Synthesis of a New Phenolate-1-methylimidazole Hexadentate Ligand and the Crystal Structure of its First Vanadyl Complex

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Reportamos neste trabalho, a síntese e a estrutura cristalina de [OV IV (Hbbimen)]PF 6 .2H 2 O [H 2 bbimen = N,N'-bis(2-hidroxibenzil)-N,N'-bis(1-metilimidazol-2-il-metil) etilenodiamina] como um raro exemplo de complexo V IV O 2+ o qual contém grupos 1-metilimidazol e fenolato coordenados simultaneamente ao centro metálico.

The synthesis and X-ray crystal structure of [OV IV (Hbbimen)]PF 6 .2H 2 O [H 2 bbimen = N,N'-bis(2-hydroxybenzyl)-N,N'-bis(1-methylimidazole-2-yl-methyl) ethylenediamine] are reported as a rare V IV O 2+ complex containing phenolate and 1-methylimidazole coordinated simultaneously to the metal center.

Keywords: imidazole-phenolate, VO 2+ complex, crystal structure

Introduction

It is well established that vanadium plays an important role in many biological processes1. In view of the recent reported binding of vanadium to tyrosinate residues in vanadium-modified transferrin2, vanadium-phenolate chemistry is receiving a great deal of attention from the inorganic chemist3-5. Despite the binding of iron(III)-transferrin has been established through crystallographic studies (NO3 coordination and CO3 2- as synergistic anion)6, the coordination environment around the vanadium centre in vanadium-transferrins is not yet entirely known. It is well known that in the +3, +4, and +5 oxidation states, vanadium binds tightly to transferrin7. In the +4 oxidation state, a vanadyl complex structure with octahedral geometry having an NO3 equatorial coordination (one tyrosinate, one aspartate, one histidine, and one monodentate carbonate) has been proposed recently for vanadium human lactoferrin, on the basis of computer simulations by using the atomic coordinates of the iron(III)- and copper(II)-lactoferrin complexes8. The coordination of histidine trans to the V=O bond has also been proposed8.

As a continuation of our work on the coordination chemistry of vanadium with biologically relevant ligands4,5, we describe herein, the preparation and structural characterization of a VO2+ complex, with a new N4O2-donor ligand which contains the ethylenediamine backbone and two phenolate-type and two 1-methyl-imidazole-2-yl methyl pendant arms. Interestingly, despite the numerous VO2+ complexes with nitrogen and oxygen donor atoms described in the literature,1 there are only very few examples of structurally characterized vanadyl(IV) complexes which contain phenolate and imidazole coordinated simultaneously to the metal center9.

Experimental

Syntheses

The ligand N,N'-bis(2-hydroxybenzyl)-N,N'-bis(1-methylimidazole-2-yl-methyl)ethylenediamine (H2bbimen) was prepared in good yield by the condensation reaction of 1-methyl-2-imidazolecarboxaldehyde10 and ethylenediamine and reduction with NaBH4, followed by alkylation of the diamine (bimen) with 2-bromo-methyl-phenyl acetate11, by the route in Scheme 1. The title complex was prepared as follows. A solution of VCl3 in dry acetonitrile was refluxed for 15 min under an argon atmosphere and equimolar quantities of H2 bbimen and Et3 N in tetrahydrofuran (thf) were added to the hot solution, followed by 30 min of reflux. After the addition of NaPF6 to the solution and cooling to room temperature under argon, a green precipitate of [VIII (bbimen)][PF 6 ] 1 was formed.
This material is stable in the solid state, even in the presence of air, but oxidizes in acetonitrile solution under aerobic conditions. The lilac complex $2$, $[\text{OV IV (Hbbimen)}][\text{PF}_6]_2\text{H}_2\text{O}$, was obtained after leaving the green solution of $1$ at room temperature over night, in the presence of air. Single crystals of $2$ suitable for X-ray crystallography were obtained by recrystallization from a propan-2-ol-acetone-acetonitrile (1:1:1) solution of $2$.

