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SYNTHESIS OF HETEROCYCLIC THIOAMIDES AND COPPER(II) COORDINATION COMPOUNDS BASED ON THEM

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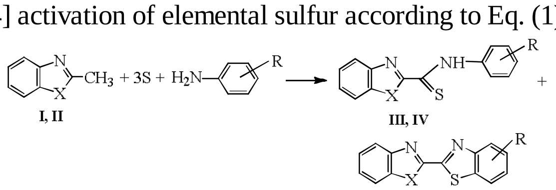
Abstract. Arylamides of hetaryl-2-thiocarbonic acid were synthesized *via* Willgerodt–Kindler modified reaction. The final products were studied by means of chemical analysis, IR- and ^{1}H NMR-spectroscopy. The coordination compounds of the general formula $[Cu(HL^4)Cl_2]_2] \cdot xCH_3OH$ (x = 0, 2) were obtained *via* traditional and direct synthesis based on benzimidazol-2-N-(4-ethoxyphenyl) carbothiamide (HL^4). Using X-ray analysis the molecular and crystal structures of $[Cu(HL^4)Cl_2]_2] \cdot 2CH_3OH$ complex were determined.

Keywords: heterocyclic thioamide, copper(II) binuclear complex, X-ray analysis.

1. Introduction

The modern development of coordination chemistry of 3*d*-metals and N,S-containing organic ligands is mainly connected with the synthesis of compounds with new biological [1], catalytic [2] and physico-mechanical [3] properties. The synthesis of heterocyclic thioamides with benzthiazol and benzimidazol fragments is complicated and connected with investigations of Willgerodt–Kindler modified reaction [4]. It is the reason for searching new methods of thioamides synthesis, their effective using in the coordination chemistry of 3*d*-metals [5] and obtaining compounds with a set of new chemical and physical properties. Previously the heterocyclic thioamides were obtained *via* thermal [6] or catalytic [3, 4] activation of elemental sulfur according to Eq. (1):



(1)

R = Alk, OAlk, Hal; X = S, **I, III, V**; X = NH, **II, IV, VI**

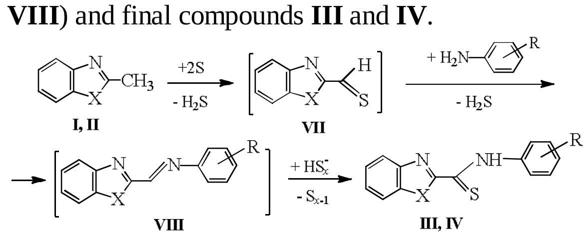
The by-products of oxidative cyclization **V** and **VI** are formed additionally to the main arylamides of hetaryl-2-thiocarbonic acid **III** and **IV.** In case of catalytic reaction, the sulfur-containing nucleophilic catalyst ($Na_2S{\cdot}9H_2O$) is used. The catalyst decomposes the initial cyclooctasulfan S_8 to the reactive nucleophilic ions HS^- and $HS_{8-x}S^-$ [4]:

$$Na_2S + H_2O \rightleftharpoons NaHS + NaOH \quad (2)$$

$$NaHS \rightleftharpoons Na^+ + HS^- \quad (3)$$

$$S_8 + HS^- \rightleftharpoons HS_{8-x}S^- + S_x, \quad x = 2 - 7 \quad (4)$$

The oxidation of active methyl group of the initial compounds **I** and **II** by sulfur (intermediate **VII**) is accompanied by formation of Schiff bases (intermediate **VIII**) and final compounds **III** and **IV**.



(5)

It should be noted that using the catalyst the yield of heterocyclic thioamides is increased by 2.0–2.5 times [3, 4] compared with the reaction thermal activation (Eq. (1)). However, in this work we propose to improve the synthesis of heterocyclic thioamides by adding dimethylsulfoxide (DMSO) that increases their yield and decreases the reaction temperature. The synthesized thioamides were analyzed as bidentate ligands while complex formation with some 3*d*-metals.

It should be also noted that nowadays the direct synthesis of coordination compounds of transition 3d-metals and thioamide ligands using HL–ROH–HCl–O_2 proton-donor systems is practically unstudied [7]. Meanwhile, such coordination compounds are widely used in engineering as additives to hydrocarbon materials [8] and model objects of copper(II) [8] and cobalt(II, III)

[9] biologically active complexes. In addition, just theoretical studies of the mechanism of the redox reactions occurred on the M^0-Ox-HL-Solv interface [10], are of particular interest.

So, the aim of this work is to investigate copper(0, II) complex formation with heterocyclic thioamides.

