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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 $[Cu(HL)Cl_2]_2$ 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 $[Cu(HL)Cl_2]_2$ we used cuprum metal powder with mass part $\geq 99.5\%$ and particles size of $8.0 \pm 1.1\ \mu m$ (75 vol %) which were determined using microsedimentometer Saishin SKC-2000S (Japan). Cuprum(I) oxide and crystalohydrate $CuCl_2 \cdot 2H_2O$ 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-C_4H_9Cl 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 4000–400 cm^{-1} were recorded using Specord 75 IR. The samples were prepared as tablets with KBr.

Arylamides of benzimidazol-2-thiocarbonic acid (HL): $C_7H_5N_2C(=S)NHC_6H_4R^{1-3}$-4, ($R^{1-3}$ = H, CH_3, Br) were synthesized by the procedure described in [4].

2.2. Direct Methods of Complex Compounds $[Cu(HL)Cl_2]_2$ 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 (3×10 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.

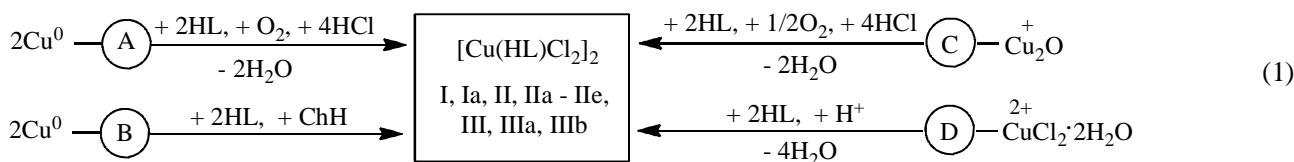## 2.3. Counter Method of Complex Compounds [Cu(HL)Cl$_2$]$_2$ Synthesis

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 CuCl$_2$·2H$_2$O 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 (3x10 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)Cl$_2$]$_2$ Obtaining

The complex compounds of the formula [Cu(HL)Cl$_2$]$_2$ were synthesized according to the general scheme:

$$2Cu^0 \xrightarrow[- 2H_2O]{+ 2HL, + O_2, + 4HCl} \boxed{\begin{array}{c} [Cu(HL)Cl_2]_2 \\ I, Ia, II, IIa - IIe, \\ III, IIIa, IIIb \end{array}} \xleftarrow[- 2H_2O]{+ 2HL, + 1/2O_2, + 4HCl} Cu_2^+O \tag{1}$$

$$2Cu^0 \xrightarrow{+ 2HL, + ChH} \qquad\qquad \xleftarrow[- 4H_2O]{+ 2HL, + H^+} CuCl_2^{2+}·2H_2O$$

HL: C$_7$H$_5$N$_2$C(=S)NHC$_6$H$_4$R$^{1-3}$; R^1 = H, **I, Ia**; R^2 = 4–CH$_3$, **II, IIa–IIe**; R^3 = 4-Br, **III, IIIa, IIIb**; ChH: CCl$_4$, CHCl$_3$, C$_2$HCl$_5$, *t*-C$_4$H$_9$Cl.

Compounds **I-III** (method A) were obtained using a proton-donor oxidative system HL–ROH–HCl–O$_2$ according to the reaction in (1). In such a system the organic ligand (HL) and organic solvent (HSolv: CH$_3$OH and C$_3$H$_7$OH) cannot compete with hydrogen chloride as a source of protons while joining oxygen in accordance with the reaction (2):

$$Cu^0 \quad 1/2O_2 \quad 2HCl \xrightarrow{} CuCl_2^{2+} + H_2O \tag{2}$$
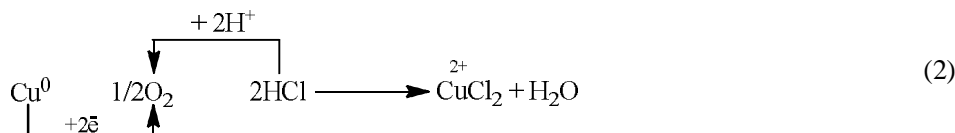
It is obvious that the oxidation rate of zero-valent cuprum and formation of complex compounds [Cu(HL)Cl$_2$]$_2$ essentially depend on the molar ratio $v(HCl)/v(Cu^0)$. Experimental results which confirm this dependence are represented in Table 2 and Figs. 1 and 2. The increase of $v(HCl)/v(Cu^0) \geq 10:1$ 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 $|Cu(HL)Cl_2|_2$

