American Journal of Chemistry 2014, 4(1): 47-50
DOI: 10.5923/j.chemistry.20140401.08

Synthesis and Structural Analysis of a Cu (II) Complex Incorporating Pyridoxal-S-Methylisothiosemicarbazone (PLITSC) Ligand

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Abstract Reaction between pyridoxal hydrochloride (PL.HCl) and S-methyilisothiosemicarbazidehydroiodide (SMeTSC.HI) in the presence of Na_2CO_3, resulted in the formation of the pyridoxal S-methylisothiosemicarbazone (PLITSC; H_2L) ligand. Reaction of the ligand with CuBr2 yielded a dark-brown, pentacoordinated Cu(II) complex, [Cu(PLITSC) $Br(CH_3OH)$] Br, having a square-pyramidal structure.

Keywords Pyridoxal-S-methylisothiosemicarbazone, Cu(II) complex, Synthesis, Crystal structure

1. Introduction

A large number of complexes incorporating PLTSC (pyridoxal-thiosemicarbazone)[1] and PLSC (pyridoxal-semicarbazone)[2,3,4] ligands has been reported, including a recent review[5], while only a couple of complexes incorporating PLITSC (pyridoxal-S- methylisothiosemicarbaz one) have been synthesized thus far[6]. Isothiosemicarbazide and his derivatives carbazons, including their complexes with metals, have been subjected to intensive research for a very long period resulting in a large number of scientific publications[7], including a monograph[8]. Arguably, the main reason for this affirmation is that this class of compounds is quite interesting due to their structural features as well as potential biological activity[9]. Coordination chemistry of isothiosemicarbazones is interesting, in general, due to a wide variety of possible ligand systems, their denticity and the nature of the donor atoms. Systematical investigations of the coordination properties of these ligands, with different denticity, unexpectedly showed, based on numerous complexes[10,11], that the isothiosemicarbazon fragments used the thioamide nitrogen atom for coordination instead of the sulfur atom. There are many complexes with tridentate ligands which were obtained based on this class of ligands especially employing pyridoxalS-methylisothiosem icarbazone (PLITSC) using the ONN set as donor atoms. The synthesis and physical properties of several iron-based complexes incorporating this ligand have already been reported, including $[Fe(PLITSC)(PLITSC-H)](NO_3)_3$, $[Fe(PLITSC)Cl_3]$. H_2O and $[Fe(PLITSC)_2]$ $OAc{\cdot}2H_2O$ [12,13,14]. Lastly, synthetic and structural investigations involving these ligand systems were a topic of a doctoral dissertation[15].

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Published online at http://journal.sapub.org/chemistry

2. Experimental

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

2.1. Synthesis of Ligand PLITSC

2.0g (10mmol) of PL·HCl and 2.30g (10mmol) of SMeTSCPL were added to 20 cm^3 of H2O and the mixture was warmed to completely dissolve the reactants. To this warm mixture 3.0 g (10 mmol) of $Na_2CO_3.10H_2O$ in 20 cm3 of H_2O was added. Immediate sedimentation of pale-yellow fibrous crystals was observed and after a couple hours they the crystalline material was collected by filtration and washed with water and ethanol. Yield: 2.40g.

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

To a warm methanol solution (10 cm^3) containing 0.14g (0.5mmol) of PLITSC was added 0.15g (0.07 mmol) $CuBr_2$ in 5 cm^3 methanol. Resulting green mixture is left at room temperature for about 50 hours, after which green monocrystals were separated. 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 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 been deposited with the Cambridge Crystallographic Data Base as CCDC reference number 735806 for the complex.

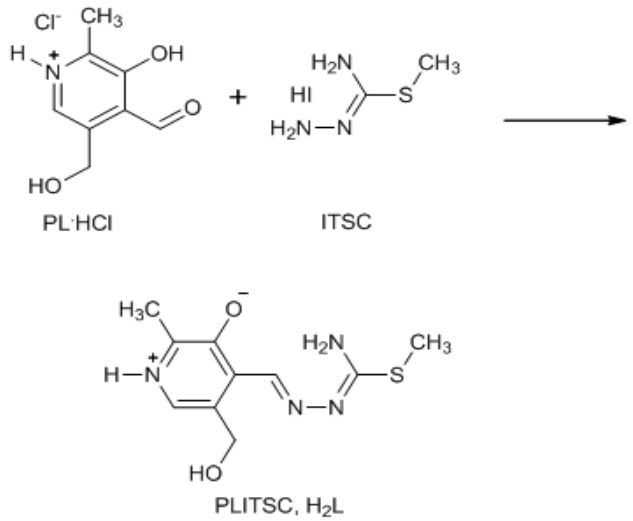
Table 1. Crystal data and structure refinement details of the complex

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 = 1 1 1 . 5 2 0 (4) γ= 111.520(4)°
Volume	857.604 (14) $Å^3$
Z	2

3. Results and Discussions

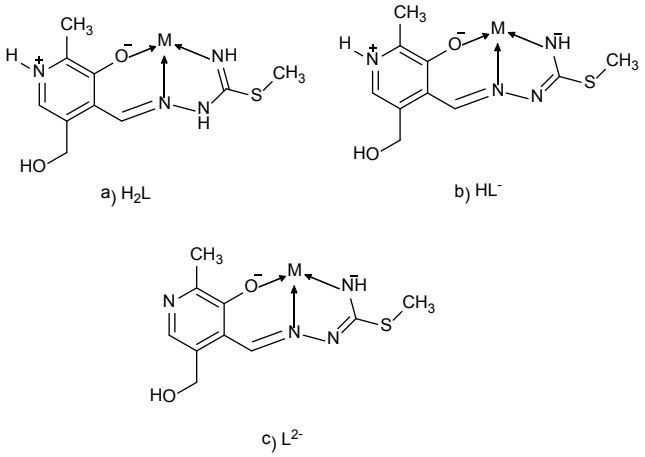
3.1. Synthesis and Structure of Complexes

Pyridoxal-Smethylisothiosemicarbazone(PLITSC, H_2L), is synthesized according to formerly described procedure[15], by reaction of a warm water mixture of PL-hydrocloride(PL.HCl), [3-hydroxi-5-(hydroxymethyl) -2-methylpyridine-4-carbaldehydehydrochloride] and S-metilisothiosemicarbazidehydroiodide (SMeTSC.H_2O) in the presence $Na_2CO_3.10H_2O$ (Scheme 1.)



