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LETTER

A new N,O-donor hexadentate ligand and its first vanadium(III) complex

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Vanadium has an important role in many biological processes. It is an essential trace element of living plants and animals and it has significant effects for normal growth [1]. However, in contrast to many other of the biologically important transition metals (Fe, Cu, Mo, etc.) the biochemistry of vanadium is still poorly understood. In view of the recent reported binding of vanadium to tyrosinate residues in vanadium-modified transferrin [2], and its interaction with the characterized polyphenol, tunichrome, in the vanadocytes of the tunicates [3], vanadium phenolate chemistry is receiving considerable attention from the inorganic chemist [4–6]. In order to understand how vanadium might function in a complex biomolecule, we have started a new programme to investigate the coordination chemistry of hexadentate ligands derived from alkyldiamines containing phenolate-type and α-pyridyl pendant arms. Herein we describe the preparation, structural characterization and electrochemical properties of such a complex.

Experimental

Synthesis of H_2BBPEN

The ligand *N,N′,N,N′*-bis[(2-hydroxybenzyl)(2-methylpyridyl)]ethylenediamine (H_2BBPEN) was prepared by alkylation of the reduced form of SALEN with 2-(chloromethyl)pyridine. ^1H NMR ($CDCl_3$; δ): 10.6 (s, two phenolic protons), 6.75–8.5 (m, 16H, phenyl and py), 3.6–3.8 (d, 8H, N–CH_2–R), 2.7–2.8 (s, 4H, N–CH_2–CH_2–N). MS: *m/z* 455.

Synthesis of $[V^{III}(BBPEN)][PF_6]$

The vanadium(III) complexes were prepared according to the following procedure. A solution of VCl_3 in dry MeCN was refluxed for 15 min under an argon atmosphere and equimolar quantities of H_2BBPEN and Et_3N were added to the hot solution. A green precipitate of $[V^{III}(BBPEN)][Cl]$ (**1**) was formed. Treatment of a hot solution of **1** with NH_4PF_6 under argon initiated the precipitation of microcrystalline $[V^{III}(BBPEN)][PF_6]$ (**2**). Single crystals suitable for X-ray crystallography were obtained by recrystallization from a 2-propanol–acetone (1:1) solution of **2**. *Anal.* Calc. for $[C_{28}H_{28}N_4O_2V][PF_6]$: C, 51.86; H, 4.43; N, 8.64. Found: C, 52.1: H, 4.5; N, 8.6%.

Results and discussion

The molecular structure** and atomic numbering scheme of **2** are shown in Fig. 1. The vanadium(III) ion is in a pseudo-octahedral environment: two phenolato oxygen and two aliphatic nitrogen atoms of the ethylenediamine backbone form the equatorial plane, where the atoms of the same nature occupy the *cis* positions with respect to each other. The remaining pyridine nitrogen atoms, mutually *trans*, complete the coordination sphere. The V–O bond distances in **2** (av. 1.887 Å) are similar to those found in the $[V^{III}(SALEN)(py)_2][ZnCl_3py]$ complex (av. 1.897 Å) [5] but significantly shorter than in the catecholato vanadium(III) complex $[K_3][V(cat)_3]1.5H_2O$ (av. 2.013 Å) [7]. In addition, it is important to note that the N(2)–V(1)–N(4) bond angle of 168.6(1)° in complex **2** is somewhat shorter than the corresponding angle of 177.1(5)° in the $[V(SALEN)(py)_2]^+$ ion complex.

The data for temperature dependence of the magnetic susceptibility of **2** using the Faraday method fit the Curie–Weiss law between 93 and 293 K with the spin only value of 2.83 μ_B for the $V^{III}(d^2)$ complex.

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Crystal data for **2: $[C_{28}H_{28}N_4O_2V][PF_6]$, $M=648.5$ triclinic, $P\bar{1}$, (C_i^1; No. 2), $a=11.036(6)$, $b=11.102(7)$, $c=12.017(7)$ Å, $\alpha=90.78(4)$, $\beta=91.46(4)$, $\gamma=108.14(4)$°, $V=1398.35$ Å^3, $Z=2$; $D_c=1.54$ g cm^{-3}. Crystal dimensions 0.19×0.26×0.42 mm; Mo Kα (0.7107 Å); $T=298$ K. AED II Siemens diffractometer. Data were reduced using SHELXTL PLUS program package and the structure was solved using this program. Hydrogen atoms were included at calculated positions with fixed U values (isotropic thermal parameters) of 0.06 Å^2; $\mu=0.47$ mm^{-1}; $8<2\theta<25$°; 6436 unique reflections; 3580 with $I>2.5\sigma(I)$; 382 least-squares parameters; $R=0.058$ ($R_w=0.050$).

