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Scientific paper

SYNTHESIS AND STRUCTURAL ANALYSIS OF A Cu(II) COMPLEX WITH PYRIDOXAL S-METHYLISOTHIOSEMICARBAZONE (PLITSC) LIGAND

SINTEZA I STRUKTURNA ANALIZA Cu(II) KOMPLEKSA SA PIRIDOKSAL S-METILIZOTIOSEMIKARBAZONOM (PLITSC) LIGANDOM

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Izvod

Reakcijom toplog vodenog rastvora piridoksal-hidrohlorida (PL·HCl) i S-metilizotiosemikarbazidhidrojodida (SMeTSC·HI), u prisustvu $Na_2CO_3 \cdot 10H_2O$, dobili smo piridoksal-metilizotiosemikarbazon (PLITSC; H_2L). Ligand i odgovarajuća so Cu se koordinuju i obrazuju kompleks: braon-obojen, penta-koordinovan, kvadratno-piramidalne strukture, mono(ligand)kompleks Cu(II) formule [Cu(PLITSC)Br(CH_3OH)]Br. U ovom radu je data sinteza i struktura kompleksa sa ligandom u neutralnoj, Zwitter jonskoj formi.

Ključne reči: *Piridoksal-S-metilizotiosemikarbazon, Cu(II) kompleks, Sinteza, Kristalna struktura.*

Abstract

Reaction between a warm water mixture of pyridoxal hydrochloride (PL·HCl), and S-methyilisothiosemicarbazidehydroiodide (SMeTSC·HI) in the presence of $Na_2CO_3 \cdot 10\ H_2O$, we got pyridoxal S-methylisothiosemicarbazone (PLITSC; H_2L). Ligand with appropriate Cu salt is coordinated, to give next complex: dark-brown, penta coordinated, square-pyramidal structure, mono(ligand)complex Cu(II) formula, [Cu(PLITSC)Br(CH_3OH)]Br.In this work is given synthesis and structure of the complex with Schiff-based ligand.

Key words: *Pyridoxal-S-methylisothiosemicarbazone, Cu(II) complex, Synthesis, Crystal structure.*

1. INTRODUCTION

A large number of complexes incorporating PLTSC [1] and PLSC [2,3,4] ligands has been reported, including a recent reviw [5], while only a couple of complexes incorporating PLITSC have been synthesized thus far [6]. Isothiosemicarbazide itself and his derivatives carbazons and

complexes with metals are subjects of labour for a longer period of years with a bigger interest, and it was seen with a bigger number of works [7], and a monograph [8]. The reasons for this affirmation are in fact that this class of compounds is interest with aspect of different kinds of crystal compositions of rewarded complexes, and they were affirmed as biology active molecules [9]. Coordination chemistry of isothiosemicarbazones is interested because of aspects of variety ligands systems, because of their dentate, and they type of sets of donors atoms. Methodical investigations for this type of compounds with different dentate were showed, that unexpectedly, isothiosemicarbazons remnant for coordination instead atom of sulfur, it use as a rule thioamide atom of nitrogen[10,11], which was assured with a larger number of affirmed compositions. There are many complexes with tridentate ligands which were become on base of this class of compounds, in that belong to, and mentioned, pyridoxal S-methylisothiosemicarbazone (PLITSC) with thirdentate ONN sets of donors atoms. In literature, there can be found special points about complexes Fe with the mentioned ligand in sense of physical chemistry and voltametric properties of complex $[Fe(ITSCPL)(ITSCPL\text{-}H)](NO_3)_3$, $[Fe(ITSCPL)Cl_3]\cdot H_2O$ and $[Fe(ITSCPL)_2]OAc\cdot 2H_2O$ [12,13,14], and investigations which were involved for these ligands systems, and they were a topic of one doctor's dissertation [15].

2. EXPERIMENTAL

All comercially obtained reagent-grade chemicals were used without further purification, except for the ligands.

