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Note

Complexes of vanadyl and uranyl ions with a benzoxazole derivative: Synthesis, structural features and remarks on luminescence properties

Davi Fernando Back [a,*], Gelson Manzoni de Oliveira [a,*], Marco Aurélio Ballin [a], Valeriano Antonio Corbellini [b]

[a] Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, UFSM, 97115-900 Santa Maria, RS, Brazil
[b] Departamento de Química e Física, Universidade de Santa Cruz, UNISC, Santa Cruz do Sul, RS, Brazil

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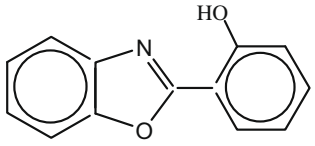
ABSTRACT

$UO_2(NO_3)_2{\cdot}6H_2O$ and $VO(acac)_2$ react with 2-(2′-hydroxylphenyl)benzoxazole (Hpbx) in methanol to give $[UO_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**). Complex **1** shows a distorted pentagonal bipyrimidal geometry, characteristic for the coordination number 7. Reciprocal OH···O interactions between neighbored molecules hold **1** in a pseudo-dimeric association with an inversion center. Complex **2** achieves a distorted octahedral geometry and the molecules "stack" along the *b* axis through secondary interactions. The molecule heaping is wholly linear, with $V^{n'}-O(1)^{n'}\cdots V^{x'}$ angles of 180°. Luminescence properties of Hpbx, **1** and **2** are discussed.

1. Introduction

It is well known that the benzene-fused oxazole ring structure (with an odor similar to pyridine) called benzoxazole is used primarily in industry and research. Being a heterocyclic compound, benzoxazole finds use as a starting material for the synthesis of larger, usually bioactive structures, and is found within the chemical structures of some pharmaceutical drugs. Because of its aromaticity it is a relatively stable compound, although as a heterocyclic it has reactive sites which allow for functionalization. Derived from 1,3-benzoxazole, the compound 2-(1,3-benzoxazol-2-yl)phenol (**A**), commonly known as 2-(2′-hydroxylphenyl)benzoxazole, has been studied for the synthesis of metal complexes with *N*,*O*-donor ligands.



A

These kinds of compounds have been used successfully as electroluminescent emitters [1–4] since the discovery that luminescent organic metal complexes are potential photoluminescent or electroluminescent materials [5]. For example, Zinc(II) complexes of 2-(2′-hydroxylphenyl)benzoxazole have been recognized as noteworthy green–blue emitters in electroluminescent devices [6,7], and further studies have shown that the introduction of a second ligand may also have important effects on the mechanism of emission [2], and, consequently, on the emitting wavelength [8,9].

The research with 2-(2′-hydroxylphenyl)benzoxazole (**A**) has been developed with the metals Zn [9–11], Re [12–14], Ru [15–17], Pt [18,19], Pd [20–22], Cu [23], Fe [24], Mn [25,26], Ga [27], including even Be [28] and Al [27,29]. The major goal of these experiments is the search of new optically tuneable luminescent materials, besides secondary interests like the catalytic oxygen atom transfer [30] and the synthesis of metallomesogens derived from heterocyclic benzoxazoles [31]. Benzoxazoles, nevertheless, are important biological substances, covering an extensive spectrum of essential and selective antimicrobial activities, such as amyloid fibril inhibitor [32,33], antimycobacterial [34], antitumor [35], immunosuppressive, antiviral [36] and antiretroviral [37].

The use of biological ligands with hard base characters for the chelation of heavy metals like uranium, thorium or lanthanides, has been a subject of interest in our group [38–42], as these kinds of ligands generally produce very stable chelate complexes. This profit makes them highly appropriates for therapeutic development of clinical chelators in safety procedures related to contamination through natural or depleted thorium and uranium, and in similar chemoprevention processes against uranium/thorium/heavy metals intoxication. On the other side, in the present days the insulin mimetic effects of vanadium complexes are well known

* Corresponding authors. Tel.: +55 55 3220 8757; fax: +55 55 3220 8031.
E-mail addresses: daviback@gmail.com (D.F. Back), manzoni@quimica.ufsm.br (G.M. de Oliveira).

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[43–45], since the discovery that vanadate ions, low-molecular-weight phosphate analogues, mimic most of the rapid actions of insulin in various cell types [46]. Curiously, an important biological compound like 2-(2′-hydroxylphenyl)benzoxazole (**A**) has not been used so far, neither for the chelation of heavy metals, nor to achieve structurally well-defined vanadium complexes, potential insulin mimetic agents.

Because our interests lay also in the metallation of biological ligands, we fill partially this gap reporting herein the synthesis and the X-ray structural characterization of the new chelate complexes of U^{VI} and V^{IV}, $[UO_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**) {Hpbx = 2-(2′-hydroxylphenyl)benzoxazole}.

2. Experimental

2.1. General

Elemental analyses for C, H and N were performed at a Shimadzu EA 112 microanalysis instrument. IR spectra were recorded on a Tensor 27 – Bruker spectrometer with KBr pellets in the 4000–400 cm^{-1} region.

2.2. Synthesis of 2-(2′-hydroxylphenyl)benzoxazole [47,48]

According to literature procedures, 2-(2′-hydroxylphenyl)benzoxazole was prepared by condensation of salicylic acid (0.65 g, 4.71 mmol) with *o*-aminophenol (0.5 g, 4.71 mmol) in polyphosphoric acid (10 ml). The mixture was heated in oil bath at 180 °C for 6½ h under N_2 atmosphere, cooled at room temperature, poured into ice, filtered, washed with water, dried, and finally purified by column chromatography over SiO_2, eluted with anhydrous dichloromethane. Yield after the elution: 56%. The colorless crystals are strongly fluorescent under ultraviolet radiation.

