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DIRECT SYNTHESIS OF CUPRUM(II) COMPLEX COMPOUNDS BASED ON THIOAMIDE LIGANDS

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Abstract. Complex compounds based on arylamides of benzimidazol-2-thiocarboxylic acid of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ have been synthesized *via* direct method. Their physico-chemical properties have been investigated.

Keywords: thioamide ligands, cuprum(II), direct synthesis.

1. Introduction

Recently the obtaining of coordinating compounds from zero-valent metals and organic ligands in anhydrous solvents is of keen interest, as well as the investigation of their electro-magnetic, mechanical, chemical and biological properties [1-3]. This interest is caused not only by preparative meaning of the direct synthesis but by the possibility to obtain heterometal coordinating compounds with various metals as well [4]. It is very important for the production of new materials with predetermined properties.

Meanwhile, the obtaining of complex compounds of transition 3d-metals and thioamide ligands *via* direct synthesis is actually unstudied, despite their wide use as antiwear and antifriction additives to oils [5-10], promoters of unsaturated rubbers sulphuric curing [11] and biologically active compounds [12, 13]. Until recently such complex compounds were obtained *via* only traditional methods [14, 15] that did not allow to use all advantages of direct synthesis [1, 2, 16, 17].

The aim of this work is to develop methods of direct synthesis of cuprum(II) complex compounds based on arylamides of benzimidazol-2-thiocarboxylic acid and to investigate their physico-chemical properties.

2. Experimental

2.1. Materials and Methods

For the synthesis of complex compounds $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ we used cuprum metal powder with mass

part $\geq 99.5\%$ and particles size of $8.0 \pm 1.1 \mu\text{m}$ (75 vol %) which were determined using microsedimentometer Saishin SKC-2000S (Japan). Cuprum(I) oxide and crystalhydrate $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were of P.A. purity. Organic solvents (CH_3OH , isopropyl alcohol (IPA), dimethylsulphoxide (DMSO)) and chlorine-containing hydrocarbons (ChH): CCl_4 , CHCl_3 , C_2HCl_5 , $t\text{-C}_4\text{H}_9\text{Cl}$ were purchased from Aldrich and Merck and used without additional purification. Cuprum(II) content in the synthesized compounds was determined by atom-absorptive spectroscopy using C-115 PKRS spectrometer. Elemental analysis for nitrogen content was carried out by the Kjeldahl method and for sulfur content – by the Schoniger method [17].

IR-spectra of ligands and complex compounds within $4000\text{--}400 \text{ cm}^{-1}$ were recorded using Specord 75 IR. The samples were prepared as tablets with KBr.

Arylamides of benzimidazol-2-thiocarboxylic acid (HL): $\text{C}_7\text{H}_5\text{N}_2\text{C}(=\text{S})\text{NHC}_6\text{H}_4\text{R}^{1-3-4}$, ($\text{R}^{1-3} = \text{H}, \text{CH}_3, \text{Br}$) were synthesized by the procedure described in [4].

2.2. Direct Methods of Complex Compounds $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ Synthesis

A. Di(m-chloro)-dichloro-bis[benzimidazol-2-N-(phenyl)carbothioamide]dicuprum(II), I. The solution of benzimidazol-2-N-(phenyl)carbothioamide (3.80 g, 15.0 mmol) in 200 ml of hot anhydrous IPA was acidified by 9 ml (90.0 mmol) of 30 % chloric acid. Then 0.95 g (15.0 mmol) of cuprum powder was added under stirring. The obtained mixture was sharply cooled to 293 K and sustained for 11 h under intensive stirring. The formed precipitate of greenish-brown color was filtrated using Schott filter, washed by anhydrous IPA ($3 \times 10 \text{ ml}$) and dried in a drying oven at 363–373 K. Product yield was 3.37 g (58 %); melting point was 508–511 K.

Compounds **II** and **III** were synthesized by the same method. Their physico-chemical characteristics are represented in Table 1.