2.1. Synthesis of ligand PLITSC

Mixture of 2.0g (10mmol) PL·HCl and 2.30g (10mmol) SMeTSC·HI ought to pour over with $20cm^3$ H_2O and ought to warm to complete dissolve of their parts. To warm mixture ought to add 3.0g (10mmol) $Na_2CO_3\cdot 10H_2O$ which was dissolved before in $20cm^3$ H_2O. Very soon comes to sedimentation of pale-yellow fibrous crystals and after a couple hours they ought to be filtrate and washed with water and ethanol. Yield: 2.40g.

2.2. Syntheses of complex $[Cu(PLITSC)Br(CH_3OH)]Br$

Warm 0.14g (0.5mmol) PLITSC in $10cm^3$ MeOH and add mixture 0.15g (0.7mmol) $CuBr_2$ in $5cm^3$ MeOH. Green mixture is got which is left behind on room temperature about 50 hours, and after that comes to separation of green monocrystals. Yield: 0.13g.

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 [16] and refined using SHELXL97 [17] on F^2 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 been deposited with the Cambridge Crystallographic Data Base as CCDC reference number 735806 for complex.

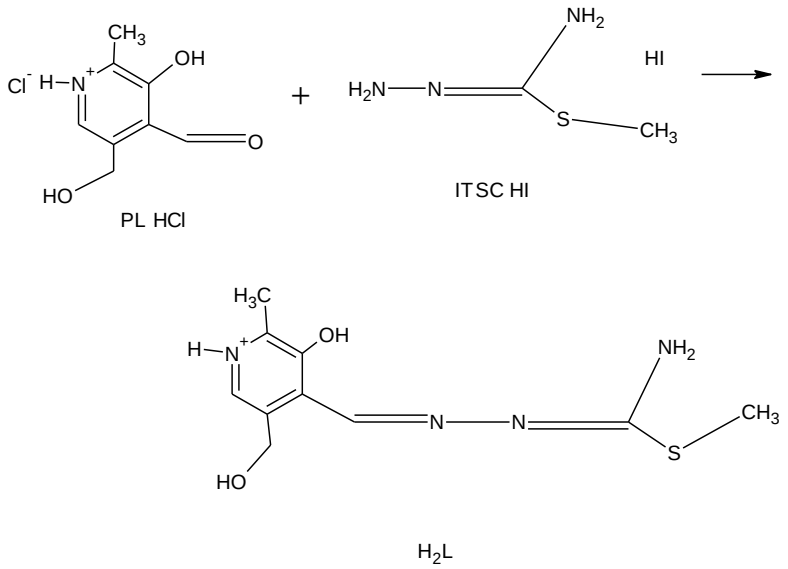
Table 1. Crystal data and structure refinement details of complex

Empirical formula	$C_{11}H_{18}Br_2Cu_1N_4O_3S_1$
Formula weight	478.67
Temperature	294K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.6945(4) α= 96.86(19)° b = 9.7045(4) Å β= 106.73(4)°. c = 13.3238(13) Å γ= 111.520(4)°
Volume	857.604 (14) $Å^3$
Z	2

