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Note

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

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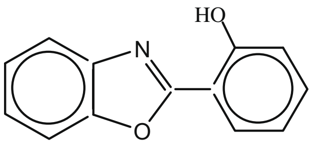
ABSTRACT

$UO_2(NO_3)_2\cdot 6H_2O$ 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

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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, $\nu(C{-}H)_{ar.}$], 1607 [strong, $\nu(C{=}N)$], 1531, 1469, 1428 [strong, $\nu(C{-}H)_{ar.}$], 1254 [strong, $\nu(C{-}O)_{Ph.}$], 1157 [medium, $\nu(H3C{-}O)$], 916 cm^{-1} [strong, $\nu_{as}(O{=}U{=}O)$].

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, $\nu(C{-}H)_{ar.}$], 1614 [s, $\nu(C{=}N)$], 1560, 1536, 1471, 1435 [s, $\nu(C{-}H)_{ar.}$], 1264 [s, $\nu(C{-}O)_{Ph.}$], 894 {$\nu_{as}(V{=}O)$ [49,50]}, 736 {$\nu_{as}(VO_2)$ [51]}, 531 {$\nu_s(VO_2)$ [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 ($e\ A^3$)	2.645 and −1.697	0.623 and −0.851

Table 2
Selected bond lengths (Å) and angles (°) for (**1**) and (**2**)

1		0(3)–U–N(2)	68.02(9)
Bond lengths		0(7)–U–N(2)	137.90(9)
U–O(3)	2.336(2)	0(2)–U–N(l)	93.84(11)
U–N(l)	2.604(3)	0(1)–U–N(1)	85.75(11)
U–0(4)	2.226(3)	0(4)–U–N(l)	69.55(9)
U–N(2)	2.568(3)	0(3)–U–N(l)	143.89(9)
U–0(7)	2.427(3)	0(7)–U–N(l)	73.85(9)
U–0(2)	1.784(3)	N(2)–U–N(l)	147.84(9)
U–O(l)	1.788(3)	**2**	
0(7)–H(l)	0.87(5)	*Bond lengths*	
H(l)···0(3)′	1.716(3)	V–O(l)	1.612(2)
Bond angles		V–0(2)	1.9421(15)
0(2)–U–0(l)	178.05(12)	V–N	2.0832(17)
0(2)–U–0(4)	94.06(11)	V–O(l)″	2.322(2)
0(l)–U–0(4)	87.59(11)	*Bond angles*	
0(2)–U–0(3)	93.50(11)	0(l)–V–0(2)	102.41(5)
0(l)–U–0(3)	85.73(11)	0(2)′–V–0(2)	155.17(9)
0(4)–U–0(3)	144.84(10)	0(1)–V–N	96.23(4)
0(2)–U–0(7)	85.47(12)	0(2)′–V–N	90.28(7)
0(l)–U–0(7)	92.58(12)	0(2)–V–N	87.05(7)
0(4)–U–0(7)	143.29(9)	N–V–N′	167.55(9)
0(3)–U–0(7)	71.56(9)	0(1)–V–0(1)″	180.000(1)
0(2)–U–N(2)	85.70(12)	0(2)–V–0(l)″	77.59(5)
0(1)–U–N(2)	95.67(12)	N–V–O(l)″	83.77(4)
0(4)–U–N(2)	78.39(9)	V–0(1)–V‴	180.0

Symmetry transformations used to generate equivalent atoms: **1** {(′) 1 − *x*, 1 − *y*, 1 − *z*}. **2** {(′) 1 − *x*, *y*, 0.5 − *z*; (″) *x*, 1 + *y*, *z*; (‴) *x*, −1 + *y*, *z*}.

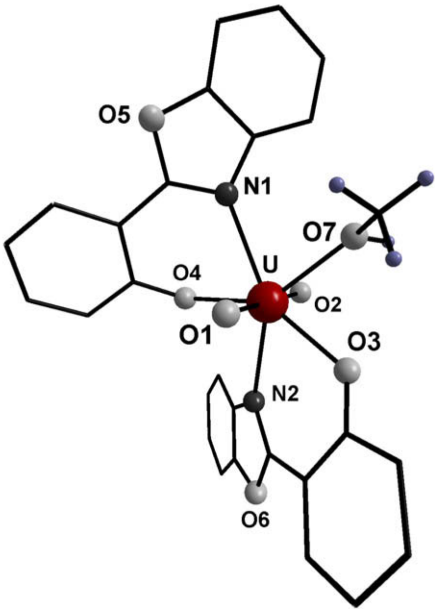


Fig. 1. Molecular structure (asymmetric unit) of $[UO_2(pbx)_2(CH_3OH)]$ (**1**). For clarity the hydrogen atoms of the pbx ligands are omitted.

and the "stacking" of the molecules of $[VO(pbx)_2]$ (**2**) along the *b* axis.

