



SPECTRAL STUDIES OF COPPER(II) COMPLEXES OF 6-(3-THIENYL)PYRIDINE-2-THIOSEMICARBAZONE

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ABSTRACT.

Two novel copper(II) complexes $[Cu(HL)Cl]Cl \cdot H_2O$ (1) and $[Cu(L)NO_3] \cdot H_2O$ (2) of the three NNS donor thiosemicarbazone ligand 6-(3-thienyl) pyridine -2-thiosemicarbazone have been synthesized. The ligand and its copper(II) complexes were characterized by elemental analysis (C, H, N, and S), FT-IR, UV-visible, magnetic susceptibility and molar conductance. The thiosemicarbazone is present either as the thione form in complex 1 or as thiol form in complex 2 and is coordinated to copper(II) atom via the pyridine nitrogen atom, the azomethine nitrogen atom and the sulfur atom. The physicochemical and spectral data suggest square planar geometry for copper(II) atoms.

Keywords: Thiosemicarbazone, Copper (II) complexes, Spectral studies.

INTRODUCTION

Thiosemicarbazone ligands obtained by the condensation of thiosemicarbazide with an aldehyde or ketone are an important class of Schiff bases compound. This importance comes as a result of their wide range of biological application specifically as antifungal, antibacterial, antioxidant and anticancer agents [1-5]. Several thiosemicarbazonecopper(II) complexes were synthesized and their biological activities were studied [6-8]. In this paper, we describe the synthesis and spectroscopic characterization of novel thiosemicarbazone ligand and its copper(II) complexes.

MATERIALS AND METHODS

General Procedure

All chemicals are reagent grade and used as commercially purchased without further purification. The elemental analysis was carried out on a flash EA1112 CHNS-O Analyser.



Melting points were determined in an open capillary tube using an Electrothermal 9100 Digital Melting Point apparatus. Infrared spectra were recorded as KBr discs, using a Perkin – Elmer FT-IR model GX infrared Spectrometer, UV spectra were obtained as DMSO solutions with UV-2450 version UV-VIS spectrometer. Magnetic moment of the complexes at 300 K was measured on a Shrewood Scientific Magnetic Susceptibility Balance. Conductance values were obtained with a EUTECH COND 610 Conductometer at 298 K from $10^{-3} \text{ mol L}^{-1}$ solutions of complexes in DMF.

Synthesis of the Ligand

A solution of thiosemicarbazide (0.091 g, 10 mmol) in ethanol (50 ml) with a few ml of distilled water was heated under reflux for half an hour to completely dissolve it. Hot ethanolic solution of 6-(3-thienyl) pyridine-2-carboxaldehyde (1.9 g, 10 mmol) was added to the thiosemicarbazide solution followed by a few drops of concentrated HCl. The mixture was heated under reflux for 2 hours. The resulting yellow coloured precipitate was filtered, washed with ethanol and dried.

Synthesis of Complexes

Synthesis of $[\text{Cu}(\text{HL})\text{Cl}]\text{Cl} \cdot \text{H}_2\text{O}$ (1)

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17 g, 1 mmol) solid was added to a solution of acetonitrile: methanol (3:1) (40 ml) of Htpytsc (1mmol, 0.26 g). The mixture was stirred for 1 hour. The complex formed was filtered, washed with acetonitrile, ether and dried in vacuo over silica gel.

Synthesis of $[\text{Cu}(\text{L})\text{NO}_3] \cdot \text{H}_2\text{O}$ (2)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.3 g, 1 mmol) solid was added to an ethanolic solution (40 ml) of Htpytsc (0.26 g, 1 mmol). The mixture was stirred for 2 hours. The complex formed was filtered, washed with ethanol, ether and dried in vacuo over silica gel.

RESULT AND DISCUSSION

Elemental analysis and physical properties of the ligand HTPYTSC and Copper (II) complexes are given in TABLE (1). The complexes are stable in air. They are soluble in DMSO,



DMF, and in most of organic solvents, but insoluble in water. The molar conductivities of complexes which have been recorded in DMF (10-3M) at room temperature show that complex 1 has value consistent with 1:1 electrolytes, indicating that one chloride anion was out of the coordination sphere, acting as counter ion[9]. However, the molar conductivity value of complex 2 suggest that is non electrolyte [10], indicating that the anion and the ligand are coordinated to the central copper(II). The magnetic susceptibilities at room temperature show that the copper(II) complexes are paramagnetic and have magnetic moments close to the theoretical spin only value (1.73 B.M) [11].

TABLE (1).Analytical data and physical properties of the ligand and copper (II) complexes.

