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Synthesis and Structural Analysis of a Dioxovanadium (V) Complex Incorporating Pyridoxal-Thiosemicarbazone (PLTSC) Ligand

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Abstract Reaction between the NH_4VO_3 and pyridoxal-thiosemicarbazone (PLTSC) in ammonia / methanol solution forms an orange, mononuclear [VO_2 (PLTSC–H)]•$2H_2O$ complex in which vanadium is in the oxidation state +5, and pyridoxal thiosemicarbazone is coordinated in its monoanionic form. The coordination environment around vanadium can be described as an almost ideal square-pyramid.

Keywords Pyridoxal-thiosemicarbazone, V(V) complex, Synthesis, Crystal structure

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1. Introduction

History of research involving mixed ligand systems based on pyridoxal (Pyridoxal, 3 -hydroxy -5 -hydroxyrnethyl -2 -methylpyridine -4 -carbaldey-de), is one of the pyridoxin forms (vitamin B6) and semi-, tiosemi- and isotiosemi-carbazones is quite recent. About 30 years have passed since the first published paper from Pelizzi group [1] describing ligand (PLTSC) synthesis, as well as its first complexes preparation.

Nevertheless, it was enough time to accumulate a substantial number of publications in this field. A large number of complexes incorporating PLTSC (pyridoxal - thiosemicarbazone) and PLSC (pyridoxal- semicarbazone) ligands has been reported. Complexes incorporating PLITSC (pyridoxal – S - methylisothiosemicarbazone) [2-16], were the main subject of a review [17] and a monograph [18].

With a variety of complex synthesized by various research groups, there was a good opportunity for compare different complexes which are composed of the same central metal (vanadium), but three different types of ligands (PLSC, PLTSC and PLITSC) around the metal center.

Specifically, in this article we will describe the structure characterization of a vanadium complex stabilized by PLTSC (pyridoxal-thiosemicarbazone). Previously vanadium complexes with PLSC [9] and PLITSC [19] were prepared.

2. Experimental

All commercially obtained reagent-grade chemicals were used without further purification, except for the ligands which were prepared as mention below in the synthesis sub-section.

2.1. Synthesis of PLTSC

Mixture of 2.03 g (10 mmol) PL HCl, 0.91 g (10 mmol) TSC i 0.70 g (10 mmol) LiOAc was perfused with 20 cm3 MeOH and refluxed for 45 min. A yellow deposit of the ligand was isolated very fast; when heated, it was percolated and washed with MeOH. Yield: 2.42 g (82 %).

2.2. Syntheses of Complex [VO_2 (PLTSC-H)] $2H_2O$

Mixture of 0.20 g (0.7 mmol) PLTSC $3H_2O$ and 0.11 g (1 mmol) NH_4VO_3 was perfused in a mixture of concentrated aqueous solution of ammonia (5 ml) and methanol (5 ml). The resulting mixture was refluxed in period of 1.5 h Orange solution was left at room temperature for 50 hours. The obtained crystals were filtered off and dried in vacuum. Yield: 0.24 g (88 %).

2.3. Crystal Structure Determination

Data for complex were collected on a Philips PW1100 diffractometer with MoKα radiation [λ= 0.7107Å]. The structure was solved using direct methods SIR92 [20] and refined using SHELXL97 [21] on F2 by full matrix least squares with anisotropic displacement parameters for all non-hydrogen atoms. Details concerning crystal data and refinement are given in Table 1. Crystallographic data have

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been deposited with the Cambridge Crystallographic Data Base as CCDC reference number 1438796 for the complex.

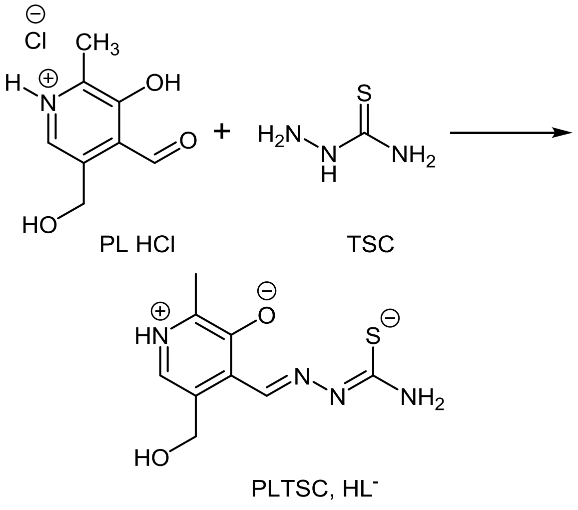
Table 1. Crystal data and structure refinement details of the complex