B. Di(m-chloro-)-dichloro-bis[benzimidazol-2-N-(4-methylphenyl)carbothioamide]dicuprum(II), IIe. 9.0 ml (80 mmol) of *tert*-butylchloride was added to the solution of 0.80 g (3.0 mmol) of benzimidazol-2-N-(4-methylphenyl)carbothioamide in 3 ml of DMSO. Then 0.19 g (3.0 mmol) of cuprum powder was added. The obtained mixture was sustained at 293 K for 2.5 h under stirring. Then the reaction flask was equipped by a back condenser, the temperature was raised to 333 K, the reaction mass was sustained for 30 min, cooled to 293 K and diluted by 15 ml of methyl alcohol. In the end of the reaction 2.2 ml (22.0 mmol) of 30 % chloride acid was added and the mixture was sustained for 10 min. The formed precipitate of green color was filtrated using Schott filter, washed by methyl alcohol (3×5 ml) and dried in the drying oven at 363–373 K. Product yield was 1.00 g (83 %); the melting point was 487–492 K.

Compounds **IIb–IId** were synthesized by the same method. Their physico-chemical characteristics are represented in Table 1.

C. Di(m-chloro-)-dichloro-bis[benzimidazol-2-N-(4-brominephenyl)carbothioamide]dicuprum(II), IIIb. 0.43 ml (3.0 mmol) of cuprum(I) oxide was added to the solution of 2.0 g (6.0 mmol) of benzimidazol-2-N-(4-brominephenyl)carbothioamide in 120 ml of hot anhydrous IPA acidified by 12 ml (120.0 mmol) of 30 % chloride acid. The obtained mixture was sustained at 333 K for 3.5 h under stirring. The formed precipitate of green color was filtrated using Schott filter, washed by anhydrous IPA (3×5 ml) and dried in drying oven at 363–373 K. Product yield was 2.21 g (79 %); the melting point was 492–495 K.

Physico-chemical characteristics of obtained coordination compound **IIIb** are represented in Table 1.

2.3. Counter Method of Complex Compounds [Cu(HL)Cl₂]₂ Synthesis

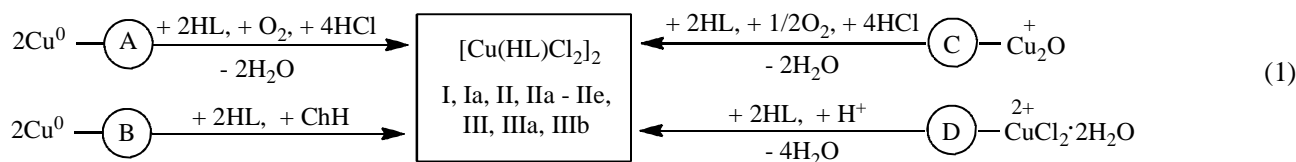
D. Di(m-chloro-)-dichloro-bis[benzimidazol-2-N-(phenyl)carbothioamide]dicuprum(II), Ia. 1.6 ml (16.0 mmol) of 30 % chloride acid and 1.04 g (6.1 mmol) of CuCl₂·2H₂O diluted in 15 ml of hot anhydrous IPA were added to the solution of 1.52 g (6.0 mmol) of benzimidazol-2-N-(phenyl)carbothioamide in 50 ml of hot anhydrous IPA. The obtained mixture was stirred at 318–323 K for 5–10 min. The formed precipitate of green color was filtrated using Schott filter, washed by anhydrous IPA (3×10 ml) and dried in the drying oven at 363–373 K. Product yield was 2.28 g (98 %); the melting point was 512–513 K.

Compounds **IIa** and **IIIa** were synthesized by the same method. Their physico-chemical characteristics are represented in Table 1.

