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Synthesis of symmetric *N*,*O*-donor ligands derived from pyridoxal (vitamin B6): DFT studies and structural features of their binuclear chelate complexes with the oxofilic uranyl and vanadyl(V) cations

Davi Fernando Back^{a,*}, Gelson Manzoni de Oliveira^{a,*}, Daiane Roman^a, Marco Aurélio Ballin^a, Roger Kober^a, Paulo Cesar Piquini^b

^a Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, UFSM, 97115-900 Santa Maria, RS, Brazil ^b Departamento de Física, Universidade Federal de Santa Maria, UFSM, 97115-900 Santa Maria, RS, Brazil

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ABSTRACT

The synthesis and the structural characterization of symmetric dimers containing uranium and vanadium atoms provide an outstanding opportunity for the study of hydrogen bonding in supramolecular architectures and unusual interactions. On the search of ligands able to coordinate itself to two metal ions simultaneously, we have synthesized the Schiff bases bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene) oxalohydrazide (H₆Pyr₂oxdihyd) and bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene) succinohydrazide (H₁₀pyr₂sucdihyd), efficient symmetric ligands with an inversion center, obtained through the reaction of pyridoxine/pyridoxal hydrochloride with oxalyl dihydrazide and succinic dihydrazide. Their reactions and the products obtained with the oxofilic uranyl(VI) and vanadyl(V) cations were discussed, as well as computational methods were used as complementary tools in the study of intra and intermolecular bonds.

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1. Introduction

A large amount of the enzymatic reactions of amino acids catalyzed by pyridoxal phosphate-containing enzymes reported earlier by Metzler et al. [1] could be reproduced by non-enzymatic reactions, in which pyridoxal [2,3] or other appropriate aldehydes [4] and a suitable metal salt act as catalysts [5,6]. Therefore, these reactions also demonstrated that the catalytic potentialities of pyridoxal phosphate *metalloenzymes* are basically those of their prosthetic group (the pyridoxal metal complex), and that the non-enzymatic and enzymatic reactions proceed by similar mechanisms. These finds increased significantly the interest for the coordination chemistry of compounds derived from the vitamin B6 complex.

We reported some reactions [7-10] of vitamin B6 derivatives with metal ions like uranium, thorium and lanthanides, and these derivatives are almost all symmetric parents of the Schiff base *N*,*N'*-bis(pyridoxylideneiminato)ethylene, derived from the condensation of pyridoxal with ethylenediamine, which has been developed to investigate substitution reactions in compounds of vanadium with the Schiff base {*N*,*N'*-ethylenediaminebis(salicylideneiminato)}, sal₂en [11].

In the search of Schiff bases presenting coordination sites with different charges and hard/soft character for the synthesis of metal complexes with N,O-donor ligands, we have further prepared the Schiff base {3-hydroxyl-5-(hydroxymethyl)-2-methylpyridine-4yl-methylene} benzohydrazidehydrochloride monohydrated, or, as acronym, (hhmmbH)Cl·H₂O [12]. This ligand is derived from the vitamin B6 (pyridoxine) and presents a hard/medium basic character. In contrast with other Schiff base ligands obtained starting from the vitamin B6, (hhmmbH)Cl·H₂O was not prepared by linkage of two pyridoxal rings through a polyamine like (for example, en or dien), being rather obtained through the reaction of pyridoxine hydrochloride with benzoic acid hydrazide, after treatment with manganese dioxide and concentrated sulfuric acid. With this ligand we obtained the chelate complexes of vanadium and uranium [VO₂(hhmmb)]·Py, [UO₂Cl(hhmmb)(H₂O)]NO₃·2H₂O and [UO₂Cl(hhmmb)(CH₃OH)]NO₃·CH₃OH [13].

In this work we describe the synthesis of the ligands H_6pyr_2 oxdihyd (bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene) oxalohydrazide) (Chart A) and $H_{10}pyr_2$ sucdihyd (bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene) succinohydrazide) (Chart B), as well as the synthesis, the structural features and DFT studies of the reaction products $[(UO_2)_2(H_6pyr_2oxdihyd-4H^+)(DMSO)_4]$ (1) and $[(VO)_2(H_{10}pyr_2sucdihyd-4H^+)(MeO)_2]$ (2). The binuclear chelate complexes of the uranyl(VI) and vanadyl (V) cations were obtained as result of the ability of the ligands to "grasp" the metal ions in both its extremities.







