.659 Å respectively for **1**, **2** and **3**. The V–O (phen) and V–N (imine) distances in **1**, **2** and **3** are longer than those observed for four- and five-co-ordinated vanadium(V) species and lie close to those observed for six-co-ordinated ones. Although complexes **1**, **2** and **3** are five-co-ordinate, their metric parameters indicate that these could be readily converted to six-co-ordinated species.[16] Elongated distances for the V=O group, 1.634 (ref. 9) and 1.649 Å[17] are observed in molecules containing VNO_4 and VN_2O_3 cores due to intermolecular hydrogen bonding. A structure reported by Pecoraro and co-workers[18] possessing neutral VO_2L moieties forms a weak dimer through V=O groups while maintaining a pseudo-square-pyramidal geometry around V.[18] In a later paper, using H_2L^1 as the ligand they obtained as asymmetric μ-oxo dinuclear vanadium(V) species $[(VOL^1)_2O]$.[8b] To our knowledge, complexes **1**, **2** and **3** are among the few examples known where the terminal V=O oxygens show considerable elongation due to hydrogen bonding; distances of similar magnitude are seen in weak dimers formed between two dioxovanadium(V) moieties.[18] Although the core in the present structures is VNO_4, the V=O bond distances in these correlate closely to the distances (1.72 Å) observed by EXAFS in the native vanadium bromoperoxidase.

IR Studies.—Complexes **1**, **2** and **6** showed only one strong and relatively sharp band ($\Delta\nu_{\frac{1}{2}}$ = 50 cm^{-1}) at *ca.* 3365 cm^{-1} due to hydrogen-bonded OH of the counter-cation. Complexes **3**, **4** and **5** showed a band around 3170 cm^{-1} with $\Delta\nu_{\frac{1}{2}}$ of 35 cm^{-1} due to strongly hydrogen-bonded OH of the counter cation. In addition **3** and **5** show bands at *ca.* 3210 cm^{1} with $\Delta\nu_{\frac{1}{2}}$ 70 cm^{-1}. The rather low energy band observed for **5** at 3212 cm^{-1} is attributable to a strongly hydrogen-bonded phenolic OH of the $[VO_2L^5]^-$ anion. These data indicate that the hydrogen-bonded pattern is equivalent in **1**, **2** and **6**, whereas it is more complicated, due to the presence of substituents, in complexes **3**, **4** and **5**. As remarked upon, this difference is reflected in the structures of **1**, **2** and **3**. The sharp spectra observed in the range 3050–2800 cm^{-1} indicate the presence symmetric and asymmetric stretches of N–H groups of the H_3N^+R in addition to ν(C–H). These complexes also showed weak combination bands around 2500 and 2100 cm^{-1} which are characteristic for salts of primary amines.[19] Complexes **1**–**6** exhibited a C=N stretch (≈1635 cm^{-1}) that indicates V–N binding of the Schiff bases. The *cis*-dioxo nature of these complexes is evidenced by the presence of two V=O stretching frequencies in the range 930–960 and 850–880 cm^{-1}. The variation in the above stretching frequencies indicates differing strengths of the V=O bonds in the series. This is consistent with the two ranges of distances, 1.607–1.621 and 1.659–1.688 Å, observed in the crystal structures of **1**, **2** and **3**. Complexes **1**–**6** are interesting examples of square-pyramidal V^V, exhibiting lower $\nu_{V=O}$ values due to hydrogen bonding. On the other hand, dimer **7** showed only one band at 960 cm^{-1} indicating the absence of *cis*-dioxovanadium units. Owing to the absence of the counter-cation [Hamp]$^+$ complex **7** does not show absorptions in the range 3000–4000 cm^{-1}. The vanadium(v) complex **8**, formed through binding of O^- and NH_2 of the amino alcohol, exhibited two bands, at 3200 and 3100 cm^{-1} arising respectively from the ν_{sym} and ν_{asym} modes of the bound NH_2 group. The appearance of two equally intense bands at 950 and 930 cm^{-1} indicates the presence of a dioxovanadium(v) centre.