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	$C_{28}H_{22}Cl_4N_6S_2Cu_2$	58
Ia	D	H	$CuCl_2 \cdot 2H_2O$	IPA, anh.	Green	512–513	10.51 / 10.84	8.59 / 8.17	16.08 / 16.39	$C_{28}H_{22}Cl_4N_6S_2Cu_2$	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	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	81
IIa	D	4-CH_3	$CuCl_2 \cdot 2H_2O$	IPA, anh.	Vinous-brown	490–491	10.15 / 10.46	7.89 / 7.98	14.42 / 15.82	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	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	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	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	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	71
IId	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	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	79
IIe	B	4-CH_3	t-C_4H_9Cl, 80 %	DMSO, 20 %	Green	487–492	10.52 / 10.46	7.81 / 7.98	15.71 / 15.82	$C_{30}H_{26}Cl_4N_6S_2Cu_2$	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	$C_{28}H_{20}Cl_4Br_2N_6S_2Cu_2$	84
IIIa	D	4-Br	$CuCl_2 \cdot 2H_2O$	IPA, anh.	Green	496–499	9.24 / 9.00	7.16 / 6.87	13.51 / 13.62	$C_{28}H_{20}Cl_4Br_2N_6S_2Cu_2$	98
IIIb	C	4-Br	HCl, 30 %	IPA, anh.	Green	492–495	9.08 / 9.00	6.93 / 6.87	13.21 / 13.62	$C_{28}H_{20}Cl_4Br_2N_6S_2Cu_2$	79

Note: HL : thioamide $C_5H_5N_2C(=S)NHC_6H_4R^{1-3}$, R^{1-3}: H, 4-CH_3, 4-Br

Table 2

Synthesis conditions of some cuprum(II) complex compounds of the general formula [Cu(HL)Cl₂]₂

Com-pound	R	Proton-donor solvent	HCl, %	Tempe-rature, K	Time, h	Molar ratio		Yield %
						$v(HL)/ v(Cu^0)$	$v(HCl)/ v(Cu^0)$	
I	H	IPA, anh	30	298	11.0	$v(HL^1)/ v(Cu^0) = 1 : 1$	6 : 1	58
II	4-CH₃	CH₃OH, anh	30	298	5.3	$v(HL^2)/ v(Cu^0) = 1 : 1$	10 : 1	81
III	4-Br	CH₃OH, anh	30	298	1.3	$v(HL^3)/ v(Cu^0) = 1 : 1$	30 : 1	84

Note: chlorine source in the complex compounds $[Cu(HL)Cl_2]_2$ – chloric acid; R – substituent in thioamide phenyl radical $C_7H_5N_2C(=S)NHC_6H_4R^{1-3}$; $R^1 = H$, $R^2 = 4\text{-}CH_3$, $R^3 = 4\text{-}Br$.
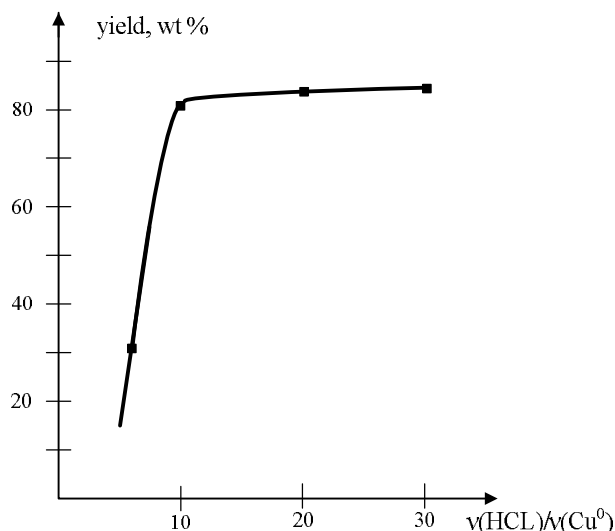
Fig. 1. Dependence of $[Cu(HL)Cl_2]_2$ yield on the molar ratio $v(HCl)/v(Cu^0)$
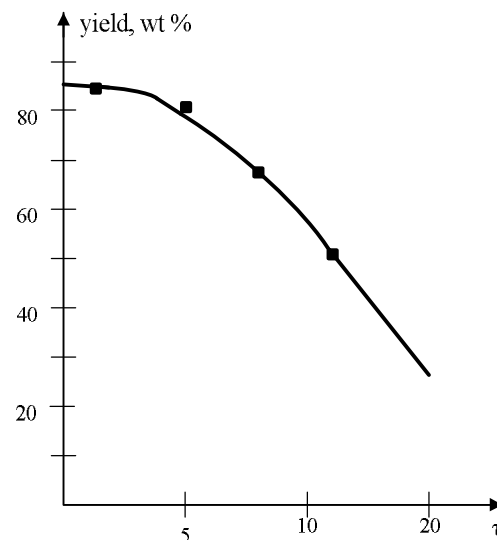
Fig. 2. Dependence of $[Cu(HL)Cl_2]_2$ yield on the reaction time at different molar ratio $v(HCl)/v(Cu^0)$

