DALTON

Structure, characterization and photoreactivity of monomeric dioxovanadium(V) Schiff-base complexes of trigonal-bipyramidal geometry

Gebray Asgedom,[a] Alavattam Sreedhara,[a] Jussi Kivikoski,[b] Erkki Kolehmainen[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, Jyvaskyla, Fin-40351, Finland*

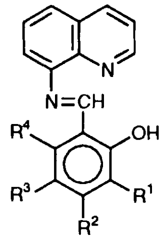
Five mononuclear *cis*-dioxovanadium(V) complexes of tridentate Schiff bases derived from salicylaldehyde and its derivatives and 8-aminoquinoline have been synthesized and characterized. Single-crystal X-ray analyses were performed with $[VO_2L^1]$ **1** and $[VO_2L^2]$ **2** (L^1 and L^2 denote the [1 + 1] Schiff-base anions derived from salicylaldehyde or naphthaldehyde and 8-aminoquinoline). While the structure of **2** was refined to a final $R = 0.074$ ($R' = 0.055$), that of **1** was refined only to $R = 0.134$ ($R' = 0.139$) due to its poor diffraction quality. The complexes contain *cis*-oxo groups in the equatorial plane and a trigonal-bipyramidal geometry around the vanadium at which the Schiff base binds meridionally. Photoirradiation of these complexes in CH_2Cl_2 yielded chloride-bound VO^{3+} species, as studied using absorption and ^{51}V NMR spectroscopy. These species are convertible back to the dioxovanadium(V) complexes upon addition of water to the photoirradiated solution.

Vanadium is an essential bioelement and is involved in various catalytic and inhibitory processes.[1,2] Vanadium(V) complexes are known as potent inhibitors for various enzymes. It has been proposed that the monomeric V^V acts as a transition-state analogue of the pentavalent trigonal-bipyramidal (*TBPY*) intermediate of phosphate hydrolysis.[3] Only a few complexes of dioxovanadium with *TBPY* geometry are known in the literature and these have mainly resulted from the dimerization of tetrahedral vanadium(V) centres.[4,5] However, a sterically hindered dioxovanadium(V) complex has been synthesized recently[6] and provides impetus for the synthesis of *TBPY* complexes. Dioxovanadium(V) complexes $[VO_2L]$ on addition of acid become protonated to give first $[VO(OH)L]^+$ and then $[V(OH)_2L]^{2+}$ formulated as $[VOL]^{2+} + H_2O$.[7,8] However, there are no reports on the formation of such species by photoirradiation.

In continuation of our investigations of oxovanadium chemistry,[9–11] we here report the synthesis, characterization by various spectral methods and photochemical conversion of five complexes possessing the VO_2^+ moiety and *TBPY* geometry, and the crystal structures of two of these.

Experimental

Absorption spectra were measured using a Shimadzu UV-260 spectrophotometer, Fourier-transform IR spectra in a KBr matrix on a Nicolet spectrometer, EPR spectra using a Varian ESR-112 spectrometer with tetracyanoethylene (tcne) as the field marker ($g = 2.002\ 77$). The ^1H, ^{13}C and ^{51}V NMR spectra were measured using a JEOL JNM GSX-270 FT spectrometer working at 270, 68.003 and 71.057 MHz, respectively, and equipped with a 10 mm tunable probe head using $(CD_3)_2SO$ and CH_2Cl_2 solutions. All free induction decays were digitally filtered by an exponential line-broadening function of digital resolution prior to Fourier transform. The ^{51}V shifts are referred to the signal of external $VOCl_3$ in a 1 mm diameter capillary tube inserted coaxially in the 10 mm NMR tube. Carbon, hydrogen and nitrogen analysis was done using a Carlo-Erba analyser. The vanadium content was determined using inductively coupled plasma atomic emission spectroscopy (ICPAES).



	R^1	R^2	R^3	R^4
HL^1	H	H	H	H
HL^2	H	H	C_4H_4	
HL^3	OMe	H	H	H
HL^4	H	H	Br	H
HL^5	H	H	OH	H

Materials

Salicylaldehyde (Hsal) was procured from local sources and distilled before use; 3-methoxy- and 4-hydroxy-salicylaldehyde were obtained from Aldrich Chemical Co. (USA). 2-Hydroxy-1-naphthaldehyde was prepared from 2-naphthol by the Duff method.[12] 8-Aminoquinoline (Lancaster, UK), vanadium pentaoxide (Loba, India), 5-bromosalicylaldehyde (SRL, India) and absolute ethanol (E. Merck, Germany) were used as received.

