Pergamon

0277-5387(94)00461-7

Polyhedron Vol. 14, No. 13-14, pp. 1873-1879, 1995

0277-5387/95 $9.50+0.00

OXOVANADIUM(V) SCHIFF BASE COMPLEXES OF TRISHYDROXYMETHYLAMINOMETHANE WITH SALICYLALDEHYDE AND ITS DERIVATIVES: SYNTHESIS, CHARACTERIZATION AND REDOX REACTIVITY*

GEBRAY ASGEDOM, A. SREEDHARA and CHEBROLU P. RAO†

Bioinorganic Laboratory, Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India

(*Received* 6 *September* 1994; *accepted* 27 *October* 1994)

Abstract—Five vanadium complexes possessing the VO^{3+} motif with NO_4 coordination have been synthesized and characterized by ^1H and ^{13}C NMR, UV–Vis, FTIR and cyclic voltammetry. These complexes favour trigonal bipyramidal geometry. In DMF solution, complexes **1** and **5** have shown reversible redox behaviour in the presence of L-ascorbic acid or L-cysteine ethyl ester in air as monitored by electronic absorption and EPR studies.

The accumulation of vanadium by plants as well as sea animals has been known since the turn of the century. For example the mushroom, *Amanita muscaria* or fly agaric concentrates vanadium and stores it in amavadin, with a proposed primary coordination possessing six oxygens and two nitrogen atoms.[1] On the other hand, tunicates accumulate vanadates from sea water and store vanadium in their blood cells in the tetravalent and trivalent states.[2a] The species actually responsible for such reductions and storage in the blood cells are still debatable. Under physiological conditions vanadium(V) is easily reduced to vanadium(IV) inside the cell by small biomolecules.[2b] While early work suggests that pyrogallol rich molecules, tunichromes,[2a] are responsible for such actions, recent studies suggest a low molecular weight component possessing a reducing sugar, vanadobin.[3] Our on going efforts in transition metal saccharide chemistry and biology have resulted in the synthesis, isolation and characterization of several saccharide complexes including vanadium.[4] However, the role of vanadium in all these is a factor to be unveiled.

Of course vanadium is also known to be present in several marine algae with a definite catalytic function such as the bromination of organic substrates by being a constituent of the catalytic site in bromoperoxidase.[5] Though the EXAFS and other studies on the enzyme and its reduced form have provided certain metric parameters, a unique solution for the primary coordination and the form of vanadium (VO^{3+} or VO_2^+) are still unknown.[6] The reduced form of the halogenoenzyme containing VO^{2+} is inactive but regains its activity by reoxidation when exposed to air.[5c]

In the vanadium nitrogenase, the metal ion is known to be present as vanadium(III) and is active in the conversion of acetylene to ethane and hence differs from the role of its counterpart in molybdenum nitrogenase as the latter stops the reaction at ethylene.[7] In order to understand various roles played by this element, the study of small molecular complexes of vanadium in various oxidation states and their redox properties using biologically relevant coordination spheres has become essential. The present paper deals with the oxovanadium(V) Schiff base complexes derived from trishydroxymethylaminomethane (TRIS) and salicylaldehyde (SAL) and its derivatives, and also 2-hydroxy-1-naphthaldehyde (HNAP).

EXPERIMENTAL

Methods and Materials

All the methods of characterization are as per an earlier paper.[4] Salicylaldehyde, and trishydroxy-

* Dedicated to Professor C. N. R. Rao, F.R.S. on his sixtieth birthday.

† Author to whom correspondence should be addressed.

methylaminomethane were purchased from local sources (Loba chemie), distilled and recrystallized respectively before use. 3-Methoxysalicylaldehyde (OMESAL) and 5-hydroxysalicylaldehyde (OHSAL) were from Aldrich and Fluka respectively. 5-Methylsalicylaldehyde (MESAL) and 2-hydroxy-1-naphthaldehyde were synthesized from *p*-cresol and *β*-naphthol respectively, by Duff's method.[8] L-Cysteine ethyl ester was purchased from Sigma Co. (U.S.A.) and L-ascorbic acid was from local sources (Loba chemie). Ammonium metavanadate was purchased from Loba chemie and $V(acac)_3$ was synthesized according to a literature procedure.[9]

