Synthesis, Structural Studies and Biological Activity of a Dioxovanadium(V) Complex with Pyridoxal Semicarbazone

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Abstract

Reaction between the NH_4VO_3 and pyridoxal semicarbazone (PLSC) in a methanol/ammonia solution forms an orange, diamagnetic, mononuclear $NH_4[VO_2(PLSC–2H)]$ complex in which vanadium is in the oxidation state +5, and pyridoxal semicarbazone is coordinated in its dianionic form. The complex cocrystallizes with a neutral molecule of PLSC and two water molecules. The coordination environment around vanadium can be described as an almost ideal square-pyramid. The complex was characterized by elemental analysis, conductometric and magnetochemical measurements, IR spectra, X-ray diffraction, and *in vitro* cytotoxicity analysis.

Keywords: Vanadium(V) complex, Pyridoxal semicarbazone, Synthesis, Physico-chemical characterization, Structural analysis, Cytotoxicity

1. Introduction

The properties of vanadium coordination compounds attract considerable interest[1], with major emphasis being placed on possible medical applications. The oxovanadium(IV), oxovanadium(V) and dioxovanadium(V) complexes are used as models for vanadium containing enzymes[2] and are also used as good oxidation catalysts[3]. Pharmacological properties of vanadium compounds include insulin-enhancing activity[4a], tumor growth inhibition and prophylaxis against carcinogenesis[4b]. Antitumor activity of vanadocene dichloride is comparable to that of cis-platinum complexes[5]. Some vanadium complexes are known to inhibit several enzymes including phosphatases, ATPases, nucleases, kinases and other enzymes[6]. Much study has been devoted to the possibility of using vanadium complexes in the treatment of diabetes mellitus[7]. Some studies suggest that vanadium compounds may also have a role in the treatment of a disease caused by protozoa *Entamoeba hystolitica*, present in tropical and subtropical regions[8].

The aforementioned observations stimulated much research into the physico-chemical properties and structure of vanadium complexes with various biologically active ligands.

Following a previous study[9] on the complexing properties of the pyridoxal thiosemicarbazone (PLTSC) and its oxygen analogue, pyridoxal semicarbazone (PLSC) (see Scheme 1), we have directed our investigations into the coordination chemistry of vanadium complexes with PLSC. Both PLTSC10 and PLSC[11] and its complexes posses biological activity though it is smaller in the case of PLSC.

The aim of this work is to investigate in more detail the coordinating behavior of PLSC towards vanadium, and the spectral and structural properties of the obtained complex.
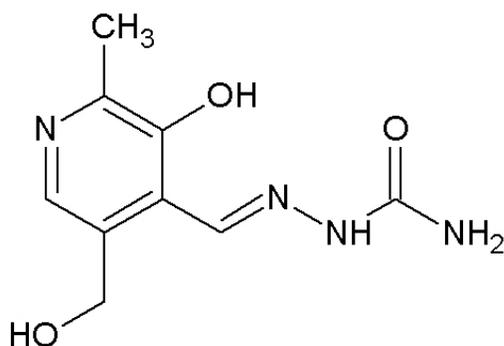
Scheme 1. Structural formula of PLSC ligand

2. Experimental

All comercially obtained reagent-grade chemicals were used without further purification, except for the ligands, wich were prepared according to the previously described procedures[11]. Elemental (C,H,N) analysis of air-dried samples was carried out by standard micromethods in the Center for Instrumental Analysis, Faculty of Chemistry, Belgrade.

2. 1. Synthesis of Complex

The complex, $NH_4[VO_2(PLSC–2H)]$ was synthesized by reacting PLSC · $2H_2O$ (0.5 mmol) and NH_4VO_3 (0.5 mmol) in a mixture of concentrated aqueous solution of ammonia (3 ml) and methanol (3 ml). The resulting mixture was refluxed for 1.5 h. On standing for 50 h at room temperature, the orange crystalline compound, $NH_4[VO_2(PLSC–2H)]$ · PLSC · $2H_2O$, separated out. The crystals were filtered off and washed with EtOH. Yield: 0.160 g (55%).