NMR Studies.—The protons of the CH_2 group of complexes **1**–**6** are shifted downfield by ≈0.3 ppm compared to the corresponding free ligands indicating binding of the alkoxo group to V. The absence of signals at *ca.* δ 14.5 in the complexes also indicated binding through phenolic O^-. Methyl signals were observed in the region δ 1.16–1.28. The OH hydrogen of the counter-cations was shifted downfield by 0.2–0.5 ppm in the complexes indicating the hydrogen-bonded environment. The protons of the primary amine salt (R^+NH_3) are observed in the range δ 7.6–7.8 in the complexes. All the complexes **1**–**6** showed similar ^1H NMR spectra, excepting marginal substitution effects inferring that the complexes are structurally similar in solution.

Comparison of the ^{13}C NMR spectra of the CH_2OH carbon of the ligands and in the corresponding vanadium complexes showed a downfield shift of 22 ppm for the dimer, **7**, and *ca.* 10 ppm for the dioxovanadium(v) complexes, **1**–**6**. This may be attributed to the strength of corresponding V–O(alkoxo) bonds as judged from the bond distances of these structures. Large downfield shifts (7–8 ppm) of the tertiary carbon in complexes **1**–**6** are also indicative of the bonding of Schiff base ligand both through the imine nitrogen as well as through the alkoxo O^-. Based on both the ^1H and ^{13}C NMR spectra of **8**, it is possible to conclude that the amino alcohol binds to vanadium both through the amino nitrogen as well as through alkoxy O^-.

UV/VIS Spectra.—The pale yellow complexes **1**–**6** did not show any electronic spectral bands in the visible region in MeOH, but only bands arising from intraligand and l.m.c.t. transitions (Fig. 4). Broad bands observed in the region 340–415 nm (ε = 2500–7000 dm^3 mol^{-1} cm^{-1}) are attributed to l.m.c.t. and those in the region 280–320 nm (ε = 2500–16 000 dm^3 mol^{-1} cm^{-1}) are attributed to $\pi \longrightarrow \pi^*$ (intraligand) transitions. Dimeric complex **7** which is red in MeOH showed a shoulder at 480 nm (ε = 600 dm^3 mol^{-1} cm^{-1}) and an intraligand transition at 340 nm (ε = 15 000 dm^3 mol^{-1} cm^{-1}). The appearance of the l.m.c.t. to lower energy in **7** as compared to complexes possessing VO_2^+ units (**1**–**6**) is expected due to the electron-rich character at the V^V centre in the latter cases.[20] Complex **8** in MeOH showed a band at 229 nm (ε = 12 549 dm^3 mol^{-1} cm^{-1}) and a shoulder at 276 nm (ε = 5 500 dm^3 mol^{-1} cm^{-1}).

Reactivity of Complexes **1**–**6** *with* H_2O_2.—Although peroxo co-ordination at vanadium is well established, the role of the resulting vanadium complex in the activation of halide oxidation has only been shown recently. The *cis*-dioxovanadium moiety has been found to give monoperoxo species in dmf according to equation (1), and the peroxo complex,

$$VO_2L^- + H_2O_2 \longrightarrow VO(O_2)L^- + H_2O \qquad (1)$$

$VO(O_2)L^-$ is claimed to be the oxidatively active species.[10] In efforts to understand the reaction products between VO_2L^- and peroxide, complex **1** was treated with H_2O_2 in dmf in ratios of 1 : 4, 1 : 6, 1 : 8 and 1 : 10, and complexes **2**, **4** and **6** were treated with H_2O_2 in a 1 : 10 ratio and the course of the reactions by absorption spectroscopy.

In the reactions of the complexes with H_2O_2 (1 : 10), the band at 360 nm showed a gradual decrease in its intensity and finally disappeared over 45 min. A new band appeared at 410 nm which increased in intensity as a function of time. Three isosbestic points (at 300, 330 and 395 nm) were observed during the progress of the reaction so indicating an equilibrium between the complex and the free Schiff-base ligand in solution. Absorption spectra in the case of complex **6** are shown in Fig. 5(*a*). When ratios of < 6 : 1 H_2O_2 : V are used, the band at 360 nm does not completely disappear. The amount of free Schiff-base ligand released was found to increase as a function of time after the addition of H_2O_2 for *ca.* 1 h and later on this free Schiff base ligand combines with the vanadium species to give the spectrum of the original complex. However the rate at which the complex formation occurs seem to depend upon the amount of H_2O_2 present in the solution; the higher the concentration of H_2O_2, the slower was the rate of the complex reformation. These trends are shown in Fig. 5(*b*). As the peroxovanadium(v) species formed in the reaction is expected to absorb light at *ca.* 430 nm,[21] its presence could not be unambiguously demonstrated due to overlap of bands from released free ligand in the same region. We, however, isolated a species from the reaction between **6** and H_2O_2 (1 : 10 mol ratio) in acetonitrile upon heating on a water-bath for a couple of minutes. The absorption spectrum of this product showed a band at 420 nm. But the FTIR spectrum of this product did not show any $\nu_{C=N}$ bands corresponding to the Schiff base ligand inferring that the Schiff-base ligand is detached from the vanadium centre. However, ν_{O-O}, ν_{V-O} and $\nu_{V=O}$ modes were identified at 666, 910