2. Experimental

2.1. Materials and Methods

To synthesize the heterocyclic thiamides **IIIa–IIIi** (Table 1) and **IVa–IVg** (Table 2) we used 2-methylbenzthiazol, 2-methylbenzimidazol and aromatic amines purchased by Aldrich and Merck. The compounds were of CP grade with the main component content of 99 %.

For the synthesis of $[Cu(HL^4)Cl_2]_2{\cdot}2CH_3OH$ complex we used the copper powder with mass part of metal ≥ 99.5 % and particles size of 8.0 ± 1.1 μm (75 vol %), determined by Saishin SKC-2000S microsedimentometer (Japan). Inorganic salts $CuCl_2{\cdot}2H_2O$ and $Na_2S{\cdot}9H_2O$ were of CP grade. Organic solvents (i-C_3H_7OH, CH_3OH and DMSO) were purchased by Merck and Aldrich and used as received without additional purification. Copper(II) content in the synthesized complex $[Cu(HL^4)Cl_2]_2{\cdot}xCH_3OH$ (x = 0, 2) was determined by atomic-absorption spectroscopy using S-115 PKRS spectrometer. The elemental analysis for nitrogen content was carried out by Kjeldahl method, sulfur content – by Sheniger method [11].

IR-spectra of **IIIa–IIIi**, **IVa–IVg** compounds and $[Cu(HL^4)Cl_2]_2{\cdot}xCH_3OH$ (x = 0, 2) complex were recorded within 4000–400 cm^{-1} using Specord 75 IR instrument. The samples were prepared as the tablets with KBr. ^1H NMR spectra were recorded using Varian VXR-200 (200 MHz) and Varian VXR-300 (300 MHz) microwave spectrometers for DMSO-d6 solutions with tetramethylsilane as an internal standard.

X-ray analysis of monocrystal **IX** was carried out at 293 K using Siemens P3/PC diffractometer (MoK_α-radiation, graphite monochromator, scanning method $q/2q$). The whole number of images are 3757, including 3401 independent ones, $R_{int} = 0.0740$. Crystals are monoclinic, $P2_{1/n}$; $a = 8.2001(3)$ Å, $b = 20.8052(5)$ Å, $c = 11.3421(4)$ Å; $\beta = 95.76(3)°$, $V = 1925.31(10)$ Å^3, $Z = 2$. For $C_{32}H_{30}Cl_4N_6O_2S_2Cu_2 \cdot 2CH_3OH$ $M = 927.74$ g/mol, $\rho_{calc.} = 1.600$ g/cm^3, $\mu(M_0K\alpha) = 1.537$ mm^{-1}, F(000) = 948.

The components structure was decoded by the direct method and specified by the least-squares method relative to F^2 in full-matrix anisotropic approximation using SHELXTL programs [12]. Hydrogen atoms of methyl groups were assigned geometrically. Two solvated molecules of methyl alcohol are present in the crystal. Full-matrix anisotropic specification of non-hydrogen atoms is completed at $R = 0.064$ according to 1918 images with $I \geq 2\sigma(I)$; $S = 1.103$.

2.2. Synthesis of Hetaryl-2-thiocarboxylic Acid Arylamides

2.2.1. Benzthiazol-2-N-(4-ethoxyphenyl)carbothiamide, IIIc

The reactor equipped by a mechanical stirrer, thermometer and backflow condenser was loaded with 14.9 g (0.1 mol) of 2-methylbenzthiazol, 13.7 g (0.1 mol) of *p*-phenetidine, 9.6 g (0.3 mol) of sulfur and 1.92 g (8 mmol) of $Na_2S{\cdot}9H_2O$. The reaction mixture was stirred and 10 ml of benzene was added. Azeotropic solution (benzene+water) was distilled at heating using Dean-Stark head. Then 5 ml of DMSO were added, the temperature was increased to 423 K and the mixture was kept under the mentioned temperature till the end of hydrogen sulfide evolving. The reaction was controlled by the qualitative reaction of lead(II) cation. After the reaction mass was cooled till 333–338 K it was extracted by 5% NaOH solution (3 x 150 ml). The alkaline extracts were collected and neutralized by diluted solution of chloride acid. The precipitate was filtered, dried at the air and recrystallized from the aqueous solutions of methyl and isopropyl alcohols. The yield was 22.6 g (72.0 %); *m.p.* was 400–401 K.

Other arylamides (**IIIa–IIIi**) were synthesized in the same way. Their physico-chemical characteristics are given in Table 1.