3. Results and Discussion

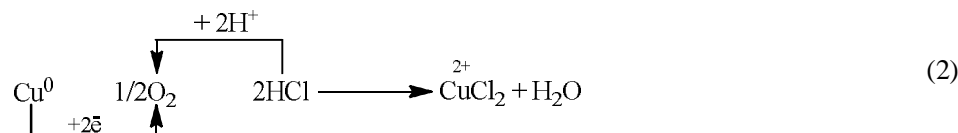
3.1. Synthetic Aspects of Complex Compounds [Cu(HL)Cl₂]₂ Obtaining

The complex compounds of the formula [Cu(HL)Cl₂]₂ were synthesized according to the general scheme:



HL: C₇H₅N₂C(=S)NHC₆H₄R¹⁻³; R¹ = H, **I, Ia**; R² = 4-CH₃, **II, IIa–IIe**; R³ = 4-Br, **III, IIIa, IIIb**; ChH: CCl₄, CHCl₃, C₂HCl₅, *t*-C₄H₉Cl.

Compounds **I–III** (method A) were obtained using a proton-donor oxidative system HL–ROH–HCl–O₂ according to the reaction in (1). In such a system the organic ligand (HL) and organic solvent (HSolv: CH₃OH and C₃H₇OH) cannot compete with hydrogen chloride as a source of protons while joining oxygen in accordance with the reaction (2):



It is obvious that the oxidation rate of zero-valent cuprum and formation of complex compounds [Cu(HL)Cl₂]₂ essentially depend on the molar ratio $v(\text{HCl})/v(\text{Cu}^0)$. Experimental results which confirm this dependence are represented in Table 2 and Figs. 1 and 2. The increase of $v(\text{HCl})/v(\text{Cu}^0) \geq 10:1$ actually has not influence on the yield of resulting metal-chelates (Fig. 1) and the decrease of the mentioned ratio doubles the reaction time (Fig. 2).

Table 1

Physico-chemical properties of cuprum(II) complex compounds of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$

Com- pound	Method	R	Cl source in the complexes	Solvent	Color	Melting point, K	Founded Calculated, %			Gross-formula	Yield, %
							N	S	Cu		
I	A	H	HCl, 30 %	IPA, anh.	Greenish- brown	508–511	10.51 10.84	7.91 8.27	16.67 16.39	$\text{C}_{28}\text{H}_{22}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	58
Ia	D	H	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	IPA, anh.	Green	512–513	10.51 10.84	8.59 8.17	16.08 16.39	$\text{C}_{28}\text{H}_{22}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	98
II	A	4-CH ₃	HCl, 30 %	CH_3OH , anh.	Chlorine	482–489	10.24 10.46	7.55 7.98	16.27 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	81
IIa	D	4-CH ₃	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	IPA, anh.	Vinous-brown	490–491	10.15 10.46	7.89 7.98	14.42 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	77
IIb	B	4-CH ₃	CCl_4 , 80 %	DMSO, 20 %	Green	478–488	10.08 10.46	7.54 7.98	15.43 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	52
IIc	B	4-CH ₃	CHCl_3 , 80 %	DMSO, 20 %	Green	481–490	10.23 10.46	7.87 7.98	15.37 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	71
IIId	B	4-CH ₃	C_2HCl_5 , 80 %	DMSO, 20 %	Yellow-green	476–483	10.17 10.46	7.76 7.98	15.30 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	79
IIe	B	4-CH ₃	<i>t</i> - $\text{C}_4\text{H}_9\text{Cl}$, 80 %	DMSO, 20 %	Green	487–492	10.52 10.46	7.81 7.98	15.71 15.82	$\text{C}_{30}\text{H}_{26}\text{Cl}_4\text{N}_6\text{S}_2\text{Cu}_2$	83
III	A	4-Br	HCl, 30 %	CH_3OH , anh.	Deep green	493–497	8.95 9.00	7.04 6.87	13.44 13.62	$\text{C}_{28}\text{H}_{20}\text{Cl}_4\text{Br}_2\text{N}_6\text{S}_2\text{Cu}_2$	84
IIIa	D	4-Br	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	IPA, anh.	Green	496–499	9.24 9.00	7.16 6.87	13.51 13.62	$\text{C}_{28}\text{H}_{20}\text{Cl}_4\text{Br}_2\text{N}_6\text{S}_2\text{Cu}_2$	98
IIIb	C	4-Br	HCl, 30 %	IPA, anh.	Green	492–495	9.08 9.00	6.93 6.87	13.21 13.62	$\text{C}_{28}\text{H}_{20}\text{Cl}_4\text{Br}_2\text{N}_6\text{S}_2\text{Cu}_2$	79