2. 1. 1. Quantitative Analysis

Anal. Calcd for $C_{18}H_{30}N_9O_{10}V$: C 37.06, H 5.18, N 21.61. Found: C 37.10, H 5.14, N 21.56.

2. 1. 2. Spectral Data for Complex

Selected IR data for $NH_4[VO_2(PLSC–2H)]$ · PLSC · $2H_2O$ (KBr pellet): 1670, 1577, 931, 922, 873, 868 cm^{-1}.

2. 1. 3. Conductometric and Magnetochemical Measurements

$\lambda_M(H_2O)$: 88.6 S cm^2 mol^{-1}; $\lambda_M(MeOH)$: 53 S cm^2 mol^{-1}.

μ_{eff} = (diamagnetic)

2. 2. Physical Measurements

Magnetic susceptibilities were measured at room temperature using a magnetic susceptibility balance MSB-MKL (Sherwood Scientific Ltd. Cambridge, England). Molar conductivities of the freshly prepared 1 × 10^{-3} M solution were measured on a Jenway 4010 conductivity meter. IR spectra (KBr disk) were recorded on a Thermo Nicolet (NEXUS 670 FT-IR) instrument.

2.3. Crystal Structure Determination

Data for $NH_4[VO_2(PLSC–2H)]$ · PLSC · $2H_2O$ were collected on a Philips PW1100 diffractometer with MoKá radiation [λ=0,7107 Å]. The structure was solved using direct methods SIR92[12] and refined using SHELXL97[13] on F^2 by full matrix least squares with anisotropic displacement parameters for all non-hydrogen atoms. One of the solvent water molecules (O2W) displayed severe disorder, and its occupancy was allowed to refine. All H atoms in the complex molecule and in the uncoordinated PLSC, were located in a difference map, except those belonging to methyl, methylene and aromatic atoms, which were calculated with standard geometries. Hydrogen atoms bonded to ammonium N5 and one of the water O1 were also located from difference map. However, severe disorder prevents location of the hydrogen atoms bonded to the second water oxygen. All hydrogen atoms were refined using the 'riding' model. Details concerning crystal data and refinement are given in Table1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Base as CCDC reference number 689739.

Table 1. Crystal data and structure refinement details of $NH_4[VO_2(PLSC–2H)]$ · PLSC · $2H_2O$

Empirical formula	$C_{18} H_{30} N_9 O_{10} V$
Formula weight	583.45
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a (Å)	8.500(8)
b (Å)	10.876(1)
c (Å)	13.810(4)
$β$ (°)	95.04(3)
$α$ (°)	100.01(2)
$γ$ (°)	100.11(2)
V(Å^3)	1229(1)
Z	2
D_{calc}(Mg/m^3)	1.577
$μ$ (mm−1)	0.477
F(000)	608
$θ$ range (°)	1.51–27.56.
HKL ranges	–11, 10; –14, 14; –17, 17
Number of reflections measured	12677
Number of unique reflections	5583 (R_{int} = 0.0313)
No. of parameters	346
Goodness-of-fit on F2	0.962
R indices (I > 2σ(I))	R1 = 0.0424; wR2 = 0.1068
R indices (all data)	R1 = 0.0672; wR2 = 0.1156
Largest diff. peak and hole (e/Å^3)	0.393 and – 0.433

2. 4. Biological Activity

The compound was evaluated for its *in vitro* cytotoxicity towards estrogen receptor positive and estrogen receptor negative breast adenocarcinoma cell lines (MCF7 and MDA-MB-231, respectively). Cytototoxic activity was evaluated by colorimetric sulforhodamine B (SRB) assay, after exposure of cells to tested compound for 24 h and 72 h.

