

PREPARATION OF COPPER COMPLEXES FROM 1-MONOSUBSTITUTED-3-BENZOYLTHIOUREA LIGANDS.

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ABSTRACT : Ligands type 1-monosubstituted-3-benzoylthiourea were prepared using the Hartman-Reuther Method. The copper complexes prepared from these ligands were characterized by ESR, IR, and Electronic Spectroscopy, Differential Thermal Analysis, and elemental analysis. These ligands have shown unexpected behavior, forming Copper (II) complexes in which their both N-H groups, were probably deprotonized, with a polymeric structure.

Key words : Ligands, 1-monosubstituted-3-benzoylthiourea, ESR spectra, copper(II) complexes.

RESUMEN : Ligandos del tipo 3-Benzoylthiourea-1-monosustituidas fueron preparados por el Método de Hartman-Reuther. Los complejos de cobre sintetizados a partir de estos ligandos fueron caracterizados por ESR, Espectroscopías IR, Espectroscopía Electrónica, y Análisis Térmico Diferencial. Los ligandos obtenidos presentaron un comportamiento inesperado, al formar complejos de Cobre (II) en los cuales sus dos grupos N-H están probablemente desprotonados con una estructura polimérica.

Palabras clave : Ligandos, Benzoylthiureas monosustituidas, Espectros ESR, Complejos de cobre (II)

INTRODUCTION

At present, hydrometallurgical processes are the predominant in the copper extraction from poor copper ores and other alternative sources as waste materials. The hydrometallurgical process are limited by the properties of used extractants, such as their selectivity, extraction kinetics, solubility at different values of pH, toxicity and cost.

Generally is stated that extractants are quelating ligands, which are forming electroneutral complexes with the central atom, and exhibiting a good solubility when are mixed with non polar solvents, allowing in this way, its separation from aqueous phase.

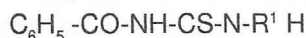
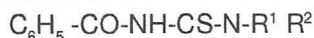
For the particular case of copper extraction, the reviewed literature reports, that quelating ligands presenting Oxygen donor atoms [1], such as the b-diketons, predominate over their ligands containing other donor atoms like N, S, Se, etc. In other way, has been observed that ligands with mixed Oxygen and Nitrogen donor atoms, also

act as copper quelating. The grate part of these mixed ligands, could be derived from the Oxygen donor ligands, changing at least one of their Oxygen atoms by the group NH, OH, or NH₂.

The diketons properties could be modified by the replacement of some groups in the periphery of ligand molecule, or due the change of the Oxygen by other donor atom, as are the cases for thio- and dithioiketons. Among the ligands used as extracting agents in hydrometallurgy, has been reported that Benzoylthiourea, have a grate chelating ability with different metal (II) ions, and particularly with copper (II) [1]. For that reason, we focused our attention on 3-Benzoylthiourea type molecules, which additionally to their Oxygen and Sulfur donor atoms, present two Nitrogen atoms, showing a variety of possible bonds.

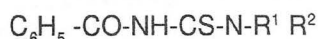
Analyzing this type of molecules, the comparison between 1,1'-disubstituted-3-benzoylthiureas and 1-monosubstituted-3-benzoylthiureas,

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shows that two NH groups are present in the later one, thus formally giving the possibility of two protons ionization.

Considering the possible ZZ', EE', ZE' and EZ' structures, together with possible dianion formation, the 1-monosubstituted-3-benzoylthioureas bring new features into studied systems, being considered as the main task of present work, to prepare and characterize different copper complexes from following 1-monosubstituted-3-benzoylthiourea ligands,



where:

R¹ = Et, CH²Ph, Ph, o-PhOH, m-PhOH, p-Ph-COOH, p-PhOMe ; R² = H

As a complementary analysis, the obtained complexes were compared with other copper complexes also prepared in this research, but from different disubstituted 3-benzoylthiourea ligands.

EXPERIMENTAL PREPARATIONS OF LIGANDS AND COMPLEXES

1. Preparation of 1-monosubstituted-3-benzoylthiourea ligands:

The 1-monosubstituted-3-benzoylthiourea (abbreviated as H(H,R-btu) ligands were prepared according to the Hartmann and Reuther method [5].