^{*} Corresponding authors. Tel.: +55 55 3220 8757; fax: +55 55 3220 8031.

E-mail addresses: daviback@gmail.com (D.F. Back), manzonideo@smail.ufsm.br (G. Manzoni de Oliveira).

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2. Experimental and computational details

2.1. General

All manipulations were conducted by use of standard argon atmosphere. 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 to 400 cm⁻¹ region.

2.2. Preparations

2.2.1. Bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4-yl)methylene) oxalohydrazide (H₆Pyr₂oxdihyd) Pyridoxine hydrochloride (0.191 g, 1 mmol) was dissolved in 100 mL of water. In this solution 0.88 g of 85% MnO₂ was suspended and 1 mL of concentrated sulfuric acid was added very slowly. Thereafter the mixture was heated in an oil-bath at 60–70 °C for ~4 h until whole dissolution of the manganese dioxide. The solution becomes brown however translucent due to the whole oxidation of pyridoxine to pyridoxal. The ligand H₆pyr₂-dihyd precipitated after the addition of 0.118 g of oxalic acid hydrazide. The mixture was heated in an oil-bath at 40 °C for about 10 min and the ligand was collected on a filter, washed with distilled water and dried. Yield: 0.167 g (86%).

Melting point: 220 °C. *Anal.* Calc: C, 51.92; H, 4.80; N, 20.19. Found: C, 51.04; H, 4.84; N, 20.02%.

IR (KBr pellets; s, strong; m, middle; w, weak): 3195 [m, v(NH)]; 3021 [w, v(CH)_{ar}]; 1718 [s, v(C=O)]; 1529 [s, v(C=N)]; 1256 cm⁻¹ [s, v(C-O)_{phenol}.].

2.2.2. $[(UO_2)_2(H_6pyr_2oxdihyd-4H^+)(DMSO)_4]$ (1)

The ligand H_6pyr_2dihyd (0.034 g, 0.05 mmol) was dissolved in 10 mL of anhydrous methanol and stirred under argon atmosphere for 15 min. After addition of $UO_2(NO_3)_2$ ·6 H_2O (0.05 g, 0.1 mmol), 0.5 mL of triethylamine were added dropwise and the mixture was refluxed for 2 h and then cooled to room temperature. After 2 days an orange precipitate was isolated by filtration and its recrystallization from DMSO yielded, after 3 days, orange crystals suitable for X-ray analysis. Yield: 0.047 g (74%).

Melting point: 212–213 °C. Anal. Calc. for $C_{26}H_{40}N_6O_{14}S_4U_2$: C, 24.69; H, 3.19; N, 6.64; S, 10.14. Found: C, 24.85; H, 3.22; N, 6.74; S, 10.05%.

IR (KBr pellets): 3125 [m, v(O-H)]; 1597 [s, v(C=N)]; 1406 [m, $\delta(S-CH3)$]; 1277 [s, $v(C-O)_{phenol.}$]; 1013 [m, $\delta(C-S=O)$]; 957 cm⁻¹ [s, $v(O=U=O)_{as}$].

2.2.3. Bis((3-hydroxy-5-(hydroxymethyl)-2-methylpyridin-4yl)methylene) succinohydrazide (H₁₀pyr₂sucdihyd)





Pyridoxal hydrocloride (0.406 g, 2 mmol), dissolved in 10 ml of anhydrous methanol, was mixed with 0.146 g (1 mmol) succinic dihydrazide. The white solution was stirred by 1 h under Ar atmosphere. The light yellow precipitate was removed by filtration. The slow evaporation of the mother solution yielded light pale yellow crystals. Yield: 82%.

Properties: light yellow crystals. Melting point: 235–238 °C. *Anal.* Calc.: C, 45.82; H, 5.19; N, 15.93. Found: C, 46.24; H, 5.33; N, 16.19%.