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

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[14]. The H_2L ligand uses three ligators atom for coordination: the phenolic oxygen, hydrazine nitrogen and nitrogen atom of the isothioamide group i.e the ONN set of atoms. In that two metallocycles are formed: one six-membered (pyridoksilydene) and one five-membered (isothiosemicarbazide derivate). PLITSC ligand can also coordinated in neutral, monoanionic or dianionic forms (Scheme 2).



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

Figure1 includes the structure of the newly synthesized Cu(II) complex, [Cu(ITSPL)Br(CH_3OH)]Br, incorporating the neutral ligand form. In Table 2, selected structural parameters are given.

Table 2. Bond lengths[Å] and angles[^{o}] 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)

Pentacoordinate copper(II) ion is in the equatorial plane surrounded by the ONN set of the ligand atoms, an oxygen atom (O6) from methanol and a bromide atom. The Br ligand is in the axial position. The lengths of Cu-ligand bond distances in the equatorial plane are very similar. The shortest connection is formed with the phenolic oxygen atom (Cu-O7 1.906(2) Å). Yet, the longest connection the central copper forms is with Br atom in theaxial position (Cu-Br1 2.776(5) Å). As already mentioned the PLITS ligand is in its netural form (Scheme 2.) which is confirmed by the presence of hydrogen atoms on N8 and N10. The existence of the last hydrogen atom is deduced from the value for the bond angle of 125.39(5)º which pyridine N10 forms with its neighboring C atoms.

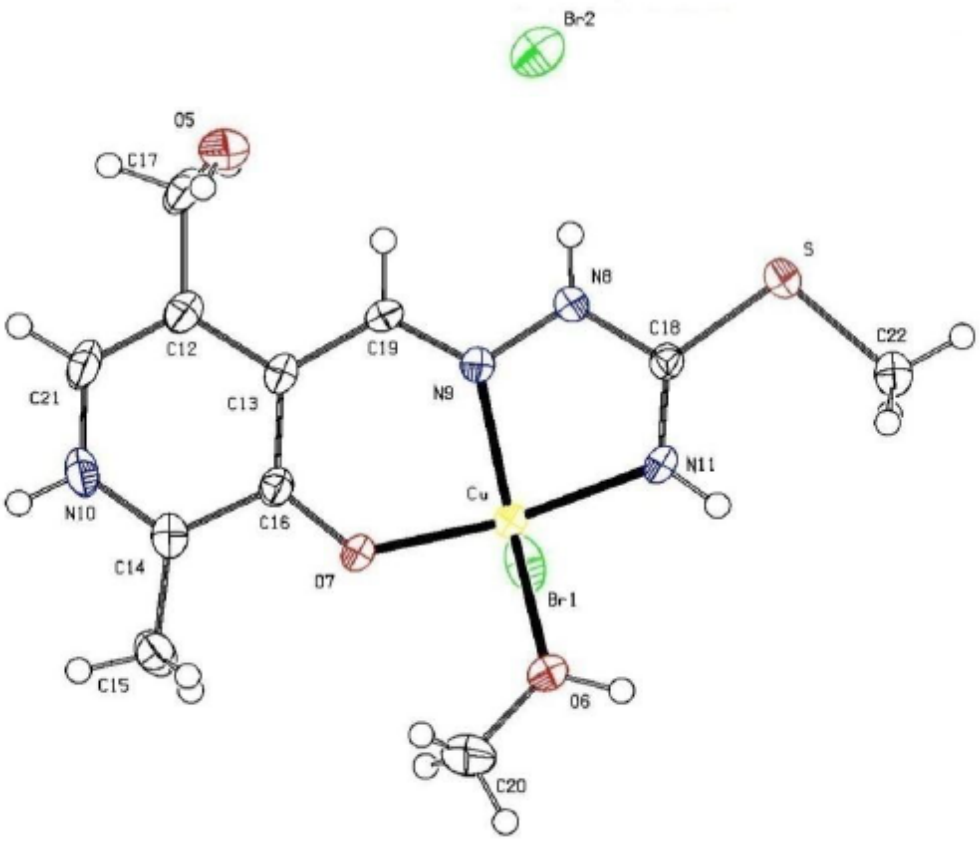


Figure 1. The molecular structure of the complex, with the atom and ring-labeling scheme

4. Conclusions

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 ligand derived from isothiosemicarbazide and pyridoxal (pyridoxal is a 3-hydroxy-5hydroxymethyl-2-methylpyridine-4-carboxaldehyde).

Ligand pyridoxal-S-methylisothiosemicarbazone (PLITS C; H_2L) is a tridentate ONN ligand. The Cu(II) environment is best described as a square pyramid. The equatorial plane is formed by the tridentate ligand and a molecule of methanol, while the Br atom 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) $Å^3$.

5. Supplementary Information

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

ACKNOWLEDGMENTS

The author acknowledge the Oxford Chemical Crystallography Service for the use of the instrumentation and many thanks D.J. Watkin research group for help.

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