Empirical formula	$C_9H_{12}V_1N_4O_5S_1$
Formula weight	339.22
Temperature	294 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 2_1/c
Unit cell dimensions	a=6.3789(2) Å α=90° b=8.8414(2) Å β=91.3963(11)° c=23.3578(7) Å γ=90°
Volume	1316.95 $Å^3$
Z	4

3. Results and Discussions

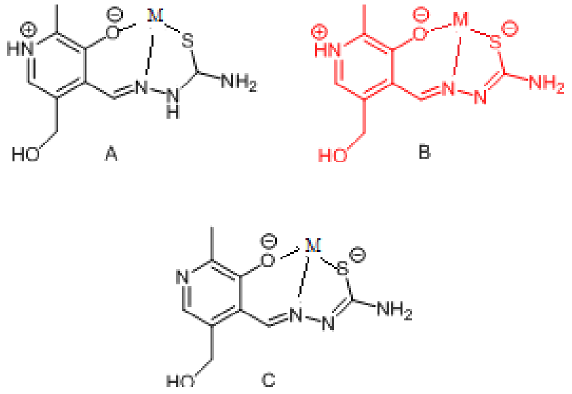
3.1. Synthesis and Structure of Complexes

Pyridoxal-thiosemicarbazone (PLTSC, H_2L), is synthesized according to formerly described procedure [18], by reaction of a warm methanol mixture of PL-hydrocloride (PL HCl),[3 -hydroxy -5 -hydroxymethyl -2 -methylpyridine -4 -carbaldehydehydrochloride] and thiosemicarbazide (TSC H_2O) in the presence Na_2CO_3 $10H_2O$ (Scheme 1.)



Scheme 1. Synthesis of Pyridoxal-thiosemicarbazone (PLTSC)

The common coordination modes, based on the X-ray analysis, for these types of lignads is presented in Scheme 2 and they are in a good agreement with similar systems [1, 18]. The H_2L ligand uses three ligators atom for coordination: the phenolic oxygen, hydrazine nitrogen and sulfur atom of the thioamide group i.e the ONS set of atoms. In that two metallocycles are formed: one six-membered (pyridoksilydene) and one five-membered (thiosemicarbazide derivate). PLTSC ligand can also be coordinated in neutral, monoanionic or dianionic forms (Scheme2.)



Scheme 2. Coordination models and ligand forms: a) neutral, b) mono- and c) dianionic

Figure 1 includes the structure of the newly synthesized V(V) complex, $[VO_2(PLTSC-H)]$ $2H_2O$, incorporating the monoligand form. In Table 2, selected structural paramethers are given.

Table 2. Bond lengths [Å] and angles[°] for the complex

C6-C17	1.365(4)	S(2)-V1-O(3)	143.78(7)
V1-S2	2.3536(9)	S(2)-V1-N (4)	77.04(7)
O11-V1	1.625(3)	S(2)-V1-O (5)	86.94(8)
O5-V1	1.655(2)	S(2)-V1-O (11)	102.52(9)
O3-V1	1.900(2)	O(3)-V1-N (4)	82.49(9)
N4-V1	2.195(3)	O(3)-V1-O (5)	97.4(1)
N7-C16	1.328(4)	O(3)-V1-O (11)	109.8(1)
C6-N7	1.345(4)	N(4)-V1-O (5)	151.0(1)
N4-N8	1.389(4)	N (4)-V1-O (11)	98.2(1)
C18-N8	1.316(4)	O (5) V1 O (11)	108.9(1)
N4-C13	1.297(4)	C(6)-N(7)-C(16)	121.0(3)
C18-S2	1.738(3)		
N15-C18	1.342(4)		

Two vanadium complexes with PLSC [8] and PLITSC [19] are already synthesized before, so we have the excellent opportunity for comparing these structures of vanadium with our structure.

All three structures are complexes of vanadium, but with different ligands systems, PLSC, PLITSC and PLTSC, respectively. The complex with PLSC is the anionic, while with PLTSĆ and PLITSC are neutral.