Syntheses

$[VO(OEt)_3]$. Vanadium pentaoxide (0.120 g) was refluxed in absolute EtOH (55 cm^3) for 24 h and filtered. The green residue (0.020 g) was discarded and the pale yellow filtrate (≈ 1 mmol) used in the following reactions.

Dioxovanadium(V) complexes 1–5. All the complexes were synthesized and purified in a similar manner and a typical procedure for **1** is given below.

Table 1 Elemental analyses for complexes **1**–**5** and **1′***

Complex	Analysis (%) C	H	N	V
1	57.75	3.25	8.35	15.80
	(58.20)	(3.35)	(8.50)	(15.45)
2	62.95	3.45	7.15	13.80
	(63.15)	(3.45)	(7.35)	(13.40)
3	56.75	3.60	7.70	14.55
	(56.70)	(3.65)	(7.80)	(14.15)
4	47.45	2.55	6.95	12.30
	(46.95)	(2.45)	(6.85)	(12.45)
5	55.65	3.20	8.05	15.35
	(55.50)	(3.20)	(8.10)	(14.70)
1′	45.35	3.20	5.95	11.55
	(45.20)	(3.10)	(6.20)	(11.30)

* Calculated values in parentheses.

To 8-aminoquinoline (1 mmol, 0.144 g) in absolute EtOH (10 cm^3) was added Hsal (1 mmol, 0.121 g) in absolute EtOH (10 cm^3) and heated for 1 h. The solution was cooled and $[VO(OEt)_3]$ (1 mmol) was added dropwise. A yellow precipitate formed immediately and the reaction mixture was heated for 3 h. The precipitate was filtered off and stirred in hot absolute EtOH for 1 h, filtered, washed with diethyl ether and dried *in vacuo*.

Complexes **1**–**5** were obtained using the ligands HL^1–HL^5 in about 55% yield. Single crystals suitable for X-ray diffraction in the case of **1** and **2** were grown from Me_2SO solution. Proton and ^{13}C NMR spectra supported the formation of the complexes and their intact nature in solution.

$[VO(OH)L^1(Cl)]\cdot CH_2Cl_2$ 1′. Complex $[VO_2L^1]$ **1** (0.033 g) was photoirradiated in CH_2Cl_2 (50 cm^3) using a 25 W fluorescent light for 7 d. The final violet-blue solution was filtered and concentrated to 5 cm^3 by slow evaporation in a moisture-free atmosphere to give a dark precipitate. The latter was filtered off and dried *in vacuo* to yield **1′**.

Elemental analyses are given in Table 1.

X-Ray crystallography

X-Ray diffraction data were collected for complex **2** on an Enraf-Nonius CAD4 diffractometer at ambient temperature in ω–2θ scan mode using Mo-Kα radiation (λ = 0.710 73 Å). The structure was solved using direct methods (SHELXS 86[13]) and refined with CRYSTALS.[14] The hydrogen atoms bonded to C were geometrically placed (C–H 1.00 Å). Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms was used. The hydrogen atoms were treated as riding atoms with a fixed thermal parameter (U_{iso} = 0.08 $Å^2$). An empirical (ψ scan) absorption correction was applied using four reflections. A residual electron density of 2.1 e $Å^{-3}$ was observed in the final Fourier-difference map and this made no interpretable contacts with the rest of the structure. Other details of the data collection and refinement (based on F^2) are provided in Table 2. Coordinates of all non-hydrogen atoms of structure **2** are given in Table 3, important bond lengths and angles in Table 4.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Table 2 Summary of crystallographic data and parameters for compound **2**

Formula	$C_{20}H_{13}N_2O_3V$
M	380.28
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal dimensions/mm	0.10 × 0.40 × 0.50
a/Å	12.637(2)
b/Å	8.994(1)
c/Å	14.589(2)
β/°	107.67(1)
U/$Å^3$	1579.8(4)
Z	4
D_c/g cm^{-3}	1.60
F(000)	776
Total reflections	4899
Unique reflections	3791
Observed reflections [$I > 3\sigma(I)$]	2714
Parameters	235
Final R	0.074
Final R'	0.055
R_{int}*	0.026

* $R_{int} = \Sigma|F^2 - (F^2)_{mean}|/\Sigma F^2$, where a Chebychev weighting scheme was employed.

