

SYNTHESIS, STRUCTURE AND PROPERTIES OF COPPER(II)
CHELATES WITH BENZIMIDAZOLE-2-*N*-ARYLCARBOTHIOAMIDESOlga Gordienko¹, Taras Titov¹, Anatolii Ranskiy^{1, *}, Olexander Gumenchuk²<https://doi.org/10.23939/chcht12.02.176>

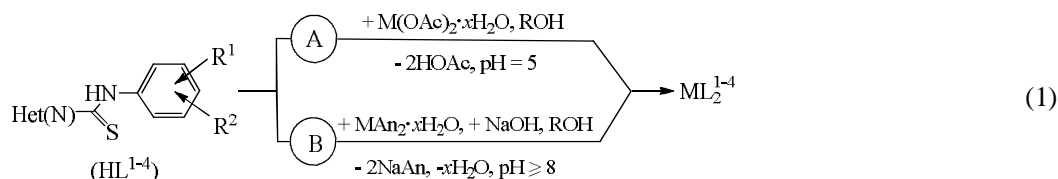
Abstract. Coordination compounds of general formula $\text{CuL}_2^{\text{I-IV}}$ have been obtained *via* complexation of copper(II) acetates and chlorides, as well as precipitated $\text{Cu}(\text{OH})_2$ with benzimidazole-2-*N*-arylcabothioamides ($\text{HL}^{\text{I-IV}}$). Monocrystal of $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S})_2] \cdot i\text{-C}_3\text{H}_7\text{OH}$ complex has been obtained by slow evaporation of CuL_2^{II} chelate saturated solution in isopropyl alcohol. The obtained compounds were investigated by means of elemental, XRD analysis and IR-spectroscopy. The investigated crystal structure is a solvate of copper(II) crystal complex of $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S})_2]$ composition and isopropyl alcohol with the ratio of 1:1. The central atom of copper(II) is coordinated by two atoms of nitrogen and sulfur of deprotonated thioamide ligand. Antiwear and

antifriction properties of lubricating compositions based on I-20A industrial oil and synthesized $\text{CuL}_2^{\text{I-IV}}$ complexes have been examined.

Keywords: heterocyclic thioamides, copper(II) chelated complexes, XRD, tribochemistry.

1. Introduction

Previously [1], the coordination compounds of some 3*d*-metals with heterocyclic thioamides of the general formula $\text{CuL}_2^{\text{I-4}}$ were synthesized according to the following schemes:

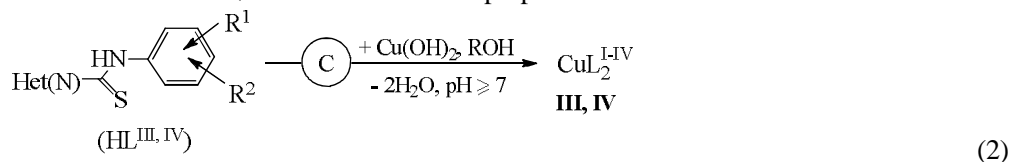


Methods A and B. HL^{I} : pyridyl-2, $\text{R}^1 = \text{H}$, $\text{R}^2 = 4\text{-CH}_3$, 4-OCH_3 , $\text{M} = \text{Cu}^{2+}$, Ni^{2+} ; HL^{II} : quinolyl-2, $\text{R}^1 = \text{H}$, $\text{R}^2 = 4\text{-CH}_3$, 4-OCH_3 , $\text{M} = \text{Cu}^{2+}$, Ni^{2+} ; Co^{2+} ; HL^{III} : benzothiazolyl-2, $\text{R}^1 = \text{H}$, $\text{R}^2 = 4\text{-CH}_3$, 4-OCH_3 , $\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+} ; HL^{IV} : benzimidazolyl-2, $\text{R}^1 = \text{R}^2 = \text{H}$; $\text{R}^1 = \text{H}$, $\text{R}^2 = 2\text{-CH}_3$, 4-CH_3 , 2-OCH_3 , 4-OCH_3 , $4\text{-OC}_2\text{H}_5$, 3-Br , 4-Br , 4-Cl , 4-F ; $\text{R}^1 = 2\text{-Br}$; $\text{R}^2 = 4\text{-CH}_3$; $\text{M} = \text{Cu}^{2+}$, Ni^{2+} , Co^{2+} , Zn^{2+} , Mn^{2+} .