2.2.2. Benzimidazol-2-N-(4-bromphenyl)carbothioamide, IVe

The reactor equipped by the mechanical stirrer, thermometer and backflow condenser was loaded with 26.4 g (0.2 mol) of 2-methylbenzimidazol, 36.1 g (0.21 mol) of *p*-bromaniline, 19.2 g (0.6 mol) of sulfur, 3.6 g (15 mmol) of $Na_2S{\cdot}9H_2O$ and 30 ml of DMSO. The reaction mixture was heated at 383–393 K for 1.5 h without backflow condenser and then at 403–413 K for 10 h with it. The mixture was cooled to 343–353 K and extracted by 5% NaOH (3 x 250 ml). The alkaline extracts were collected. The hot solution was filtrated, cooled to the ambient temperature and acidified by diluted sulfuric acid till pH became 5–6. The yellow precipitate was filtered, dried at the air and recrystallized from the aqueous solution of isopropyl alcohols. Then it was re-precipitated from the diluted NaOH solution and again recrystallized from the aqueous solution of CH_3OH. The yield was 46.8 g (70.5 %); *m.p.* was 432.5–433 K.

Other arylamides (**IVa–IVg**) were synthesized in the same way. Their physico-chemical characteristics are given in Table 2.

2.3. Synthesis of $[Cu(HL^4)Cl_2]_2] \bullet xCH_3OH$ (x = 0, 2) Coordination Compounds

2.3.1. Di(μ-chloro)-dichloro-bis[benzimidazol-2-N-(4-ethoxyphenyl)carbothiamide]copper(II) solvated by methanol, IX. Method A.

4.46 g (15.0 mmol) of benzimidazol-2-N-(4-ethoxyphenyl) carbothiamide were dissolved in 200 ml of hot unhydrous methyl alcohol. The solution was acidified by 9 ml (90.0 mmol) of 30% HCl and then 0.95 g (15.0 mmol) of copper powder was added under stirring. The obtained mixture was quickly cooled to 293 K and intensively stirred for 11 h. The precipitate of violet-brown color was filtrated using Schott filter, washed by unhydrous methanol (3 × 10 ml) and dried in desiccator over $CaCl_2$. The yield was 5.96 g (92 %); melting point 473–480 K (with decomp.). Found, %: N 5.98; S 6.57; Cu 13.54. For $[Cu(C_{32}H_{30}N_6O_2S_2)Cl_4]\cdot 2CH_3OH$ calculated, %: N 6.04; S 6.91; Cu 13.70.

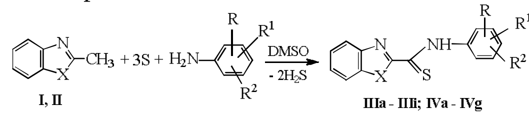
2.3.2. Di(μ-chloro)-dichloro-bis[benzimidazol-2-N-(4-ethoxyphenyl)carbothiamide]copper(II), X. Method B.

2.59 g (15.2 mmol) of $CuCl_2\cdot 2H_2O$ dissolved in 45 ml of hot unhydrous methyl alcohol and 4.0 ml (40.0 mmol) of 30% HCl were added to 4.46 g (15.0 mmol) of benzimidazol-2-N-(4-ethoxyphenyl) carbothiamide dissolved in 100 ml of hot unhydrous methyl alcohol under constant stirring. The solution was stirred at 318–323 K for 30 min. The formed precipitate of violet-brown color was filtrated using Schott filter, washed by unhydrous methanol (3 × 25 ml) and dried in desiccator at 363–373 K till the weight became constant. The yield was 6.15 g (95 %); melting point 473–480 K (with decomp.). Found, %: N 9.41; S 7.36; Cu 14.45. For $[Cu(C_{32}H_{30}N_6O_2S_2)Cl_4]\cdot 2CH_3OH$ calculated, %: N 9.73; S 7.43; Cu 14.72.

3. Results and Discussion

3.1. Synthesis of Heterocyclic Thioamides

To continue the investigations of new heterocyclic thioamides synthesis *via* Willgerodt–Kindler modified reaction [3, 4] we obtained **IIIa–IIIi** and **IVa–IVg** compounds by adding aprotic solvent DMSO to the reaction products:



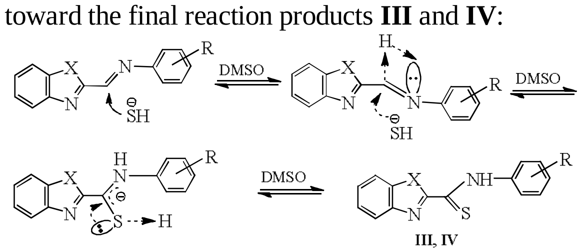
(6)