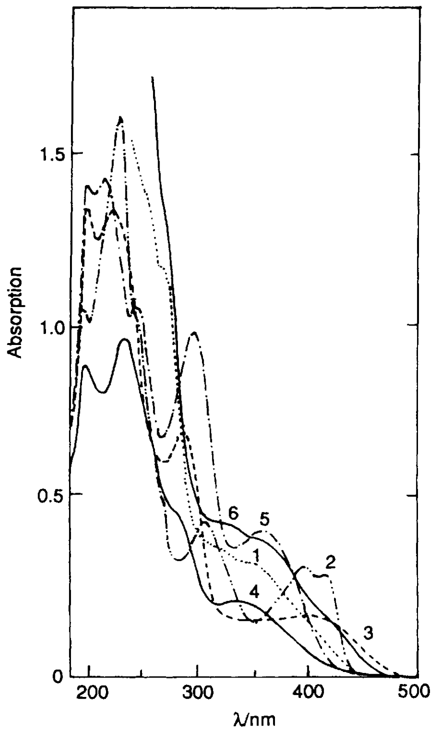


Fig. 4 Electronic absorption spectra of complexes **1**–**6** in MeOH

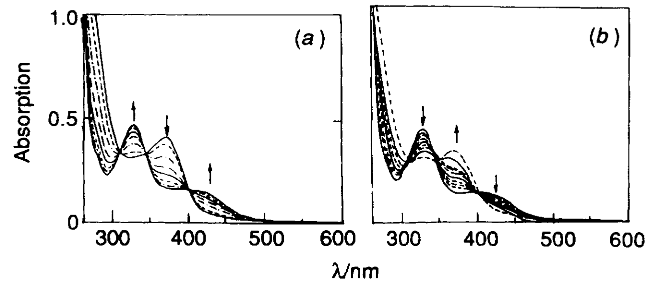


Fig. 5 Absorption spectra as a function of time for the reaction mixture **6** : H_2O_2 (1 : 10); (*a*) during first 45 min; (*b*) between 45 min and 24 h

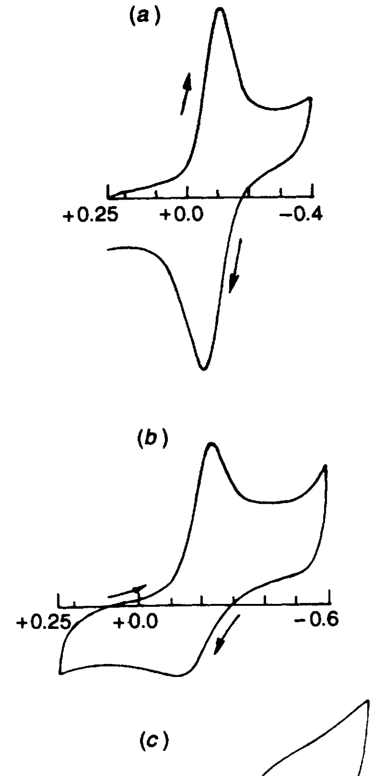


Fig. 6 Cyclic voltammograms of complexes, **6** (*a*), **4** (*b*) and **8** (*c*) in MeOH at a platinum electrode at a scan speed of 0.1 V s^{-1}; supporting electrolyte NEt_4Br, reference electrode Ag–AgCl

and 990 cm^{-1} respectively;[22] the product separated from the reaction between **1** and H_2O_2 under the same conditions showed identical absorption and FTIR spectral features.