The reaction was carried out in a subacid or neutral medium using alcohol solutions of metal acetates (method

A) or in alkaline medium using alcohol-alkaline solutions of metal chlorides (method B), which provided deprotonation of the thioamide ligand and the formation of $\text{ML}_2^{\text{I-4}}$ metal chelates [1].

In this work we obtained copper(II) chelates **I-IV**, using copper salts (methods A and B), precipitated $\text{Cu}(\text{OH})_2$ (method C) and the new thioamides $\text{HL}^{\text{I-IV}}$. We investigated their structure, physico-chemical and functional properties.



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Methods A and B. HL^{I, II}: benzimidazolyl-2, **I**: R¹ = H, R² = 2-Cl; **II**: R¹ = 2-CH₃, R² = 4-CH₃.

Method C. HL^{III, IV}: benzimidazolyl-2, **III**: R¹ = H, R² = 3-CH₃; **IV**: R¹ = H, R² = 3-CF₃.

In addition to scientific issues of studying copper(II) complexation with heterocyclic thioamides in the organic solvents, this work has a practical significance, since the synthesized compounds **I-IV** are potential thermostabilizers and accelerators of sulfuric vulcanization of polyisopropene based rubber, polyfunctional additives to industrial oils and lubricants, as well as biologically active substances [2-4].

The purpose of the work is the synthesis of new coordination compounds of copper(II) with benzimidazole-2-*N*-arylcarbothioamides, the investigation of their structure and possible use as antiwear and antifriction additives for industrial oils.

2. Experimental

2.1. Materials and Methods

To obtain the coordination compounds CuL₂^{I-IV}, the initial heterocyclic thioamides HL^{I-IV} were synthesized according to the procedures described in [5]. The content of copper(II) in the synthesized complexes **I-IV** was determined using EDTA complexometric titration. Elemental analysis regarding the nitrogen content was carried out by the Kjeldahl method, and sulfur – by the Sheniger method [6].

IR spectra of compounds **I-IV** in the range of 4000–400 cm⁻¹ were recorded on Specord 75 IR device, the samples were prepared as tablets with KBr.

To carry out XRD analysis the bis[benzimidazole-2-*N*-(2,4-dimethylphenyl)carbothioamidato]copper(II) monocrystal solvated with isopropyl alcohol (compound **V**) was obtained by slow evaporation of chelate **II** saturated solution in isopropyl alcohol. XRD analysis was carried out at 293 K using Xcalibur-3 diffractometer (MoK_α-radiation, CCD-detector, graphite monochromator, ω-scan, 2θ_{max} = 50°). Totally 10092 images were obtained, 3305 of them are independent, *R*_{int} = 0.085. The crystals were found to be monoclinic, spatial group C₂/s; *a* = 35.516(4) Å, *b* = 7.560(1) Å, *c* = 15.189(2) Å; *b* = 109.25(1)°, *V* = 3850.4(8) Å³, *z* = 4. For C₃₂H₂₈N₆S₂Cu·C₃H₇OH the molecular weight *M* = 744.48 g/mol, ρ_{calc.} = 1.284 g/cm³, μ(MoK_α) = 0.716 mm⁻¹, *F*(000) = 1564.