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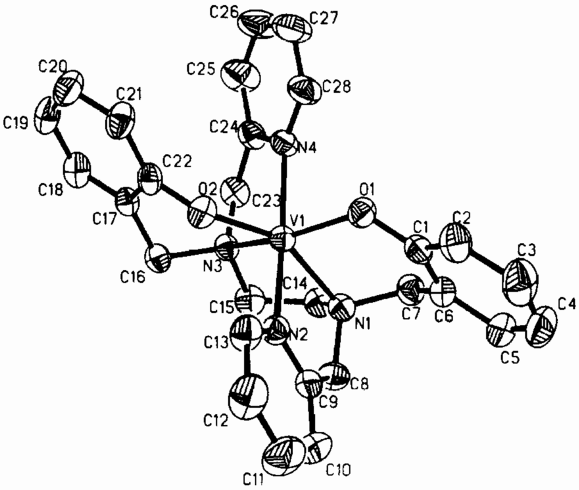

Fig. 1. X-ray structure of cation in crystals of **2**. Selected bond lengths (Å) and angles (°): V–O(1) 1.884(3), V–O(2) 1.891(3), V–N(1) 2.238(4), V–N(2) 2.144(4), V–N(3) 2.225(4), V–N(4) 2.139(4), O(1)–V–O(2) 111.5(1), O(1)–V–N(1) 88.9(1), O(1)–V–N(2) 90.4(2), O(1)–V–N(3) 151.5(1), O(1)–V–N(4) 85.1(2), O(2)–V–N(1) 153.1(1), O(2)–V–N(2) 85.3(2), O(2)–V–N(3) 89.5(1), O(2)–V–N(4) 86.7(1), N(1)–V–N(2) 76.8(1), N(1)–V–N(3) 78.5(2), N(1)–V–N(4) 113.4(1), N(2)–V–N(3) 111.0(1), N(2)–V–N(4) 168.6(1), N(3)–V–N(4) 77.0(1).

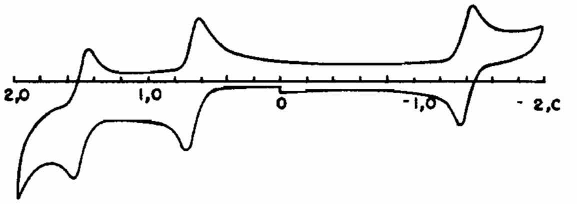

Fig. 2. Cyclic voltammogram of [V^{III}(BBPEN)][PF_6] in MeCN (0.1 M [Bu_4N][PF_6] supporting electrolyte, platinum working electrode, ferrocene internal standard, scan rate 200 mV s^{-1}).

The electronic spectrum of **2** measured in MeCN solution consists of the following transitions at λ_{max} (nm) (ϵ (1 mol^{-1} cm^{-1})): 612 (76), 500sh, 348 (2280). The weak broad absorption at 612 nm is assigned to the $^3T_{1g} \rightarrow {}^3T_{2g}$ transition in pseudo-octahedral symmetry whereas the intense band at 348 nm is assigned to a phenolato-to-vanadium(III) charge-transfer (CT) transition.

The redox properties of [V(BBPEN)][PF_6] in MeCN have been investigated by cyclic voltammetric (CV) and coulometric techniques (Fig. 2). At scan rates of 20–500 mV/s three quasi-reversible one-electron transfer processes were detected at $E^{1-3}_{1/2}$ of +1.11, +0.27 and −1.79 V versus Fc^+/Fc. These data are consistent with the process shown in eqn. (1).

$$
\begin{aligned}
&[V^{V}(BBPEN)]^{3+} + e^- \overset{E^1_{1/2}}{\rightleftharpoons} \\
&[V^{IV}(BBPEN)]^{2+} + e^- \overset{E^2_{1/2}}{\rightleftharpoons} \\
&[V^{III}(BBPEN)]^{+} + e^- \overset{E^3_{1/2}}{\rightleftharpoons} [V^{II}(BBPEN)] \qquad (1)
\end{aligned}
$$

Controlled potential coulometric measurements on **2** at 0.35 V versus Fc^+/Fc, revealed that this species is oxidized by 1.00±0.05 electrons per vanadium center. The CVs of this solution and **2** are identical under the same conditions, but the oxidized species decomposes slowly. The electronic spectra of the deep purple oxidized species consist of two very intense overlapping bands at λ_{max} (nm) (ϵ (1 mol^{-1} cm^{-1})) 580 (3900) and 480 (4000). Similar spectra have been reported for the vanadium(IV) catecholato [7] and [LV^{IV}][BPh_4] [6] L=1,4,7-tris(5-t-butyl-2-hydroxybenzyl-1,4,7-triazacyclononane non-oxo complexes. From this information, we suggest that the $[V(BBPEN)]^{2+}$ ion complex could be formed in solution without changing the coordination sphere at the vanadium centre. In contrast to many vanadium(III) Shiff base complexes described in the literature [4, 5], it is worth noting that $[V(BBPEN)]^+$ is a new example of a vanadium(III) complex containing N,O-donors atoms, which shows three quasi-reversible one-electron waves, indicating the accessibility of V(II), V(III), V(IV) and V(V) formal oxidation states. To our knowledge, only the complex of Wieghardt and co-workers [6] [VL] shows a similar behaviour. Further preparative, structural and electrochemical studies on both V(IV) and V(V) complexes are in progress in our laboratory and will be reported later in a full paper.

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