2-*Salicylideniminato*-2-(*hydroxymethyl*)-1,3-*dihydroxypropane-oxovanadium*(*V*) **(1)**. 2-Salicylideniminato-2-(hydroxymethyl)-1,3-dihydroxypropane (SALTRIS) was prepared by the addition of TRIS (20 mmol, 2.420 g) dissolved in 10 cm^3 of water to SAL (20 mmol, 2.442 g) dissolved in 10 cm^3 of MeOH. Yellow solution was observed immediately and crystals of SALTRIS started to appear and were allowed to grow for 5 days. The crystals were filtered, washed with ether and dried *in vacuo*, and found to be satisfactory based on elemental analysis, ^1H NMR and FTIR studies. To SALTRIS (0.450 g, 2 mmol) dissolved in 10 cm^3 MeOH was added $VO(acac)_2$ (0.530 g, 2 mmol) in 15 cm^3 MeOH. The mixture changed to brown with the formation of a precipitate. This was heated for 4 h, cooled to room temperature and filtered. Pure product of **1** was obtained by first suspending the residue in MeOH and separation and later by dissolving in DMSO, followed by reprecipitation with excess MeOH. The product was dried *in vacuo* following an ether wash to yield 70%. Found C, 46.0; H, 4.5; N, 5.0; V, 17.2; Calc. for $C_{11}H_{12}NO_5V$: C, 45.7; H, 4.1; N, 4.8; V, 17.6%. ^1H NMR: 9.03 (imine, 1H); 7.69–6.82 (ph, m, 4H); 5.46 (OH, t,1H); 5.10–4.95 (CH_2, m, 3H); 4.38–4.35 (CH_2, d, 1H); 3.91–3.80 (CH_2, m, 2H). ^{13}C NMR: 164.6 (imine); 162.7, 136.8, 135.5, 120.9, 119.6, 118.1 (ph); 80.0 (tertiary C); 86.7, 82.0, 63.1 (CH_2).

Compound **1** can also be prepared by other synthetic routes where *in situ* generated Schiff base ligand in MeOH was reacted with NH_4VO_3 or $V(acac)_3$. Irrespective of the starting material used, the final product has always been vanadium(V) complex due to aerial oxidation of the vanadium(III) or the vanadium(IV).

2-(5-*Methylsalicylideniminato*)-2-(*hydroxymethyl*)-1,3-*dihydroxypropane-oxovanadium*(*V*) **(2)**. To TRIS (5 mmol, 0.605 g) dissolved by heating in 20 cm^3 MeOH was added MESAL (5 mmol, 0.685 g) also in 10 cm^3 MeOH. The yellow solution formed was allowed to reflux gently for 30 min. $VO(acac)_2$ (5 mmol, 1.325 g) was added in 30 cm^3 MeOH to this solution and heated for 4 h, cooled to room temperature and filtered to give a solid product **2**. Purification was followed as for **1**. Found C, 47.5; H, 5.0; N, 4.8; V, 16.5. Calc. for $C_{12}H_{14}NO_5V$: C, 47.5; H, 4.6; N, 4.6; V, 16.8%. ^1H NMR: 8.95 (imine, 1H); 7.47–6.72 (ph, m, 3H); 5.42 (OH, b, 1H); 5.07–4.92 (CH_2, m, 3H); 4.35–4.32 (CH_2, d, 1H); 3.83 (CH_2, b, m, 2H); 2.30 (CH_3, 3H). ^{13}C NMR: 164.2 (imine); 160.8, 137.3, 134.7, 127.8, 120.4, 117.4 (ph); 79.6 (tertiary C); 86.3, 81.8, 63.0 (CH_2); 20.3 (CH_3).

2-(5-*Hydroxysalicyclideniminato*-2-(*hydroxymethyl*)-1,3-*dihydroxypropane-oxovanadium*(*V*) **(3)**. To TRIS (2 mmol, 0.242 g) dissolved by heating in 20 cm^3 MeOH was added OHSAL (2 mmol, 0.276 g) also in 10 cm^3 MeOH and the resulting yellow solution was refluxed gently for 30 min. $VO(acac)_2$ (2 mmol, 0.530 g) was added in 15 cm^3 MeOH to the *in situ* generated ligand and heated for 4 h, cooled to room temperature and filtered to give a solid product **3**. Purification was followed as for **1**. Found C, 42.9; H, 4.2; N, 3.9; V, 16.5. Calc. for $C_{11}H_{12}NO_6V$: C, 43.3; H, 3.9; N, 4.6; V, 16.7%. ^1H NMR: 10.38 (phenolic OH, 1H); 8.77 (imine, 1H); 7.47–8.14 (ph, m, 3H); 5.40–5.37 (OH, t, 1H); 5.04–4.87 (CH_2, m, 3H); 4.31–4.28 (CH_2, d, 1H); 3.87–3.75 (CH_2, m, 2H). ^{13}C NMR: 164.5 (imine); 165.3, 162.4, 136.5, 114.0, 108.6, 102.8 (ph); 79.4 (tertiary C); 86.1, 82.1, 63.2 (CH_2).