A solution of 0.2 mol of Benzoylchloride in 50 mL of Acetone was under stirring, quickly added to a solution of 0.2 mol of KSCN in 100 mL of Acetone. The resulting mixture was heated to 328 K and kept under reflux for two hours. After cooling to room temperature a cold solution of 0.25 mol of the primary amine was dropwise added to this mixture. As the resulting reaction released a considerable amount of heat, the amine addition must be slow to keep solvent just under slow reflux. The reaction mixture was stirred during additional two hours and then was added to a diluted water solution of HCl (1:1 v/v) to destroy unused residuals of Benzoylisothiocyanate.

Crude products were recrystallized from Ethanol. The purity of ligands were

checked by elemental analysis and by melting point determination.

2. Preparation of the Cu (Et-btu) complex:

A solution of 500 mg (2.5 mmol) in 70 mL of Methanol was mixed with a solution of 1104,1 mg (5mmol) of H(H, Et-btu) in Acetone (25 mL) at room temperature and under stirring. After one hour the light yellow precipitate was filtered off and washed with Methanol-Diethylether (1:1) and dried.

Yield 650 mg, m.p. 403- 405 K.

Analysis.. calc. For [CuC₁₀H₁₁N₂SO]_n :

Calc.: C, 44.35; H, 4.09; N, 10.34; S, 11.84; Cu, 23.47%.

Found: C, 43.73; H, 4.05; N, 9.91; S, 12.00; Cu, 23.50%.

3. Preparation of the Cu(Bzy-btu) complex:

A solution of 600 mg (3 mmol) of Cu (CH₃COO)₂·H₂O in 90 mL of Methanol, was added to a solution of 811 mg of H(H, Bzy-btu) (wazzu 3 mmol) in 20 mL of Acetone. The resulting mixture was kept under stirring at room temperature for one hour. The light green product was filtered off and washed with Methanol-Diethylether (1:1) and dried.

Yield 650 mg, m.p. 412- 413 K.

Analysis calc. For [CuC₁₅H₁₃N₂SO]_n :

Calc.: C, 54.12; H, 3.94; N, 8.42; S, 9.63; Cu, 19.09%.

Found: C, 54.83; H, 3.82; N, 8.69; S, 9.88; Cu, 18.46%.

4. Preparation of the Cu (Ph-btu) complex:

A solution of 500 mg (2.5 mmol) of Cu (CH₃COO)₂·H₂O in 50 mL of Methanol was mixed with a solution of 1282 mg (5 mmol) of H(H,Ph-btu) in 30 mL of Acetone, and resulting mixture was kept under stirring at room temperature for one hour. The yellow product was filtered off and washed with diethylether and dried.

Yield 850 mg, m.p. 395-397 K.

Analysis calc. For CuC₁₄H₁₁N₂SO:

Calc.: C, 52.73; H, 3.47; N, 8.79; S, 10.06; Cu, 19.93%.

Found: C, 51.40; H, 3.49; N, 8.42; S, 10.87; Cu, 19.20%.

5. Preparation of the Cu(p-PhOMe-btu) complex:

A 570 mg (2 mmol) of H(H,PhOMe-btu) was solved in 80 mL of Acetone, and were mixture with a solution of 200 mg (1 mmol) of Cu(CH₃COO)₂·H₂O in Methanol. The reaction was kept under stirring at room temperature for one hour. The mixture changes from its original green color to chest-

nut yellow, and a precipitate of the same colour was filtered off, washed with Methanol and dried.

Yield 350 mg, m.p. 425- 425.5 K.

Analysis calc. For $\text{CuC}_{15}\text{H}_{13}\text{N}_2\text{SO}_2$:

Calc.: C, 51.64; H, 3.76; N, 8.03; S, 9.19; Cu, 18.21%.

Found : C, 50.63; H, 3.71; N, 8.01; S, 9.55; Cu, 18.31%.

6. Preparation of the $\text{Cu}_3(\text{o-PhO-btu})_2$ complex:

A solution of 599 mg (3 mmol) of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ in Methanol (60 mL) was added to a solution of 817 mg (3 mmol) of $\text{H}(\text{H}, \text{o-PhOH-btu})$ in 75 mL of Acetone, and was kept under stirring at room temperature for 3/2 hours. The dark brown product was filtered off and washed with ether and dried.