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

Atom	x	y	z
V	0.304 70(5)	0.1496 4(6)	0.388 11(4)
O(1)	0.241 2(2)	0.026 0(4)	0.464 3(2)
O(51)	0.317 3(3)	0.029 4(3)	0.309 5(2)
O(52)	0.198 3(2)	0.255 2(3)	0.340 1(3)
N(1)	0.436 8(2)	0.174 9(3)	0.521 9(2)
N(2)	0.416 5(2)	0.296 7(3)	0.354 3(2)
C(1)	0.268 1(3)	−0.029 4(4)	0.550 0(3)
C(2)	0.192 5(3)	−0.132 6(5)	0.570 0(3)
C(3)	0.213 0(4)	−0.193 7(5)	0.657 2(3)
C(4)	0.309 3(3)	−0.157 4(4)	0.734 8(3)
C(5)	0.327 8(4)	−0.220 0(5)	0.826 2(3)
C(6)	0.419 2(4)	−0.183 7(6)	0.901 9(3)
C(7)	0.496 3(4)	−0.082 5(5)	0.885 6(3)
C(8)	0.482 1(3)	−0.021 1(5)	0.796 3(3)
C(9)	0.386 9(3)	−0.055 7(4)	0.717 6(2)
C(10)	0.366 6(3)	0.007 8(4)	0.622 2(2)
C(11)	0.444 2(3)	0.109 3(4)	0.603 7(2)
C(12)	0.524 9(3)	0.272 2(3)	0.517 2(2)
C(13)	0.617 5(3)	0.308 7(4)	0.592 4(3)
C(14)	0.696 2(3)	0.408 4(4)	0.576 1(3)
C(15)	0.685 0(3)	0.466 9(4)	0.487 6(3)
C(16)	0.591 0(3)	0.431 3(4)	0.409 5(2)
C(17)	0.570 2(3)	0.488 5(4)	0.315 6(3)
C(18)	0.474 4(3)	0.452 1(5)	0.245 7(3)
C(19)	0.399 5(3)	0.354 9(4)	0.268 1(2)
C(20)	0.511 0(2)	0.334 0(3)	0.426 0(2)

Table 4 Selected bond lengths (Å) and angles (°) for complex **2**

V–O(1)	1.912(3)	V–N(1)	2.161(3)
V–O(51)	1.619(3)	V–N(2)	2.100(3)
V–O(52)	1.621(3)		
O(51)–V–O(1)	99.9(2)	N(1)–V–O(52)	129.9(1)
O(52)–V–O(1)	98.8(2)	N(2)–V–O(1)	159.0(1)
O(51)–V–O(52)	109.4(2)	N(2)–V–O(51)	92.1(1)
N(1)–V–O(1)	83.2(1)	N(2)–V–O(52)	93.3(1)
N(1)–V–O(51)	119.6(1)	N(2)–V–N(1)	75.9(1)

Results and Discussion

With monobasic tridentate ligands, the dioxovanadium(V) complexes formed are usually dimeric and six-co-ordinated. However, when these ligands are modified with additional steric groups, rare mononuclear *cis*-dioxovanadium(V) five-co-ordinate complexes with *TBPY* geometry are obtained. The dimerization of such mononuclear complexes requires rearrangement. On the other hand, the square-pyramidal mononuclear complexes can easily dimerize through axial ligation. We have been able to synthesize a set of five mononuclear *cis*-

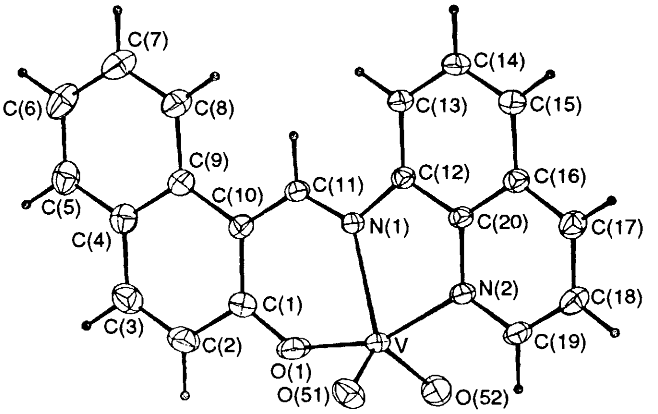


Fig. 1 An ORTEP[15] diagram of complex **2** showing 50% probability level thermal ellipsoids for all non-hydrogen atoms. Small circles indicate hydrogen positions

dioxovanadium(v) (VO_2^+) complexes with *TBPY* geometry **1**–**5** from reactions between $[VO(OEt)_3]$ and rigid monobasic tridentate Schiff bases. On the other hand, reactions between $[VO(acac)_2]$ (acac = acetylacetonate) and the same Schiff bases led to the formation of mixtures of vanadium-(IV) and -(V) species. These were not used for further studies.