Note: HL : thioamide $\text{C}_7\text{H}_5\text{N}_2\text{C}(=\text{S})\text{NHC}_6\text{H}_4\text{R}^{1-3}$, R¹⁻³: H, 4-CH₃, 4-Br

Table 2

Synthesis conditions of some cuprum(II) complex compounds of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$

Compound	R	Proton-donor solvent	HCl, %	Temperature, K	Time, h	Molar ratio		Yield %
						$\nu(\text{HL})/\nu(\text{Cu}^0)$	$\nu(\text{HCl})/\nu(\text{Cu}^0)$	
I	H	IPA, anh	30	298	11.0	$\nu(\text{HL}^1)/\nu(\text{Cu}^0) = 1:1$	6:1	58
II	4-CH ₃	CH ₃ OH, anh	30	298	5.3	$\nu(\text{HL}^2)/\nu(\text{Cu}^0) = 1:1$	10:1	81
III	4-Br	CH ₃ OH, anh	30	298	1.3	$\nu(\text{HL}^3)/\nu(\text{Cu}^0) = 1:1$	30:1	84

Note: chlorine source in the complex compounds $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ – chloric acid; R – substituent in thioamide phenyl radical $\text{C}_7\text{H}_5\text{N}_2\text{C}(=\text{S})\text{NHC}_6\text{H}_4\text{R}^{1-3}$; R¹ = H, R² = 4-CH₃, R³ = 4-Br.

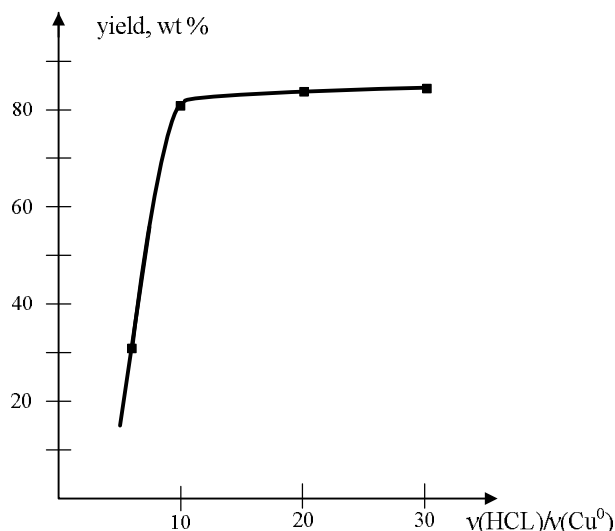


Fig. 1. Dependence of $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ yield on the molar ratio $\nu(\text{HCl})/\nu(\text{Cu}^0)$

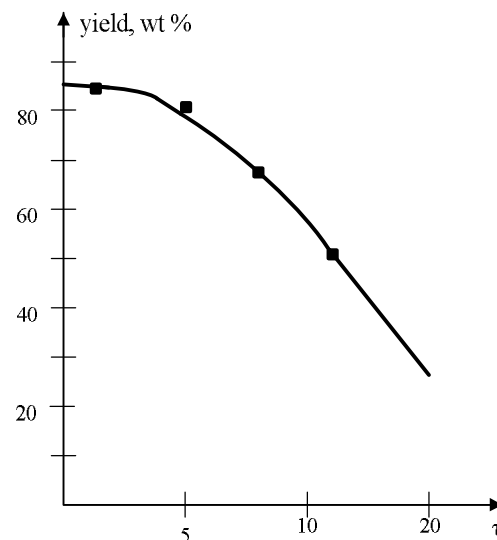


Fig. 2. Dependence of $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ yield on the reaction time at different molar ratio $\nu(\text{HCl})/\nu(\text{Cu}^0)$

The conditions of **I-III** complex compounds obtained by method A are represented in Table 2.