The cells were grown in Dulbecco's Modified Eagle's Medium with 4.5% of glucose (DMEM, PAA Laboratories) supplemented with 10% foetal calf serum (FCS). Cells were seeded into 96-well microtiter plates at the density 5,000 cells/0.1 ml/well, and 24 h after seeding, exposed in triplicate to serial dilutions (100 μM – 0.4 μM) of sample dissolved in dimethyl sulfoxide (DMSO). Control and blank wells were included in each plate. After 24 h and 72 h SRB assay was carried out. The cells were fixed in trichloroacetic acid (TCA) (25 μl of 50% w/v TCA per well) for 1 h at 4 °C, washed five times with distilled water, and stained with 50 μl of 0.4% SRB in 1% acetic acid for 30 min. The cells were washed five times with 1% acetic acid and air-dried. The stain was solubilized in 10 mM TRIS (pH 10.5) light absorption was measured using a plate reader (ThermoLabsystems) on 492 nm, with reference wavelength 690 nm. Cell cytotoxicity was expressed as a percentage of corresponding control value (nontreated cells) obtained in two independent experiments. The original data were analysed by a one-way ANOVA, followed by Duncan's multiple-range post hoc test. Differences were considered significant at $P < 0.05$. The IC50 values, defined as a dose of compound that inhibits cell growth by 50%, were calculated from concentration-response curves.

3. Results and Discussion

3. 1. Synthesis and Physical Characteristics of the Complex

In a number of cases, coordination of tridentate ligand to vanadium(V) is achieved through the formation of dimeric oxovanadium(V) species. In the case of the title ligand, the formation of a dimeric complex with the metal atoms bridged by the $[N_3]^-$ ligand, $[Ni_2(PLSC)_2-(\mu_{1,1}N_3)_2(N_3)_2] \cdot 2H_2O^{14a}$, and complexes monomeric $[Ni(PLSC)(H_2O)_3]^{2+}$ [14b], dimeric $[Ni_2(PLSC)_2(H_2O)_4]^{4+}$ [14b], and finally complexes $Ni(PLSC)Cl_2 \cdot 3.5H_2O$, $[Ni(PLSC)(H_2O)_3](NO_3)_2$, $Ni(PLSC)(NCS)_2 \cdot 4H_2O$, $[Ni(PLSC–2H)NH_3] \cdot 1.5H_2O^{14c}$ were recently reported. Several other monomeric complexes incorporating PLSC ligand have been reported including $[Pt(PLSC–H)Cl_3]^{115a}$, $[Cu(PLSC–Br_2]^{15b}$ and $[Fe(PLSC)(H_2O)_2SO_4]$; $[Fe(PLSC)(H_2O)Cl_2]Cl^{15c}$. In the case of the vanadium, the formation of binuclear species can be prevented and reaction can be tuned towards the formation of mononuclear $[V^VO_2L]^{-}$ [16]

complexes if a suitable base is introduced in the reaction mixture. Under the reaction conditions described in the Experimental part, the formation of the mononuclear complex was achieved. The anionic complex crystallizes with ammonium, as a counter ion, an uncoordinated neutral PLSC ligand, and two solvent water molecules. The orange crystalline substance obtained is soluble in H_2O and slightly soluble in EtOH and this suggests an electrolytic character which is in accordance with the measurement of the molar conductivity. Moreover the diamagnetic nature of the title complex indicates that the vanadium atom is in the +5 oxidation state. The analysis of the IR spectra allows the following considerations. The band at 1670 cm^{-1} corresponds to the $v(C=O)^{17,18}$ of the free ligand as the double deprotonation of the coordinated ligand leads to formation of its enol form resulting in the absence of the $v(C=O)$ for the coordinated ligand. The band at 1577 cm^{-1} can be assigned to $v_{C=N}$ vibrations. Two intense bands are observed at 931 and 873 cm^{-1} and these can be asigned to the vibrations of the VO_2 group, as already observed in the similar salicylaldehyde-S-methylthiosemicarbazonato complex,[19] where the bands are at 922 and 868 cm^{-1}.

