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Article

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

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Reportamos neste trabalho, a síntese e a estrutura cristalina de $[OV^{IV}(Hbbimen)]PF_6.2H_2O$ [H_2bbimen = *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 $[OV^{IV}(Hbbimen)]PF_6.2H_2O$ [H_2bbimen = *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

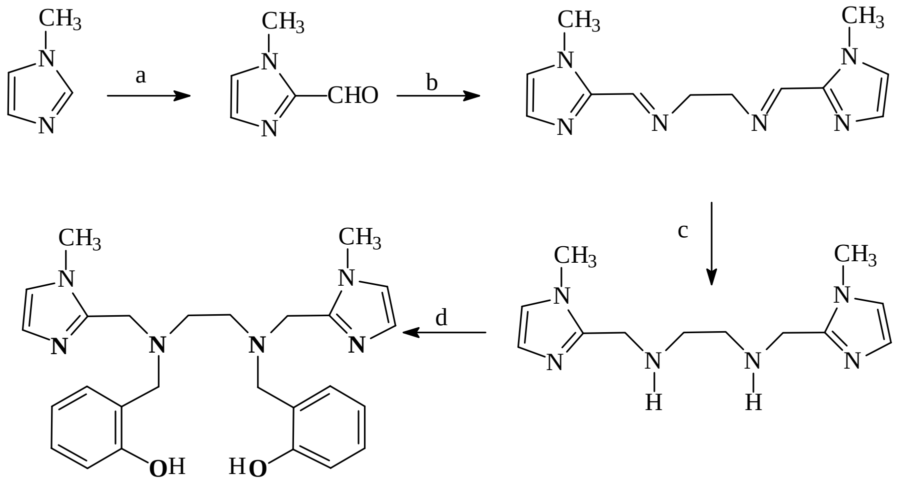
It is well established that vanadium plays an important role in many biological processes[1]. In view of the recent reported binding of vanadium to tyrosinate residues in vanadium-modified transferrin[2], vanadium-phenolate chemistry is receiving a great deal of attention from the inorganic chemist[3-5]. Despite the bindidng of iron(III)-transferrin has been established through crystallographic studies (NO_3 coordination and $CO_3$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 tighly to transferrin[7]. In the +4 oxidation state, a vanadyl complex structure with octahedral geometry having an NO_3 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 complexes[8]. The coordination of histidine *trans* to the V=O bond has also been proposed[8].

As a continuation of our work on the coordination chemistry of vanadium with biologically relevant ligands[4,5], we describe herein, the preparation and structural characterization of a VO^{2+} complex, with a new N_4O_2-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 VO^{2+} 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 center[9].

Experimental

Syntheses

The ligand *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(1-methylimidazole-2-yl-methyl)ethylenediamine (H_2bbimen) was prepared in good yield by the condensation reaction of 1-methyl-2-imidazolecarboxaldehyde[10] and ethylenediamine and reduction with $NaBH_4$, followed by alkylation of the diamine (bimen) with 2-bromo-methylphenyl acetate[11], by the route in Scheme 1. The title complex was prepared as follows. A solution of VCl_3 in dry acetonitrile was refluxed for 15 min under an argon atmosphere and equimolar quantities of H_2bbimen and Et_3N in tetrahydrofuran (thf) were added to the hot solution, followed by 30 min of reflux. After the addition of $NaPF_6$ to the solution and cooling to room temperature under argon, a green precipitate of $[V^{III}(bbimen)][PF_6]$ **1** was formed.



H$_2$bbimen

Scheme 1. Synthesis of the ligand H$_2$bbimen: *reagents and conditions:* a) n-BuLi/dmf, Et_2O; b) $H_2NCH_2CH_2NH_2$, diisopropyl ether; c) $NaBH_4$/MeOH; d) i) 2-BrCH$_2\phi$OOCCH$_3$/Et$_3$N, thf, argon; ii) KOH/CH$_3$OH; iii) HCl.

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**, [OV^{IV}(Hbbimen)][PF$_6$].2H$_2$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 [$C_{26}H_{31}N_6O_3V$].PF$_6$.2H$_2$O, M = 707.51, triclinic, P-1, (No. 2), Z = 2, a = 10.703(2), 13.857(3), c = 14.166(3) Å, α = 118.70(3), β = 103.77(3), γ= 102.78(3)°, V = 1645.2(6) Å^3, D$_c$ = 1.428 g cm^{-3}, F(000) = 730, μ = 0.428 mm^{-1} for Mo-Kα radiation (λ = 0.71073 Å, crystal size 0.13 x 0.13 x 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[12].

