

## Synthesis, Structure and Electrochemical Characterization of a New Non-oxo Vanadium(IV) Complex

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Reaction of *N,N,N',N'*-tetrakis(2-hydroxybenzyl)ethylenediamine ( $H_4tben$ ) with  $VCl_3$  in tetrahydrofuran in the presence of  $Et_3N$  affords  $[Et_3NH][V^{III}(tben)]$  which is oxidized by oxygen to the stable  $[V^{IV}(tben)]$  complex; the X-ray crystal structure, and the electrochemical, magnetic and electronic spectroscopic properties of  $[V^{IV}(tben)] \cdot CH_2Cl_2$  are reported.

It is well established that vanadium is present at the active site of certain enzymes, including haloperoxidases in sea algae and lichens<sup>1</sup> and some nitrogenases in nitrogen-fixing *Azotobacter*.<sup>2</sup> Furthermore, vanadium ions are bound to tyrosinate residues in vanadium-modified transferrin<sup>3</sup> and amavadim,<sup>4</sup> and certain sea squirts or tunicates<sup>5</sup> (polyphenol ascidians) are able to store vanadium in high concentrations. In view of the importance of the interaction of  $V^{III}$ ,  $V^{IV}$  and  $V^V$  with tyrosinate residues,<sup>3,5</sup> vanadium-phenolate chemistry is receiving considerable attention.<sup>6</sup> However, in contrast to the well known vanadium(IV)/(V)-phenolate complexes containing  $VO^{2+}$  or  $VO^{3+}$  units, only very few octahedral non-oxo  $V^{IV}$  and  $V^V$  complexes, the so-called 'bare' complexes, have been isolated and structurally characterized.<sup>7</sup> The  $[V^{IV}(\text{cat})_3]^{2-}$  (cat = catecholato)<sup>8</sup> and  $[LV^{IV}]^+$  [ $H_3L = 1,4,7$ -tris(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane]<sup>9</sup> ion complexes represent two structurally well characterized examples. More recently, we<sup>10</sup> reported the electrochemical and electronic spectroscopic characterization of the less stable  $[V^{IV}(\text{bbpen})]^{2+}$  [ $H_2\text{bbpen} = N,N'$ -bis(2-hydroxybenzyl)-*N,N'*-bis(2-pyridylmethyl)ethylenediamine] ion complex, for which the X-ray structure of the corresponding  $[V^{III}(\text{bbpen})]^+$  has been described.<sup>10</sup> In this work, we report the preparation, structural characterization, and electrochemical and electronic spectroscopic properties of a non-oxo vanadium(IV) complex, with a new  $N_2O_4$ -donor ligand which contains the ethylenediamine backbone and four phenolate-type pendant arms. This is part of our programme for preparation and characterization of vanadium complexes with bioinorganic relevance.

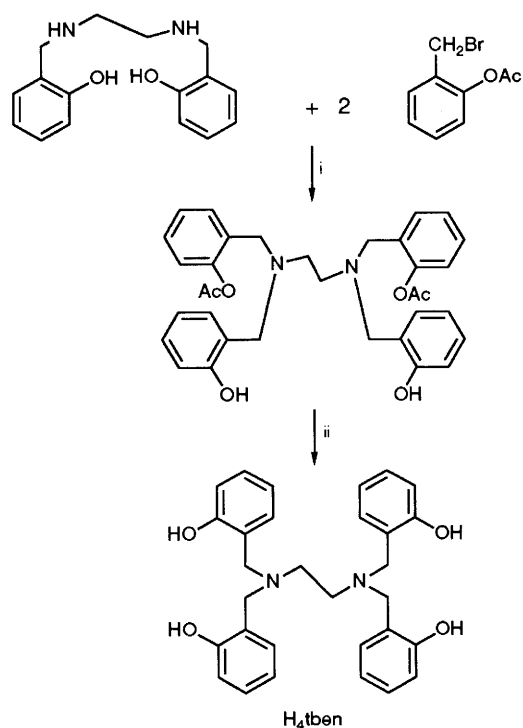
The ligand *N,N,N',N'*-tetrakis(2-hydroxybenzyl)ethylenediamine ( $H_4tben$ ) was prepared in good yield by alkylation of *N,N'*-bis(2-hydroxybenzyl)ethylenediamine ( $H_2\text{bben}$ )<sup>11</sup> with 2-bromomethylphenyl acetate,<sup>12</sup> by the route in Scheme 1. The vanadium(III) complex was prepared as follows. A

solution of  $VCl_3$  in dry tetrahydrofuran (thf) was refluxed for 30 min under an argon atmosphere and equimolar quantities of  $H_4tben$  and  $Et_3N$  were added to the hot solution. A green precipitate of  $[Et_3NH][V(tben)]$  **1** was immediately formed. This material is very air-sensitive, and was characterized only by IR spectroscopy. Treatment of a hot solution of **1** in  $CH_2Cl_2$  with dry  $O_2$  afforded a clear deep-purple solution. After cooling the solution to 5 °C, a microcrystalline precipitate of purple  $[V^{IV}(tben)] \cdot CH_2Cl_2$  was formed, which was filtered off, washed with ethanol and air dried.† Single crystals of **2** suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a  $CH_2Cl_2$  solution of **2**.