2-(3-*Methoxysalicylideniminato*)-2-(*hydroxymethyl*)-1,3-*dihydroxypropane-oxovanadium*(*V*) **(4)**. To TRIS (3 mmol, 0.363 g) dissolved by heating in 20 cm^3 MeOH was added OMESAL (3 mmol, 0.456 g) also in 10 cm^3 MeOH and the reaction mixture was refluxed gently for 30 min. $VO(acac)_2$ (3 mmol, 0.795 g) was added in 20 cm^3 MeOH to this mixture and heated for 4 h, cooled to room temperature and filtered to give a solid product **4**. Purification was followed as for **1**. Found C, 44.6; H, 4.1; N, 3.8; V, 15.7. Calc. for $C_{12}H_{14}NO_6V$: C, 45.1; H, 4.4; N, 4.4; V, 16.0%. ^1H NMR: 9.00 (imine, 1H); 7.28–6.87 (ph, m, 3H); 5.47–5.43 (OH, t, 1H); 5.06–4.95 (CH_2, m, 3H); 4.34–4.31 (CH_2, d, 1H); 3.89–3.78 (CH_2 and OCH_3, m, 5H). ^{13}C NMR: 164.4 (imine); 153.2, 148.5, 126.4, 120.8, 118.7, 118.2 (ph); 79.7 (tertiary C); 86.4, 81.9, 63.1 (CH_2); 56.8 (OMe).

2-(2-*Hydroxy*-1-*naphthalideniminato*)-2-(*hydroxymethyl*)-1,3-*dihydroxypropane-oxovanadium*(*V*) **(5)**. To TRIS (5 mmol, 0.605 g) dissolved by heating in 20 cm^3 MeOH was added HNAP (5 mmol, 0.860 g) also in 10 cm^3 MeOH and the solution was refluxed gently for 30 min. $VO(acac)_2$ (5 mmol, 1.325 g) was added in 30 cm^3 MeOH to this solution and heated for 4 h, cooled to room

temperature and filtered to give a solid product **5**. Purification was followed as for **1**. Found C, 53.1; H, 4.2; N, 4.0; V, 15.3. Calc. for $C_{15}H_{14}NO_5V$: C, 53.1; H, 4.1; N, 4.1; V, 15.0%. ^1H NMR: 9.83 (imine), 1H); 8.48–7.11 (naph, m, 6H); 5.58–5.54 (OH, t, 1H); 5.28–5.13 (CH_2, q, 2H); 5.04–5.00 (CH_2, d, 1H); 4.46–4.43 (CH_2, d, 1H); 4.05–3.96 (CH_2, m, 2H). ^{13}C NMR: 163.6 (imine); 159.0, 137.3, 133.5, 129.4, 128.8, 128.1, 124.1, 120.8, 110.8 (naph); 80.5 (tertiary C); 86.8, 81.8, 63.0 (CH_2).

RESULTS AND DISCUSSION

Electronic absorption spectral studies

Complexes **1–5** showed two interesting LMCT transitions in DMF in the ranges 475–520 and 340–380 nm as reported in the literature.[10] Typical spectra are shown in Fig. 1. The spectra are generally characteristic of vanadium either in VO^{3+} or bare vanadium(V) form, while the former is confirmed by FTIR spectra. The LMCT transition (475–520 nm; ε: 300–400 M^{-1} cm^{-1}) is attributed to a charge transfer from a p_π orbital on the phenolate to the empty *d*-orbitals. A decrease in the LMCT energy is observed from **1** to **5**, with a maximum shift of about 1280 cm^{-1} in the case of **4** and **5** with respect to **1**. This may be attributed to the easy oxidizability of the ligand. The other LMCT bands observed in the UV region (340–380 nm; ε: 4800–6300 M^{-1} cm^{-1}) is generally attributable to either the alkoxo bound or phenolate bound vanadium(V) species. The molar absorptivity (ε) of these transitions are in agreement with those obtained for similar transitions in the literature.[10c] An identical spectral behaviour was observed for these complexes in DMSO.