Complexes **1** and **3** are soluble in Me_2SO and CH_2Cl_2 whereas **2** and **4** are less soluble. Complex **5** is soluble only in Me_2SO. All the complexes have given satisfactory elemental analyses (Table 1).

Structure of complex 2

The single-crystal structure was determined for complex **2**. The molecular structure is shown in Fig. 1 and selected bond lengths and angles in Table 4. The $[VO_2L^2]$ complex is a neutral mononuclear unit where V is co-ordinated to two nitrogen atoms, one phenolate oxygen and two terminal oxo groups. The ligand assumes a meridional binding through its three donor atoms. The geometry around vanadium can best be described as a distorted trigonal bipyramid. The V=O(51), V=O(52) and the imine nitrogen N(1) form the triangular plane, and O(1) and the nitrogen in the ring, N(2), are *trans* to each other (159°). This arrangement is rather rare as the known square-pyramidal and octahedral cases exhibit one V=O in equatorial position and the other V=O in apical position. Such a geometry is expected to reflect the physicochemical properties. The equatorial angles are in the range 109–130°. It is possible that when the bulky ring approaches from the *trans* position it pushes O(52) closer to O(51), the O(51)–V–O(52) angle being 109.4°, and hence leads to distortion. However, this angle is similar to those of mononuclear dioxovanadium(v) complexes of *TBPY* (109.8),[6] square-pyramidal[9] (110.1) and octahedral[16,17] (106.5 and 107.1°) geometries. Further, the metal deviates from the trigonal plane by 0.1 Å towards O(1). The V=O distances, 1.619 and 1.621 Å, are typical of non-hydrogen bonded V=O groups.[18] The V–N(1) and V–N(2) distances (2.16 and 2.10 Å) are in accord with literature values for imine and aromatic ring nitrogens respectively.[19]

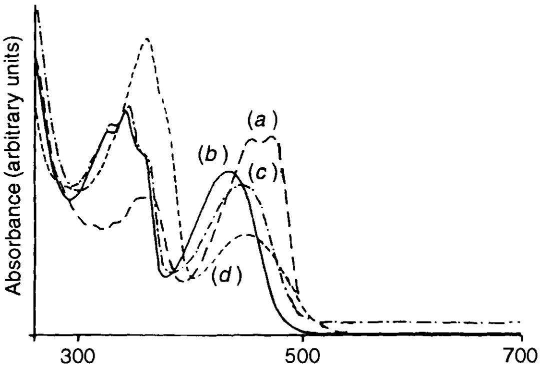


Fig. 2 Electronic absoption spectra of complexes **2** (*a*), **1** (*b*), **4** (*c*) and **3** (*d*) in CH_2Cl_2

Five-co-ordinate dioxovanadium(v) complexes tend to dimerize, in many cases, to six-co-ordinated species. The mononuclear compounds generally have square-pyramidal geometry and to our knowledge only one Schiff-base complex of *TBPY* geometry is known, where the dimerization was prevented using a bulky Bu^t group in the 3 position of salicylidinimine.[6] Though the molecule does not form a dimer, intermolecular hydrogen-bonding interactions predominate. The *trans* angle for **2** is similar to that observed for the uridinevanadate complex (162°) in ribonuclease.[6] Comparison of the geometry parameters of **2** with the *TBPY* structure in the literature suggested that the metal geometry is less distorted in the present case. The rigidity and the tridentate nature of the ligand favours a meridional geometry leading to a *TBPY* structure with both the V=O groups in the equatorial position rather than the generally seen square-pyramidal one. The residual electron density for **2** (2.1 and 0.56 e Å^{-3}) does not make any interpretable bonding or non-bonding contacts with the rest of the molecule.