In the uranyl complex $[UO_2(pbx)_2(CH_3OH)]$ (**1**) the uranium atom is the center of a distorted pentagonal bipyramide, characteristic for the coordination number 7. The seventh coordination position in $[UO_2(pbx)_2(CH_3OH)]$ (**1**) is accomplished by a methanol molecule, which interacts through the OH group with the O(3) atom of a neighbor molecule (see Fig. 3). These reciprocal hydrogen bridges have a distance of 1.716(3) Å and hold the molecules in pairs, with a pseudo-dimeric association, completed by an inversion center. The U–O bonds are shorter than the U–N ones, and this can be assigned to the harder basic character of the oxygen atom in respect to nitrogen. In the case of U–O(1) and U–O(2) the noteworthy short distances also reflect the covalent character of these two bonds.

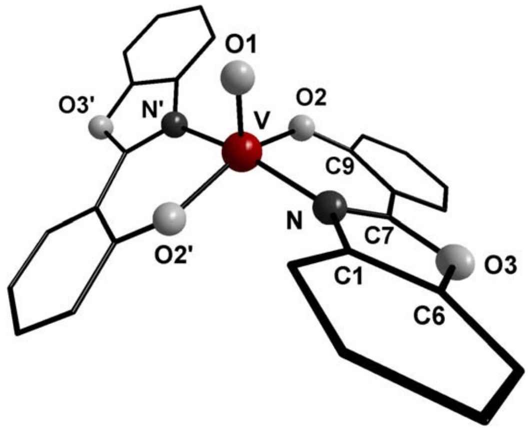


Fig. 2. Molecular structure of $[VO(pbx)_2]$ (**2**). Symmetry transformations used to generate equivalent atoms: (′) 1−*x*, *y*, 0.5−*z*. For clarity the hydrogen atoms of the pbx ligands are omitted.

In the complex $[VO(pbx)_2]$ (**2**) the metal centers attain a distorted octahedral geometry, since the molecules stack symmetrically along the *b* axis through secondary $\mathrm{V}^{n'}\cdots\mathrm{O}(1)^{x'}$ bonds, represented in dashed lines in Fig. 3. These interactions have the same distance, 2.322(2) Å, and are very longer than the V–O(1) bonds, which measure 1.612(2) Å. The molecule "heaping" along the *b* axis is rightly linear, as the $\mathrm{V}^{n'}\text{–}\mathrm{O}(1)^{n'}\cdots\mathrm{V}^{x'}$ bonds have angles of 180° (see Fig. 3 and Table 2). In the complex **2** the harder basic character of the oxygen atoms is not so evident like in complex **1**: the V–O(2) and the V–N bonds are very similar, with distances of 1.9421(15) and 2.0832(17) Å, respectively. This is probably due to the small size of the vanadium atoms, in comparison with the bulky uranium centers. Finally, it would be appropriate to underline the impossibility to differentiate oxygen and nitrogen atoms crystallographically. The C–O(N) distances, however, can be unmistakably measured, so that we can design the molecule configuration also with basis on X-ray data. In the case of complex **2**, for example, the occurrence of two V–N bonds is also confirmed by the fact that the C–N distances in the ligand Hpbx are not alike (see **A**). The single/double bond characters of the ligand are maintained in the complex: the double N–C(7) bond measures 1.3127(26) Å, while the single N–C(1) one is correspondently longer, with 1.3991(40) Å. The O(3)–C(7) and O(3)–C(6) distances are 1.3633(29) and 1.3833(39) Å, respectively. The O(2)–C(9) bond is the shorter of its species (1.3165(21) Å), since the ligand atom O(2) was originally a hydroxyl group (see Fig. 2).

3.2. Optical properties

Studies on the biological activity of complex **2** are in progress, and preliminary results allow considering this compound as a probable insulin mimetic agent. The luminescence properties of the 2-(2′-hydroxylphenyl)-*N*,*O*-, *N*,*N*- and *N*,*S*-species seem to result from the tautomeric equilibrium shown in Scheme 1.