X = S; R = R^1 = H, R^2 = CH_3-3, **IIIa**; R = R^1 = H, R^2 = OCH_3-2, **IIIb**; R = R^1 = H, R^2 = OC_2H_5-4, **IIIc**; R = H, R^1 = CH_3-2, R^2 = CH_3-4, **IIId**; R = H, R^1 = CH_3-2, R^2 = CH_3-5, **IIIe**; R = CH_3-2, R^1 = CH_3-4, R^2 = CH_3-6, **IIIf**; R = R^1 = H, R^2 = Cl-2, **IIIg**; R = R^1 = H, R^2 = Cl-4, **IIIh**; R = R^1 = H, R^2 = Br-4, **IIIi**.
X = NH; R = H, R^1 = CH_3-2, **IVa**; R = H, R^1 = OCH_3-2, **IVb**; R = H, R^1 = OC_2H_5-4, **IVc**; R = CH_3-2, R^1 = CH_3-4, **IVd;** R = H, R^1 = Cl-4, **IVe;** R = H, R^1 = Br-4, **IVf;** R = H, R^1 = F-4, **IVg**

It was previously noted that $Na_2S\cdot 9H_2O$ nucleophilic catalyst activates S_8 cyclooctasulfone and provides the formation of HS^-, $HS_{8-x}S^-$ reactive nucleophilic ions and final heterocyclic thioamides **III** and **IV** (Eqs. (2)–(5)). The additional introduction of DMSO aprotic solvent increases thioamides yield by 15–27 % due to the following possible reasons:

– the increase in $HS_{8-x}S^-$ ion nucleophilicity;

– the increase in the rate of 2-methylhetarenes methyl group thiolation reaction (formation of intermediate **VII**) and shift of thione-thiol equilibrium toward the final reaction products **III** and **IV**:



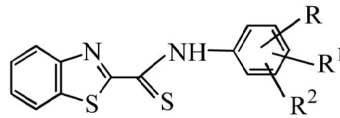
(7)

Physico-chemical properties of the synthesized heterocyclic thioamides are represented in Tables 1 and 2. The composition and structure of all synthesized compounds were investigated by elemental analysis and ^1H NMR spectroscopy. In addition, the structure of the compounds **IVa–IVf** was studied by IR-spectroscopy.

So, for the compounds **IVa–IVf** the most typical vibrations are stretching vibrations of ν(N–H) thioamide group of average or high intensity in the area of 3370–3260 cm^{-1}, stretching vibrations of ν(N–H) of heterocyclic fragment of average intensity within 3095–3015 cm^{-1} and multiplex vibrations of thioamide group which were interpreted as vibrations of “B”-, “D”- and “E”-band [7]. The typical stretching vibrations of “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 and “E”-band (C=S + C–N) with greater contribution of C=S group are represented in Table 3.

Table 1

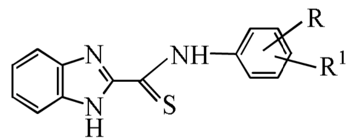
Physico-chemical characteristics of benzthiazolyl-2-thiocarboxylic acid arylamides