The reactions of synthesis of these three complexes are very similar, almost identical. (Scheme.3)

The structures of complexes are very similar, also (Figure 1, 2 and 3). These are vanadium penta coordinated complexes. Three coordinated place is coming from ligands systems (PLSC, PLITSC and PLTSC): phenolic O, hydrazine N it is same for all. The difference is the third place coordination and it is carbonyl O atom (PLSC), the nitrogen of the isothioamide group (PLITSC) and the sulfur of thioamide group (PLTSC) (Scheme 4). Other two coordination places are occupied by two oxygen.

The geometry of the all complexes is almost ideal square pyramid.

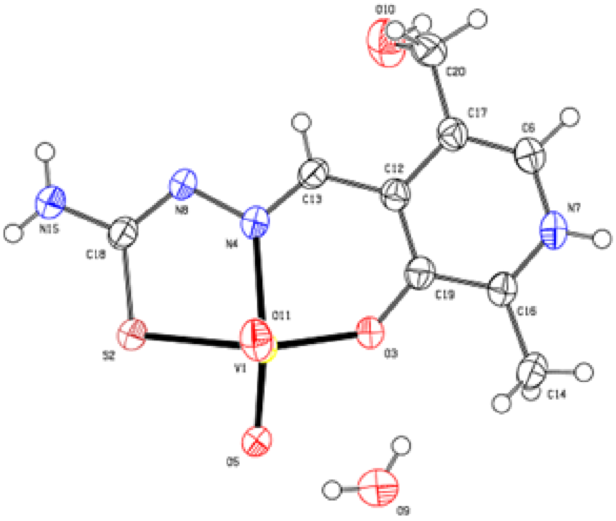
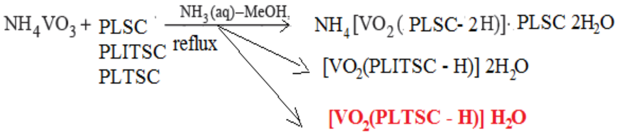


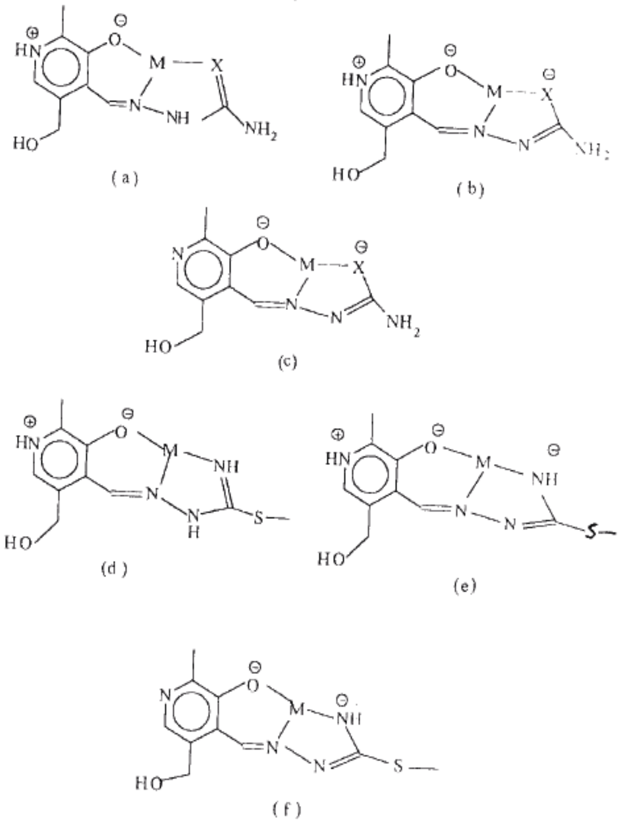
Figure 1. The molecular structure of the complex [VO$_2$(PLTSC-H)] 2H$_2$O, with the atom and ring-labeling scheme



Scheme 3. Formation of the dioxovanadium (V) complexes with PLSC, PLITSC and PLTS ligands

It is interesting that the form of the ligand PLSC that is coordinated is in dianionic form, while the remaining two PLITSC and PLTSC are in monoanionic form. (Scheme 3 and 4).