The absorption of the complexes **1–5** in the solid showed a broad shoulder $\simeq$ 500 nm and a broad band in the range 300–400 nm similar to that observed in solution suggesting that the structure of the complexes is retained in the solution as well.

FTIR studies

FTIR spectra of complexes **1–5** were measured in a KBr matrix and those of **1**, **2** and **5** are shown in Fig. 2. Complex **5** exhibited an extremely sharp band for ν_{OH} at 3546 cm^{-1} ($\Delta\nu_{1/2}$ = 17 cm^{-1}) for a completely free OH group; however, the ν_{OH} region for the complexes **1–4** possess a broad asymmetric band ($\Delta\nu_{1/2} \sim 320$ cm^{-1}) with two very weak shoulders positioned one on the higher and the other on the lower energies. While the main stretching vibration in this region (3390–3430 cm^{-1}) is assigned to intermolecular hydrogen bonding, the higher energy shoulder (3490–3530 cm^{-1}) to free

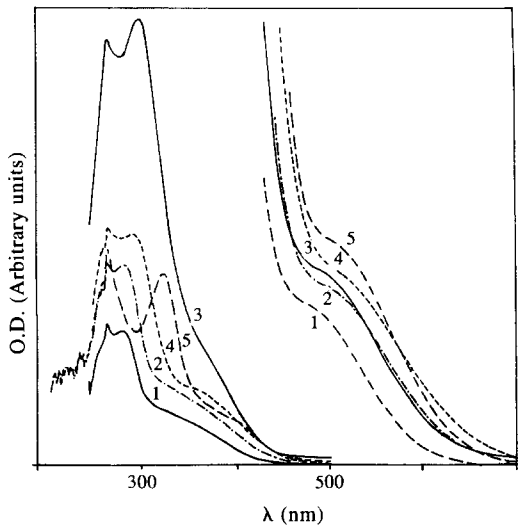

Fig. 1. Absorption spectra of complexes **1–5**. Numbers on spectra indicate the compound number.

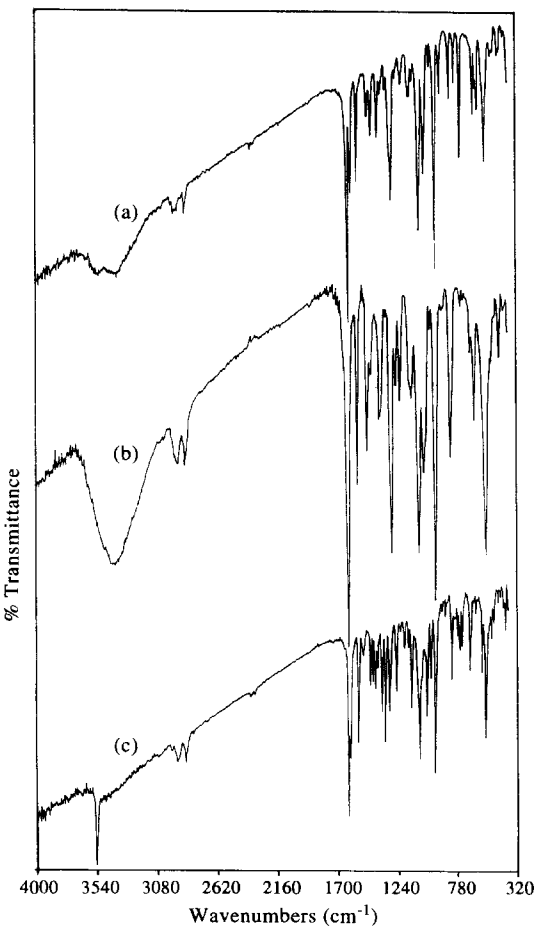

Fig. 2. FTIR spectra of complexes: (a) **1**; (b) **2**; and (c) **5**; in KBr matrix.