Electrochemistry.—The electrochemical properties of the dioxovanadium(V) complexes **1**–**6** and **8** were examined by cyclic voltammetry in the potential range −1.2 to +1.0 V in MeOH at a Pt working electrode. All the complexes exhibited a well defined voltammetric response due to the V^V–V^{IV} couple. While complexes **1**, **2**, **3**, **5** and **6** showed electrochemical reversibility with $E_{\frac{1}{2}}$ values of −64, −69, −77, −79 and −82 mV, complex **4** showed quasireversible behaviour (E_p^c = −240 mV and $E_{\frac{1}{2}}$ = −181 mV). By contrast complex **8** showed an irreversible V^V–V^{IV} process (E_p^c, −250 mV). The peak to peak separation (ΔE) in the reversible cases was 70 ± 10 mV (the ferrocenium–ferrocene couple under the same conditions has shown values of 70 mV). Representative voltammograms for reversible (**6**), quasireversible (**4**) and irreversible couples (**8**) are shown in Fig. 6. The near linearity of the i_p^c *vs.* $\nu^{\frac{1}{2}}$ (ν in the range 50–500 (mV s^{-1}) for all the complexes showed that these are diffusion controlled processes. The independence of $E_{\frac{1}{2}}$ with ν, the ΔE behaviour and the near unity of the ratio of i_{p_a}/i_{p_c} for **1**, **2**, **3**, **5** and **6** indicated that the V^V–V^{IV} redox processes are reversible under these experimental conditions. No other peaks were observed in the potential range scanned. Substitution on the aromatic ring does not affect the redox potentials of the V^V–V^{IV} couple to any great extent except for **4**, where the potentials were more cathodic than those of the unsubstituted complex **1**; this is expected owing to the electron donating nature of the *tert*-butyl groups. Vanadium(V) complexes of Schiff bases generated from tris(hydroxymethyl)aminomethane with a similar NO_4 core have more negative V^V–V^{IV} potentials,[23] indicating that redox potentials are dependent upon the nature of the primary co-ordination. The low potentials and the near reversibility observed in our systems are indicative of the ability of these ligands in stabilizing the metal in the high oxidation states IV and V.

The stability of these complexes in MeOH under ambient conditions was checked by recording voltammograms after 48 h. All but **5**, which showed an irreversible reduction peak after about 20 h, were unchanged.

Photoreduction of Complexes **1**–**6**.—When solid complexes **1**–**6** were exposed to light (25 W), **1**, **2** and **6** underwent a colour change from yellow to green, with loss of crystallinity while complexes **3**, **4** and **5** were unaltered. The colour change for **1**, **2** and **6** was accompanied by photoreduction from V^V to V^{IV} as indicated by the appearance of eight-line EPR spectra characteristic of V^{IV}, and by the solid state absorption spectra of the photoreduced products. The solid-state absorption spectra showed d–d transitions at *ca.* 600 and 740 nm. By contrast, photoirradiation of *solutions* of the vanadium(V) complexes did not lead to any changes even over a period of one week. Interestingly, when the green photoproducts were dissolved in acetonitrile they reverted back to the original yellow vanadium(V) species as confirmed both by absorption and voltammetric studies. Therefore the photoreactivity is a solid-state phenomenon presumably arising from the molecular packing. Various *N*-salicylideneamine derivatives, upon irradiation by visible light show tautomerization induced by an intramolecular proton transfer accompanied by p-electron configurational changes.[24] Although we expect that all the complexes would have a similar geometry around the metal, as affirmed for complexes **1**–**3**, the crystal packing is greatly influenced by the substitution on the aromatic ring. The non-photoreactivity of **3** can be attributed to the changes in the hydrogen-bonded network of this lattice (relative to **1** and **2**) that is essentially caused through the breakage of the apical V=O(51) hydrogen bond and the involvement of the phenyl substituted OMe group in hydrogen-bond formation. However, complete mechanistic aspects of this reactivity are not yet available. However, Pecoraro and co-workers[25] have recently shown that the weakly dimeric dioxovanadium(V) complex $[(VO_2L')_2]$ [HL′ = *N*-(2-hydroxyethyl)-*N*′-salicylideneethylenediamine] is photoreducible *both* in the solid state and in dmf solution. On the other hand, when the same compound with the corresponding reduced Schiff-base ligand was studied, the resulting complex with a similar structure was not photoreducible.

Acknowledgements

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