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 \([\text{Cu(HL)Cl}_2]_2\) 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 sulphur 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-thio-carboxylic acid and to investigate their physico-chemical properties.

2. Experimental

2.1. Materials and Methods

For the synthesis of complex compounds \([\text{Cu(HL)Cl}_2]_2\) we used cuprum metal powder with mass part ≥ 99.5 % and particles size of 8.0 ± 1.1 μm (75 vol %) which were determined using microsedimentometer Saishin SKC-2000S (Japan). Cuprum(I) oxide and crystalohydrate CuCl\(_2\)⋅2H\(_2\)O were of P.A. purity. Organic solvents (CH\(_3\)OH, isopropyl alcohol (IPA), dimethylsulphoxide (DMSO)) and chlorine-containing hydrocarbons (ChH): CCl\(_4\), CHCl\(_3\), C\(_2\)HCl\(_5\), t-C\(_4\)H\(_9\)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 4000–400 cm\(^{-1}\) were recorded using Specord 75 IR.

Arylamides of benzimidazol-2-thiocarboxylic acid (HL): C\(_7\)H\(_5\)N\(_2\)C(=S)NH\(_2\)H\(_4\)R\(_1\)-3-4, (R\(_1\)-3 = H, CH\(_3\), Br) were synthesized by the procedure described in [4].
B. Di(µ-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 mass was filtered and the mixture was sustained for 10 min. The formed precipitate of green color was filtered using Schott filter, washed by anhydrous IPA, 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 30 min. 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 acidified by 12 ml (120.0 mmol) of 30 % chloride acid. 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 anhydrous IPA, 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-IIId were synthesized by the same method. Their physico-chemical characteristics are represented in Table 1.

C. Di(µ-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. 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 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} Obtaining

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

\[
\begin{align*}
2\text{Cu}^{0} & \xrightarrow{\text{A}} + 2\text{HL} + \text{O}_{2} + 4\text{HCl} - 2\text{H}_{2}\text{O} & & \text{[Cu(HL)Cl]}_{2} \\
2\text{Cu}^{0} & \xrightarrow{\text{B}} + 2\text{HL} + \text{CH}_{2} & & \text{C}^{+} \xrightarrow{\text{Cu}_{2}\text{O}} \\
& & & \text{D}^{2+} \xrightarrow{\text{2CuCl}} 2\text{H}_{2}\text{O}
\end{align*}
\]

HL: C_{6}H_{5}N_{2}C(=S)NHCH_{2}R^{13}; R^{1} = \text{H, I, II, IIa-IIe, III, IIIa, IIIb}; \text{CH}_{2}: \text{CCL}_{1}, \text{CHCl}_{2}, \text{C}_{2}\text{HCl}_{5}, \text{t-C}_{4}\text{H}_{6}\text{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_{2}H_{5}OH) cannot compete with hydrogen chloride as a source of protons while joining oxygen in accordance with the reaction (2):

\[
\begin{align*}
\text{Cu}^{0} & \xrightarrow{-2\text{e}^{-}} 1/2\text{O}_{2} + 2\text{HCl} \xrightarrow{\text{2+}} \text{CuCl}_{2} + \text{H}_{2}\text{O}
\end{align*}
\]