The structure was decoded by direct method using the SHELXTL program [7]. The positions of hydrogen atoms were found from the difference in electron density and specified according to the “rider” model with *U*_{iso} = *n*·*U*_{eq} of a non-hydrogen atom bound with hydrogen

one (*n* = 1.5 for methyl groups and *n* = 1.2 for other atoms of hydrogen). The components structure was specified by the least-squares method relative to *F*² in full-matrix anisotropic approximation for non-water atoms up to *wR*₂ = 0.076 relative to 3238 reflections (*R*₁ = 0.045 relative to 3238 reflections with *F* > 4σ(*F*), *S* = 0.675).

Antiwear (*I*_g) and antifriction (*f*_{fr}) properties of lubricant compositions based on I-20A industrial oil and **I-IV** synthesized compounds were determined using SMTs-2 friction machine with a “bronze-steel” friction pair with a slip velocity of 3.0 m/s and sliding distance of 3·10³ m. Roller material was Steel-45, pads material – bronze BrAZh 9-4. Coefficient of mutual overlap was 0.13. Initial roughness was 0.30–0.62 μm for a steel sample and 0.62–0.80 μm – for bronze. Wear was recorded by gravimetric method using the analytical scales with the second-grade accuracy. The temperature in the friction zone was measured by a chromel-copel thermocouple, and the friction force – with the help of a strain gauge [8].

2.2. Synthesis of Coordination

Compounds of the General Formula

CuL₂, I-IV

2.2.1. Bis[benzimidazole-2-*N*-(2-chlorophenyl)carbothioamidato]copper(II), I

Method A. 1.0 g (5.0 mmol) of copper(II) acetate dissolved in 15 ml of boiling water was added to a solution of 2.88 g (10.0 mmol) of benzimidazole-2-*N*-(2-chlorophenyl)carbothioamide in 150 ml of hot methanol under constant stirring. The reaction mixture was heated to boiling and kept with backflow condenser for 20 min. After cooling to room temperature, the precipitated brown product was filtered, washed with hot methanol (2 × 10 ml) and distilled water (2 × 10 ml), and then dried in a drying chamber at 373 K till the weight became constant. Yield: 2.9 g (91 %), m.p. 473–481 K (decomposes). Found, %: N 12.77; S 9.69; Cu 10.27. For [Cu(C₁₄H₉ClN₃S)₂] calc.: N 13.19; S 10.07; Cu 9.97. IR (KBr, ν, cm⁻¹): NH_{het} 3075 m; “B”-band 1570 s, 1527 m, 1490 m, 1465 s, 1320 s; “D”-band 1286 m, 1220 m; “E”-band 800 m, 725 s; (ν, C=N_{het.}) 1615 m; (*n*, C–Cl) 1042 m.

2.2.2. Bis[benzimidazole-2-*N*-(2,4-dimethylphenyl)carbothioamidato]copper(II), II

Method B. A solution of 0.56 g (10.0 mmol) KOH in 5 ml of distilled water was added to a solution of 2.81 g (10.0 mmol) benzimidazole-2-*N*-(2,4-dimethylphenyl)carbothioamide in 150 ml of hot anhydrous isopropyl alcohol under constant stirring. Then 0.67 g (5.0 mmol) of

Thus, we found that the **III**, **IV** are formed in a neutral or weak-alkaline environment using precipitated copper(II) hydroxide according to the equilibrium reactions shown in schemes (2)-(7).

The composition and structure of the synthesized compounds **I-IV** were established by elemental, XRD analysis and IR-spectroscopy. In IR spectra of the compounds **I-IV** we observe weak stretching vibrations $\nu(\text{N-H})$ of benzimidazole fragment at 3075–3063 cm^{-1} and mixed vibrations of thioamide group ($-\text{C}(-\text{S}^-)=\text{N}-$): “B”-band 1575–1515 and 1490–1380 cm^{-1} ; “D”-band 1286–1215 and 926–922 cm^{-1} ; “E”-band 850–800 and 747–710 cm^{-1} . The absence of valence vibrations $\nu(\text{N-H})$ of thioamide group ($-\text{S}(=\text{S})\text{NH}-$) indicates the deprotonated form of ligands in the CuL_2^{I-IV} coordination compounds. The obtained results are also confirmed by XRD (compound **V**) and literature data [5, 6].