Table 2. Bond distances (Å) and angles (°) involving vanadium and coordinated atoms

V1–O1 1.950(2)	O1–V1–O2	147.17(8)
V1–O2 1.863(2)	O1–V1–O4	91.53(9)
V1–O4 1.648(2)	O1–V1–O5	102.67(9)
V1–O5 1.622(2)	O1–V1–N3	73.75(8)
V1–N3 2.154(3)	O2–V1–O4	96.59(9)
	O2–V1–O5	104.68(9)
	O2–V1–N3	82.16(8)
	O4–V1–O5	108.66(9)
	O4–V1–N3	146.22(9)
	O5–V1–N3	104.23(9)

3. 2. Description of the Structure of $NH_4[VO_2(PLSC–2H)] \cdot PLSC \cdot 2H_2O$

Previous studies[9,11] show that pyridoxal semicarbazone (PLSC) acts as a tridentate ligand coordinated to the metal atom through the phenolic O, hydrazine N and carbonyl O atom. While the denticity of the ligand is preserved, its charge may vary depending on the degree of deprotonation and PLSC may therefore coordinate to the metal in its neutral, monoanionic or dianionic form. It was also observed that PLSC may also coordinate in a zwitterionic form[14b], obtained by the shifting of phenolic H, to the pyridine N. In the title compound the PLSC is coordinated to vanadium as a dianion.

The asymmetric unit of coordination compound consists of the complex anion $[VO_2(PLSC–2H]^{-}$ (as stated in figure caption of Figure 2), neutral molecule of PLSC (Fig.1), an ammonium cation, and two water molecules.

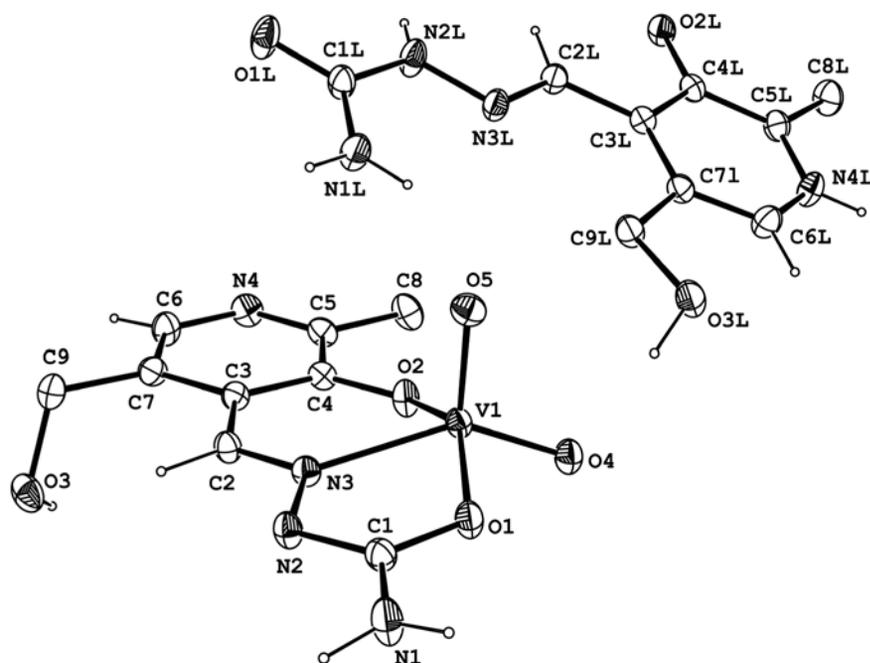**Figure 1.** A view of the anionic complex a NH$_4$[VO$_2$(PLSC–2H)] · PLSC · 2H$_2$O

Bond distances and angles around vanadium are given in Table 2. The molecular structure of complex anion reveals a five-coordinate stereochemistry (Table 2).

Vanadium(V) is a d^0 ion has no preferential geometries due to LFSE (Ligand Field Stabilisation Energies) and when pentacoordinated it tends to assume a whole variety of geometries intermediate between the two extremes: square pyramid and triangular bipyramid. For assessing the shape of the coordination polyhedron the distortion parameter τ can be used[20]. It may assume values from 0 to 1, where 0 correspond to an ideal square pyramid and 1 corresponds to an ideal trigonal bipyramid. In the case of the title complex, τ = 0.02, which correspond to an almost ideal square pyramid, with oxygen O5 in the axial position (Fig. 1).