Compound	c olour	Y ield	M .p(° C)	Found (Calcd) %				M(B.M.)	Λ M*
				C	H	N	S		
HTPYTSC	Y ellow	9 5%	2 16- 218	4 6.63 (5 0.37)	4 .79 (3.8 5)	2 0.62 (2 1.36)	2 1.27 (2 4.44)	-	-
[Cu(HL)Cl]C H ₂ O (1)	G reen	7 5%	1 78- 180	3 1.35 (31.85)	2 .22 (13.51) 2.92	1 2.54 (5.46)	1 5.52 (1 5.46)	1.7	8 0
[Cu(L)NO ₃] .H ₂ O(2)	G reen	6 0%	2 30- 232	3 3.88 (3 2.63)	1 .84 (2.74	1 6.03 (17.30)	1 4.83 (5.84)	1.7	5 0



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ΛM^* Molar conductivity of 10^{-3} M DMF solution, in $Scm^2 mol^{-1}$

The principal IR bands of the ligand and copper(II) complexes are listed in TABLE (2). The IR spectra of the ligand (HTPYTSC) shows $\nu(N-H)$ in the range of $3391 - 3275 cm^{-1}$ for $(-NH_2)$ and at $3175 cm^{-1}$ for $(-NH-)$. In the spectra of complexes these bands shift to lower energies [12]. Suggesting differences in hydrogen bonding of $(-NH)$ between the uncomplexed and complexed thiosemicarbazone. The band at $3175 cm^{-1}$ in the spectrum of free ligand due to $\nu(-NH-)$ is absent in the spectrum of complex 2 providing strong evidence for deprotonation of the thiosemicarbazone and chelation in the thiolate form. The strong band observed at $1607 cm^{-1}$ in the spectrum of the ligand can be assigned to $\nu(C=N)$ [13]. This later frequency shifts to higher region frequency [14-15] in the spectra of the copper (II) complexes, indicating the coordination of nitrogen of the azomethine group to the central metal atom in these complexes. The presence of a new band at $497 cm^{-1}$ and $491 cm^{-1}$ due to $\nu(Cu-N)$ for complex 1 and 2, respectively, thus confirming the coordination via the azomethine nitrogen [16-17]. The band appearing around $1351 cm^{-1}$ in the spectrum of the ligand has been shifted to lower frequency indicating coordination of thiolate/thionesulfur [16]. This coordination is confirmed by the presence of a new band at $373 cm^{-1}$ and $389 cm^{-1}$ [18-19] that can be assigned to $\nu(Cu-S)$ for the copper(II) complexes. Coordination of the pyridine nitrogen is indicated by a positive shift of the ring deformation band found around $612 cm^{-1}$ in the spectra of the thiosemicarbazone ligand to above $612 cm^{-1}$ in the complexes spectra [20-21]. Pyridine nitrogen coordination is further proved by bands observed at $280 cm^{-1}$ and $308 cm^{-1}$ assignable to $\nu(Cu-Npy)$ [22] in the spectrum of copper(II) complexes. The $\nu(Cu-Cl)$ band in complex 1 has been assigned in the $315 cm^{-1}$ [23-24]. The spectrum of 2 exhibits strong band at $1384 cm^{-1}$ and a weak band at $1011 cm^{-1}$ together with the combination band at $1763 cm^{-1}$ indicating the presence monodentate nitrate ion [25].



TABLE (2). Principle IR bands of the ligand and copper (II) complexes (cm⁻¹).

Compound	ν [-NH ₂]	ν [-NH-]	ν (C=N)	ν (C=S)	ρ γ (ip)	ν (M-N)	ν (M-S)	ν (M- Npy)	ν (M- Cl)	ν (M- NO ₃)
3391	3		1	1	6	-	-	-	-	-
3275	175		607	351	12					
[Cu(HL)Cl]	3	3	1	1	6	4	3	28	3	-
Cl H ₂ O (1)	264	129	627	334	19	97	73	0	15	
[Cu(L)NO	3	-	1	1	6	4	3	30	-	2
3]. H ₂ O(2)	232		616	323	15	91	89	8		63

The tentative assignment of the significant electronic spectral band of the ligand and copper(II) complexes are presented in TABLE (3). The UV-Visible spectra of the ligand show two bands. An absorption at 37313cm⁻¹ is assigned to a ring $\pi - \pi^*$ transition and the band in the 28653cm⁻¹ is assigned to n - π^* transition within the thiosemicarbazone moiety involving mainly C=N and C=S [26-27]. The spectra of the complexes generally show the higher energy band unshifted, but the n - π^* transition associated with pyridine ring is shifted to higher energies indicating coordination via the pyridine nitrogen [28]. In addition to showing the $\pi - \pi^*$ and n - π^* the electronic spectra of the complexes display a S – Cu charge transfer (LMCT) band at 24038 cm⁻¹ and 24510 cm⁻¹ for complex 1 and 2 , respectively [29].