IR (KBr pellets cm⁻¹): 3561 [m, v(N-H)]; 3107,2932 [w, v(O-H)];

1694 [s, v(C=O)]; 1623 [m, v(C=N)]; 1544 [s,v(Py-H)]; 1142 [s, v(C-O)_{alcohols}].

2.2.4. $[(VO)_2(H_{10}pyr_2sucdihyd-4H^+)(MeO)_2]$ (2)

least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions, but those hydrogen atoms that realize special bonds were located in the Fourier map. Crystal data and more details of the data collection and refinements of the complexes **1** and **2** are contained in Table 1.

2.4. Computational details

The interactions stabilizing the resulting molecular packing in the molecular crystals have been studied through a methodology that treats differently the parts of the molecules directly involved in the intermolecular interactions from those that are secondary to these stabilizing interactions. Each of the molecules in the molecular crystal is divided in two layers (ONIOM approach) [15]. A first principles density functional theory (DFT) is used to



The ligand $H_{10}pyr_2sucdihyd$ (0.2 mmol, 0.104 g) was dissolved in 8 ml of methanol and mixed with 0.2 mmol (0.052 mg) of 98% vanadyl(IV) acetylacetonate and 200 µL of Et₃N. The mixture was stirred for 3.5 h at 60 °C. The few precipitate was removed by filtration and after 3 days the solvent evaporation (under normal conditions of temperature and pressure) yielded deep red crystals. Yield: 94%.

Properties: deep red crystals. Melting point (decomp.): 147 °C. Anal. Calc. for $C_{22}H_{26}N_6O_{10}V_2$ (636): C, 41.37; H, 4.38; N, 13.16. Found: C, 40.02; H, 4.33; N, 12.64%. IR (KBr, cm⁻¹): 3431 [sh, m(O-H)_{alcohols}]: 2924 [w, v(C-H)]; 1604 [s, v(C=O)]; 1510 [m, v(C=N)]; 1303 [m, v(C-N)]; 1219 [m, v(C-O)_{alcohols}] 984 [m, v(VO)_{sym}].

2.3. X-ray crystallography

Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo K α radiation. The structure was solved by direct methods using SHELXS [14]. Subsequent Fourier-difference map analyses yielded the positions of the non-hydrogen atoms. Refinements were carried out with the SHELXL package [14]. All refinements were made by full-matrix

treat the layer that is most directly involved in the interaction between the molecules, while the remaining atoms in the complementary layer are studied through the semi-empirical PM6 methodology [16]. The DFT approach uses the hybrid CAM-B3LYP functional to describe the exchange and correlation interactions [17], and the 6-31+G(d, p) basis set to represent the molecular orbitals. Our calculations are performed on a model system containing three molecules, according to Fig. 6, which contains all the relevant structural informations that are necessary to study the intermolecular interactions in the molecular crystal. This "three molecules" model is obtained directly from the molecular crystal, keeping the structure of each molecule and their relative configurations as in the bulk. Fig. 6 shows the atomic layers: a small one that is treated with the density functional theory (represented by balls), and a larger one for which the semi-empirical approach is used (represented by sticks). Total energy calculations for this model system are performed according to the scheme illustrated in Fig. 7. The total energy is calculated using the PM6 approach for the whole molecule plus the total energy of the smaller layer using the DFT approach, minus the total energy of this same smaller layer calculated through the PM6 methodology.

Table 1						
Crystal data and	structure	refinement	for	1	and	2.