Compound	 R	R[1]	R[2]	Brutto-formula	Found/Calculated, % N	Found/Calculated, % S	^{1}H NMR (δ), ppm	Melting point (*m.p.*), K	Yield*, %
IIIa	H	H	CH_3-3	$C_{15}H_{12}N_2S_2$	10.16 / 9.85	22.18 / 22.55	2.40s (3H, CH_3); 7.12d, 7.33t, 7.51–7.63m (4H, C_{Ar}-H), 7.75t, 8.14d (4H, C_{Het}-H); 12.18s (1H, NH)	377–379	17.2
IIIb	H	H	OCH_3-2	$C_{15}H_{12}N_2OS_2$	8.94 / 9.33	21.14 / 21.35	3.99s (3H, CH_3); 7.03t, 7.17d, 7.31t, 8.65d (4H, C_{Ar}-H); 7.54t, 7.61t, 8.13m (4H, C_{Het}-H); 11.74s (1H, NH)	379–380	64.8
IIIc	H	H	OC_2H_5-4	$C_{16}H_{14}N_2OS_2$	9.24 / 8.91	20,08 / 20,40	1.38m (3H, CH_3); 4.07m (2H, CH_2); 6.94d, 7.88d (4H, C_{Ar}-H); 7.52t, 7.58t, 8.10d (4H, C_{Het}-H); 12.21s (1H, NH)	400–401	72.0
IIId	H	CH_3-2	CH_3-4	$C_{16}H_{14}N_2S_2$	9.67 / 9.39	21.80 / 21.49	2.22s, 2.35s (6H, 2-CH_3, 4-CH_3); 7.05–7.25m (3H, C_{Ar}-H); 7.52–7.62m, 8.10–8.16t (4H, C_{Het}-H); 12.12s (1H, NH)	412–414	68.5
IIIe	H	CH_3-2	CH_3-5	$C_{16}H_{14}N_2S_2$	9.05 / 9.39	21.84 / 21.49	2.12s, 2.35s (6H, 2-CH_3, 5-CH_3); 7.08d, 7.17t (3H, C_{Ar}-H); 7.54t, 7.60t, 8.10–8.16m (4H, C_{Het}-H); 12.10s (1H, NH)	405–406	61.7
IIIf	CH_3-2	CH_3-4	CH_3-6	$C_{17}H_{16}N_2S_2$	9.24 / 8.97	20.11 / 20.53	2.11s, 2.26s (9H, 2-CH_3, 4-CH_3, 6-CH_3); 6.90s (2H, C_{Ar}-H); 7.55m, 8.06m (4H, C_{Het}-H); 12.20s (1H, NH)	448.5–451	80.5
IIIg	H	H	Cl-2	$C_{14}H_9ClN_2S_2$	9.64 / 9.19	20.65 / 21.04	7.38t, 7.43t, 7.59d, 7.94d (4H, C_{Ar}-H); 7.54t, 7.60t, 8.09d, 8.15d (4H, C_{Het}-H); 12.09s (1H, NH)	441–442	22.0
IIIh	H	H	Cl-4	$C_{14}H_9ClN_2S_2$	9.43 / 9.19	21.75 / 21.04	7.46d, 7.98d (4H, C_{Ar}-H); 7.53t, 7.60t, 8.13d, 8.16d (4H, C_{Het}-H); 12.40s (1H, NH)	432–434	29.2
IIIi	H	H	Br-4	$C_{14}H_9BrN_2S_2$	8.37 / 8.02	17.96 / 18.36	7.59d, 7.95d (4H, C_{Ar}-H); 7.54t, 7.60m, 8.15m (4H, C_{Het}-H); 12.37s (1H, NH)	431.5–432.5	51.0

Note: yield of the compounds **IIIa–IIIi** is given after threefold recrystallization according to the following sequence: I – aqueous *i*-C_3H_7OH; II – aqueous 5% solution of NaOH; III – aqueous CH_3OH

Table 2

Physico-chemical characteristics of benzimidazolyl-2-thiocarboxylic acid arylamides

Compound	 R	R[1]	Brutto-formula	Found/Calculated, % N	Found/Calculated, % S	^{1}H NMR (δ), ppm	Melting point (*m.p.*), K	Yield*, %
IVa	H	CH_3-2	$C_{15}H_{13}N_3S$	15.40/15.72	11.71/11.99	2.30s (3H, CH_3); 7.30m, 7.47t, 7.63d, 7.75d (8H, C_{Ar}-H, C_{Ar}-H); 11.92s, 12.90s (2H, NH, NH)	397–399	54.6
IVb	H	OCH_3-2	$C_{15}H_{13}N_3OS$	14.60/14.83	11.74/11.32	4.00s (3H, CH_3); 7.04t, 7.17d, 7.30t, 7.62d, 7.76d, 8.98d (8H, C_{Ar}-H, C_{Ar}-H); 11.77s, 12.92s (2H, NH, NH)	444.5–446	60.2
IVc	H	OC_2H_5-4	$C_{16}H_{15}N_3OS$	14.51/14.13	10.45/10.78	1.40m (3H, CH_3), 4.00–4.10m (2H, CH_3); 6.97d, 7.92d (4H, C_{Het}-H); 12.05s, 12.85s (2H, NH, NH)	444–445	69.7
IVd	CH_3-2	CH_3-4	$C_{16}H_{15}N_3S$	14.54/14.93	11.75/11.40	2.26s, 2.35s (6H, CH_3, CH_3); 7.08t, 7.30t, 7.62d, 7.74d (7H, C_{Ar}-H, C_{Ar}-H); 11.90s (1H, NH), 12.85s (1H, $NH_{гет}$)	415–417	64.3
IVe	H	Cl-4	$C_{14}H_{10}ClN_3S$	14.88/14.60	11.45/11.14	7.42d, 7.06d, (4H, C_6H_4); 7.28t, 7.68s (4H, C_{Het}-H); 12.22s (1H, NH), 12.90s (1H, $NH_{гет}$)	441–442	40.2
IVf	H	Br-4	$C_{14}H_{10}BrN_3S$	12.41/12.65	9.82/9.65	7.59d, 8.00d, (4H, C_{Ar}-H); 7.30d, 7.62–7.82m (4H, C_{Het}-H); 12.20s, (1H, NH); 12.92s (1H, $NH_{гет}$)	432.5–433.5	70.5
IVg	H	F-4	$C_{14}H_{10}FN_3S$	15.31/15.49	11.42/11.82	2.50d, 3.04s (3H, CH_3); 7.27m, 7.68m, (4H, C_{Het}-H); 7.55s, 7.88d (3H, C_{Ar}-H); 11.80s, (1H, NH); 12.90s (1H, $NH_{гет}$)	446–448	39.9