TABLE (3). Electronic spectral data (cm^{-1}) of thiosemicarbazone ligand and its copper
(II) complexes

Compound	$\pi - \pi^*$	$n - \pi^*$	CT
HTPYTSC	37313	28653	-
[Cu(HL)Cl]Cl H ₂ O (1)	37037	30303	24038
[Cu(L)NO ₃]. H ₂ O(2)	37173	32680	24510

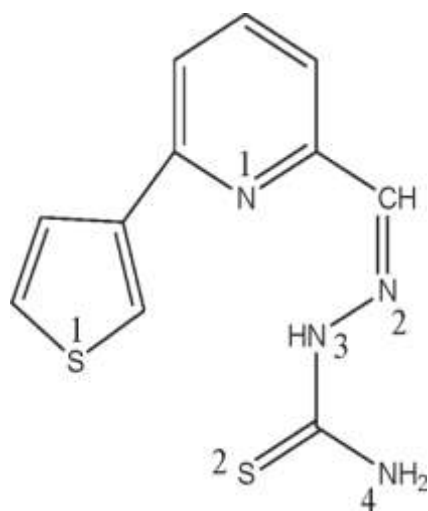


FIGURE 1.6-(3-thienyl) pyridine-2-thiosemicarbazone ligand.

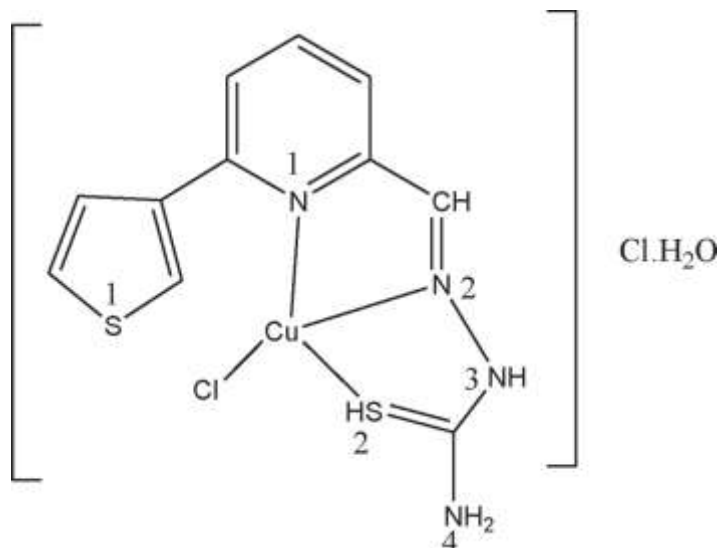


FIGURE 2. Proposed structure of complex 1.

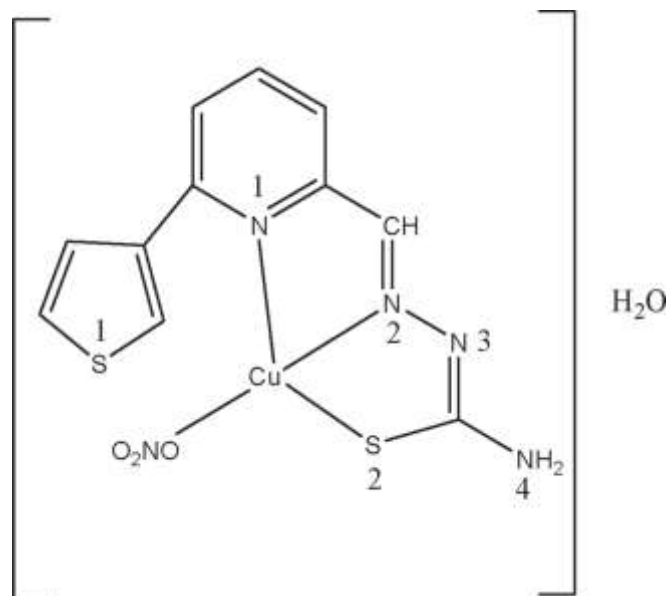


FIGURE 3. Proposed structure of complex 2.

CONCLUSION

It may be concluded that the 6-(3-thienyl)pyridine-2-thiosemicarbazone HTPYTSC ligand coordinated to the copper (II) atom as a tridentate N,N,S donor leading to the formation of six membered chelate ring. The chelate are proposed to have a square planar geometry.



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