The molecular‡ structure and atomic numbering scheme of **2** are illustrated in Fig. 1. The vanadium(IV) ion is in a pseudo-octahedral environment, in which each of the two symmetrical halves of the  $tben^{4-}$  ligand are in a facial arrangement (*fac*- $NO_2$  donor set): two phenolate oxygen and two aliphatic nitrogen atoms of the ethylenediamine backbone

† All new compounds gave satisfactory elemental analysis (C, H, N).

‡ Crystal data for **2**:  $[C_{30}H_{28}N_2O_4V] \cdot CH_2Cl_2$ ,  $M = 616.44$ : monoclinic,  $P2_1/c$ , ( $C_{2h}^5$ ; No. 14),  $a = 10.360(1)$ ,  $b = 20.984(5)$ ,  $c = 13.322(4)$  Å,  $\beta = 103.0(2)^\circ$ ,  $V = 2822(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.48$  g cm<sup>-3</sup>. Crystal dimensions  $0.13 \times 0.45 \times 0.25$  mm, Mo-K $\alpha$  ( $\lambda = 0.7107$  Å);  $T = 298$  K. Enraf-Nonius CAD-4 diffractometer. Data were reduced using the Structure Determination Package (SDP) and the structure was solved with the SHELX-76 program package. Hydrogen atoms were located from Fourier difference maps and fixed with  $B$  values of 3.95 Å<sup>2</sup>;  $\mu = 5.25$  cm<sup>-1</sup>; 4919 unique reflections; 2287 with  $I > 3\sigma(I)$ ; 362 least-squares parameters;  $R = 0.052$  ( $R_w = 0.051$ ). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



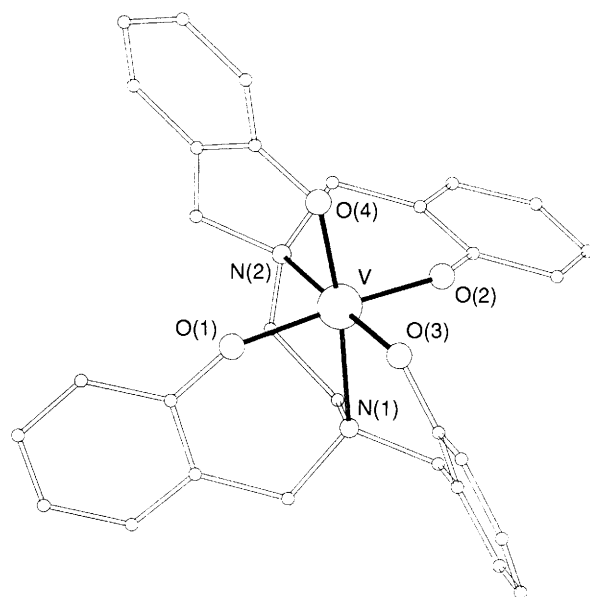
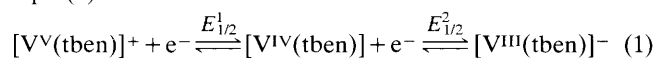
**Scheme 1** Synthesis of the ligand  $H_4tben$ : reagents and conditions: i, thf,  $Et_3N$ , argon; ii, methanol, KOH

form the equatorial plane, where atoms of the same type occupy *cis*-positions with respect to each other. The remaining phenolate oxygen atoms, mutually *trans*, complete the coordination sphere. The V–N (amine) and V–O bond lengths [av. 2.182(5) and 1.874(4) Å] in the equatorial plane of **2** are 0.05 and 0.013 Å, respectively, shorter than the corresponding bond distances in the  $[V^{III}(bbpen)]^+$  complex,<sup>10</sup> consistent with the higher oxidation state of the former. On the other hand, the mean value of the four V–O bond distances of 1.863(4) Å is significantly shorter than in the catecholate vanadium(IV) complex  $[Et_3NH][V^{IV}(cat)_3] \cdot MeCN$  [av. 1.930(3) Å]<sup>8</sup> and somewhat longer than in the  $[V^{IV}L][BPh_4]$  complex [av. 1.827(5) Å].<sup>9</sup>