Note: yield of the compounds **IVa–IVg** is given after threefold recrystallization according to the following sequence: I – aqueous *i*-C_3H_7OH; II – aqueous 5% solution of NaOH; III – aqueous CH_3OH

Table 3

IR-spectra of thioamides IVa–IVf and complexes IX, X

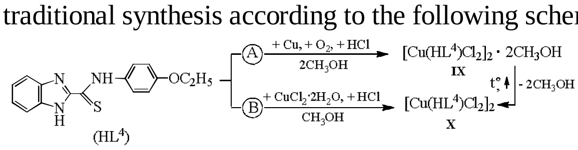
Compound	–NH– group, cm^{-1}		–C(=S)NH– group, cm^{-1}						Other vibrations, cm^{-1}
	Thioamide group	Benzimidazol fragment	“B”-band		“D”-band		“E”-band		
			C=N	N–H	C–N	C=S	C=S	C–N	
IVa	3370h 3270h	3045a	1555h 1510a	1395h 1315h	1240a 1185a	1085a	850l	755h	1287, 1150, 1240, 950, 775, 880
IVb	3300h 3260h	3063l	1536h	1380h 1320h	1280a	1110a	944a	762a 745h	1598,1465,1423
IVc	3330h 3260h	3075a	1532h 1515a	1390h 1315a	1280a 1185h	965a	832a	750h	1225, 1125, 870, 680
IVd	3324h 3290h	3065a	1540h 1506h	1387h 1316h	1287a 1194h	933h	812h	738h 732h	1575, 1146, 900, 700
IVe	3260h	3015a	1595h 1546h 1500h	1387h 1320a	1290a 1196h	1085h	960l	745h	2975, 1455, 772, 870, 835, 695
IVf	3260h	3015l	1596h 1535h 1488h	1384vh 1316h	1280l	1072vh 1006a	820h	730vh	1610, 950, 930, 620, 504, 432
IX	3270a 3219a	3075a	1545h 1520h	1392a 1324a	1303a 1177h	933a	815a	742h	2935, 2875, 1150, 1435
X	3270a 3210a	3075a	1544h 1520h	1392a	1306a 1117h	935a	815a	746h	1610, 1435, 1324

Note: “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 and “E”-band (C=S + C–N) with greater contribution of C=S group. The intensity of vibrations: vh – very high; h – high; a – average; l – low

[1]H NMR spectra of the compounds **IIIa–IIIi** (Table 1) represent proton signals of aromatic nuclei, benzthiazol fragment and NH thioamide group. Proton signals of 1,4-disubstituted phenylene (compounds **IIIc, IIIh** and **IIIi**) usually appear as two doublets within 6.94–7.98 ppm and signals of 1,2-substituted fragment (**IIIb** and **IIIg**) – as two doublets and two triplets within 7.03–8.65 ppm. Proton signals of methyl group in N-tolylamide fragment (**IIIa**, **IIId**, **IIIe** and **IIIf**) appear as a singlet within 2.11–2.40 ppm. However, protons of the same groups in metoxyl fragment (**IIIb**, **IIIc**) appear as the singlet in a lower field (3.99 ppm), methyl group (**IIIc**) – in the area of 1.38 ppm and methylene group – in the area of 4.07 ppm. Proton signals of benzthiazol fragment usually appear as two doublets (8.06–8.16 ppm) and two triplets (7.52–7.61 ppm). Protons of NH-group appear as the singlet within 12.10–12.40 ppm, except for **IIIb**, the proton of which gives signal at 11.74 ppm. Relation of proton signals of 1,4- and 1,2-disubstituted phenylene, methyl and methoxyl groups of the compounds **IVa–IVg** are similar to those of thioamides **IIIa–IIIi** (Table 2). [1]H NMR spectra of the compounds **IVa–IVg** differ by two NH-groups in their structure: thioamide and benzimidazol fragments. Signals of NH proton of thioamide group (**IVa–IVg**) appear as the singlet within 11.77–12.22 ppm; protons of benzimidazol fragment – within 12.85–12.92 ppm.