The square pyramid geometry may seem at first sight not the more stable geometry because, based on a VSEPR (Valence Shell Electron Pair Repulsion) model, it does not minimize the repulsion of bonding electron pairs. To shed light on the problem we have carried out a simple DFT (Density Functional Theory) calculation with GAUSSIAN03[21] at the B3LYP (Becke, three-parameter, Lee-Yang-Parr) level using the 6-31G(3d) basis set in the gas phase to compare the energy difference between the observed structure with a model with an ideal trigonal bipyramid geometry and we found that between the two geometries there is a difference of only 6.2 Kcal/mol that can therefore be easily overcome by other molecular interactions such as hydrogen bonds and van der Waals forces.

Searching the CSD (Cambridge Structural Database)[22] and limiting our search to dioxovanadium(V) and tri-dentate ligands we carried out a study on the data of analogous systems present in the literature.
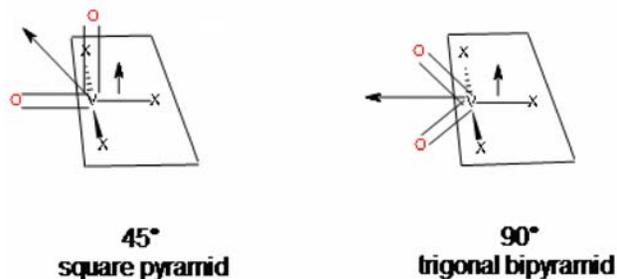
Scheme 2: The α angle between the normal to the plane and the bisector defines the geometry

In the search, to describe the geometry, we have adopted the following model: the ligand with its three donor atoms (X) is represented by the plane and the dioxovanadium moiety is defined by the vector bisecting the OVO angle. The α angle between the normal to the plane and the bisector defines the geometry: 45° corresponds to an ideal square pyramid while 90° corresponds to the trigonal bipyramid (see Scheme 2). What we observe is that, in agreement with the theoretical calculations, there is an almost uniform spread between the two extreme geometries (the average value of the α angle is 74(1)°) with only a slight preference towards the trigonal bipyramid.

In our case we observe (see Fig. 2) a strong hydrogen bond between the pyridoxal hydroxyl group (O3-H)

and a dioxovanadium oxygen (O4i' = 1-x,1-y,z) [O···O 2.828 Å OHO 172.51°] and the square planar geometry favors van der Waals interactions between the PLSC–2H ligands that face one other.
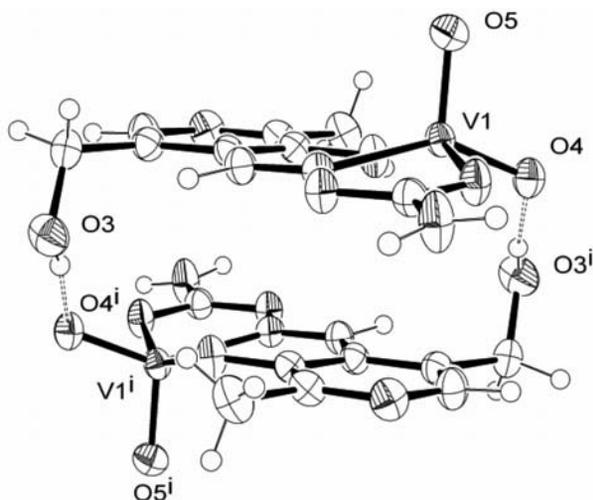

Figure 2. A view of the hydrogen bond between the two [VO₂(PLSC–2H)]⁻ complex anions