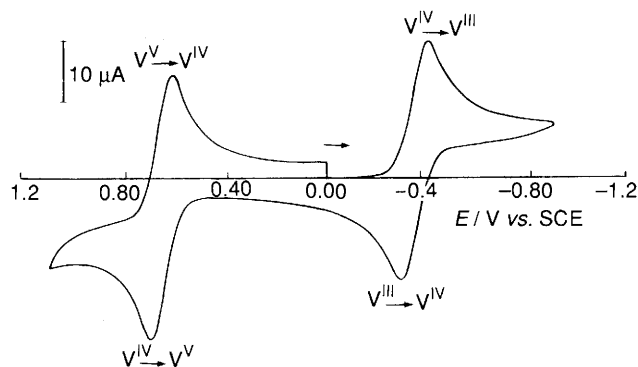
The data for temperature dependence of the magnetic susceptibility of **2**, using the Faraday method, fit the Curie–Weiss law between 4.2 and 284.5 K with  $\mu_{eff} = 1.64 \mu_B$ , which is expected for a mononuclear complex of vanadium(IV) ( $d^1$  configuration) with no or very small intermolecular magnetic coupling.

The electronic spectrum of **2** measured in MeCN solution consists of the following transitions at  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ): 512 (9800) and 400 (6500). The lowest energy band at 512 nm is assigned, by analogy with other reported 'bare' vanadium(IV) complexes,<sup>8–10</sup> as being a phenolate-to-vanadium(IV) charge-transfer (CT) transition. The higher energy transition at 400 nm, which is absent in the free ligand, is also assigned to a phenolate-to-vanadium(IV) CT transition and probably arises from the different V–O bond lengths in **2**.

The electrochemical properties of **2** in dimethylformamide (dmf) have been investigated by cyclic voltammetric (CV) and coulometric techniques (Fig. 2). At scan rates of 50–400  $mV s^{-1}$  two well defined reversible one-electron-transfer waves were detected at  $E_{1/2}^1 + 0.16 V$  and  $E_{1/2}^2 - 0.84 V$  vs.  $Fc^+/Fc$ . These data are consistent with the process shown in eqn. (1).



**Fig. 1** X-Ray structure of **2**. Selected bond lengths (Å) and angles ( $^\circ$ ): V–O(1) 1.848(4), V–O(2) 1.853(4), V–O(3) 1.877(4), V–O(4) 1.872(4), V–N(1) 2.192(5), V–N(2) 2.171(5); O(1)–V–O(2) 168.0(2), O(1)–V–O(3) 96.6(2), O(1)–V–O(4) 90.3(2), O(1)–V–N(1) 84.8(2), O(1)–V–N(2) 88.0(2), O(2)–V–O(3) 91.1(2), O(2)–V–O(4) 98.3(2), O(2)–V–N(1) 85.9(2), O(2)–V–N(2) 83.8(2), O(3)–V–O(4) 94.4(2), O(3)–V–N(1) 91.1(2), O(3)–V–N(2) 173.9(2), O(4)–V–N(1) 173.0(2), O(4)–V–N(2) 89.6(2), N(1)–V–N(2) 85.2(2).



**Fig. 2** Cyclic voltammogram of  $[V^{IV}(tben)] \cdot CH_2Cl_2$  in dmf (0.1 mol  $dm^{-3}$   $[Bu_4N][PF_6]$  supporting electrolyte, platinum working electrode, ferrocene internal standard, scan rate 400  $mV s^{-1}$ ) (SCE = standard calomel electrode)

Controlled potential coulometric measurements on **2** at 0.4 V vs.  $Fc^+/Fc$  revealed that this species is oxidized by  $1.00 \pm 0.05$  electrons per vanadium centre. The CVs of this solution and **2** are identical under the same conditions, and the starting material can be regenerated with reelectrolysis at 0.0 V vs.  $Fc^+/Fc$ . The deep-blue oxidized species is stable for at least 48 h, and its electronic spectra consists of two very intense bands at  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ): 678 (15000) and 318 (14000). This spectrum is similar to that reported for the  $[V^VL]^{2+}$  ion complex,<sup>9</sup> but red shifted by 40 nm, consistent with the presence of four  $O_{phenolate}$  donors in **2**. The coulometric reduction of **2** at  $-1.2 V$  vs.  $Fc^+/Fc$  confirms the result obtained from CV studies, indicating that this is also a one-electron-transfer process, involving the  $[V^{III}(tben)]^-$  complex. A more detailed characterization of the  $[V^{III}(tben)]^-$  and  $[V^V(tben)]^+$  'bare' complexes, as well as the structural and electrochemical characterization of two new

VO<sup>2+</sup> and VO<sup>3+</sup> derivatives with tben<sup>4-</sup>, are in progress and will be published elsewhere.

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