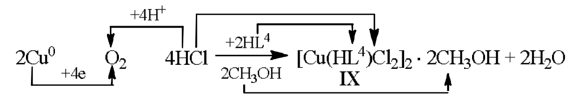
3.2. Synthesis of $[Cu(HL^4)Cl_2]_2$•$2CH_3OH$ Complex

Earlier we assumed [7] that the coordination compounds obtained *via* the direct synthesis, have a dimeric structure. Their general formula is: $[Cu(HL^{1-3})Cl_2]_2$, where HL^1 – $C_7H_5N_2C(=S)NHC_6H_5$, HL^2 – $C_7H_5N_2C(=S)NHC_6H_4CH_4$-4, HL^3 – $C_7H_5N_2C(=S)NHC_6H_4Br$-4. To confirm this assumption here we obtain metal-chelates **IX** and **X** *via* direct and traditional synthesis according to the following scheme:



(8)

The same synthesis conditions for the compounds of the general formula $[Cu(HL^{1-3})Cl_2]_2$ [7] and complex **IX** confirm the identity of their compositions and presence of dimeric structure. CH_3OH solvent and ligands of different nature (thioamide, HCl) may be the potential donors of hydrogen cation. However, neither methyl alcohol (autoprotolysis: $2CH_3OH \rightleftharpoons CH_3\overset{\ominus}{O} + CH_3O\overset{\oplus}{H}_2$), nor thioamide ligand (dissociation of weak NH acid: $HL \rightleftharpoons \overset{\oplus}{H} + \overset{\ominus}{L}$) are capable to compete with the dissociation of strong acid $HCl \longrightarrow \overset{\oplus}{H} + \overset{\ominus}{Cl}$ and its further participation in formation of compound **IX** dimeric structure:



(9)

The composition of compounds **IX** and **X** was determined by elemental analysis, their structure – by IR-investigations (Table 3). The comparison of **IVc** and **IX, X** IR-spectra confirms the proceeding of complexation reaction and their structure (Scheme (8)).

IR-spectra of the compounds **IX** and **X** are practically identical. There is the shift of thioamide group ν(N–H) bond vibrations by 60 cm^{-1} compared with **IVc** whereas stretching vibrations of benzimidazol fragment ν(N–H) bond are the same. For ν(N–H) bonds (band "B") the strong stretching vibrations are typical, as well as their shift toward the high field by 13 and 9 cm^{-1} for the compounds **IX** and **X**, respectively. Stretching vibrations of ν(C–H) and ν(C=S) bonds (band "D") of the average intensity shift toward high and low fields by 23 and 29 cm^{-1}, respectively. For the band "E" the shift of ν(C=S) stretching vibrations toward low field by 17 cm^{-1} is typical. The spectral data are confirmed by the results of other investigations [7] and prove the structure of the compounds **IX** and **X** obtained *via* both direct and traditional synthesis.

3.3. X-ray Analysis of $[Cu_2(C_{32}H_{30}N_6O_2S_2)Cl_4]$•$2CH_3OH$, IX

The general view of the molecule, bonds length and valence angles of the compound **IX** are represented in Fig. 1.

Crystal structure of the compound **IX** is a copper(II) bicyclic complex of $Cu_2(HL)_2Cl_4$ ($HL = C_{16}H_{15}N_3OS$) with methyl alcohol (1:2). Binuclear complex has two structurally equivalent copper atoms located at the distance of 3.620 Å between each other. Every copper atom is five-coordinated by three atoms of chlorine, two of which are bridge ones, and atoms of nitrogen and sulfur of (HL^4) thioamide ligand. The coordination polyhedron is a strongly deformated bipiramide, where N(1) and Cl(2A) atoms are in the axial position and S(1), Cl(1) i Cl(2) – in the equatorial one (valence angles N(1)–Cu(1)–Cl(2A) 170.4(1)°; S(1)–Cu(1)–Cl(1) 131.54(8)°; S(1)–Cu(1)–Cl(2) 117.12(7)° and Cl(1)–Cu(1)–Cl(2) 117.12(7)°). The atom of Cu(1) is actually in the plane of equatorial atoms (deviation is 0.028(1)Å).According to X-ray analysis (Fig. 1) there are three planar fragments in the molecule of thioamide ligand: benzimidazole bicycle (fragment *A*, mean square deviation of atoms from the plane is 0.013 Å); S(1), N(3), C(8) and C(9) atoms, (fragment *B*, deviation is 0.011 Å) and ethoxyphenyl radical (fragment *C*, deviation is 0.036 Å). The rotation angles of fragments *B* and *C* relative to *A* are 16.8 and 111.6 °, respectively.