Though complex **1** yielded poor-quality crystals a single-crystal X-ray analysis was performed* and it was found that the structure is similar to that of **2** with a distorted trigonal-bipyramidal geometry at the metal and both the V=O groups in the equatorial plane.†

Fourier-transform IR spectra

Complexes **1**–**5** showed ν(C=N) in the 1607–1624 cm^{-1} region; **1** and **2** showed ν(V=O) at 926 cm^{-1}, perhaps characteristic of both V=O bonds in the equatorial plane as observed in the structures of **1** and **2**. Substitution of the salicylaldehyde ring, on the other hand, is expected to alter the crystal packing and thereby the ν(V=O) pattern. Changes were noticed in the crystal packing in the case of the $[VO_2L]^-$ complexes, where L is a Schiff base derived from salicylaldehyde (or its derivatives) and 2-amino-2-methylpropan-1-ol, upon changing the substituent on the salicylaldehyde ring.[9] Complex **3** showed bands at 926 and 945 cm^{-1} and **5** at 907 and 953 cm^{-1}. The ν(V=O) stretching vibration observed at low energy for **5** is attributable to hydrogen bonding in the crystal lattice. This is further supported by a broad band observed around 3150 cm^{-1}. Complex **4** alone showed three sharp bands in the region 919–940 cm^{-1}.

---

* Crystal data: $C_{16}H_{11}N_2O_3V$ **1** monoclinic, space group $P2_1/n$, a = 9.861(13), b = 10.673(19), c = 13.206(16) Å, β = 107.75(10)°, U = 1324(3) Å^3, Z = 4, D_c = 1.668 g cm^{-3}. The structure was solved by SHELXS 86 and refined by CRYSTALS using direct methods to give final R = 0.134 and R' = 0.139. Among the 2588 unique reflections measured, 1722 [$I \geqslant 3\sigma(I)$] were used in refining 200 parameters. The hydrogen atoms bonded to C were placed geometrically (C–H 1.00 Å) and treated as riding atoms with a fixed thermal parameter (U_{iso} = 0.08 Å^2). A residual electron density of 2.59 e Å^3 was observed in the final Fourier-difference map which made no interpretable contacts with the rest of the structure. Selected bond lengths and angles: V–O(1) 1.897(6), V–O(51) 1.599(8), V–O(52) 1.608(6) and V–N(1) 2.171(6), V–N(2) 2.112(6) Å; O(51)–V–O(1) 104.0(3), O(52)–V–O(1) 98.3(3), O(51)–V–O(52) 110.4(5), N(1)–V–O(1) 84.0(2), N(1)–V–O(51) 114.7(3), N(1)–V–O(52) 132.8(4), N(2)–V–O(1) 156.6(2), N(2)–V–O(51) 94.0(3), N(2)–V–O(52) 89.1(3) and N(2)–V–N(1) 74.8(2)°.

† *Note added at proof:* A recent crystal structure determination of an azide chloroperoxidase showed a trigonal bipyramidal vanadium centre with both of the oxo groups occupying the equitorial plane,[20] hence our studies are of paramount importance in the context of the structure and the photochemical enhancement of the reactivity of the native enzyme.[21]

Table 5 Electronic absorption spectra in CH_2Cl_2 solution

Compound	λ/nm (ε/dm^3 mol^{-1} cm^{-1})
1	328 (sh, 14 521), 342 (16 501), 355 (sh, 13 201), 430 (11 551)
2	330 (sh, 4 500), 360 (5 700), 455 (8 100), 475 (8 200)
3	360 (23 636), 380 (s, 17 773), 450 (sh, 7 636)
4	328 (sh, 7 022), 342 (8 511), 355 (sh, 7 763), 442 (4 733)
5*	330 (sh, 13 805), 350 (15 044), 425 (23 008)
1′	330 (sh, 17 326), 370 (23 762), 548 (3 267), 690 (2 640)
2′	320 (sh, 11 000), 410 (20 000), 550 (3 100), 840 (1 900)
3′	360 (24 000), 380 (sh, 17 636), 450 (5 454), 730 (1 818)
4′	355 (sh, 13 888), 370 (17 776), 545 (3 222), 700 (3 000)

* In Me_2SO; the primed numbers indicate the products obtained upon photoirradiation of the corresponding compounds with unprimed numbers in CH_2Cl_2.