Complex	1	2
Empirical formula	$C_{26}H_{40}N_6O_{14}S_4U_2$	$C_{22}H_{26}N_6O_{10}V_2$
Formula weight	1264.94	636.37
T (°K)	273(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system, space group	monoclinic, P2 ₁ /c	monoclinic, P2 ₁ /n
Unit cell dimensions		
a (Å)	6.2867(10)	8.5426(6)
b (Å)	31.201(4)	14.9955(13)
<i>c</i> (Å)	10.0480(12)	9.5856(7)
α (°)	90	90
β(°)	102.906(6)	94.895(5)
γ (°)	90	90
$V(\dot{A}^3)$	1921.1(4)	1223.44(16)
Z, d_{calc} (g cm ⁻³)	2, 2.187	2, 1.727
Absorption coefficient (mm ⁻¹)	8.706	0.836
F(000)	1196	652
Crystal size (mm)	$0.265 \times 0.094 \times 0.051$	$0.18 \times 0.10 \times 0.09$
θ range (°)	2.18-28.30	1.72-28.43
Index ranges	$-8\leqslant h\leqslant$ 3,	$-10\leqslant h\leqslant 10$,
	$-41 \leqslant k \leqslant 30$,	$-17\leqslant k\leqslant 19$,
	$-13 \leqslant l \leqslant 13$	$-12 \leqslant l \leqslant 12$
Reflections collected	17016	16431
Reflections unique	4633 $[R_{int} = 0.0754]$	2598 [R _{int} = 0.0925]
Completeness to theta max. (%)	98.6	98.3
Absorption correction	GAUSSIAN	GAUSSIAN
Maximum and minimum transmissions	0.738 and 0.6197	0.9286 and 0.8641
Refinement method	full-matrix least- squares on F ²	full-matrix least- squares on F ²
Data/restraints/parameters	4633/0/212	2598/1/176
Goodness-of-fit (GOF) on F^2	1.081	1.017
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0588$,	$R_1 = 0.0662$,
	$wR_2 = 0.1035$	$wR_2 = 0.1531$
R indices (all data)	$R_1 = 0.0969$,	$R_1 = 0.1247$,
	$wR_2 = 0.1174$	$wR_2 = 0.1841$
Largest difference in peak and hole (e $Å^{-3}$)	2.694 and -2.376	0.832 and -0.835

All calculations have been done using the GAUSSIAN 09 simulation package [18]. The ball and sticks figures are made using the VMD code [19], while the 2D graphs are obtained through the use of the Grace code [20].

3. Results and discussion

3.1. Crystal structure

The molecular structure of the chelate, binuclear complex $[(UO_2)_2(H_6pyr_2oxdihyd-4H^+)(DMSO)_4]$ (1) is represented in Fig. 1. Selected bond lengths and angles of complex 1 are resumed in Table 2.

In the molecule of **1** two uranyl cations are chelated at the extremities of the ligand H_6Pyr_2dihyd , which undergoes deprotonation in the two NH groups, as well as in the phenolic OH group of both rings. Two molecules of DMSO complete the coordination number seven and the characteristic distorted pentagonal bipyramidal geometry of both the uranyl cations. The double (covalent) bonds U–O3 (1.778) and U–O4 (1.766 Å) are shorter than the coordinative ones U–O1 (2.230), U–O5 (2.323), U–O6 (2.391), U–O7 (2.387) and U–N2 (2.569 Å).

The molecule of $[(UO_2)_2(H_6pyr_2oxdihyd-4H^+)(DMSO)_4]$ (1), as well as the ligand $H_6Pyr_2oxdihyd$, present an inversion center between the atoms C10 and C10'. The attainment of N–H intermolecular [21,22] interactions allowed the visualization of supramolecular assemblies along the two-dimensional plane *bc*.



Fig. 1. Molecular structure of the binuclear chelate $[(UO_2)_2(H_6pyr_2oxdihyd-4H^*)(-DMSO)_4]$ (1).

Table 2

Selected bond lengths (Å) and angles (°) for $[(UO_2)_2(H_2pyr_2oxdihyd)(DMSO)_4]$ (1) and $[(VO)_2(H_6pyr_2sucdihyd)(MeO)_2]$ (2).

1		2	
Bond lengths		Bond lengths	
U-04	1.766(7)	V05	1.607(6)
U-03	1.778(7)	V04	1.7249(12)
U-01	2.230(7)	V-01	1.857(5)
U05	2.323(7)	V03	1.930(5)
U-07	2.387(7)	V—N2	2.102(5)
U-06	2.391(7)	Bond angles	
U—N2	2.569(8)	05–V–04	103.4(2)
S2-07	1.516(8)	05-V-01	102.6(3)
Bond angles		04-V-01	101.38(15)
04–U–03	179.2(3)	05–V–03	100.0(3)
04-U-01	87.3(3)	04-V-03	93.00(15)
03–U–01	92.6(3)	01-V-03	149.5(2)
04–U–05	88.5(3)	05-V-N2	92.4(3)
03—U—05	91.0(3)	01-V-N2	83.3(2)
01U-05	131.1(2)	04VN2	161.95(17)
04—U—07	90.9(3)	03V—N2	75.5(2)
03—U—07	89.6(3)	C2-01-V	133.1(4)
01–U–07	153.4(2)		
05—U—07	75.3(2)		
03U—06	86.2(3)		
01-U-06	78.6(3)		
05—U—06	150.3(3)		
07—U—06	75.1(3)		
03—U—N2	81.9(3)		
01-U-N2	69.1(3)		
05—U—N2	63.1(2)		
07—U—N2	137.3(3)		
06-U-N2	144.9(3)		
04—U—06	94.6(3)		
S2-07-U	142.8(4)		
S1-06-U	143.0(5)		