3.2. XRD Investigations of Complex Compound $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S}_2)] \times i\text{-C}_3\text{H}_7\text{OH}$, **V**

General view of the molecule, the most important bond lengths and valence angles of the compound **V** are shown in Fig. 1. The crystal structure of the compound **V** is a chelate complex of copper(II) of the composition $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S}_2)]$ and isopropyl alcohol with the ratio of 1:1. Copper atom is at the center of the complex symmetry and is coordinated by sulfur and nitrogen atoms of two deprotonated thioamide ligands. The coordination number of copper atom is 4, and the coordination polyhedron can be described as a distorted square with the angle of turn between thioamide ligands atoms equal to 23.8° (torsion angle $\text{N}(2)-\text{S}(1)-\text{N}(2\text{A})-\text{S}(1\text{A})$), which form coordination bonds with the copper atom.

The length of $\text{S}(1)-\text{C}(8)$ bond of thioamide anion is 1.712 Å, which, according to [10], corresponds to $\text{C}_{\text{sp}^2}-\text{S}$ chemical bond. The length of $\text{N}(3)-\text{C}(8)$ bond is 1.295 Å and corresponds to $\text{C}_{\text{sp}^2}-\text{N}$ bond (average value is 1.302 Å). Such distribution of electronic density in the thioamide fragment allows us to assert that the negative

charge of the thioamide anion is localized on the sulfur atom. The bicyclic fragment and thioamide group are in the same plane with the accuracy of 0.03 Å. Dimethylphenyl substituent is turned relative to the thioamide group at the angle of 34.4(5)° (torsion angle $\text{C}(8)-\text{N}(3)-\text{C}(9)-\text{C}(10)$). The possible reason is the repulsion between the atoms of thioamide group and aromatic ring (shortened intramolecular bonds $\text{H}(10)\dots\text{S}(1)$ 2.66 Å (a sum of Van der Waals radii [15] 3.01 Å), $\text{H}(10)\dots\text{C}(8)$ 2.81 Å (2.87 Å)).

In the molecule crystal the copper(II) chelate generates endless chains along the crystallographic direction [001], which are bound *via* bridge molecules of isopropanol due to intermolecular bonds $\text{N}(1)-\text{H}(1\text{N})\dots\text{O}(1\text{S})'(x, 1-y, 0.5+z)$ $\text{H}\dots\text{O}$ 1.98 Å, $\text{N}-\text{H}\dots\text{O}$ 158° and $\text{O}(1\text{S})-\text{H}(10\text{S})\dots\text{S}(1)'(x, 1-y, z)$ $\text{H}\dots\text{S}$ 2.60 Å, $\text{O}-\text{H}\dots\text{S}$ 142°.

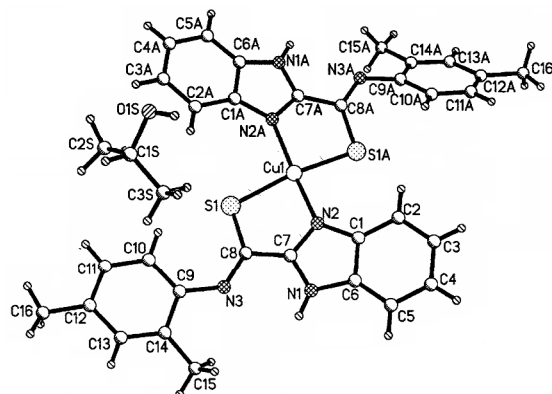
3.3. Investigations of Coordination Compounds CuL_2^{I-IV} as Additives to I-20A Industrial Oils