The conditions of **I-III** complex compounds obtained by method A are represented in Table 2.
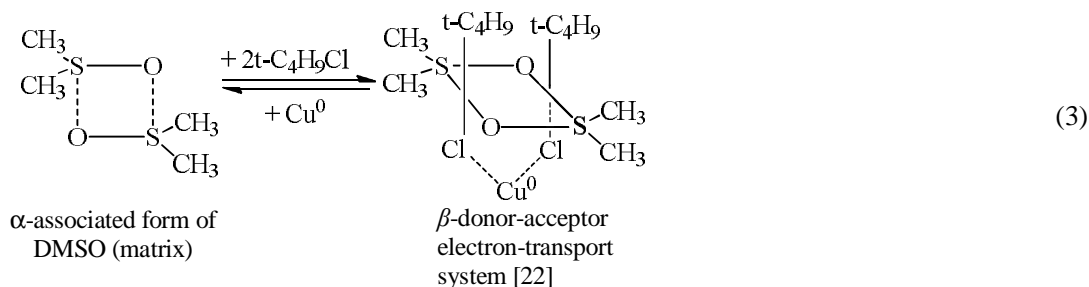
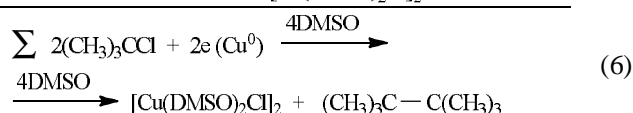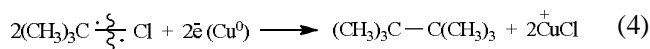Compounds **IIb-IIe** (method B) were obtained using two-stage oxidative system:

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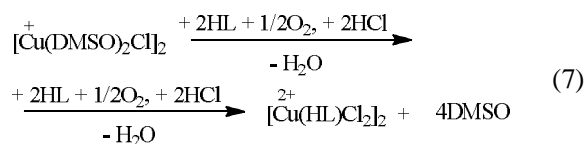
At the same time the determinative factor is a dissolving of zero-valent cuprum under the action of oxi-

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).
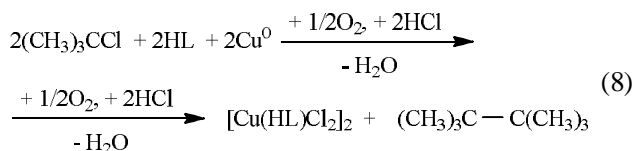

(3)

α-associated form of DMSO (matrix)

β-donor-acceptor electron-transport system [22]

$$2(CH_3)_3C \overset{\cdot\,S\,\cdot}{\underset{\cdot\cdot}{-}} Cl + 2\bar{e}\,(Cu^0) \longrightarrow (CH_3)_3C - C(CH_3)_3 + 2\overset{+}{C}uCl \quad (4)$$

$$2\overset{+}{C}uCl + 4DMSO \longrightarrow [\overset{+}{C}u(DMSO)_2Cl]_2 \quad (5)$$

$$\sum 2(CH_3)_3CCl + 2e\,(Cu^0) \xrightarrow{4DMSO}$$
$$\xrightarrow{4DMSO} [Cu(DMSO)_2Cl]_2 + (CH_3)_3C - C(CH_3)_3 \quad (6)$$