In the singlet ground state the tautomerization of the *enol* to the *keto* form is a very fast process because of the existence of an intramolecular hydrogen bond between the hydroxyl group and the nitrogen atom of the oxazole ring (O–H···N). Thus, after light absorption the compound emits fluorescence and gives a large Stokes shift. The triplet excited state of the enol form cannot be achieved directly via intersystem crossing due to the extremely rapid tautomerization process [53,54].

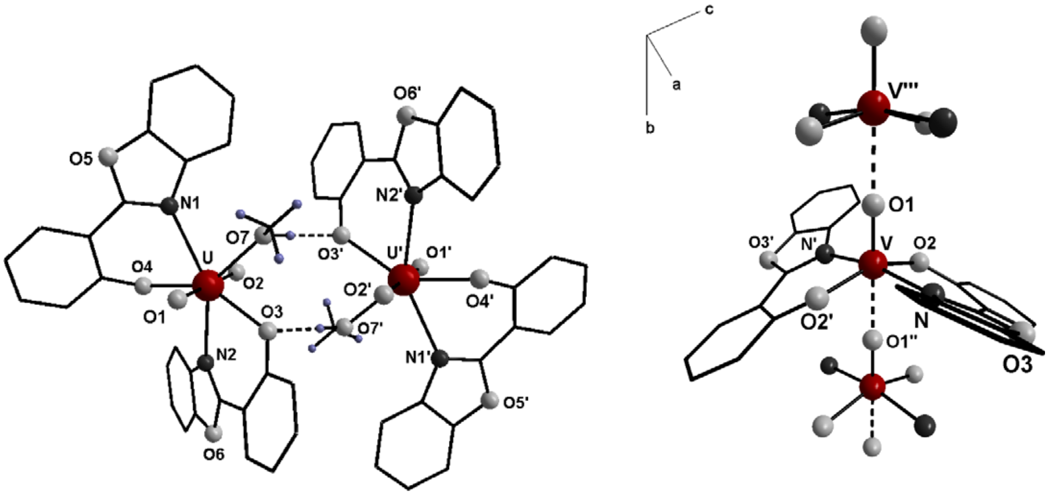
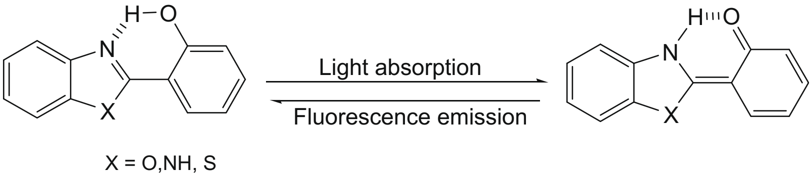


Fig. 3. Pseudo-dimeric association of $[UO_2(pbx)_2(CH_3OH)]$ (**1**, symmetry transformations used to generate equivalent atoms: (′) 1−*x*, 1−*y*, 1−*z*), and the "stacking" of the molecules of $[VO(pbx)_2]$ (**2**) along the *b* axis. Symmetry transformations used to generate equivalent atoms: (′) 1−*x*, *y*, 0.5−*z*; (″) *x*, 1 + *y*, *z*; (‴) *x*, −1 + *y*, *z*. For clarity the hydrogen atoms of the pbx ligands are omitted.



Scheme 1.

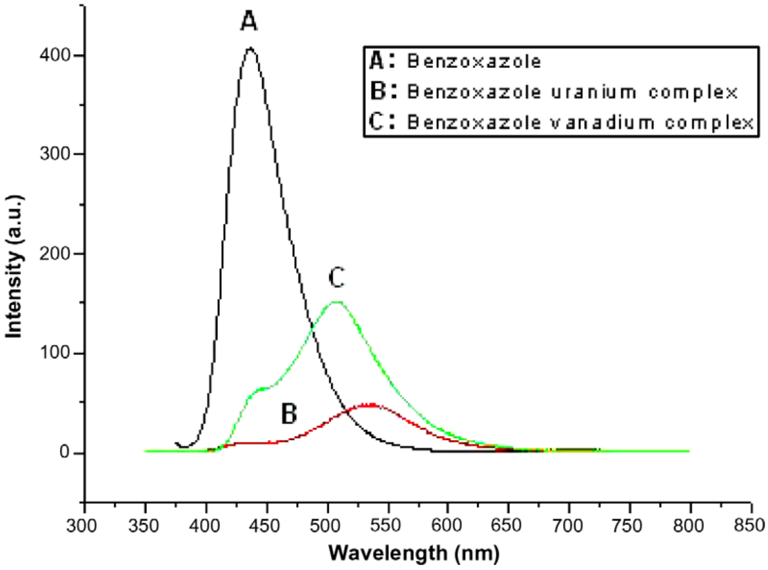


Fig. 4. Emission spectrum of the ligand 2-(2′-hydroxylphenyl)benzoxazole (A) and of the complexes $[UO_2(pbx)_2(CH_3OH)]$ (**1**, B) and $[VO(pbx)_2]$ (**2**, C). The emission bands of **1** and **2** are broad and weak on the contrary of the sharp and intense band of the ligand.