It should be noted that tribotechnical properties (I_g , f_{fr}) of lubricating compositions using modifying additives of the general formula CuL_2 are described in a limited number of works [1, 8]. V. Sytar *et al* [1] studied the antifriction properties of polyamide phenylone, graphite and modifying additive – copper(II) complex with heterocyclic thioamides CuL_2 . Antifriction properties were found to be improved by 12.5 %, wear resistance and hardness of the coating increase by 2.2 and 1.8 times, respectively. In the continuation of the above-mentioned works on the study of tribotechnical properties of lubricating compositions based on industrial oils, we synthesized complex compounds CuL_2^{I-IV} . Moreover, the complexes $\text{CuL}_2^{\text{VI,VII}}$ (Table, No. 5, 6) were synthesized earlier by the methods given in [1] and investigated under the same conditions as additives to lubricating compositions. The obtained results (I_g , f_{fr}) were used to analyze the dependence of tribotechnical characteristics on the structure for more expanded range of obtained additives ($\text{CuL}_2^{I-IV} + \text{CuL}_2^{\text{VI,VII}}$).

Fig. 1. Molecular structure of the compound **V**

The most important lengths of the bonds Å: $\text{Cu}(1)-\text{S}(1)$ 2.297(1), $\text{Cu}(1)-\text{N}(2)$ 1.978(2), $\text{Cu}(1)-\text{S}(1\text{A})$ 2.297(1), $\text{Cu}(1)-\text{N}(2\text{A})$ 1.978(2), $\text{S}(1)-\text{C}(8)$ 1.728(3), $\text{C}(7)-\text{C}(8)$ 1.459(4), $\text{C}(7)-\text{N}(2)$ 1.333(3), $\text{C}(7)-\text{N}(1)$ 1.347(3), $\text{C}(8)-\text{N}(3)$ 1.295(3), $\text{C}(12)-\text{C}(16)$ 1.497(5), $\text{C}(14)-\text{C}(15)$ 1.473(4), $\text{C}(18)-\text{C}(35)$ 1.442(5), $\text{C}(18)-\text{O}(18)$ 1.391(4).

Valence angles, degree: $\text{N}(2)-\text{Cu}(1)-\text{S}(1)$ 86.54(8), $\text{S}(1)-\text{Cu}(1)-\text{N}(2\text{A})$ 95.63(8), $\text{N}(2\text{A})-\text{Cu}(1)-\text{S}(1\text{A})$ 86.54(8), $\text{S}(1\text{A})-\text{Cu}(1)-\text{N}(2)$ 95.63(8), $\text{S}(1)-\text{Cu}(1)-\text{S}(1\text{A})$ 160.44(6), $\text{N}(2)-\text{Cu}(1)-\text{N}(2\text{A})$ 167.20(2), $\text{N}(3)-\text{C}(8)-\text{S}(1)$ 131.9(3), $\text{C}(8)-\text{N}(3)-\text{C}(9)$ 125.1(3), $\text{C}(10)-\text{C}(9)-\text{N}(3)$ 124.7(2)



**Investigation results of tribotechnical properties of coordination compounds $\text{CuL}_2^{\text{I-IV}}$
and $\text{CuL}_2^{\text{VI, VII}}$ added to I-20A industrial oil**

No. of lubricating composition	Components of the lubricating composition, %			$I_g \cdot 10^{-4}$, g	$f_{fr} \cdot 10^{-2}$
	CuL_2	DMF	I-20A		
1	$\text{CuL}_2^{\text{I}} / 0.05$	3.0	up to 100	1.53	3.83
2	$\text{CuL}_2^{\text{II}} / 0.05$	3.0	up to 100	1.79	4.85
3	$\text{CuL}_2^{\text{III}} / 0.05$	3.0	up to 100	1.87	4.60
4	$\text{CuL}_2^{\text{IV}} / 0.05$	3.0	up to 100	0.31	4.34
5	$\text{CuL}_2^{\text{VI}} / 0.05$	3.0	up to 100	1.70	4.42
6	$\text{CuL}_2^{\text{VII}} / 0.05$	3.0	up to 100	0.60	4.17
7	I-20A		100	8.00	5.20

Note. Investigation conditions: contact load – 8 MPa, $T = 298$ K, $\tau = 3$ h. Ligand symbols: HL^{VI} – *N*-phenylbenzimidazole-2-carbothioamide, HL^{VII} – *N-p*-bromophenylbenzimidazole-2-carbothioamide. DMF – *N,N*-dimethylformamide.