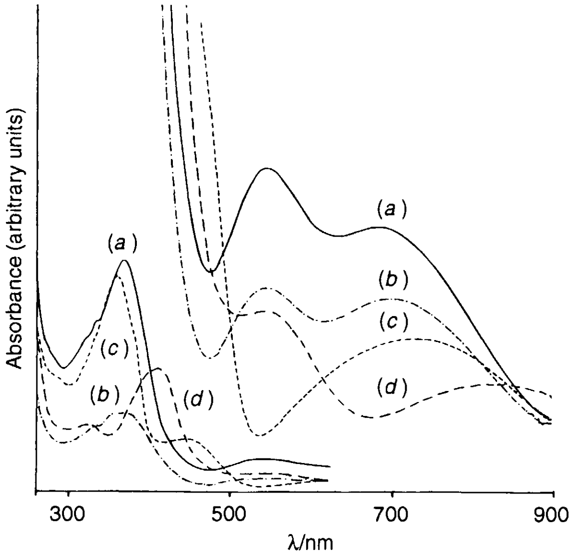


Fig. 3 Electronic absorption spectra of photoirradiated solutions: (*a*) complex **1′**, (*b*) **4′**, (*c*) **3′** and (*d*) **2′**, in CH_2Cl_2

Electronic absorption spectra

The ligands of complexes **1**–**5** (HL^1–HL^5), except for **2**, in both CH_2Cl_2 and Me_2SO solutions showed strong bands in the region 330–350 nm and a very weak band around 470 nm. The ligand in **2** (HL^2) exhibited bands at 326, 456 and 479 nm. Complexes **1** and **3**–**5** showed strong bands in the range 335–360 and 430–450 nm. The new bands around 440 nm are assignable to ligand-to-metal charge transfer (l.m.c.t.) transitions and those around 350 nm to intraligand transitions (Fig. 2). The appearance of l.m.c.t. transitions at high energy for dioxovanadium(v) complexes is expected to be due to the decrease in net positive charge at the metal.[22] Complex **2** exhibited bands at 360, 455 and 475 nm. However, the l.m.c.t. transition could not be assigned unambiguously as it is obscured by strong ligand bands. The absorption data are given in Table 5.

^{51}V NMR spectra

The ^{51}V NMR studies of complexes **1**–**5** dissolved in Me_2SO showed single resonances at δ -534.9, -535.9, -533.4, -531.2 and -533.9, respectively. These values are as expected for dioxo complexes of V^V having co-ordination spheres of O_4N or O_3N_2.[8,21] The observation of a single signal also indicated that they are stable in Me_2SO solution.

Photochemistry

Complexes **1**–**5** are stable in the solid state, and in Me_2SO or MeCn solutions, even after exposure to fluorescent light over a period of 4–5 d. On the other hand, dichloromethane solutions of **1**–**4** exposed to fluorescent light for 4–24 h exhibited considerable changes in colour and hence were studied using UV/VIS and ^{51}V NMR spectroscopy. The photoirradiated product of **1** was isolated in the solid state and characterized.

UV/VIS spectra. Under fluorescent light complexes **1**–**4** were converted into **1′**–**4′**, changing from yellow to violet blue (**1′**, **4′**), red-brown (**2′**) or dark green (**3′**). However, the corresponding ligands were not affected by light in the solid state or in CH_2Cl_2 solution under identical experimental conditions. Solutions of **1′**, **2′** and **4′** showed two new bands in the visible region; one at 545 and the other in the 680–840 nm range. The bands in the visible region are very broad and asymmetric. The original bands in the 400–500 nm range disappeared and new ones appeared at higher energy with larger absorption coefficients. On the other hand, the absorption pattern exhibited by **3′** is different from the rest and showed only one band at 730 nm without any change in that at 360 nm even after exposure to light for 2–3 weeks (Fig. 3). The qualititative rate of conversion of these complexes in CH_2Cl_2 under identical photoirradiation conditions follow a trend, **4′** > **1′** > **2′** > **3′**, based on the growth of the bands in the region 500–900 nm. In solution, **1′**–**3′** are stable for 2–3 weeks, whereas **4′** precipitates in 1 d. The large ε values are indicative of l.m.c.t. transition. Such l.m.c.t. transitions in the visible region arise either from VO^{3+}, bare V^{5+} or V^{4+} bound to phenolate.[19,22] Based on EPR studies, the presence of V^{IV} is ruled out. Therefore conversion of $VO_2{}^+$ to VO^{3+} is envisaged in the presence of light.