Yield 700 mg, m.p. 591.5 - 592 K.

Analysis calc. For $\text{Cu}_3\text{C}_{28}\text{H}_{19}\text{N}_4\text{S}_2\text{O}_4$:

Calc.: C, 46.05; H, 2.62; N, 7.67; S, 8.78; Cu, 26.11%.

Found : C, 46.42; H, 2.67; N, 7.78; S, 8.78; Cu, 24.21%.

7. Preparation of the $\text{Cu}(\text{H}, \text{m-PhOH-btu})$ complex:

To 1630mg (6 mmol) of $\text{H}(\text{H}, \text{m-PhOH-btu})$ in 30 mL of Acetone, were added 600 mg (3 mmol) of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ in 180 mL of Methanol, and kept under stirring for one hour. The light brown product was separated and washed with Diethylether and dried.

Yield 1200mg, m.p. 419 - 420 K.

Analysis calc. For $\text{CuC}_{14}\text{H}_{11}\text{N}_2\text{SO}_2\cdot 1/2\text{MeOH}$:

Calc. : C, 49.63; H, 3.73; N, 7.98; S, 9.14; Cu, 18.11%.

Found : C, 49.12; H, 3.58; N, 7.82; S, 10.59; Cu, 18.02%.

8. Preparation of the $\text{Cu}(\text{H}, \text{p-PhCOO-btu})$ complex:

A solution of 600 mg (2 mmol) of $\text{H}(\text{H}, \text{p-PhCOOH-btu})$ in 100 mL of hot Acetone was mixture under stirring with a solution of 200 mg $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (1 mmol). The obtained green mixture changes after two minutes to yellow colour. One hour later, the yellow precipitate was filtered off, washed with Diethylether and dried

Yield 350 mg, m.p. 427 - 433 K

Analysis calc. For $\text{CuC}_{15}\text{H}_{11}\text{N}_2\text{SO}_3$:

Calc. : C, 49.79; H, 2.79; N, 7.35; S, 8.86; Cu, 17.56%.

Found : C, 46.53; H, 2.89; N, 7.19; S, 9.73; Cu, 17.16%.

RESULTS AND DISCUSSION

Several experiments with different molar ratios of reactants and different solvents were performed with prepared ligands. Except the $\text{H}(\text{H}, \text{o-PhOH-btu})$ all used ligands behave as H_2LL acids and have formed complexes with the $\text{Cu}(\text{LL})$ stoichiometry, however is important to point out, have been found that it is possible to isolate from the filtrates of the reactive mixtures other type of copper (II) complexes [6]. The exceptional $\text{H}(\text{H}, \text{o-PhOH-btu})$ ligand formed the product of the $\text{Cu}_3(\text{LL})_2$ stoichiometry. All compounds are stable in air and are soluble in Chloroform.

The thermogravimetric measurements were realized on a derivatograph MOM Budapest by heating 100 mg of sample up to 773 K. Thermal stability of all complexes up to ca. 473 K are consistent with $\text{Cu}(\text{R}_2\text{btu})_2$ stoichiometry. The thermal decomposition of all complexes precedes in one step and no intermediates existence was registered.

The infrared spectra of nujol suspensions in the region $400 - 4000 \text{ cm}^{-1}$ were measured on a PU 9800 FTIR instrument. The IR spectra of the ligands contain (Table 1) the bands between $3400 - 3140 \text{ cm}^{-1}$ range assignable to the N-H or to the O-H (if present) vibrations. The strong bands in this region were found only for the $\text{Cu}(\text{m-PhOH-btu})\cdot 1/2\text{MeOH}$ complex which is in good agreement with presence of O-H groups. All other complexes have shown no bands, or very weak bands in this region, perhaps due to moisture, which can be taken as the additional argument with observed stoichiometry, for supporting the possibility of both N-H group ionization in complex formation. It is necessary to states that no bands in this region were found for the complex of the $\text{Cu}_3(\text{o-PhO-btu})_2$ stoichiometry.