ν_{OH} and the lower energy shoulder (3320–3350 cm^{-1}) to a ν_{OH} that is involved in a moderately strong intermolecular hydrogen bonding. Involvement of the C=N group in metal coordination is evidenced through the shift of the $\nu_{C=N}$ by 20–30 cm^{-1} to lower energy in the complexes **1–5**. ν_{V-N} is noted in the range 568–578 cm^{-1}.[11] The characteristic $\nu_{V=O}$ stretching frequency[12] that is observed in the region 950–960 cm^{-1} seems to indicate no influence of the intermolecular hydrogen bonding in **1–4**, but may be indicative of $\nu_{V=O}$ stretch that has *trans* coordination. Thus based on the FTIR study it is possible to deduce that while the unbound OH in **5** is free from intermolecular hydrogen bonding, the same is involved in extensive hydrogen bonding in the cases **1–4**. Further the deprotonated hydroxyls of the neighbouring molecules act as hydrogen bond acceptors.

NMR studies

Proton NMR spectra of all the complexes are characteristic of the loss of protons from the phenolic OH and two alkoxy OH groups thereby suggesting a binding of three oxygens to the vanadium(V) centre in the complexes. The downfield shift of about 0.52 ppm for the imine hydrogens also confirms the binding of the imine nitrogen to the vanadium(V) centre. The three CH_2 groups which are equivalent in the ligand spectra have become nonequivalent due to the considerable perturbation which occurs upon complexation. Typical proton NMR spectra of the ligand (SALTRIS) and its complex **(1)** in this region are shown in Fig. 3. While one of the CH_2 groups is found unperturbed, the other two have shown a large downfield shift. The hydrogens of these two CH_2 groups were observed as one multiplet accounting for three hydrogens and another doublet accounting for one hydrogen, where the centre of the multiplet and the doublet are separated by 0.57–0.69 ppm in complexes **1–5** depending upon the substitution on the salicylaldehyde. Thus the proton NMR spectra are indicative of the involvement of only two CH_2OH groups in metal binding while the third CH_2OH group is free. This is further supported by the presence of a triplet corresponding to a free CH_2OH group in the spectra of complexes. The observed pattern of the perturbed CH_2OH groups in the spectra may be attributed to the stereochemical orientation of these groups, with respect to the V=O group.

The information obtained from ^1H NMR is fully supported by the ^{13}C NMR spectra of these complexes where the δ of one CH_2 carbon is unperturbed and the other two have shown downfield

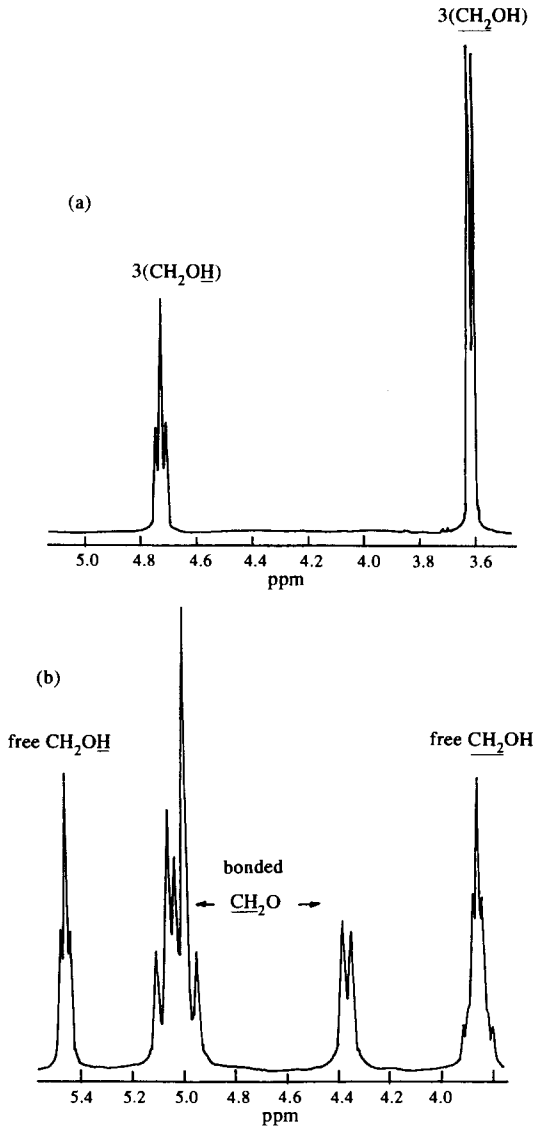

Fig. 3. A region of ^1H NMR spectra of (a) SALTRIS ligand and (b) complex **1**.

shifts of about 20 and 24 ppm respectively. Appropriate downfield shifts were observed with imine, tertiary carbon and phenolic carbons indicating the binding of the Schiff base to the vanadium(V) centre. Assignment of the tertiary carbon and the methylene carbon resonances was done based on a partially decoupled experiment.