The asymmetric unit consists of a tridentate ONS monodeprotonated ligandchelating the VO^{2+} and two water molecules. The well-separated complex units of [VO$_2$ (PLTSC–H)] and H$_2$O are connected by hydrogen bonds. Pentacoordinated vanadium (V) ion is in the equatorial plane surrounded by the ONS set of the ligand atoms and an oxygen atom (O5). Other oxygen atom (O11) are in the axial position. The lengths of V-ligand bond distances in the equatorial plane are very similar. The shortest connection is formed with the oxygen atom (V-O5 1.655(2) Å). The same length is also, for other oxygen O11, but in axial position. Yet, the longest connection the central vanadium forms is with S atom (V1- S2 2.3536(9) Å). As already mentioned the PLTS ligand is in its monoanionic form (Scheme 2.) which is confirmed without the presence of hydrogen atoms on N8. On the other hand, the existence of the last hydrogen atom is deduced from the value for the bond angle of 125.39(5) ° which pyridine N7 forms with its neighboring C atoms. The basal plane (O11, N4, O3, S2) of the coordination polyhedron is slightly tetrahedrally deformed. The VO$_2$ group is in the *cis*-configuration with an O–V–O angle of 109.8(1) ° (Table 2). A very similar square-pyramidal arrangement around the vanadium (V) ion was also found in the crystal structure of [VO$_2$(PLITSC–H)] 2H$_2$O [19].



Scheme 4. The mode of coordination and ligands form for PLSC, PLTSC (X= O or S) (a,b,c) and PLITSC (d,e,f)

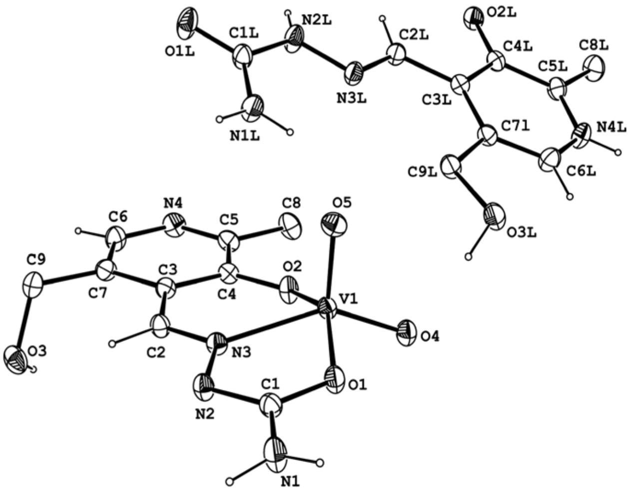


Figure 2. A view of the anionic complex a NH$_4$ [VO$_2$ (PLSC–2H)] PLSC 2H$_2$O

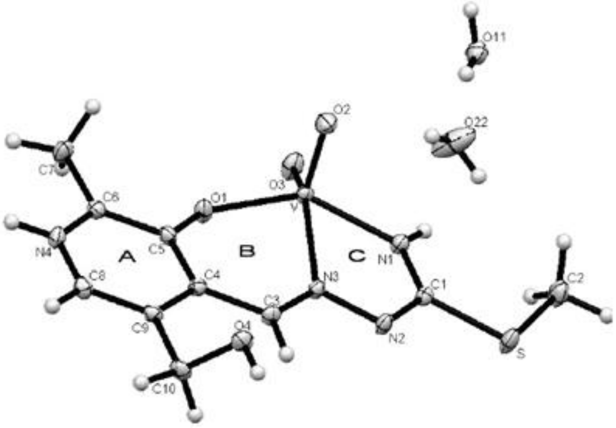


Figure 3. MERCURY view of [VO_2(PLITSC–H)] $2H_2O$ shown with 50 % probability level of the thermal ellipsoids

4. Conclusions

The structure of the title compound $C_9H_{12}V_1N_4O_5S_1$, is an interesting metal complex with a Schiff base ligand derived from thiosemicarbazide and pyridoxal (pyridoxal is a 3-hydroxy-5hydroxymethyl-2-methylpyridine-4-carboxaldehyde). Ligand pyridal-thiosemicarbazone (PLTSC; H_2L) is a tridentate ONS ligand. The V (V) environment is best described as a square pyramid. The equatorial plane is formed by the tridentate ligand and a two molecule of oxigen. This compound crystallizes in monoclinic symmetry, in space group P $2_1/c$, with lattice constants: a=6.3789(2)Å, b=8.8414(2)Å, c=23.3578(7)Å, α=90°, β=91.3963(11)°, γ=90°, V=1316.95 $Å^3$.

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