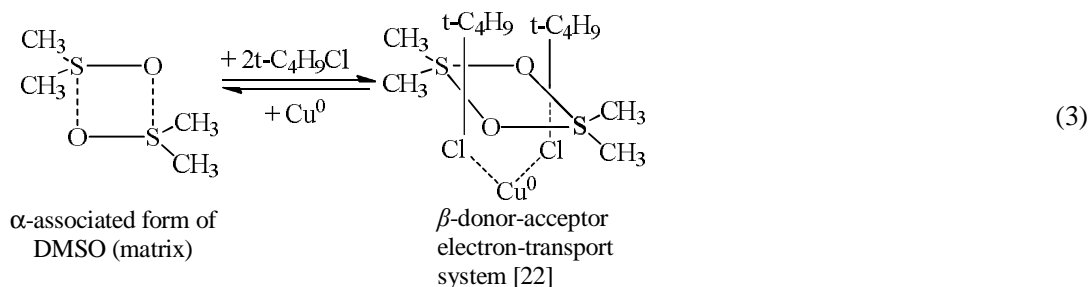
Compounds **IIb-IIe** (method B) were obtained using two-stage oxidative system:

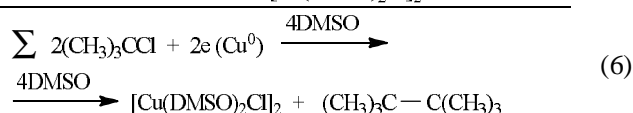
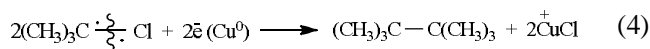
– at the first stage HL – DMSO – *t*-C₄H₉Cl (dissolving of metal cuprum);

– at the second stage HL – DMSO – CH₃OH – HCl – O₂ (formation of resulting metal-chelates) in accordance with the reaction in Scheme (1).

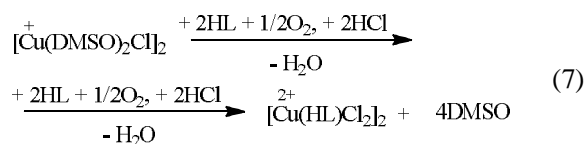
At the same time the determinative factor is a dissolving of zero-valent cuprum under the action of oxi-

dative system HL – *t*-C₄H₉Cl – DMSO. At room temperature thioamides and dimethylsulphoxide as an aprotic solvent with high solvating (coordinating) ability (DN = 29.8) [19] forms complexes with charge transfer (CCT): (CH₃)₂SO·HL [20] and deactivates in such a way their coordinating ability. The dissolving of zero-valent cuprum under the action of oxidative system *t*-C₄H₉Cl – DMSO (I stage) occurs with the formation of possible molecular complexes [21] on the metal surface (Scheme 3) followed by chemical transformations (4)–(6).

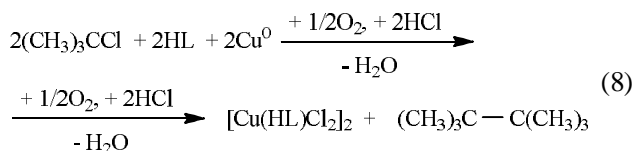




At the same time it is necessary to examine the reaction (4) as one-electron oxidation of metal cuprum followed by the formation of $[\text{Cu}(\text{DMSO})_2\text{Cl}]_2$ dimeric complex and recombination of possible *tert*-butyl radicals $(\text{CH}_3)_3\text{C}^\bullet$ to 2,2,3,3-tetramethylbutane. It should be noted that cuprum(I) chloride is stabilized due to $[\text{Cu}(\text{DMSO})_2\text{Cl}]_2$ complex formation and its transfer from metal surface into the solution [23]. The resulting complex $[\text{Cu}(\text{HL})\text{Cl}]_2$ is formed under the action of $\text{HL} - \text{DMSO} - \text{CH}_3\text{OH} - \text{HCl} - \text{O}_2$ oxidative system due to the heating to 333 K for 30 min (II stage). At the same time the decomposition takes place according to the scheme: $\text{HL} \cdot \text{DMSO} \rightarrow \text{HL} + \text{DMSO}$. The additional introduction of methyl alcohol to the system increases the oxidation rate $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ in the similar systems [22]. The second stage of zero-valent cuprum oxidation proceeds according to the reaction (7):