Complex **1′**, isolated from a photoirradiated solution in CH_2Cl_2, showed a broad ν(OH) vibration at 3440 cm^{-1} and a strong ν(V=O) band at 975 cm^{-1} in the Fourier-transform IR spectrum. The absorption spectrum of this product upon redissolution in CH_2Cl_2 was the same as that observed for the photoirradiated product of **1** in CH_2Cl_2, with a low-energy band at 687 nm and another at 546 nm. The analytical data are consistent with a formula $[VO(OH)L^1(Cl)]\cdot CH_2Cl_2$.

Addition of acid. Absorption spectra observed upon addition of HCl to CH_2Cl_2 solutions of complexes **1**–**4** in 1 : 1 or 1 : 2 ratios are equivalent to those for the photoconverted products in CH_2Cl_2 solution (**1′**–**4′**). However, complete conversion of the species **1**–**4** to **1′**–**4′** was observed only when the acidic solutions were further exposed to fluorescent light for at least 30 min. In the absence of HCl, these conversions required irradiation periods of 4–24 h.

The effects of acid (HCl and CF_3SO_3H) were also studied in MeCN solutions for complexes **1** and **3**. Addition of 100 μl of concentrated HCl to 25 cm^3 of a 0.001 mol dm^{-3} solution of the complexes gave spectra similar to those obtained from photoirradiation in CH_2Cl_2 solution (**1′** and **3′**). Addition of CF_3SO_3H to complexes **1** and **3** resulted in a change from yellow to red and a broad band was observed around 580–590 nm with ε = 420–451 dm^3 mol^{-1} cm^{-1} but no low-energy bands (unlike the HCl reaction); the species are assignable to $[VO(OH)L]^+$. All these studies are indicative of the formation

$$[\mathrm{VO_2L}] \xrightleftharpoons[+\text{water}]{\mathrm{CH_2Cl_2},\,h\nu} [\mathrm{VO(OH)L(Cl)}] \xrightleftharpoons[h\nu]{+\text{water (100 µl)}} [\mathrm{VO_2L}]$$

Scheme 1

$$[\mathrm{VO_2L'}] \xrightleftharpoons[+\text{water}]{\mathrm{CH_2Cl_2},\,h\nu} [\mathrm{VO(OH)L'Cl)}] \xrightleftharpoons[\cancel{h\nu}]{+\text{water}} [\mathrm{VO_2L'}]$$

Scheme 2

of [VO(OH)L(Cl)] species upon photoirradiation of the original products in CH_2Cl_2 and this is better understood from ^{51}V NMR studies.

Addition of water. A 100 µl volume of water was added to 25 cm^3 of complex **1′**, **3′** or **4′** and the changes were monitored by absorption spectroscopy. The band in the visible region disappeared and bands identical to those of the $VO_2{}^+$ complexes (**1**, **3** and **4**) were noted after stirring for 15 min. When the aqueous solutions of **1′** and **4′** were once again exposed to fluorescent light they gave absorption spectra identical to those of **1′** and **4′**. This clearly suggested that, at least in the case of **1** and **4**, the photochemical reactions followed by addition of water are reversible and cyclic. While photoirradiation gives a chloro product, this upon water addition yields a dioxo product. This is explained as in Scheme 1. However these conversions were found to be non-cyclic in the case of **2** and **3**, as the water-containing CH_2Cl_2 solution of **2′** and **3′** is not affected by photoirradiation even over 1 week (Scheme 2). The formation of chloro species and their conversion to dioxo species are further supported by ^{51}V NMR studies.

^{51}V NMR spectra. The ^{51}V NMR spectra of photoirradiated solutions of complexes **1**–**4** in their **1′**–**4′** forms in CH_2Cl_2 were measured. While **2′** and **3′** showed a peak at δ −539 ± 1, those from **1′** and **4′** did not. This can be explained by the slow photoconversion of **2** and **3** as this peak is expected from the unchanged starting dioxovanadium(v) complexes **2** and **3**. Complex **1′** showed only one peak shifted downfield at δ −310, strongly indicating the formation of a monooxochloro species. Solutions of **2′** and **3′** also exhibited weak signals at δ −277 and −253 respectively, corresponding to their monochloro species. Even for **4′**, two signals were observed at δ −311 and −228 indicating the presence of both the mono- and di-chlorovanadium species. This is consistent with the inverse electronegativity principle observed among ^{51}V NMR chemical shifts.[23] For monooxomonochloro complexes, values previously found were δ −280 for $[VO(Cl)(pbha)_2]$ (pbha = *N*-phenylbenzohydroxamate),[23] δ −324 for di-µ-pinacolato-bis[chlorooxovanadium(v)][4] and δ −387 for $[\{VO(Cl)(OCH_2CH_2O)\}_2]$.[24] However, the trichloro complex, *mer*-$[VOCl_3(nppyc)]$ [nppyc = *N*-(2-nitrophenyl)pyridine-2-carboxamide] showed a peak at δ −83.[25]

Addition of water. Addition of water to the photoirradiated complexes in CH_2Cl_2 was also monitored by ^{51}V NMR spectroscopy. In all cases, the downfield signals completely disappeared and only a peak at δ −538 ± 1 was seen, indicating the conversion of the chloro species back to the dioxo ones.