The bond lengths in both coordinated (dianion) and uncoordinated (neutral) PLSC molecule are shown in Table 3. As expected the largest differences in the bond distances are observed for the atoms involved in coordination to vanadium. Thus, the bonding of O1 and O2 to V leads to extension of the corresponding C1-O1 and C4-O2

bonds for 0.07 and 0.03 Å respectively. The coordination of N3 to V does not influence other bonds to N3, however deprotonation of neighboring N2 leads to shortening of N2-C1 bond for 0.04 Å. The value of 118.98(2) for the C5-N4-C6 angle of the pyridine ring is another evidence for the deprotonation of the ligand as the value of 122.43(2) is observed for the non-coordinated ligand. It is also worth mentioning that the vanadium cation is about 0.44 Å above the plane of the ligand and that configuration of the coordinated and non-coordinated ligands differ because during coordination hydrazine nitrogen in the free ligand moves in the same orientation as carbonyl and phenyl oxygen atoms in order to coordinate to the vanadium centre.

The packing is determined by an extended network of hydrogen bonds. The most significant intermolecular contacts are listed in Table 4. Besides the hydrogen bond

Table 3. Bonding distances (Å) in the anionic and neutral form of PLSC

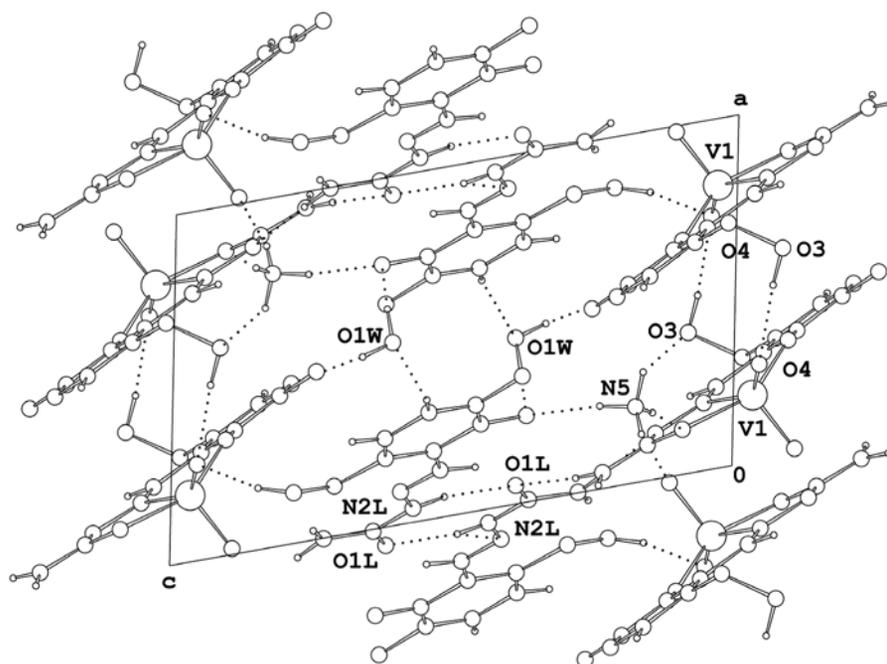|	Anionic	Neutral
O1 – C1	1.312(3)	1.245(3)
O2 – C4	1.325(3)	1.297(3)
O3 – C9	1.433(3)	1.420(3)
N1 – C1	1.321(4)	1.307(3)
N2 – C1	1.320(3)	1.357(4)
N2 – N3	1.375(3)	1.369(3)
N3 – C2	1.294(3)	1.278(3)
C2 – C3	1.444(4)	1.454(3)
C3 – C4	1.393(4)	1.427(4)

Figure 3. View of the unit cell emphasizing the formation of molecular dimers and the role of solvent molecules in the formation of the crystal structure (Table 4)

Table 4. Selected hydrogen bonds in the crystal structure of NH$_4$[VO$_2$(PLSC–2H)] · PLSC · 2H$_2$O