It is obvious that the oxidation rate of zero-valent cuprum and formation of complex compounds [Cu(HL)Cl]_{2} essentially depend on the molar ratio \(\nu(\text{HCl})/\nu(\text{Cu}^{0})\). Experimental results which confirm this dependence are represented in Table 2 and Figs. 1 and 2. The increase of \(\nu(\text{HCl})/\nu(\text{Cu}^{0}) \geq 10:1\) 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>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>R</th>
<th>Cl source in the complexes</th>
<th>Solvent</th>
<th>Color</th>
<th>Melting point, K</th>
<th>Founded Calculated %</th>
<th>Gross-formula</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>H</td>
<td>HCl, 30 %</td>
<td>IPA, anh.</td>
<td>Greenish-brown</td>
<td>508–511</td>
<td>N: 10.51 10.84 S: 7.91 8.27 Cu: 16.67 16.39</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>58</td>
</tr>
<tr>
<td>Ia</td>
<td>D</td>
<td>H</td>
<td>CuCl_{2} · 2H_{2}O</td>
<td>IPA, anh.</td>
<td>Green</td>
<td>512–513</td>
<td>N: 10.51 10.84 S: 8.59 8.17 Cu: 16.08 16.39</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>98</td>
</tr>
<tr>
<td>II</td>
<td>A</td>
<td>4-CH_{3}</td>
<td>HCl, 30 %</td>
<td>CH_{3}OH, anh.</td>
<td>Chlorine</td>
<td>482–489</td>
<td>N: 10.24 10.46 S: 7.55 7.98 Cu: 16.27 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>81</td>
</tr>
<tr>
<td>IIa</td>
<td>D</td>
<td>4-CH_{3}</td>
<td>CuCl_{2} · 2H_{2}O</td>
<td>IPA, anh.</td>
<td>Vinous-brown</td>
<td>490–491</td>
<td>N: 10.15 10.46 S: 7.89 7.98 Cu: 14.42 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>77</td>
</tr>
<tr>
<td>IIb</td>
<td>B</td>
<td>4-CH_{3}</td>
<td>CCl_{4}, 80 %</td>
<td>DMSO, 20 %</td>
<td>Green</td>
<td>478–488</td>
<td>N: 10.08 10.46 S: 7.54 7.98 Cu: 15.43 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>52</td>
</tr>
<tr>
<td>IIc</td>
<td>B</td>
<td>4-CH_{3}</td>
<td>CHCl_{3}, 80 %</td>
<td>DMSO, 20 %</td>
<td>Green</td>
<td>481–490</td>
<td>N: 10.23 10.46 S: 7.87 7.98 Cu: 15.37 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>71</td>
</tr>
<tr>
<td>IIId</td>
<td>B</td>
<td>4-CH_{3}</td>
<td>C_{2}HCl_{6}, 80 %</td>
<td>DMSO, 20 %</td>
<td>Yellow-green</td>
<td>476–483</td>
<td>N: 10.17 10.46 S: 7.76 7.98 Cu: 15.30 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>79</td>
</tr>
<tr>
<td>IIe</td>
<td>B</td>
<td>4-CH_{3}</td>
<td>t-C_{4}H_{4}Cl, 80 %</td>
<td>DMSO, 20 %</td>
<td>Green</td>
<td>487–492</td>
<td>N: 10.52 10.46 S: 7.81 7.98 Cu: 15.71 15.82</td>
<td>C_{22}H_{12}Cl_{12}N_{2}S_{2}Cu_{2}</td>
<td>83</td>
</tr>
<tr>
<td>III</td>
<td>A</td>
<td>4-Br</td>
<td>HCl, 30 %</td>
<td>CH_{3}OH, anh.</td>
<td>Deep green</td>
<td>493–497</td>
<td>N: 8.95 9.00 S: 7.04 6.87 Cu: 13.44 13.62</td>
<td>C_{22}H_{12}Cl_{12}Br_{2}N_{2}S_{2}Cu_{2}</td>
<td>84</td>
</tr>
<tr>
<td>IIIa</td>
<td>D</td>
<td>4-Br</td>
<td>CuCl_{2} · 2H_{2}O</td>
<td>IPA, anh.</td>
<td>Green</td>
<td>496–499</td>
<td>N: 9.24 9.00 S: 7.16 6.87 Cu: 13.51 13.62</td>
<td>C_{22}H_{12}Cl_{12}Br_{2}N_{2}S_{2}Cu_{2}</td>
<td>98</td>
</tr>
<tr>
<td>IIIb</td>
<td>C</td>
<td>4-Br</td>
<td>HCl, 30 %</td>
<td>IPA, anh.</td>
<td>Green</td>
<td>492–495</td>
<td>N: 9.08 9.00 S: 6.93 6.87 Cu: 13.21 13.62</td>
<td>C_{22}H_{12}Cl_{12}Br_{2}N_{2}S_{2}Cu_{2}</td>
<td>79</td>
</tr>
</tbody>
</table>

Note: HL: thioamide C_{2}H_{3}N_{2}C(=S)NHCH_{3}R^{1-3}, R^{1-3}: H, 4-CH_{3}, 4-3r
Synthesis conditions of some cuprum(II) complex compounds of the general formula [Cu(HL)Cl₂]₂

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>Proton-donor solvent</th>
<th>HCl, %</th>
<th>Temperature, K</th>
<th>Time, h</th>
<th>Molar ratio</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>H</td>
<td>IPA, anh</td>
<td>30</td>
<td>298</td>
<td>11.0</td>
<td>(v(HL)/v(Cu⁰) = 1 : 1)</td>
<td>6 : 1</td>
</tr>
<tr>
<td>II</td>
<td>4-CH₃</td>
<td>CH₂OH, anh</td>
<td>30</td>
<td>298</td>
<td>5.3</td>
<td>(v(HL)/v(Cu⁰) = 1 : 1)</td>
<td>10 : 1</td>
</tr>
<tr>
<td>III</td>
<td>4-Br</td>
<td>CH₂OH, anh</td>
<td>30</td>
<td>298</td>
<td>1.3</td>
<td>(v(HL)/v(Cu⁰) = 1 : 1)</td>
<td>30 : 1</td>
</tr>
</tbody>
</table>

Note: chlorine source in the complex compounds [Cu(HL)Cl₂]₂ – chloric acid; R – substituent in thioamide phenyl radical \(C_7H_5N_2C(=S)NHC₆H₄R\); \(R^1 = H, R^2 = 4-\text{CH}_3, R^3 = 4-\text{Br}\).