Acknowledgements

G. A. thanks the Indian Council for Cultural Relations for financial support and the Government of Ethiopia for leave, A. S. the Department of Atomic Energy, India for a Dr. K. S. Krishnan research fellowship, C. P. R. the Department of Science and Technology, New Delhi for financial support and J. K. and E. K. the Academy of Finland for financial support. We are grateful to Mr. R. Kauppinen for his help in running the ^{51}V NMR spectra.

References

1 D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 148.
2 A. Butler and C. J. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61.
3 R. N. Lindquist, J. L. Lynn, jun., and G. E. Lienhard, *J. Am. Chem. Soc.*, 1973, **95**, 8762.
4 D. C. Crans, R. A. Felty and M. M. Miller, *J. Am. Chem. Soc.*, 1991, **113**, 265.
5 F. Hillerns, F. Olbrich, U. Behrens and D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 447.
6 L. M. Mokry and C. J. Carrano, *Inorg. Chem.*, 1993, **32**, 6119.
7 X. Li, M. S. Lah and V. L. Pecoraro, *Inorg. Chem.*, 1988, **27**, 4657.
8 C. A. Root, J. D. Hoeschele, C. R. Cornman, J. W. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1993, **32**, 3855.
9 G. Asgedom, A. Sreedhara, J. Kivikoski, J. Valkonen and C. P. Rao, *J. Chem. Soc., Dalton Trans.*, 1995, 2459.
10 G. Asgedom, A. Sreedhara and C. P. Rao, *Polyhedron*, 1995, **14**, 1873.
11 A. Sreedhara, M. S. S. Raghavan and C. P. Rao, *Carbohydr. Res.*, 1994, **264**, 227.
12 J. C. Duff, *J. Chem. Soc.*, 1934, 1351.
13 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
14 D. J. Watkin, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Chemical Crystallography Laboratory, University of Oxford, 1990.
15 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
16 W. R. Scheidt, D. M. Collins, and J. L. Hoard, *J. Am. Chem. Soc.*, 1971, **93**, 3873.
17 A. Giacomelli, C. Floriani, A. O. de Souza Dvarte, A. Chiesi-villa and C. Guastini, *Inorg. Chem.*, 1982, **21**, 3310.
18 C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944.
19 C. R. Cornman, G. J. Colpas, J. D. Hoeschele, J. Kampf and V. L. Pecoraro, *J. Am. Chem. Soc.*, 1992, **114**, 9925.
20 L. H. Simons, P. Barnett, E. G. M. Vollenbroek, H. L. Dekker, A. O. Muijsers, A. Messerschmidt and R. Wever, *Eur. J. Biochem.*, in the press; A. Messerschmidt and R. Wever, *J. Inorg. Biochem.*, 1995, **59**, in the press.
21 R. Wever, M. G. M. Tromp, B. E. Krenn, A. Marjani and M. Van Tol, *Environ. Sci. Technol.*, 1991, **25**, 446.
22 J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, 1986, **108**, 4088.
23 V. Vergopoulos, W. Priebsch, M. Fritzsche and D. Rehder, *Inorg. Chem.*, 1993, **32**, 1844.
24 S. R. Cooper, Y. B. Koh and K. N. Raymond, *J. Am. Chem. Soc.*, 1982, **104**, 5092.
25 D. Rehder, C. Weidemann, A. Duch and W. Priebsch, *Inorg. Chem*, 1988, **27**, 584.
26 D. C. Crans, R. A. Felty, O. P. Anderson and M. M. Miller, *Inorg. Chem.*, 1993, **32**, 247.
27 T. A. Kabanos, A. D. Keramidas, A. Papaioannou and A. Terzis, *Inorg. Chem.*, 1994, **33**, 845.

Received 7th August 1995; *Paper* 5/05279C