Intermolecular interactions of the type $O \cdots H$, as well as $C - H \cdots \pi$ contacts have not been detected in compound **1**.

The occurrence of binuclear complexes of the uranyl cation is not uncommon, since chelate complexes of $UO_2^{2^+}$ with oligodentate ligands have been already reported [23–26]. Along the crystallographic direction 010 could be observed the existence of a classic hydrogen bond, as shown in Fig. 2, between the atoms N3(A)…H2#–O2#(D) (A = acceptor; D = donator), in order of 0.850 Å in length (D–H); 2.008(9) Å (H…A), and 2.789(1) Å



Fig. 2. Molecular assembly and hydrogen interaction in complex 1. Symmetry operations used to generate equivalent atoms: (#) -x, 0.5 + y, 2.5 - z.



Fig. 3. Hydrogen interactions in complex 1 (dashed lines). Symmetry operations used to generate equivalent atoms: (#) 1 + x, y, z.

 $(D \cdots A)$, with an angle of $158.84(51)^{\circ}$ $(D-H \cdots A)$. Symmetry transformations used to generate equivalent atoms: (#) -x, -0.5 + y, 2.5 - z.

However, when the *ac* crystallographic plane of complex **1** is observed, also bifurcated hydrogen bonds of the type "receptor forked", with two donors atoms, are identified [27,28]. The O3 atom of the uranyl cation acts as acceptor for two hydrogen bonds from the hydrogens of the methyl groups of the neighboring dimethyl sulfoxide groups. These type of atomic interactions allow us to link this structure with species of three-dimensional stairs (Fig. 3, symmetry transformations used to generate equivalent atoms: (#) 1 + *x*, *y*, *z*) [29]. The intermolecular bonds and distances showed in Table 3 for the atoms C—H···O3(#) support the evi-

Table 3	
Selected bond lengths (Å) and angles (°) for complex 1.	

(D—H···A)	D—H (Å)	H···A (Å)	D· · ·A (Å)	D—H···A(°)
03#…H11a—C11	0.960(11)	2.423(7)	3.204(14)	138.24(75)
03#…H14a—C14	0.959(13)	2.631(7)	3.568(15)	165.37(74)

dences of growth of the supramolecular assembly of complex **1** along the crystallographic plane *ac* (see Fig. 3).

Similarly to what happens with complex **1**, the ligand $H_{10}pyr_{2}$ sucdihyd contains a "spacer" (succinohydrazide), which allows the complexation of two (VO)⁺³ cations at two ligand places, as represented in Fig. 4. Each "side" of the hexadentate ligand occupies



Fig. 4. Molecular structure of the binuclear chelate [(VO)₂(H₁₀pyr₂sucdihyd-4H⁺)(MeO)₂] (2).

three coordination positions at each oxidocation $(VO)^{+3}$: one oxygen atom from the deprotonated phenolic group, a bond from the substituent C=N (imino) and the third bond is formed by the negative charged oxygen of the group.

The two cations (VO)⁺³ achieve a distorted quadratic pyramidal geometry through further coordination to two deprotonated molecules of methanol.

The deprotonation of the hydroxilic methanol groups can be easily confirmed by comparison of the V—O (methanol) distances listed en Table 4, for both protonated and not protonated hydroxyl methanolic groups, which are considerably lower than in protonated cases [28,30–32].

As in the complex of uranium (1), in compound 2 the hydrogen of the fragment of the primary alcohol from pyridoxal performs connections between the nitrogen atoms of the neighboring pyridines (Table 5).