D–H...A	H...A (Å)	D–H...A (°)	Symm. code of acceptor A
N1–H1...O3L	2.11	160	1 + x,1 + y, −1 + z
N1–H2...O1L	1.94	176	1 + x, y, −1 + z
N1L–H1L...N2	2.14	167	−1 + x, y, 1 + z
N2L–H4N2...O1L	1.98	168	−x, 1 − y, 1 − z
O3–H4...O4	1.92	173	1 − x, 1 − y, −z
O3L–H4L...O4	1.81	165	1 − x,1 − y, 1 − z
N5–H1A...O2L	1.83	170	x, 1 + y, z
N5–H2A...O1	2.05	172	1 − x, 2 − y, −z
N5–H4A...O5	2.05	162	−1 + x, y, z
O1W–H1W...N4	1.88	162	
O1W–H2W...O2L	1.77	163	

already cited above, noteworthy is the N2L-H4N2...O1L interaction between adjacent molecules of neutral PLSC. An extensive network of hydrogen bonds involving the solvent molecules links the molecular dimers into a crystal structure (Fig. 3).

3. 3 Results of Cytotoxicity Analysis

Cytotoxic effects of vanadium complex were examined using SRB colorimetric assay, based on bonding of SRB compound with the total proteins of the living cells[23]. Fig. 4 shows the IC50 values for the two cell lines and incubation times. The results suggest that vanadium complex exhibit potent inhibitory action on MDA-MB-231 cell proliferation , where IC50 values for both incubation times were in the range of 3 μM. In MCF7 cell line cytotoxic effect is more pronounced after 72 h treatment, with IC50 value of 5 μM. Similar cytotoxic effects on MCF7 cell line were reported for nickel complexes of naphthaquinone thiosemicarbazone and semicarbazone, with IC50 values ranging from 2–4 μM[23].
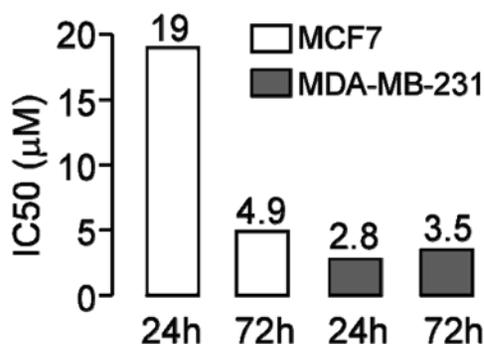

Figure 4. Cytotoxic effects of vanadium complex on MCF7 and MDA-MB-231 human breast cancer cell lines after 24 h and 72 h of treatment

4. Conclusions

Pyridoxal semicarbazone (PLSC) reacts with NH$_4$VO$_3$ under the basic conditions (methanol/ammonia) to give a vanadium mononuclear anionic complex. The ligand PLSC, in its dianionic form, is coordinated by dioxovanadium as tridentate. In the resulting complex vanadium atom is in almost ideal square-planar environment. The presence in the crystal structure of the PLSC as coordinated (dianionic) and non-coordinated (neutral) molecules allow comparison of the geometry between the two forms of the same molecule. It was found that coordination and deprotonation at imino N are the major sources of structural changes between the two forms. Moreover, obtained results clearly demonstrated that NH$_4$[VO$_2$(PLSC–2H)] · PLSC · 2H$_2$O expressed strong inhibition of cell proliferation towards MCF7 and MDA-MB-231 breast adenocarcinoma cell lines.

5. Acknowledgements

5. 1 Appendix and Supplementary Material

CCDC 689739 contains the supplementary crystallographic data for the complex. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Chambridge, CB2 1EZ, UK (fax:+44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Povzetek

Pri reakciji NH$_4$VO$_3$ s piridoksal semikarbazonom (PLSC) v amoniakalni metanolni raztopini nastane oranžen, diamagneten, mononuklearni kompleks NH$_4$[VO$_2$(PLSC-2H)], v katerem ima vanadij oksidacijsko število +5, piridoksal semikarbazon pa je koordiniran v obliki dvakrat deprotoniranega aniona. Kompleks kokristalizira z nevtralno molekulo PLSC in dvema molekulama vode. Koordinacijski polieder okrog vanadija je skoraj idealna kvadratna piramida. Kompleks smo okarakterizirali z elementno analizo, konduktometričnimi in magnetokemijskimi meritvami, IR spektri, rentgensko strukturno analizo in *in vitro* citotoksično analizo.