The C-O vibration of free ligands was found in the region from 1691 to 1579 cm^{-1} (Table 1), while for all complexes these bands were observed in region between 1711 and 1572 cm^{-1} . The C-S vibration might be for the prepared ligands found in the $1197 - 1134 \text{ cm}^{-1}$ range, while those bands for complexes were found between 1186 and 1122 cm^{-1} .

The prepared complexes are of brown to yellow colour and their reflectance spectra exhibit very broad and poorly resolved bands in the form of shoulders in the $500 - 900 \text{ nm}$ region of wave lengths.

The electronic spectra of nujol suspensions in the region from 330 to 800 nm were measured on a SPECORD M 400 instrument. There were observed three different types of ESR spectrum of the powdered polycrystalline sample. The ESR spectrum of the Cu(Et-btu) is of the axial type with hyperfine splitting of g_{\parallel} component (Figure 1). Using the simulation program for ESR spectra the $g^{\perp} = 2.048$, $g_{\parallel} = 2.30$ and $A_{\parallel} = 158$ G values were obtained by fitting calculated and experimental data. The ESR spectrum is in good agreement with proposed square coplanar geometry for this complex. The ESR spectra of other two complexes (Cu(Bzy-btu) and Cu₃(o-PhO-btu)₂) show

rather broad isotropic signals at g-values 2.094 and 2.085 respectively. The ESR spectra of the other complexes are rather complicated (Figures 2 - 5), showing partially axial symmetry type, but indicating possible presence of different type of copper atom coordination. The ESR spectra of polycrystalline samples in X-band zone were taken on a EPR BRUKER ER 200E-SRC instrument at 293 K.

The magnetic susceptibility measurements were carried out on a Laje Shore Susceptometer in temperature region from 80 to 300 K, and showed for prepared complexes, weak signals similar to that of benzoylthiourea complexes.

Table 1. Selected data from Infrared Spectra of H(H,R-btu) ligands and their Cooper complexes.

Compound	thioamide bands						
	$\nu(\text{N-H})$ cm ⁻¹	$\nu(\text{C-O})$ cm ⁻¹	I	II	III	IV	$\nu(\text{C-S})$ cm ⁻¹
H (H,Et-btu)	3219sb	1676vs 1601m	1560s 1525sb 1487m	1331m 1319sh 1302w	1259s	1093m 1080m 1064m 1024m 999m	1196s 1147m
Cu (Et-btu)	3175wb	1604s	1556s	1342s 1489w 1290mb	1219m 1313m	1095w 1070w 1045w 1024w	1176w 1153w
H (H,Bzy-btu)	3258sb 3163sb	1672s 1603m 1585sh	1549s 1489m	1319w 1300w	1253s 1207w	1097w 1082w 1064m 1028w 1001w 825w	1190vw 1167s
Cu (Bzy-btu)	3377wb 3173vw	1601m 1585s	1533vw 1481s 1400sb	1348m 1307w 1290w	1251w 1209m	101m 1076m 1026m 1001w 985w	1178m 1157w
H (H,Ph-btu)	3277sb	1672m 1606vs	1568vs 1535s 1489s 1485s	1361vs 1315m 1300m	1257s	1084m 1028w 999w 979vw	1188m 1147s
Cu (Ph-btu)		1711m 1676w 1606vs 1589s,sh	1570vs 1531vs 1452s	1327vs	1286vs	1084m 1070m 1024m 1003w 970w	1170m
H(H,p-PhOMe-btu)	3370mb 3175mb	1668s 1647s 1597s	1533vs 1512vs	1338s 1300m	1271s 1250s	1109m 1086m 1072w 1020s 999w	1184m 1172w 1118w
Cu(p-PhOMe-btu)		1604mb 1585m	1510vs	1338sh	1294w 1246s 1209mb	1105sh 1089m 1033m	1174m 1122vw

Table 1. Selected data from Infrared Spectra of H(H,R-btu) ligands and their Cooper complexes (continuación).