Electrochemical studies

The electrochemical properties of oxovanadium(V) complexes **1–5** were examined with cyclic voltammetry in DMF solution at a Pt electrode. While complexes **1**, **2**, **4** and **5** showed reversible redox behaviour corresponding to a $V^V \rightleftarrows V^{IV}$ couple, complex **3** showed an irreversible reduction. All the voltammograms and their peak potentials

are shown in Fig. 4. The reversible redox nature of **1**, **2**, **4** and **5** was also reflected in their i_p^c/i_p^a ratios and from their ΔE_p values when compared with the standard ferrocene measured under the same conditions. The calculated $E_{1/2}$ values for these complexes are in the range −470 to −400 mV with respect to Ag/AgCl. It is noteworthy that the potentials of the V^V/V^{IV} couple in these complexes are more negative than those observed for the other vanadium(V) complexes.[13] The stabilization of the higher oxidation state in these complexes may be attributed to strong π donation of the alkoxy groups to the vanadium centre. In the case of complex **4** the reduction of $VO^{3+} \rightarrow VO^{2+}$ is easier than the unsubstituted complex **1**. Based on model molecules it has been understood that the easier the reduction of vanadium(V), the lower the energy of its LMCT band.[10] In fact the LMCT band in the absorption spectrum of **4** was found at the lowest energy of all reported in this paper. Molecular modelling experiments in the case of substituted SALOPHEN complexes have indicated that the substituents in the 3-position brings crowding which might result in tilting of the aromatic ring out of the planar arrangement.[14] This results in a coordinatively less favoured orientation for phenolic oxygen atom and thus makes 3-OMe-SALTRIS a poorer donor overall than SALTRIS and hence its electrochemical and absorption behaviour. However, no such steric influence is possible for 5-substituted ones. Since the LMCT band was found as a shoulder around 315 nm in the native bromoperoxidase, it was suggested that it is difficult to reduce the vanadium(V) centre and the enzyme.[10c]

Structures of these complexes have been proposed based on these studies and a representative one is shown in Fig. 5 along with the sketch of the ligand.

Chemical redox in solution

Solution redox reactivity of complexes **1** and **5** was studied using L-ascorbic acid and L-cysteine ethyl ester as reducing agents at a 1 : 2 mole ratio and were monitored by absorption and EPR spectra. The absorption pattern for complex **1** using L-ascorbic acid as reductant is shown in Fig. 6. Upon reacting the complexes with the reducing agent in DMF, a gradual change of the colour from red to green was observed initially. This resulted in the decrease in intensity of the broad bands observed around 490 nm in parental complexes as a function of time and finally shifted to 540 nm after periods of 70 and 120 min in case of L-ascorbic acid (Fig. 6a) and L-cysteine ethyl ester respectively for complex **1**. For complex **5**, these periods were 30 and 75 min, respectively, for L-ascorbic acid and L-cysteine ethyl ester. During the same period a new band

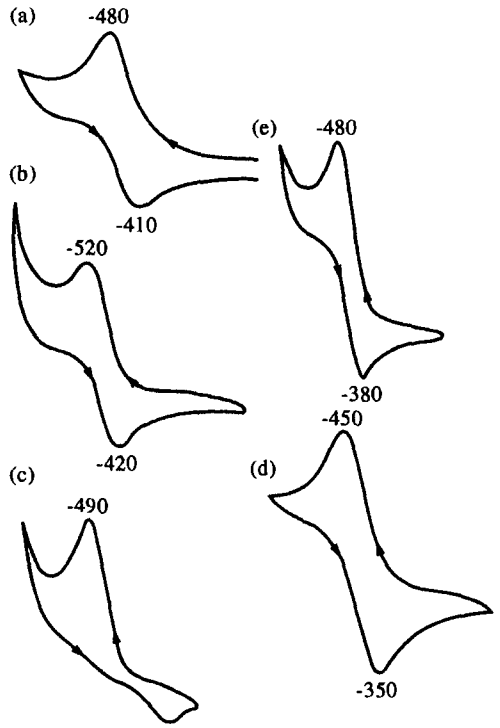

Fig. 4. Cyclic voltammetry of complexes (a) **1**; (b) **2**; (c) **3**; (d) **4**; and (e) **5**. Working electrode: Pt; scan speed: 100 mV s^{-1}; supporting electrolyte: 0.1 M Et_4NBr; Reference electrode: Ag/AgCl.