At the same time it is necessary to examine the reaction (4) as one-electron oxidation of metal cuprum followed by the formation of $[Cu(DMSO)_2Cl]_2$ dimeric complex and recombination of possible *tert*-butyl radicals $(CH_3)_3C^\bullet$ to 2,2,3,3-tetramethylbutane. It should be noted that cuprum(I) chloride is stabilized due to $[Cu(DMSO)_2Cl]_2$ complex formation and its transfer from metal surface into the solution [23]. The resulting complex $[Cu(HL)Cl_2]_2$ is formed under the action of HL – DMSO – CH_3OH – HCl – 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: $HL \cdot DMSO \rightarrow HL + DMSO$. The additional introduction of methyl alcohol to the system increases the oxidation rate $Cu^+ \rightarrow Cu^{2+}$ in the similar systems [22]. The second stage of zero-valent cuprum oxidation proceeds according to the reaction (7):

$$[\overset{+}{C}u(DMSO)_2Cl]_2 \xrightarrow[-H_2O]{+2HL+1/2O_2,+2HCl}$$
$$\xrightarrow[-H_2O]{+2HL+1/2O_2,+2HCl} [Cu(HL)Cl_2]_2^{2+} + 4DMSO \quad (7)$$

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

$$2(CH_3)_3CCl + 2HL + 2Cu^0 \xrightarrow[-H_2O]{+1/2O_2,+2HCl}$$
$$\xrightarrow[-H_2O]{+1/2O_2,+2HCl} [Cu(HL)Cl_2]_2 + (CH_3)_3C - C(CH_3)_3 \quad (8)$$

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-C_4H_9Cl 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 HL – i-C_3H_7OH – HCl – O_2 in accordance with the reaction given in Scheme 1. To our mind the obtaining of $[Cu(HL)Cl_2]_2$ *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):

$$\overset{+4H^+}{\underset{+2\bar{e}}{\Big\updownarrow}}$$
$$\overset{+}{C}u_2O \quad 1/2O_2 \quad 4HCl \longrightarrow 2CuCl_2 + 2H_2O \quad (9)$$
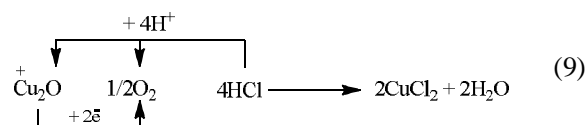
It is obvious that the same regulations are typical of this interaction and above-mentioned method A (Scheme 2).

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 –C(=S)NH– thioamide group (having complex valent-deformational nature) with similar vibrations in the complex compounds. Thioamides have stretching vibrations of thioamide group $v(N–H)$ of the mean intensity in the area of 3356–3256 cm^{-1}, weak vibrations $v(N–H)$ 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 $C\overset{\cdots}{-}N$ fragment increases and order of C=S bond decreases due to the possible formation of boundary structures A and B:
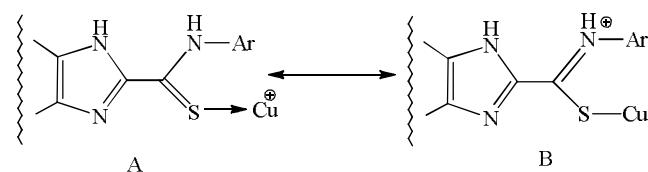
The boundary structure B shifts stretching vibrations of thioamide group $v(N–H)$ and $v(C=N)$ toward the high field by 102–55 and 20–15 cm^{-1}, respectively ("B"-band). At the same time stretching vibrations $v(N–H)$ of benzimidazol fragment are without changes indicating that cuprum(II) coordination 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 ($\approx$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 $[Cu(HL)Cl_2]_2$ obtained *via* direct and counter synthesis.