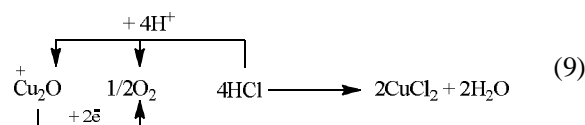
Adding (6) and (7) we obtain the general equation of zero-valent cuprum oxidation in the presence of chlorine-containing hydrocarbons:



As follows from Eq. (8), the contribution of chloride ligands into the resulting coordinating compounds **IIb-IIe** is equivalent: 50 % due to the reduction of *t*-C₄H₉Cl and 50 % – due to Cl⁻ anion of chlorine acid. The conditions of compounds **IIb-IIe** obtaining *via* method B are given in Table 3.

The compound **IIIb** (method C) was obtained using cuprum(I) oxide and proton-donor oxidative system $\text{HL} - i\text{-C}_3\text{H}_7\text{OH} - \text{HCl} - \text{O}_2$ in accordance with the reaction given in Scheme 1. To our mind the obtaining of $[\text{Cu}(\text{HL})\text{Cl}]_2$ *via* method C is not a classic direct synthesis including zero-valent cuprum oxidation because

cuprum is already in the oxidated form Cu_2^+O and re-oxidized according to the reaction (9):

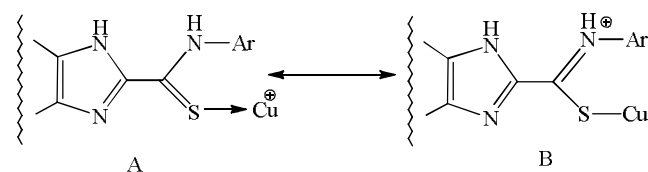


It is obvious that the same regulations are typical of this interaction and above-mentioned method A (Scheme 2).

3.2. IR-Spectroscopic Investigations

The compositions of the synthesized compounds **I-III**, **Ia**, **IIa-IIe**, **IIIa**, **IIIb** were determined using elemental analysis (Table 1) and their structure – using IR-spectroscopy. We compared the vibrations of thioamide ligands, namely N–H bond of thioamide group and benzimidazol fragment, as well as vibrations of $-\text{C}(=\text{S})\text{NH}-$ thioamide group (having complex valent-deformational nature) with similar vibrations in the complex compounds. Thioamides have stretching vibrations of thioamide group $\nu(\text{N}-\text{H})$ of the mean intensity in the area of 3356–3256 cm⁻¹, weak vibrations $\nu(\text{N}-\text{H})$ of heterocyclic fragment in the area of 3095–3060 cm⁻¹ and complex vibrations of thioamide group which were interpreted as vibrations “B”-, “D”- and “E”-bands [24] (Table 4).

While forming coordinating compounds the double character of $\text{C} \cdots \text{N}$ fragment increases and order of C=S bond decreases due to the possible formation of boundary structures A and B:



The boundary structure B shifts stretching vibrations of thioamide group $\nu(\text{N}-\text{H})$ and $\nu(\text{C}=\text{N})$ toward the high field by 102–55 and 20–15 cm⁻¹, respectively (“B”-band). At the same time stretching vibrations $\nu(\text{N}-\text{H})$ of benzimidazol fragment are without changes indicating that cuprum(II) coordination with this fragment is absent. The significant increase of vibrations intensity of C=S group and its shift by 140–17 cm⁻¹ toward the high field is typical of stretching vibrations of thioamide group (“E”-band). Stretching vibrations of C–N group slightly shift (≈ 10 cm⁻¹) toward the high field (structure A). The obtained spectral data are in agreement with the results of other researchers [14, 25, 26] and confirm the structure of complex compounds of the general formula $[\text{Cu}(\text{HL})\text{Cl}]_2$ obtained *via* direct and counter synthesis.