These interactions are considered strong to moderate, since the distances between the atoms are in the range of 0.987 Å (O2–H2) and 1.860(6) Å (O3 \cdots H2#). The bond angle is 165°. These values are in agreement with the models proposed by T. Steiner and G.A. Jeffrey [41,42].

Although this hydrogen bond can be considered strong-moderate due to a preferential spatial arrangement, the oxygen O2 from the alcohol function makes interactions between the atoms O3# (ketone function), N2# (imine function) O1# (phenol function) and O1# (deprotonated methanol oxygen). The major interaction

 Table 4

 Bond lengths (Å) of selected vanadium compounds described in the literature.

Reference	V—O distance (deprotonated methanol)	V—O distance (protonated methanol)
[33]	1.775	2.398
[34]	1.768	2.346
[35]	1.767	2.398
[36]	1.775	2.333
[36]	1.761	2.340
[37]	1.769	2.327
[38]	1.793	2.311
[39]	1.781	2.236
[40]	1.776	2.295

Table 5		
Secondary interactions: lengths	(Å) and angles (•) for complex 2.

	e	ē (,,	-	
(D—H· · · A)	D—H (Å)	H· · ·A (Å)	D···A (Å)	D–H···A (°)
02—H2···03#	0.987(1)	1.860(6)	2.827(7)	165.64(16)

Table 6	
Selected bond lengths	(Å) for complex 2.
Atom	

D· · ·A (Å)
2.774(6)
2.942(7)
2.915(4)
3.032(2)

occurs between the atoms O2—O4# (3.032 (2) Å), being also in agreement with the sum of the Van der Waals radii listed in Table 6. Fig. 5 shows the above related interactions between the atoms (red dashed lines).

3.2. Theoretical statements

In complex **2** there are two main interactions responsible for the crystalline stabilization: (i) the one between the O2 atom in molecule A and the V-centered group of atoms in molecule B (see Fig. 6), and (ii) the hydrogen bond interaction between the H2 atom in molecule A and the N1# atom in molecule C. In order to compare the relative importance of these interactions on the stabilization of the crystal structure, total energy calculations for different O2–V and H2–N1# interatomic separations have been performed.

For the O2—V interaction between molecules A and B, we displace molecules A and C relative to each other as a rigid block along the vector joining the O2 and V atoms. No geometry optimization is performed. The total energy curve obtained for each O2—V interatomic separation is shown in Fig. 8.

The calculated equilibrium distance of 2.58 Å is in close agreement with the crystallographic data (2.592 Å). In order to understand which atoms are most affected by this interaction, the natural atomic charges are calculated and their variation relatively to their values at a O2–V distance of 15 Å is displayed in Fig. 9 (the charge variation for O2–V distances from 4 to 15 Å follow a monotonic path, not shown in Fig. 9). As can be seen from this Figure, the greater variations are observed at the V atom that turns more and



Fig. 5. Multiple interactions in complex 2. Symmetry operations used to generate equivalent atoms: (#) - 0.5 + x, 1.5 - y, 0.5 + z and (2#) 0.5 + x, 1.5 - y, -0.5 + z.



Fig. 6. The three molecules model used to calculate the total energy and Mulliken charges. Letters A, B, and C are used to label the different molecules while the atomic labels distinguish the atoms relevant to the analysis in the text.



Fig. 7. Scheme used to calculate the total energy of the model system. The left side shows the layers treated by the DFT (balls) and PM6 (sticks) approaches. The total energy is obtained by calculating the total energy of the two layers using the PM6 approach (first term on the right side), plus the total energy of the smaller layer using the DFT approach (second term on the right side), minus the total energy of the smaller layer using the PM6 approach (third term on the right side).



Fig. 8. Calculated potential energy profiles for both the hydrogen bonding between atoms H2 and N1# atoms (black curve) and the electrostatic interaction between the O2 and V atoms (red (deeper) curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 9. The calculated Natural charge variation on selected atoms as a function of the O2–V interatomic separation. The values are taken relatively to the ones at a O2–V distance of 15 Å.

more negatively charged until the O2—V (equilibrium) distance of 2.58 Å where this tendency is stopped and slightly reverted. An opposite behavior is observed for the N2# and O2 atoms, which turn more and more positively charged (relatively to its value at long distances) as the O2 atom at molecule A approaches the V center at molecule B. The O2 atom revert this behavior for O2—V distances lower than the one corresponding to the lowest total energy.