3. RESULTS AND DISCUSSION

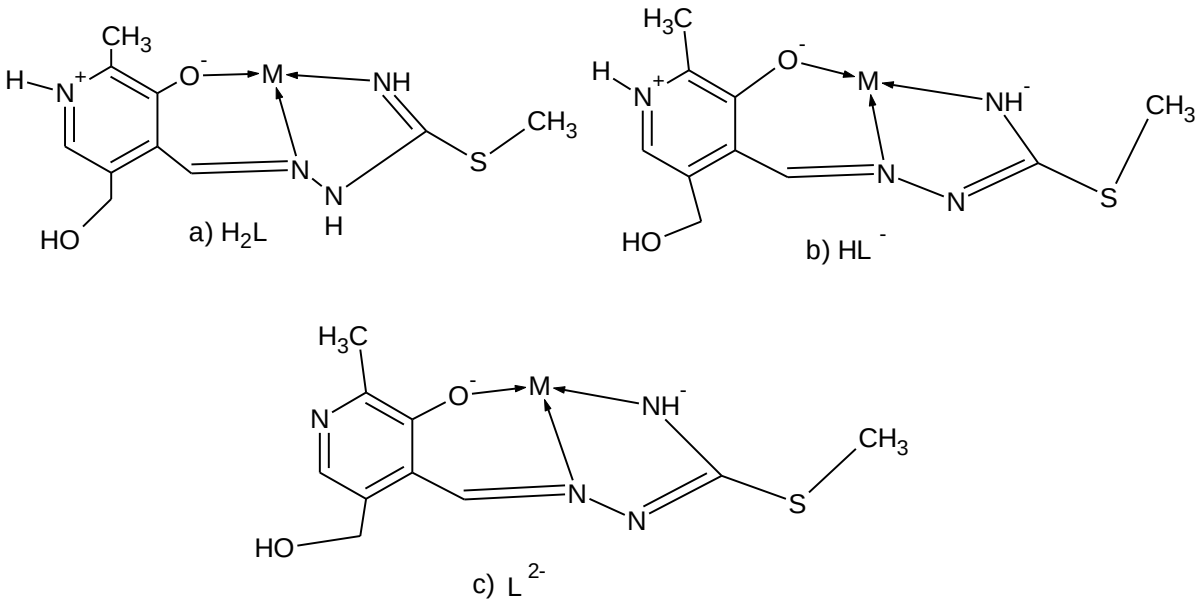
3.1. Synthesis and structure of complexes

Pyridoxal S-methylisothiosemicarbazone (PLITSC; H_2L), is synthesized according to formely described action [15], reaction with some warm water mixture pyridoxal hydrochloride (PL·HCl),[3-hydroxy-5-(hydroxymethyl)-2-methylpyridine-4-carbaldehydehydrochloride]and S-metyilisothiosemicarbazidehydroiodide (SMeTSC·HI) in presence $Na_2CO_3 \cdot 10\ H_2O$ (Scheme 1).



Scheme 1. Synthesis of pyridoxal S-methylisothiosemicarbazone (PLITSC)

The common coordination mode of this and ligand form of PLITSC is presented in Scheme 2, and they are taken out base of results X-ray analysis compositions PLITSC and which is in harmony with former well known compositions [14]. H_2L ligand for coordination use three ligators atom: are the phenolic oxygen, hydrazine nitrogen and atom of nitrogen of the isothioamide group. In that case ONN ligand PLITSC, two metallocycles are formed: one six-membered (pyridoksilydene) and one five-membered (isothiosemicarbazide derivate). PLITSC ligand can coordinated in neutral, monoanionic or dianionic forms (Scheme 2).



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

On the picture Figure 1 is given a structure of a neuter mono(ligand)complex [Cu(ITSPL)Br(CH_3OH)]Br, and in Table 2 are given the length of connections metal-ligand and angles among connections in coordinate sphere of metal.