Thioamide Bands							
Compound	$\nu(\text{N-H})$	$\nu(\text{C-O})$	I	II	III	IV	$\nu(\text{C-S})$
	cm^{-1}	cm^{-1}	cm^{-1}				cm^{-1}
H(H,o-PhOH-btu)							
	3310sb	1658m	1560vs	1342m	1282m	1101m	1197m
	3127sb	1606s	1537vs	1317s	1259s	1080m	1180m
	(OH)	1599s	1504s			1037w	1159m
			1489s			1026w	1145m
Cu₃(o-PhO-btu)₂							
		1653vw	1520vw	1398s	1280m	1078m	1186w
		1603w	1489sh	1302m	1259s	1039w	
	1153w						
		1583m				1026w	
		1572m					
H(H,m-PhOH-btu)							
	3321s	1672m	1552s	1329s	1290vs	1099m	1176s
	1610sh	1525vs	1304s	1261s	1080m	1161s	
		1597m			1238s	1022w	1142s
						1001w	
Cu(m-PhO-btu)							
	3402s	1689m	1556vs	1338vs	1290s	1087m	1174w
	3304s	1595s	1537vs	1305s	1238m	1070w	1147s
	(OH)	1572s			1205m	1026w	
H(H,p-PhCOOH-btu)							
	3258sb	1691vs	1560sh	1331s	1298s	1103w	1192w
		1674m	1527s	1317s	1261s	1084w	1178w
		1591s	1489m		1241w	1072w	1167m
		1579sh				1014vw	1157m
						1134w	
Cu(H,p-PhCOO)							
		1691s	1529s	1323m	1284m	1101w	1169mw
		1603m	1489vw			1084w	
		1579sh				1068w	
						1016w	
						945w	

w = weak

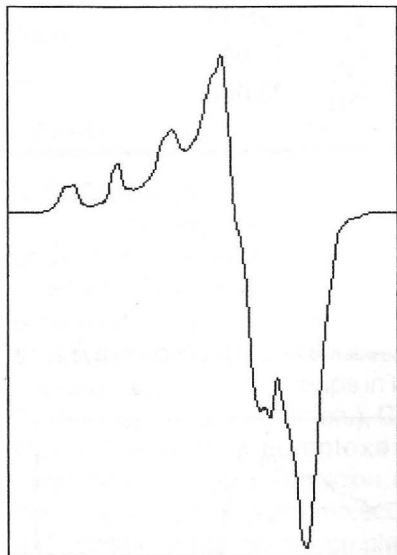
s = strong m = medium

vs = very strong

b = broad

sh = shoulder

Figura 1. The ESR Spectrum of polycrystalline powder of $\text{Cu}(\text{Et-btu})$ at 293 K



$\text{Cu}(\text{Et-btu})$

$g_{\perp} = 2.048$

$g_{\parallel} = 2.300$

$A_{\parallel} = 158.0$

Figura 2. The ESR Spectrum of polycrystalline powder of $\text{Cu}(\text{p-PhOMe-btu})$ at 293 K

$\text{Cu}(\text{p-PhOMe-btu})$

$g_{\perp} = 2.0313$

$g_{\parallel} = 2.300$

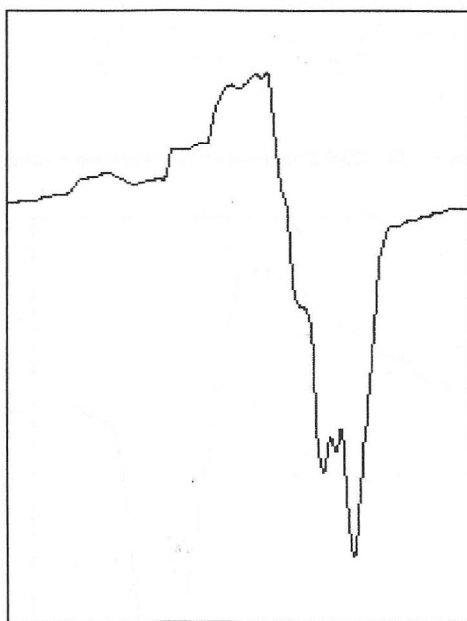
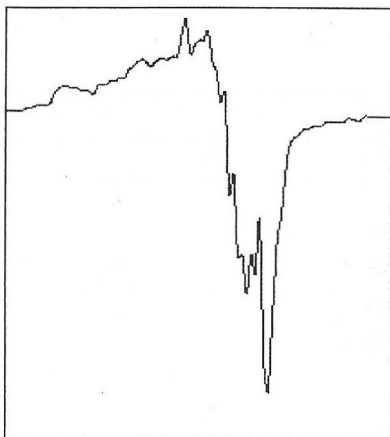