Table 3

Synthesis conditions for compounds IIb–IIe of the general formula $[Cu(HL)Cl_2]_2$

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-CH₃	CCl₄, 80 % + DMSO, 20 %	274.1–293 274.2–298	1.1–1.5 1.2–1.5	$\nu(HL^1)/\nu(Cu^0) = 1.0$; $\nu(CCl_4)/\nu(Cu^0) = 5.0$; $\nu(CCl_4)/\nu(DMSO) = 0.13$; $\nu(Cl)/\nu(Cu^0) = 20.0$	CH₃OH, 97	323–333	0.5	$\nu(HCl)/\nu(Cu^0) = 30.0$; $\nu(CH_3OH)/\nu(DMSO+CCl_4) = 2.5$	3.5	52
IIc	4-CH₃	CHCl₃, 80 % + DMSO, 20 %	274.1–293 274.2–298	1.1–1.3 1.2–1.5	$\nu(HL^2)/\nu(Cu^0) = 1.0$; $\nu(CHCl_3)/\nu(Cu^0) = 27.0$; $\nu(CHCl_3)/\nu(DMSO) = 2.7$; $\nu(Cl)/\nu(Cu^0) = 81.0$	CH₃OH, anh	323–333	1.0	$\nu(HCl)/\nu(Cu^0) = 10.0$; $\nu(CH_3OH)/\nu(DMSO+CHCl_3) = 10.0$	3.8	71
IId	4-CH₃	C₂HCl₅, 80 % + DMSO, 20 %	298	1.0	$\nu(HL^2)/\nu(Cu^0) = 1.0$; $\nu(C_2HCl_5)/\nu(Cu^0) = 5.0$; $\nu(C_2HCl_5)/\nu(DMSO) = 0.1$; $\nu(Cl)/\nu(Cu^0) = 25.0$	CH₃OH, 80	323–333	1.0	$\nu(HCl)/\nu(Cu^0) = 40.0$; $\nu(CH_3OH)/\nu(DMSO+C_2HCl_5) = 3.0$	2.0	79
IIe	4-CH₃	t-C₄H₉Cl, 80 % + DMSO, 20 %	274.1–293 274.2–298	1.1–1.5 1.2–1.5	$\nu(HL^2)/\nu(Cu^0) = 1.0$; $\nu(t\text{-}C_4H_9Cl)/\nu(Cu^0) = 28.0$; $\nu(t\text{-}C_4H_9Cl)/\nu(DMSO) = 2.0$; $\nu(Cl)/\nu(Cu^0) = 28.0$	CH₃OH, 97	323–333	0.5	$\nu(HCl)/\nu(Cu^0) = 7.0$; $\nu(CH_3OH)/\nu(DMSO+t\text{-}C_4H_9Cl) = 1.0$	3.5	83

Table 4

IR-spectra of thioamides and their complex compounds of the general formula [Cu(HL)Cl₂]₂

| Compound | General formula | ν(N–H), cm⁻¹ | | group –C(=S)NH–, 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	
–	HL¹	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
–	HL²	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
–	HL³	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	[Cu(HL¹)Cl₂]₂	3195 m	3062 w	1565 s	1449 s	1252 w	1140 w	960 vs	760 s, 742 s	1606
Ia	[Cu(HL¹)Cl₂]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	[Cu(IIL²)Cl₂]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	[Cu(HL²)Cl₂]₂	3140 m	3065 w	1560 m, 1510 m	1324 s	1250 m	1186 m	965 s	760 m, 746 s	1145
IIIb	[Cu(HL³)Cl₂]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: $C_7H_3N_2C(=S)NHC_6H_4R^{1-3}$; R^1 = H (HL¹), R^2 = 4-CH₃ (HL²), R^3 = 4-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 – сильна; m – mean; w – weak

4. Conclusions

Cuprum(II) complex compounds based on arylamides of benzimidazol-2-thiocarboxylic acid of the general formula $[Cu(HL)Cl_2]_2$ have been obtained *via* direct synthesis method.

We investigated the action of HL–ROH–HCl–O_2 oxidative system in alcohol medium, HL–DMSO–ChH (metal cuprum dissolving) and HL–DMSO–CH_3OH–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 $[Cu(HL)Cl_2]_2$.

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 [Cu(HL)Cl₂]₂ та досліджено їх фізико-хімічні властивості.*

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