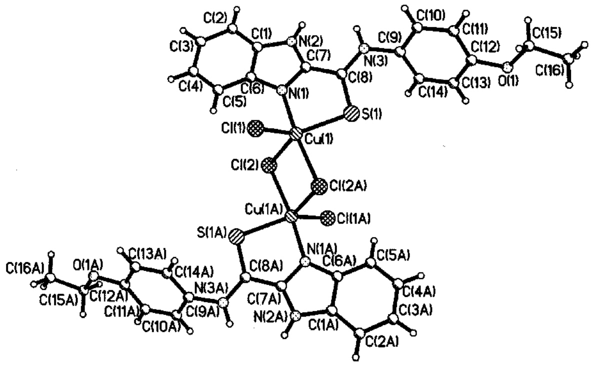


Fig. 1. Molecular structure of the compound **IX.** The main bonds length (Å): Cu(1)–Cl(1) 2.313(2), Cu(1)–Cl(2) 2.563(2), Cu(1)–Cl(2A) 2.271(2), Cu(1)–S(1) 2.293(2), Cu(1)–N(1) 1.949(4), S(1)–C(8) 1.632(6), O(1)–C(12) 1.362(7), O(1)–C(15) 1.439(7), N(1)–C(7) 1.341(7), N(1)–C(6) 1.396(6). Valence angles: N(1) Cu(1) Cl(2A) 170.4(1)°, N(1) Cu(1) S(1) 84.8(1)°, S(1) Cu(1) Cl(2A) 88.33(7)°, N(1) Cu(1) Cl(1) 94.1(1)°, Cl(1) Cu(1) Cl(2A) 95.55(6)°, S(1) Cu(1) Cl(1) 131.54(8)°, N(1) Cu(1) Cl(2) 89.3(1)°, Cl(2) Cu(1) Cl(2A) 87.78(6)°, S(1) Cu(1) Cl(2) 117.12(7)°, Cl(1) Cu(1) Cl(2) 111.29(6)°, Cu(1) Cl(2) Cu(1A) 92.22(6)°

Methyl alcohol molecules occupy the position in external sphere and are bounded by hydrogen bonds between each other and nitrogen and oxygen atoms of N(3)–H(3N)···O(1S) thioamide ligand (H···O 1.97 Å, N–H···O 153°).

The length of N(1)–C(7) bond in benzimidazol fragment is 1.341(7) Å, that approximates to the mean value of carbon–nitrogen double bond (1.339 Å) [13]. At the same time C(8)–S(1) bond is shorter than typical values of C=S double bond (cf. 1.632(6) and 1.671 Å). The length of other bonds is typical [14].

4. Conclusions

New arylamides of hetaryl-2-thiocarbonic acid were synthesized *via* Willgerodt–Kindler modified reaction. The introduction of DMSO aprotic solvent into the reaction mass increases the yield of heterocyclic thioamides by 15–27 %. The composition and structure of the final products were studied by means of chemical analysis, IR- and ^{1}H NMR-spectroscopy.

We synthesized di(μ-chloro)-dichloro-bis[benzimidazol-2-N-(4-ethoxyphenyl)carbothiamide]copper(II) coordination compound solvated by methanol. Its composition and binuclear structure were studied using IR-spectroscopy and X-ray analysis.

X-ray analysis was used to examine the dimeric structure of the complex compounds of general formula $[Cu(HL^{1-4})Cl_2]_2 \cdot xCH_3OH$ (x = 0, 2). It was determined that crystals are monoclinic: a = 8.2001(3) Å, b = 20.8052(5) Å, c = 11.3421(4) Å, spatial group $P2_{1/n}$, Z = 2. Copper(II) binuclear coordination compound has four chloride anions, two of which are bridge ones, two neutral molecules of benzimidazol-2-N-(4-ethyxyphenyl)carbthioamide (HL), and two solvated molecules of methyl alcohol.

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СИНТЕЗ ГЕТЕРОЦИКЛІЧНИХ ТІОАМІДІВ ТА КООРДИНАЦІЙНИХ СПОЛУК КУПРУМУ(ІІ) НА ЇХ ОСНОВІ

Анотація. *Модифікованою реакцією Вільгеродта-Кіндлера синтезовані ариламіди гетарил-2-тіокарбонової кислоти. Отримані сполуки досліджені методами хімічного аналізу, ІЧ- та ^{1}Н ЯМР-спектроскопією. Методами традиційного та прямого синтезу на основі бензімідазол-2-N-(4-етоксифеніл)карботіоаміда (HL^4) отримано кординаційні сполуки загальної формули $[Cu(HL^4)Cl_2]_2] \cdot xCH_3OH$ (x = 0, 2). Молекулярна і кристалічна структура комплексу $[Cu(HL^4)Cl_2]_2] \cdot 2CH_3OH$ встановлена методом рентгеноструктурного аналізу.*

Ключові слова: *гетероциклічні тіоаміди, біядерні комплекси купруму(ІІ), рентгеноструктурний аналіз.*