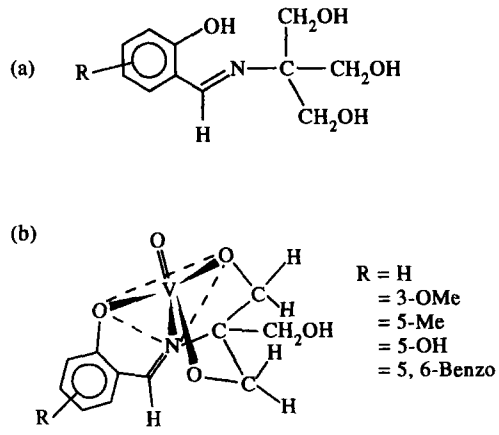

Fig. 5. Schematic representations of the ligand (a) and its proposed vanadium complex (b).

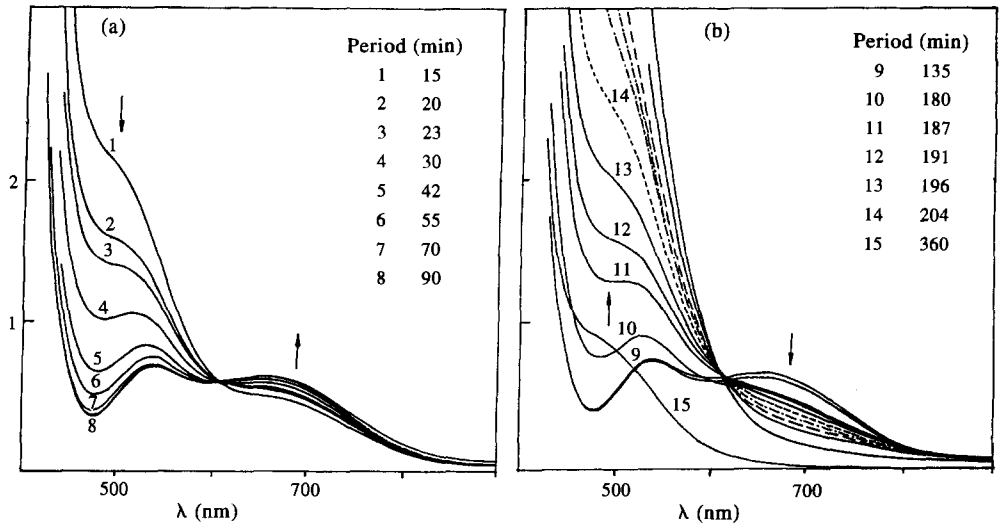

Fig. 6. Absorption spectra of complex **1** in the presence of L-ascorbic acid in 1 : 2 ratio: (a) during reduction and (b) during reoxidation of the reduced species. (A 5 cm cell was used for recording all the absorption spectra except for 15 where a 1 cm cell was used.)

appeared at 660 nm whose intensity increases as a function of time and the spectra goes through an isosbestic point at 610 nm. These spectral changes are indicative of the interconversion of oxidized [vanadium(V)] and reduced vanadium(IV) species. This information is supported by the formation of incremental amounts of vanadium(IV) signal in EPR as a function of time. When the solutions were left in air for periods beyond the complete reduction, the colour changes back to the original indicating reoxidation of the reduced species. These changes were also monitored by both absorption and EPR spectra. Typical spectra for the reoxidation process for **1** with L-ascorbic acid are shown in Fig. 6b. The spectral changes are indicative of a reversible redox reactivity of complexes **1** and **5** in the presence of 1 : 2 ratio of complex to the reducing agents. Use of excess reducing agent (more than 1 : 6 ratio) delays the reoxidation. This solution behaviour indicates that the redox nature is of simple electron transfer type rather than forming any stable complexes with the reducing agents, L-ascorbic acid and L-cysteine ethyl ester. Complex **1** was also found to be reduced in acidic DMF solutions.