Table 3

Synthesis conditions for compounds IIb–IIe of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$

Compound	R-substituent in phenyl radical	First stage				Second stage				Total time, h	Yield, %
		Solvent, %	T, K	Time, h	Stoichiometric ratio of the reagents	Solvent, %	T, K	Time, h	Stoichiometric ratio of the reagents		
IIb	4-CH ₃	CCl ₄ , 80% + DMSO, 20 %	274.1– 293 274.2– 298	1.1–1.5 1.2–1.5	$\nu(\text{HL}^-)/\nu(\text{Cu}^0) = 1.0$; $\nu(\text{CCl}_4)/\nu(\text{Cu}^0) = 5.0$; $\nu(\text{CCl}_4)/\nu(\text{DMSO}) = 0.13$; $\nu(\text{Cl}^-)/\nu(\text{Cu}^0) = 20.0$	CH ₃ OH, 97	323–333	0.5	$\nu(\text{HCl})/\nu(\text{Cu}^0) = 30.0$; $\nu(\text{CH}_3\text{OH})/\nu(\text{DMSO} + \text{CCl}_4) = 2.5$	3.5	52
IIc	4-CH ₃	CHCl ₃ , 80 % + DMSO, 20 %	274.1– 293 274.2– 298	1.1–1.3 1.2–1.5	$\nu(\text{HL}^-)/\nu(\text{Cu}^0) = 1.0$; $\nu(\text{CHCl}_3)/\nu(\text{Cu}^0) = 27.0$; $\nu(\text{CHCl}_3)/\nu(\text{DMSO}) = 2.7$; $\nu(\text{Cl}^-)/\nu(\text{Cu}^0) = 81.0$	CH ₃ OH, anh	323–333	1.0	$\nu(\text{HCl})/\nu(\text{Cu}^0) = 10.0$; $\nu(\text{CH}_3\text{OH})/\nu(\text{DMSO} + \text{CHCl}_3) = 10.0$	3.8	71
IIId	4-CH ₃	C ₂ HCl ₃ , 80 % + DMSO, 20 %	298	1.0	$\nu(\text{HL}^-)/\nu(\text{Cu}^0) = 1.0$; $\nu(\text{C}_2\text{HCl}_3)/\nu(\text{Cu}^0) = 5.0$; $\nu(\text{C}_2\text{HCl}_3)/\nu(\text{DMSO}) = 0.1$; $\nu(\text{Cl}^-)/\nu(\text{Cu}^0) = 25.0$	CH ₃ OH, 80	323–333	1.0	$\nu(\text{HCl})/\nu(\text{Cu}^0) = 40.0$; $\nu(\text{CH}_3\text{OH})/\nu(\text{DMSO} + \text{C}_2\text{HCl}_3) = 3.0$	2.0	79
IIe	4-CH ₃	<i>t</i> -C ₄ H ₉ Cl, 80 % + DMSO, 20 %	274.1– 293 274.2– 298	1.1–1.5 1.2–1.5	$\nu(\text{HL}^-)/\nu(\text{Cu}^0) = 1.0$; $\nu(\text{t-C}_4\text{H}_9\text{Cl})/\nu(\text{Cu}^0) = 28.0$; $\nu(\text{t-C}_4\text{H}_9\text{Cl})/\nu(\text{DMSO}) = 2.0$; $\nu(\text{Cl}^-)/\nu(\text{Cu}^0) = 28.0$	CH ₃ OH, 97	323–333	0.5	$\nu(\text{HCl})/\nu(\text{Cu}^0) = 7.0$; $\nu(\text{CH}_3\text{OH})/\nu(\text{DMSO} + \text{t-C}_4\text{H}_9\text{Cl}) = 1.0$	3.5	83

Table 4

IR-spectra of thioamides and their complex compounds of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$