Fig. 1. Dependence of [Cu(HL)Cl₂]₂ yield on the molar ratio \(v(HCl)/v(Cu⁰)\)

Fig. 2. Dependence of [Cu(HL)Cl₂]₂ yield on the reaction time at different molar ratio \(v(HCl)/v(Cu⁰)\)

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 oxidative 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 (1 stage) occurs with the formation of possible molecular complexes [21] on the metal surface (Scheme 3) followed by chemical transformations (4)–(6).

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{S} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{α-associated form}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{S} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{β-donor-acceptor}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_3 \quad \text{CH}_3 \quad \text{S} \quad \text{O} \quad \text{S} \quad \text{O} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{electron-transport}
\end{array}
\]

\[
\text{system [22]}
\]
Direct Synthesis of Cuprum(II) Complex Compounds Based on Thioamide Ligands

\[
2\text{CH}_3\text{C}^+\text{Cl}^- + 2\text{E(C}^6\text{)} \rightarrow (\text{CH}_3\text{C}^+\text{C(}\text{CH}_3\text{)}_2 + 2\text{HCl}) \tag{4}
\]

\[
2\text{CuCl} + 4\text{DMSO} \rightarrow [\text{Cu(DMSO)}_2\text{Cl}_2] \tag{5}
\]

\[
\sum \text{2CH}_3\text{C}^+\text{Cl}^- + 2\text{E(C}^6\text{)} \rightarrow 4\text{DMSO} \rightarrow [\text{Cu(DMSO)}_2\text{Cl}_2] + (\text{CH}_3\text{C}^+\text{C(}\text{CH}_3\text{)}_2) \tag{6}
\]

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)$_2$Cl$_2$] dimeric complex and recombination of possible tert-butyl radicals (CH$_3$)$_3$C to 2,2,3,3-tetramethylbutane. It should be noted that cuprum(I) chloride is stabilized due to [Cu(DMSO)$_2$Cl$_2$] complex formation and its transfer from metal surface into the solution [23]. The resulting complex [Cu(HL)Cl$_2$] is formed under the action of HL – DMSO – CH$_3$OH – 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 · DMSO → HL + DMSO. The additional introduction of methyl alcohol to the system increases the oxidation rate Cu$^+$ → Cu$^{2+}$ in the similar systems [22]. The second stage of zero-valent cuprum oxidation proceeds according to the reaction (7):

\[
[\text{Cu(DMSO)}_2\text{Cl}_2] + 2\text{HL} + 1.2\text{O}_2 + 2\text{HCl} \rightarrow \text{CuO} + 1.2\text{HCl} + 1.2\text{H}_2\text{O} \tag{7}
\]

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

\[
2\text{CH}_3\text{C}^+\text{Cl}^- + 2\text{HL} + 2\text{Cu}^0 \rightarrow 1.2\text{O}_2 + 2\text{HCl} \rightarrow \text{CuO} + 1.2\text{HCl} + 1.2\text{H}_2\text{O} \tag{8}
\]

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$_6$H$_5$Cl and 50 % – due to Cl$^-$ anion of chloride 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$_6$H$_5$OH – HCl – O$_2$ in accordance with the reaction given in Scheme 1. To our mind the obtaining of [Cu(HL)Cl$_2$] via method C is not a classic direct synthesis including zero-valent cuprum oxidation because cuprum is already in the oxidized form Cu$^{2+}$O and re-oxidized according to the reaction (9):

\[
\begin{array}{c}
\text{CuO} + 1/2\text{O}_2 + 4\text{HCl} \rightarrow 2\text{CuCl}_2 + 2\text{H}_2\text{O}
\end{array} \tag{9}
\]

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-II, 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 ν(N–H) of the mean intensity in the area of 3356–3256 cm$^{-1}$, weak vibrations ν(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$\equiv$N fragment increases and order of C=S bond decreases due to the possible formation of boundary structures A and B:

![Structure A - Cu]  

![Structure B - Cu]  

The boundary structure B shifts stretching vibrations of thioamide group ν(N–H) and ν(C=) toward the high field by 102–55 and 20–15 cm$^{-1}$, respectively (“B”-band). At the same time stretching vibrations ν(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 (=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$_2$] obtained via direct and counter synthesis.
### Table 3