**X-ray Crystallography**

Crystal data for $[\text{C}_{26}\text{H}_{31}\text{N}_6\text{O}_3\text{V}].\text{PF}_6.2\text{H}_2\text{O}$, $M = 707.51$, triclinic, $P-1$, $(\text{No. 2})$, $Z = 2$, $a = 10.703(2)$, $b = 13.857(3)$, $c = 14.166(3)$ Å, $\alpha = 118.70(3)$, $\beta = 103.77(3)$, $\gamma = 102.78(3)$, $V = 1645.2(6)$ Å$^3$, $D_c = 1.428$ g cm$^{-3}$, $\mu = 0.428$ mm$^{-1}$ for Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å, crystal size $0.13 \times 0.13 \times 0.46$ mm. Nonius CAD4 diffractometer, $T = 293$ K. Measured reflections: 6021, with 4049 unique reflections of which 2071 had $I > 2\sigma(I)$.

The structure was solved by direct methods, full-matrix refinement on $F^2$, anisotropic refinement for all non-H atoms of the complex molecule, isotropic refinement for water molecules and disordered PF$_6$ group. The number of refined parameters was 390, $R = 0.127$, $wR = 0.273$.

The quality of the refinement was limited by the intrinsic quality of the data and by the high thermal motion of the disordered PF$_6$ group. All the H atoms were placed at geometrically calculated positions, except those of the water molecules that were not found. Crystallographic calculations were performed using the MOLEN, SHELXS86, SHELXL93 and ZORTEP computer program packages.

**Results and Discussion**

The structure and atomic numbering scheme of $2$ are shown in Fig. 1. The vanadium (IV) ion is in a pseudo-octahedral environment, in which one phenolate oxygen, one amine, and two 1-methylimidazole nitrogen atoms in *trans* positions, form the equatorial plane. The other amine nitrogen atom of the ethylenediamine backbone, in the *trans* position with respect to the terminal oxo group, completes the coordination sphere. It is important to note that, despite the similarities between the hexadentate H$_2$bbimen and H$_2$bbpen$^5$ ligands, $[\text{H}_2\text{bbpen} = \text{N,N’-bis(2-hydroxybenzyl)-N,N’-bis(2-pyridylmethyl)ethylenediamine}]$, there are significant structural differences in their corresponding VO$^{2+}$ complexes. While in $[\text{OV IV (bbpen)}]$, one pyridyl group of the ligand H$_2$bbpen is pendant, in $2$ one phenol group of H$_2$bbimen is not coordinated to the vanadium (IV) center. This most probably arises due to distinct basicities of the coordinating pyridyl and 1-methylimidazole nitrogen atoms. As expected, the V-N$_{\text{amine}}$ of 2.36(1) Å *trans* to the V=O bond in $2$, is 0.13 Å longer than the V-N$_{\text{amine}}$ bond in the equatorial plane and is a consequence of the strong *trans* influence of the oxo group. A similar trend in these bond lengths has been observed in $[\text{OV IV (bbpen)}]$, but with longer V-N$_{\text{amine}}$ bonds (0.05 and 0.03 Å for *trans* and *cis* to the oxo group, respectively) in complex 2. This fact can be associated with the higher rigidity of 2, due to the presence of three five- and one six-membered rings compared to $[\text{OV IV (bbpen)}]$, which possesses two five- and two six-membered rings. In addition, the displacement of the V atom from the N$_3$O plane (0.331 Å) for the present complex is smaller compared with that (0.345 Å) in $[\text{OV IV (bbpen)}]$. The V-O (phenolate) distance in $2$ (1.905(8) Å) is similar to those found in the $[\text{OV IV (bbpen)}]$ complex$^5$.
but is shorter than in the isostructural VO\textsuperscript{2+}-(imidazole)(phenolate) complexes (1.981-1.973 Å) which contain the [OV\textsuperscript{IV}(salim\textsubscript{H})] fragment \{Hsalim\textsubscript{H} = 4-(2-(salicylideneamino)ethyl)imidazole\} and variable bidentate ligands\textsuperscript{9}. The V-N\textsubscript{(1-methylimidazole)} distances (av. 2.08 Å) \textit{cis} to the V=O bond, are similar to the V-N\textsubscript{(imidazole)} bond of 2.099 Å observed in the [OV\textsuperscript{IV}(salim\textsubscript{H})(acac)] complex\textsuperscript{9}.

Finally, further preparative, structural and physicochemical (UV-Vis, EPR and electrochemical) studies on both V\textsuperscript{III} and V\textsuperscript{IV} complexes are in progress in our laboratory in order to compare with the corresponding properties of V\textsuperscript{III}- and V\textsuperscript{IV}-transferrins. These results will be reported later in a full paper.

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\textbf{References}

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