These results show that when the O2 atom of molecule A approaches the V center in molecule B, a charge transfer occurs from atoms N2# to the V atom within molecule B that drives the electrostatic interaction between molecules A and B. This mechanism is effective until an O2—V distance around 2.58 Å. For shorter O2—V distances this interaction turns repulsive, with the charge on atoms O2 and V remaining approximately constant or even changing the sign of their variation.

Total energy calculations for the hydrogen bond interaction between molecules A and C have been performed for different H2—N1# interatomic distances by displacing molecules A and C relative to each other, as rigid blocks, along the vector joining the H2 and N1# atoms. Again no geometry optimization is performed. The total energies for each considered H2—N1# separation are shown in Fig. 8. An equilibrium distance of 2.16 Å is obtained, which is relatively larger (16%) than the one obtained from the crystallographic data (1.86 Å). The variation of the atomic natural charges relatively to their values at a H2—N1# separation of 10 Å



Fig. 10. Calculated Natural charge variation on selected atoms (see Fig. 1), as a function of the H2–N1# interatomic separation, relatively to their values at a H2–N1# distance of 10 Å.

are shown in Fig. 10. From these Natural charges one can see that the most pronounced charge variation appears for the N1# and O2 atoms. As shorter the H2—N1# distance more negatively charged turns the N1# atom, until the H2—N1# distance is shorter than 2.0 Å, when its charge remains the same, independently of the H2—N1# bond distance. Further, the charge variations on H2 and V atoms show opposite behaviors, with the H2 and V turning positively and negatively charged, respectively, as the H2—N1# distance turns shorter. These tendencies are reverted for H2—N1# distances lower than 2.0 Å. A very similar behavior is observed for the Natural charges of the O3# e N2# atoms, as can be seen in Fig. 10.

The relative influences of the O2–V and H2–N1# interactions for the molecular crystal stabilization can be estimated by comparing the potential energy profiles in Fig. 8. It should be stressed that the absolute values for the binding energies obtained from calculations using the ONIOM approach are far from being conclusive, since we are not taken into account the basis set superposition error [43]. We will then focus on the differences between the potential energy profiles.

The O2—V interaction presents a sharper potential energy profile, while the hydrogen bond shows a broader one. It indicates that the H2—N1# hydrogen bond is softer (lower vibrational frequencies) than the O2—V electrostatic interaction.

From this analysis it could be suggested that the H2—N1# hydrogen bond interaction drives the initial steps of the crystallization process but, when the molecules turn closer to each other, the O2—V electrostatic interaction would effectively stick the molecules together, stabilizing the crystalline packing.

4. Conclusions

The reactions reported in this work, together with already published results [7–10], make evident that pyridoxal and pyridoxine derivatives present a remarkable ability to react with $[UO_2]^{2+}$ and $[VO]^{+3}$ attaining the chelation of two metal atoms pro ligand molecule.

The ligands H_6Pyr_2dihyd and $H_{10}pyr_2sucdihyd$, like other pyridoxal- or pyridoxine-containing Schiff base ligands, combine the metabolic potential of the vitamin B6 family with its chemical ability to form stable chelate complexes. Because of that, and in theory, the synthesis and the structure elucidation of the title complexes **1** and **2** should also represent a previous qualitative contribution to the research on models of chelation of oxofilic elements.

We have also observed that molecules containing pyridoxal have been shown a differentiated behavior regarding the formation of supramolecular assemblies, since this molecule (pyridoxal) has more potential sites for hydrogen bonding and specific interactions. The theoretical (computational) data presented are useful tools to qualify and quantify the intra and intermolecular interactions involved in the title compounds.

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Appendix A. Supplementary material

CCDC 845588 and 935327 contains the supplementary crystallographic data for complexes **1** and **2**, respectively. 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 http://dx.doi.org/10.1016/j.ica.2013.12.008.

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