Acknowledgements—G.A. is under the Cultural Exchange Programme from Ethiopia. A.S. thanks the Department of Atomic Energy, Government of India, for the award of the Dr K. S. Krishnan research fellowship. Financial support by DST, India, to C.P.R. is gratefully acknowledged. Thanks are also due to Ms S. Sukeerthi for some experimental help.

REFERENCES

1. H. Kneifel and E. Bayer, *Angew. Chem., Int. Ed. Engl.* 1973, **12**, 508.
2. (a) M. J. Smith, D. Kim, B. Horenstein, K. Nakanishi and K. Kustin, *Acc. Chem. Res.* 1991, **24**, 117; (b) H. Sakurai, S. Shimomura and K. Ishizu, *Inorg. Chim. Acta* 1981, **55**, L67.
3. H. Michibata, T. Miyamoto and H. Sakurai, *Biochem. Biophys. Res. Commun.* 1986, **141**, 251.
4. (a) C. P. Rao, P. S. Sarkar, S. P. Kaiwar and S. Vasudevan, *Proc. Ind. Acad. Sci. (Chem. Sci.)* 1990, **102**, 219; (b) C. P. Rao and S. P. Kaiwar, *Inorg. Chim. Acta.* 1991, **186**, 11; (c) C. P. Rao and S. P. Kaiwar, *Carbohydr. Res.* 1992, **237**, 203; (d) C. P. Rao, K. Geetha and R. P. Bandwar, *BioMed. Chem. Lett.* 1992, **2**, 997; (e) C. P. Rao, K. Geetha and M. S. S. Raghavan, *BioMetals* 1994, **7**, 25; (f) C. P. Rao, S. P. Kaiwar and M. S. S. Raghavan, *Polyhedron* 1994, **12**, 1895; (g) R. P. Bandwar, M. S. S. Raghavan and C. P. Rao, *BioMetals*, 1995, **8**, 19; (h) A. Sreedhara, M. S. S. Raghavan and C. P. Rao, *Carbohydr. Res.* 1994, **264**, 227; (i) S. P. Kaiwar, R. P. Bandwar, M. S. S. Raghavan and C. P. Rao, *Proc. Indian Acad. Sci., (Chem. Sci.)* 1994, **106**, 743.
5. (a) H. Vitler, *Phytochemistry* 1984, **23**, 1387; (b) R. Wever, E. de Boer, H. Plat and B. E. Krenn, *FEBS Lett.* 1987, **216**, 1; (c) K. Knuttel, A. Muller, D. Rehder, H. Vitler and V. Wittneben, *FEBS Lett.* 1992, **302**, 11.
6. J. M. Arber, E. de Boer, C. D. Garner, S. S. Hasnain and R. Wever, *Biochemistry* 1989, **28**, 7968.
7. R. L. Robson, R. R. Eady, T. H. Richardson, R. W.

Miller, M. Hawkins and J. R. Postgate, *Nature* 1986, **322**, 388.
8. (a) J. C. Duff, *J. Chem. Soc.*, 1941, 541; (b) J. C. Duff, *J. Chem. Soc.* 1934, 1305.
9. D. Grdenic and B. Korpar-Colig, *Inorg. Chem.* 1964, **3**, 1328.
10. (a) C. J. Carrano, K. Spartalian, G. V. N. Appa Rao, V. L. Pecoraro and M. Sundaralingam, *J. Am. Chem. Soc.* 1985, **107**, 1651; (b) J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.* 1986, **108**, 4088; (c) C. J. Carrano, M. Mohan, S. M. Holmes, R. de la Rosa, A. Butler, J. M. Charnock and C. D. Garner, *Inorg. Chem.* 1994, **33**, 646.
11. G. A. Kolawole and K. S. Patel, *J. Chem. Soc., Dalton Trans.* 1981, 1241.
12. (a) A. Syamal and K. S. Kale, *Inorg. Chem.* 1979, **18**, 992; (b) A. Syamal and L. J. Theriot, *J. Coord. Chem.* 1973, **2**, 193.
13. (a) J. Chakravarthy, S. Dutta, S. K. Chandra, P. Basu and A. Chakravorthy, *Inorg. Chem.* 1993, **32**, 4249; (b) U. Auerbach, B. S. P. C. Della Vedova, K. Weighardt, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.* 1990, 1004.
14. R. K. Boggess, J. W. Hughes, W. M. Coleman and L. T. Taylor, *Inorg. Chim. Acta* 1980, **38**, 183.