<table>
<thead>
<tr>
<th>Compound</th>
<th>R-substituent in phenyl radical</th>
<th>First stage</th>
<th>Second stage</th>
<th>Total time, h</th>
<th>Yield, %</th>
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</thead>
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<tr>
<td></td>
<td>Solvent, %</td>
<td>7, K</td>
<td>Stoichiometric ratio of the reagents</td>
<td>Solvent, %</td>
<td>7, K</td>
</tr>
<tr>
<td>IIb</td>
<td>CCl₄, 80% + DMSO, 20%</td>
<td>274.1–293</td>
<td>1.1–1.5</td>
<td>1.2–1.5</td>
<td>CH₂OH, 97</td>
</tr>
<tr>
<td>IIc</td>
<td>CCl₄, 80% + DMSO, 20%</td>
<td>274.1–293</td>
<td>1.1–1.3</td>
<td>1.2–1.5</td>
<td>CH₂OH, anh</td>
</tr>
<tr>
<td>IId</td>
<td>C₃H₇Cl, 89% + DMSO, 20%</td>
<td>298</td>
<td>1.0</td>
<td></td>
<td>CH₂OH, 80</td>
</tr>
<tr>
<td>IIe</td>
<td>C₆H₄Cl, 80% + DMSO, 20%</td>
<td>274.1–293</td>
<td>1.1–1.5</td>
<td>1.2–1.5</td>
<td>CH₂OH, 97</td>
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### Table 4

<table>
<thead>
<tr>
<th>Compound</th>
<th>General formula</th>
<th>$\nu$(N–H), cm$^{-1}$</th>
<th>“B”-band</th>
<th>“D”-band</th>
<th>“E”-band</th>
<th>Other vibrations, cm$^{-1}$</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>C=N</td>
<td>N–H</td>
<td>C–N</td>
<td>C=S</td>
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<tr>
<td>–</td>
<td>HL$^1$</td>
<td>3356 m 3256 m 3060 w</td>
<td>1597 s</td>
<td>1384 vs</td>
<td>1216 w</td>
<td>948 m</td>
</tr>
<tr>
<td>–</td>
<td>HL$^2$</td>
<td>3340 m 3267 m 3067 w</td>
<td>1590 m</td>
<td>1380 vs</td>
<td>1280 w</td>
<td>896 m</td>
</tr>
<tr>
<td>–</td>
<td>HL$^3$</td>
<td>3260 m 3095 w 1596 s</td>
<td>1535 s</td>
<td>1384 vs</td>
<td>1280 w</td>
<td>820 s</td>
</tr>
<tr>
<td>I</td>
<td>[Cu(HL$^1$)Cl$_2$]</td>
<td>3195 m 3062 w 1565 s</td>
<td>1449 s</td>
<td>1252 w</td>
<td>1140 w</td>
<td>960 vs</td>
</tr>
<tr>
<td>Ia</td>
<td>[Cu(HL$^1$)Cl$_2$]</td>
<td>3195 m 3145 m 3095 m 3060 w</td>
<td>1565 vs 1494 m</td>
<td>1450 s 1416 vs 1386 m</td>
<td>1244 w 1143 w 1091 w</td>
<td>963 vs 763 s 745 vs 696 vs</td>
</tr>
<tr>
<td>IIa</td>
<td>[Cu(HL$^1$)Cl$_2$]</td>
<td>3155 m 3085 m 3060 w</td>
<td>1564 m 1512 vs</td>
<td>1435 s 1392 m</td>
<td>1258 vs 1177 s</td>
<td>963 s 742 s</td>
</tr>
<tr>
<td>IIb</td>
<td>[Cu(HL$^1$)Cl$_2$]</td>
<td>3140 m 3065 w 1560 m 1510 m</td>
<td>1324 s</td>
<td>1250 m</td>
<td>1186 m</td>
<td>965 s 760 m 746 s</td>
</tr>
<tr>
<td>IIb</td>
<td>[Cu(HL$^1$)Cl$_2$]</td>
<td>3135 w 3065 w</td>
<td>1552 s</td>
<td>1486 vs</td>
<td>1440 s 1324 m</td>
<td>1240 w 1145 m 1080 m</td>
</tr>
</tbody>
</table>

**Notes:** $\text{C}_x\text{H}_y\text{N}_z$($\text{C}=\text{S})\text{NH}_c\text{H}_d\text{R}^{1+}$; $\text{R}^1 = \text{H (HL$^1$), R}^2 = \text{4-CH}_3\text{(HL$^2$)$, R}$ $^3 = \text{4-Br (HL$^3$)}$. “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 – strongly; 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 HL–ROH–HCl–O\(_2\) oxidative system in alcohol medium, HL–DMSO–CH\(_3\)OH–O\(_2\) (formation of resulting metal-chelates) two-stage oxidative system in halogen hydrocarbons medium. Within the frame of β-donor-acceptor electron-transfer 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.

References


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

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

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