The results (*vide* Table) indicate that the functional properties of the complexes in the lubricating compositions vary significantly depending on the substituents in *N*-aryl fragment of the thioamide ligand. Thus, the antiwear properties of lubricating compositions (1)-(6) are improved by 4.3–25.8 times, and antifriction properties – by 1.1–1.4 times compared with those of pure I-20A oil (No. 7). It was determined that the introduction of halogens of various nature into the thioamide ligands (No. 1, 4, 6) significantly improves the performance characteristics of the investigated compounds. It should be noted that the effect of the trifluoromethyl group (No. 4) in the thioamide ligands on the functional properties of CuL_2^{IV} complex is likely to be related not to electron effects, but to their possible destruction and to the formation of fluoropolymer layers (Teflon type) on metal surfaces of friction pairs.

4. Conclusions

New chelates of copper(II) with benzimidazole-2-*N*-arylcarrbothioamides were synthesized; their composition and structure were established by elemental analysis and IR-spectroscopy. Based on the general theory of solvosystems, we propose a scheme of chemical reactions with the formation of chelates of the general formula $\text{CuL}_2^{\text{I-IV}}$.

The spatial structure of the complex compound $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S})_2] \cdot i\text{-C}_3\text{H}_7\text{OH}$ was confirmed using XRD. This compound is the chelate of copper(II) and isopropyl alcohol complex with the ratio of 1:1.

The antiwear and antifrictional properties of lubricating compositions based on I-20A industrial oil and copper(II) chelates of the general formula CuL_2 were investigated for the friction pair “bronze-steel”. The mentioned properties were found to be significantly improved in comparison with those of “pure” I-20A oil.

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**СИНТЕЗ, БУДОВА І ВЛАСТИВОСТІ
ХЕЛАТІВ КУПРУМУ(II) З
БЕНЗІМІДАЗОЛ-2-N-АРИЛКАРБОТІОАМІДАМИ**

Анотація. Комплексоутворенням ацетатів і хлоридів купруму(II), а також свіжоосадженого $\text{Cu}(\text{OH})_2$ з бензімідазоліл-2-N-арилкарботіоамідами ($\text{HL}^{\text{I-IV}}$) отримано координаційні сполуки загальної формули $\text{CuL}_2^{\text{I-IV}}$. Монокристал комплексу $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S})_2] \cdot \text{C}_3\text{H}_7\text{OH}$ отримано повільним випаровуванням насиченого розчину хелату CuL_2^{II} в ізопропіловому спирті. Отримані сполуки досліджено методами

елементного, рентгеноструктурного аналізу та ІЧ-спектроскопією. Досліджена кристалічна структура монокристалу є сольватом комплексу купруму(II) складу $[\text{Cu}(\text{C}_{16}\text{H}_{14}\text{N}_3\text{S})_2]$ та ізопропілового спирту в співвідношенні 1:1. Центральний атом купруму(II) координований двома атомами нітрогену та сульфуром депротонованого тіоамідного ліганду. Досліджено протизношувальні та антифрикційні властивості мастильних композицій на основі індустріальної оливи I-20A та синтезованих комплексів $\text{CuL}_2^{\text{I-IV}}$.

Ключові слова: гетероциклічні тіоаміди, хелатні комплекси купруму(II), рентгеноструктурний аналіз, трибохімія.