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, [H$_2$bbpen = *N,N'*-bis(2-hydroxybenzyl)-*N,N'*-bis(2-pyridylmethyl)ethylenediamine], there are significant structural differences in their corresponding VO^{2+} complexes. While in [OV^{IV}(bbpen]^5 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$_{(amine)}$ of 2.36(1) Å *trans* to the V=O bond in **2**, is 0.13 Å longer than the V-N$_{(amine)}$ bond in the equatorial plane and is a consequence of the strong *trans* influence of the oxo group. A similar trend in these bond lenghts has been observed in [OV^{IV}(bbpen)], but with longer V-N$_{(amine)}$ 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 [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 [OV^{IV}(bbpen)]. The V-O$_{(phenolate)}$ distance in **2** (1.905(8) Å) is similar to those found in the [OV^{IV}(bbpen)] complex[5]

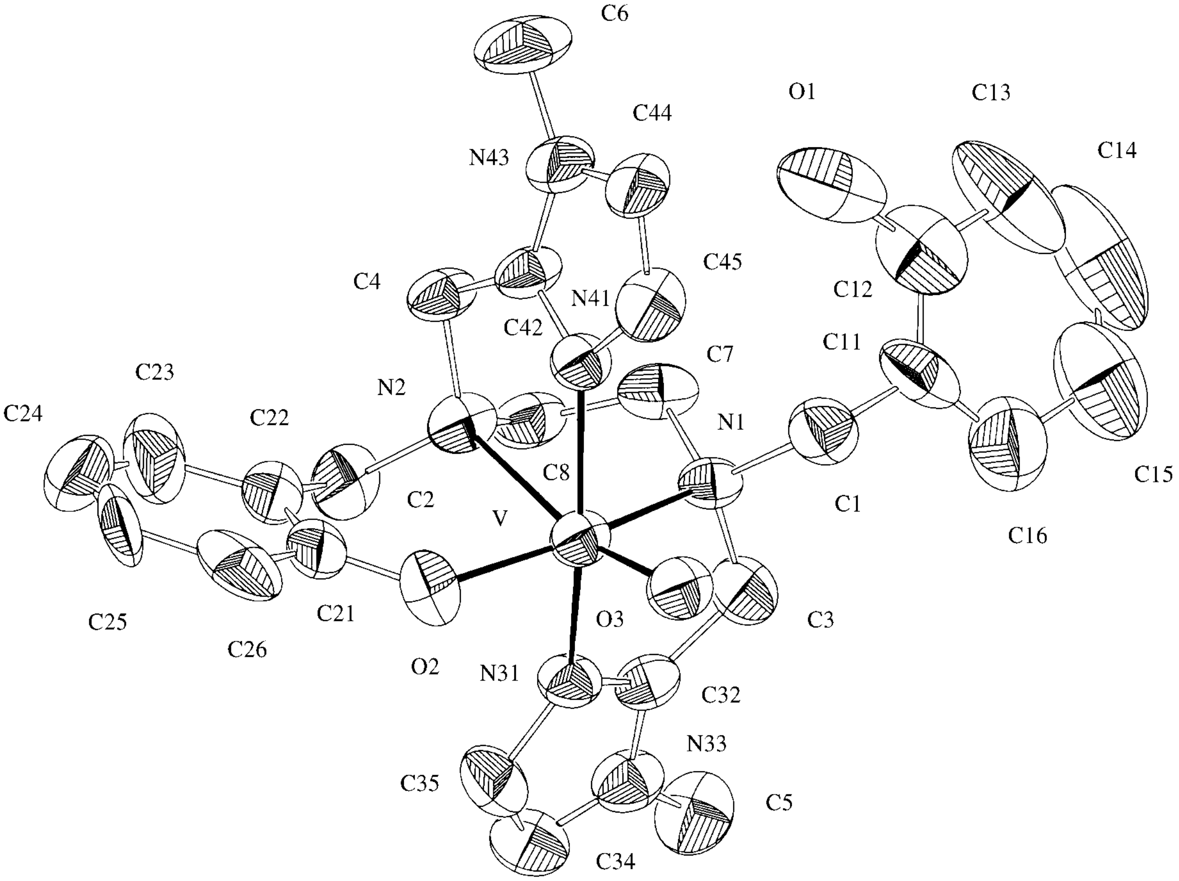


Figure 1. X-ray structure of 2. Selected bond lenghts (Å) and angles (°): V-O3 1.588(8), V-O2 1.905(8), V-N1 2.234(9), V-N2 2.360(9), V-N31 2.072(9), V-N41 2.088(9), O3-V-O2 106.4(4), O3-V-N1 93.7(4), O3-V-N2 165.9(4), O3-V-N31 101.0(4), O3-V-N41 95.0(4), O2-V-N1 157.8(3), O2-V-N2 84.7(4), O2-V-N31 89.9(4), O2-V-N41 96.6(4), N1-V-N2 77.1(4), N1-V-N31 76.9(4), N1-V-N41 90.7(4), N2-V-N31 87.4(4), N2-V-N41 74.7(3), N31-V-N41 160.2(4).

(av. 1.923 Å) but is shorter than in the isostructural VO^{2+}-(imidazole)(phenolate) complexes (1.981-1.973 Å) which contain the $[OV^{IV}$(salimH)] fragment {HsalimH = 4-(2-(salicylideneamino)ethyl)imidazole} and variable bidentate ligands[9]. The V- $N_{(1\text{-methylimidazole})}$ distances (av. 2.08 Å) *cis* to the V=O bond, are similar to the V-$N_{(\text{imidazole})}$ bond of 2.099 Å observed in the $[OV^{IV}$(salimH)(acac)] complex[9].

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

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