Although our results on the luminescence properties of Hpbx, $[UO_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**) are preliminary and inconclusive (in particular because neither absorption nor excitation spectra are presented), crude emission spectra, resumed in Fig. 4, show that all compounds exhibit luminescence, and this find is not surprising for **1**, as uranyl complexes are well known as notoriously good emitters under the proper circumstances. Nevertheless, the excitation at 280 nm is not adequate for complexes with the uranyl group, so that for complex **1** some vibronic structure should be expected, particularly exciting at 400 nm. In addition, the emission spectra presented in Fig. 4 are probably distorted by self-absorption from the colored complexes. The preliminary spectra allow also concluding that the luminescence of the ligand is much more intense than that of the complexes **1** and **2**, and the vanadyl complex is approximately three times more fluorescent than the uranyl compound. Since the fluorescence

$$V^{4+}{=\!=}\,O^{2-} \underset{\text{fluorescence}}{\overset{\text{light absorption}}{\rightleftharpoons}} V^{3+}\!\!-\!\!-\,O^{-}$$

Scheme 2.

properties of the ligand seem to be strongly dependent on the tautomeric equilibrium depicted in Scheme 1, the deprotonation of the hydroxyl group of the phenyl ring – occurred on the occasion of the formation of **1** and **2** – should restrain its (ligand) luminescence, because the main luminescence mechanism has been hindered. Thus, the luminescence of complexes **1** and **2** seems not to be associated to the "antenna effect" of the ligand [55] (i.e., energy transfer from the ligand to the metal ion, which emits the light) but instead, to transitions associated with the O=U=O and V=O double bonds of the chelated uranyl and vanadyl moieties, since in this kind of species the luminescence is associated with the M=O double bonds [56]. In the case of complex **2**, the lowest energy absorption band should correspond to electron transfer from O^{2-} to V^{4+}, while luminescence corresponds to the V^{3+}–O^{-} excited state going back to the V=O ground state, as illustrated in Scheme 2.

The luminescence of the uranyl complex **1** should be correlated with the same kind of transition involving electrons transfer.

4. Conclusion

In the refinement procedures for complex **1** we have found a relatively significant residual electronic density, with an uncommon value (2.645 e $Å^{-3}$) for the largest difference peak (see Table 1). This residual electronic density, however, can not be assigned to any concrete atom, since the distance between the nearest peak and the metal center is approximately 0.770 Å, shorter even than the sum of the covalent radii of C and H, for example. On the other hand, if this electronic density is attributed to any specific atom, the discordance indices R_1, wR_2 (final R indices), and R_1 (all data), undergo an unsuitable increase. Also eventual positional disorders were discarded, since the crystallographic refinement using *PART Instruction* [57] did not stabilize the thermal ellipsoids calculation. Thus, the acquired crystallographic data allow us, beyond doubt, to present the structure of Fig. 1 as the real structure of complex **1**.

Even though the theoretical predictions discussed above in the second paragraph of the preceding subsection assign luminescence only to the *keto* form of the ligand Hpbx, the luminescence of the *enol* form cannot be ruled out. Although further examples of metal complexes of Hpbx could not be found for comparison, the deprotonation of the hydroxyl group to form complexes probably also leads to emission from the complexed ligand, as in our case. This supposition should be supported by the fact that numerous benzoxazole-substituted ligands are used as luminescence sensitizers- and modulators of lanthanides and other transition metals [58–61]. Anyway, we are yet not able to make conclusive comparisons between the luminescence properties of the ligand 2-(2′-hydroxylphenyl)benzoxazole, Hpbx, and that of the complexes $[UO_2(pbx)_2(CH_3OH)]$ (**1**) and $[VO(pbx)_2]$ (**2**).

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Appendix A. Supplementary material

CCDC 712123 and 712124 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.033.

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