Figura 3. The ESR Spectrum of polycrystalline powder of Cu(Ph-btu) at 293 K



Cu(Ph-btu)

$$g_{\perp} = 2.0335$$

$$g_{\parallel} = 2.204$$

$$A_{\parallel} = 70.00\text{G}$$

Figura 4. The ESR Spectrum of polycrystalline powder of Cu(H,m-PhOH-btu) at 293 K

Cu(H,m-PhOH-btu)

$$g_{\perp} = 2.048$$

$$g_{\parallel} = 2.300$$

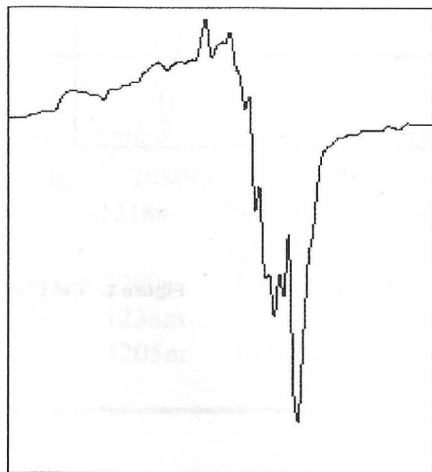
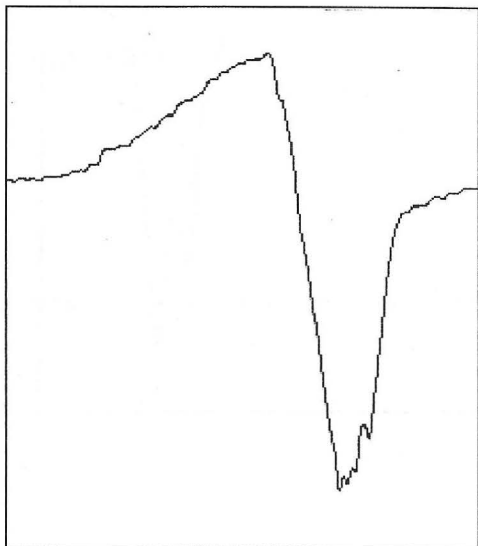


Figura 5. The ESR Spectrum of polycrystalline powder of Cu(H,p-PhCOO-btu) at 293 K



Cu(H,p-PhCOO-btu)

$$g_{\perp} = 2.052$$

$$g_{\parallel} = 2.320$$

ABREVIATIONS:

The following abbreviations of 1-monosubstituted-3-benzoylthiourea ligands ($R^1=H$) are used throughout this work..

R^2	HLL abbreviation	R^2	HLL abbreviation
Et	H(H, Et-btu)	o-PhOH	H(H, o-PhOH-btu)
PhCH ₂	H(H, Bzy-btu)	m-PhOH	H(H, m-PhOH-btu)
Ph	H(H, Ph-btu)	p-PhCOOH	H(H, p-PhCOOH-btu)
p-PhOMe	H(H, p-PhOMe-btu)		

CONCLUSIONS

The prepared complexes have shown unexpected behaviour and gave the products in which both NH group of monosubstituted benzoylthioureas were probably deprotonized and copper (II) complexes were formed. The deprotonization of NH groups in the Cu(Et-btu), Cu(Ph-btu), Cu(p-MeOPh-btu), Cu(Bzy-btu) and Cu(m-PhOH-btu) complexes cannot be explained without assumption of using other donor atoms from ligand molecule and without assumption of polymeric complexes formation. The other unexpected result within this group of complexes is the Cu₃(o-PhO-btu)₂ complex formation, which existence could for copper (II) explained only if LL³⁻ ligand is formed from H(H,o-PhOH-btu) molecule. The last complex of this group has shown deprotonization of carboxylate group on the periphery of ligand, which can in future stimulate research in this field. All cooper(II) complexes have not exhibited properties which are in contradiction with probable square coplanar geometry.

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