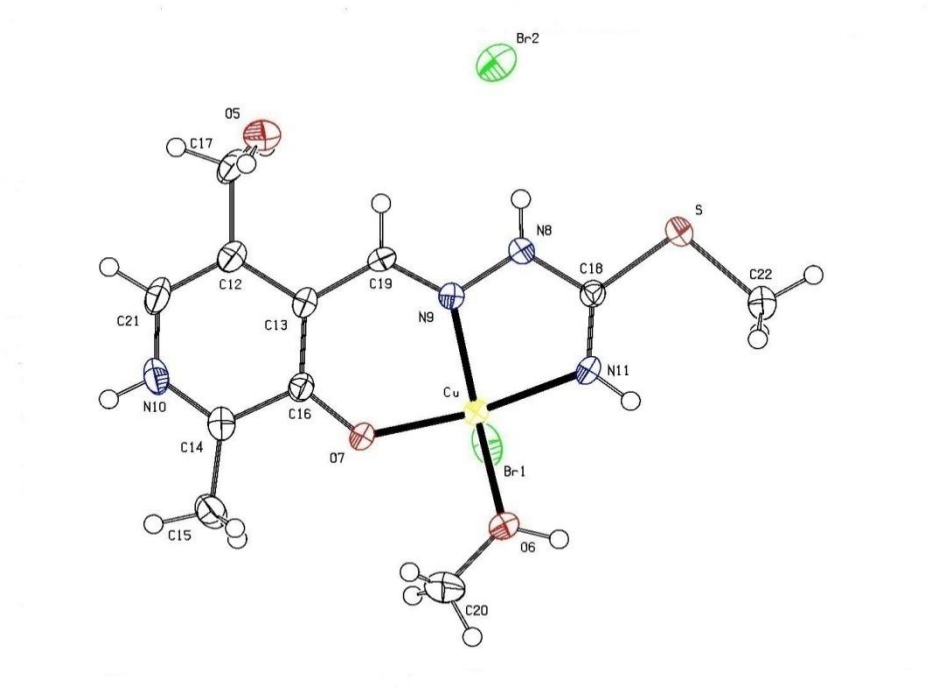


Figure 1. The molecular structure of the complex, with the atom-and ring-labeling scheme

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

Br1-Cu	2.776(5)	N(11)-Cu-N(9)	80.79(15)
Cu-O6	2.008(2)	N(9)-Cu-O(7)	45.84(17)
Cu-O7	1.906(2)	O(7)-Cu-O(6)	46.36(14)
Cu-N9	1.972(2)	O(6)-Cu-N(11)	95.87(16)
Cu-N11	1.964(2)	N(11)-Cu-Br(1)	94.97(16)
		O(6)-Cu-Br(1)	93.16(14)
		O(7)-Cu-Br(1)	95.25(18)
		N(9)-Cu-Br(1)	103.68(15)
		O(7)-Cu-N(11)	168.25(14)
		O(6)-Cu-N(9)	163.09(17)
		C(14)-N(10)-C(21)	125.39(5)

Penta coordinate copper in equatorial plane is surrounded with 5 atoms, three of ONN ligand and one atom oxygen O6 from methanol. Structure of square pyramid gives Br atom in the axial position. The lengths of Cu-ligand connections in equatorial plane are in the very close value. The shortest is connection of phenolic oxygen O7 (Cu-O7 1.906(2) Å). Yet, the longest connection with copper is with Br atom in axial position (Cu-Br1 2.776(5) Å). This complex has a molecule of

ligand is neuter form (H_2L) (see Schema 2.). Affirmation of this is presence atom of hydrogen on nitrogen N8, pyridine N10, as his value of angle which pyridine N10 has with neighbouring C atoms and it is 125.39(5)º.

4. CONCLUSION

The structure of the title compound $C_{11}H_{18}Br_2Cu_1N_4O_3S_1$, is an interesting metal complex with a Schiff base derived from isothiosemicarbazide and pyridoxal (pyridoxal is a 3-hydroxy-5 hydroxymethyl-2-methylpyridine-4-carboxaldehyde). Ligand pyridoxal-Smethylisothiosemi-carbazone (PLITSC; H_2L) is tridentate ONN ligand. The Cu^{II} environment is a square pyramid coordination, the equatorial plane of which is formed by the tridentate ONN-coordinated pyridoxal-Smethylisothiosemicarbazone and one methanol molecule, while the atom Br is in the apical position. This compound crystallizes in triclinic symmetry, in space group P-1, with lattice constants: a=7.6945(4) Å, b=9.7045(4) Å, c=13.3238(13) Å, α=96.86(19)°, β=106.73(4)°, γ=111.520(4)°, V=857.604(14)Å^3, Z=2.

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APENDIX AND SUPLEMENTARY MATERIAL

CCDC 735806 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 http://www.ccdc.cam.ac.uk)

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