2.3. Synthesis of $[UO_2(pbx)_2(CH_3OH)]$ (**1**)

To a solution of Hpbx (0.026 g, 0.125 mmol) in 15 mL of methanol, $UO_2(NO_3)_2{\cdot}6H_2O$ (0.031 g, 0.0625 mmol) was added. After heating for 1½ h at 70 °C the yellow solution turned bright red. Prismatic red crystals were formed from the solution after one day. Yield: 0.036 g, 81% based on Hpbx. Melting point: 361 °C. *Anal.* Calc. for $C_{27}H_{20}N_2O_7U$: C, 44.87; H, 2.77; N, 3.87. Found: C, 44.93; H, 2.84; N, 3.89%. IR spectra (KBr): 3047 [medium, ν(C−H)$_{ar.}$], 1607 [strong, ν(C=N)], 1531, 1469, 1428 [strong, ν(C−H)$_{ar.}$], 1254 [strong, ν(C−O)$_{Ph.}$], 1157 [medium, ν(H3C−O)], 916 cm^{-1} [strong, ν_{as}(O=U=O)].

2.4. Synthesis of $[VO(pbx)_2]$ (**2**)

To a solution of Hpbx (0.029 g, 0.2 mmol) in 15 mL of methanol, $VO(acac)_2$ (0.026 g, 0.1 mmol) was added. After heating for 1 h at 60 °C a yellow solid precipitated. The solid was redissolved in pyridine and after two days brown crystals were formed from the solution. Yield: 0.041 g, 84% based on Hpbx. Melting point: 295.4 °C. *Anal.* Calc. for $C_{26}H_{16}N_2O_5V$: C, 64.00; H, 3.28; N, 5.74. Found: C, 64.13; H, 3.31; N, 5.78%. IR spectra (KBr): 3100–3010 [m, ν(C−H)$_{ar.}$], 1614 [s, ν(C=N)], 1560, 1536, 1471, 1435 [s, ν(C−H)$_{ar.}$], 1264 [s, ν(C−O)$_{Ph.}$], 894 {ν_{as}(V=O) [49,50]}, 736 {ν_{as}(VO_2) [51]}, 531 {ν_s(VO_2) [51]}, 467, 407 cm^{-1} {V−O, V−N [51]}.

2.5. X-ray crystallography

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo Kα radiation. The structures were solved by direct methods using SHELXS [52]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [52]. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions.

2.6. Luminescence experiments

A Cary Eclypse (Varian) spectrofluorimeter was used to obtain fluorescence spectra at 25 °C. The spectra were obtained in the corrected mode with excitation wavelength of 280 nm and the slit opening was adjusted at 10.0 mm for the ligand (Hpbx) and 20.0 nm for **1** and **2**, to compensate the high fluorescence of the ligand in comparison with the low intensities of the complexes. All the measures were carried out in dimethylsulfoxide solutions.

3. Results and discussion

3.1. Crystal structure

The X-ray crystal data and the experimental conditions for the analyses of the complexes $[UO_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**) are given in Table 1. Table 2 presents selected bond distances and angles for the title compounds. Figs. 1 and 2 show, respectively, the molecular structures of compounds **1** and **2**. Fig. 3 displays the pseudo-dimeric association of $[UO_2(pbx)_2(CH_3OH)]$ (**1**)

Table 1
Crystal data and structure refinement for $[U0_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**)

	1	**2**
Empirical formula	$C_{27}H_{20}N_2O_7U$	$C_{26}H_{16}N_2O_5V$
Formula weight	722.48	487.35
T (K)	293(2)	293(2)
Radiation, X1A	0.71073	0.71073
Crystal system, space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$
Unit cell dimensions		
a (Å)	13.477(3)	29.3399(6)
b (Å)	19.344(4)	3.93430(10)
c (Å)	9.3029(19)	21.6908(5)
α (°)	90	90
β (°)	92.306(5)	126.141(3)
γ (°)	90	90
V (Å^3)	2423.4(9)	2022.00(8)
Z, D_{Calc} (g cm^{-3})	4, 1.980	4, 1.601
Absorption coefficient (nm^{-1})	6.749	0.536
F (0 0 0)	1376	996
Crystal size (mm)	0.409 × 0.384 × 0.360	0.198 × 0.143 × 0.107
θ Range (°)	1.84–30.58	1.72–28.43
Index ranges	$-19 \leqslant h \leqslant 19$, $-27 \leqslant k \leqslant 25$, $-13 \leqslant l \leqslant 12$	$-38 \leqslant h \leqslant 38$, $-5 \leqslant k \leqslant 5$, $-28 \leqslant l \leqslant 28$
Reflections collected	29 601	21 774
Reflections unique	7423 [R_{int} = 0.0321]	2534 [R_{int} = 0.0461]
Completeness to theta max.	99.6%	99.5%
Absorption correction	semi-empirical from equivalents	Gaussian
Maximum and minimum transmission	1 and 0.467496	0.989 and 0.897
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	7423/0/338	2534/0/155
Goodness-of-fit (GOF) on F^2	1.035	1.159
Final R indices [$I > 2\sigma(7)$]	R_1 = 0.0321, wR_2 = 0.0724	R_1 = 0.0377, wR_2 = 0.1142
R indices (all data)	R_1 = 0.0499, wR_2 = 0.0791	R_1 = 0.0564, wR_2 = 0.1402
Largest difference in peak and hole (e Å^3)	2.645 and −1.697	0.623 and −0.851