Compound	General formula	$\nu(\text{N-H}), \text{cm}^{-1}$		group $-\text{C}(=\text{S})\text{NH}-, \text{cm}^{-1}$						Other vibrations, cm^{-1}
		thioamide group	hetero-cyclic fragment	"B"-band		"D"-band		"E"-band		
				C=N	N-H	C-N	C=S	C=S	C-N	
-	HL ¹	3356 m 3256 m	3060 w	1597 s 1540 s 1497 s	1384 vs 1310 m	1216 w	1168 m 1076 vs	948 m 900 m	754 s 734 s	1618, 1138, 1028, 688, 640, 492
-	HL ²	3340 m 3267 m	3067 w	1590 m 1550 vs	1380 vs 1313 m	1280 w	1183 m 1076 vs	896 m	789 s 740 vs	2915, 1669, 1160, 1140, 668, 611, 494
-	HL ³	3260 m	3095 w	1596 s 1535 s 1488 s	1384 vs 1316 s	1280 w	1072 vs 1006 m	820 s	730 vs	1610, 950, 930, 620, 504, 432
I	$[\text{Cu}(\text{HL}^1)\text{Cl}_2]_2$	3195 m	3062 w	1565 s	1449 s	1252 w	1140 w	960 vs	760 s 742 s	1606
Ia	$[\text{Cu}(\text{HL}^1)\text{Cl}_2]_2$	3195 m 3145 m 3095 m	3060 w	1565 vs 1494 m	1450 s 1416 vs 1386 s	1244 w	1143 w 1091 w	963 vs	763 s 745 vs 696 vs	2962, 1606, 1507, 1324, 1205, 782
IIa	$[\text{Cu}(\text{HL}^2)\text{Cl}_2]_2$	3155 m 3085 m	3060 w	1564 m 1512 vs	1435 s 1392 m	1258 vs	1177 s	963 s	742 s	2985, 2875, 1475, 1147, 1085, 1042, 1005, 921, 815
IIb	$[\text{Cu}(\text{HL}^2)\text{Cl}_2]_2$	3140 m	3065 w	1560 m 1510 m	1324 s	1250 m	1186 m	965 s	760 m 746 s	1145
IIIb	$[\text{Cu}(\text{HL}^3)\text{Cl}_2]_2$	3135 w	3065 w	1552 s	1486 vs 1440 s 1324 m	1240 w	1145 m 1080 m	961 vs 820 s	740 s	1608, 1592, 725, 492

Notes: $\text{C}_7\text{H}_5\text{N}_2\text{C}(=\text{S})\text{NHC}_6\text{H}_4\text{R}^{1-3}$; $\text{R}^1 = \text{H}$ (HL¹), $\text{R}^2 = 4\text{-CH}_3$ (HL²), $\text{R}^3 = 4\text{-Br}$ (HL³). "B"-band (C=N + N-H) with greater contribution of N-H group; "D"-band (C-N + C=S) with greater contribution of C-N group; "E"-band (C=S + C-N) with greater contribution of C=S group. Vibrations intensity: vs – very strong; s – strong; m – mean; w – weak

4. Conclusions

Cuprum(II) complex compounds based on arylamides of benzimidazol-2-thiocarboxylic acid of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ have been obtained *via* direct synthesis method.

We investigated the action of $\text{HL}-\text{ROH}-\text{HCl}-\text{O}_2$ oxidative system in alcohol medium, $\text{HL}-\text{DMSO}-\text{ChH}$ (metal cuprum dissolving) and $\text{HL}-\text{DMSO}-\text{CH}_3\text{OH}-\text{O}_2$ (formation of resulting metal-chelates) two-stage oxidative system in halogen hydrocarbons medium. Within the frame of *b*-donor-acceptor electron-transport system we proposed the possible scheme of metal-chelates complex formation reaction of the general formula $[\text{Cu}(\text{HL})\text{Cl}_2]_2$.

The composition and structure of the synthesized coordinating compounds have been confirmed by physico-chemical investigations and counter synthesis.

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ПРЯМИЙ СИНТЕЗ КОМПЛЕКСНИХ СПОЛУК КУПРУМУ(II) НА ОСНОВІ ТІОАМІДНИХ ЛІГАНДІВ

Анотація. Методом прямого синтезу отримано комплексні сполуки на основі ариламідів бензімідазол-2-тіокарбонової кислоти загальної формули $[\text{Cu}(\text{HL})\text{Cl}_2]_2$ та досліджено їх фізико-хімічні властивості.

Ключові слова: тіоамідні ліганди, купрум(II), прямий синтез.