Transition metals in the process of complexation with organic ligands containing heteroatoms in the structure

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Abstract. The synthesis and research of copper subgroup metal complexes with organic ligands, which have several heteroatoms in their structure, is highly perceptive. Since the resulting complex compounds differ in physical and chemical properties from the original organic compounds they will have a set of new characteristics of practical significance. In this study, 2-mercaptanicotinic acid and 2-mercapto-4(3H)-quinazolinone were used. During the research, complex compounds of metals of the copper subgroup were obtained from aqueous and water-alcohol solutions. The resulting compounds represent colored powder-like materials. The coordination of the organic reagent to metal ions was established by instrumental methods of analysis. The effect of the introduced reagent (alkali, ammonia) on the coordination of the organic reagent was investigated.

1. Introduction
The separation, concentration, and quantitative determination of transition metals are carried out using organic reagents, during interaction with which the transition metals form strong complex compounds. Compounds containing functional-analytical groups with almost all known donor atoms - O, N, S, P - are most often used as organic reagents. These are amines, phenolic and alcohol oxides, mercaptans, thioacids, and other S-analogs of oxygen-containing compounds [1].

In addition, complex compounds of transition metals can be used in medicine. In practical medicine, preparations based on gold, silver, copper (protargol, collargol, silver sulfadiazine, gold thiosulfate, auronofin, etc.) are used. Silver preparations have an antibacterial, astringent and cauterizing effect, due to their ability to disrupt the enzyme systems of microorganisms and to precipitate proteins. Gold compounds are used in the treatment of malignant tumors, pulmonary tuberculosis, skin and autoimmune diseases [2–4]. Medicines containing gold nanoparticles are widely used in the treatment of chronic arthritis [5]. Copper compounds in medicine are used as an antimicrobial and cauterizing agent. Effective drugs with copper-containing compounds (cupralene, dicupren or cuprimil, copper morruate, permalon) were used in the treatment of acute and chronic arthritis, chronic polyarticular gout, ankylosis and multiple spondylitis, rheumatoid fever, erythema.

According to the Pearson's hard and soft acids and bases principle, metal ions of the copper subgroup with the electronic configuration d⁹ (oxidation state +2) can be attributed to soft acids. Therefore, they
form the most stable compounds with soft bases. Ligands of this type include compounds containing O, N, and S atoms that act as electron donors. The softest bases are sulfur-containing ligands, due to the diffusivity of the donor electron pair of the sulfur atom and the energy proximity of their 3d orbitals to the metal ion orbitals. Among the metals of the copper subgroup, this type of configuration is typical for copper. Gold (II) and silver (II) compounds are fragile, so the production and isolation of such compounds is accompanied by number difficulties. Most compounds can be obtained only as intermediate complexes [6].

Gold (I) with the d10 configuration, being a "soft" metal center, has a strongly pronounced tendency to form stable complexes with easily polarizable soft donor atoms, such as sulfur and phosphorus [3]. According to the Pearson's hard and soft acids and bases principle, silver (I) being a stronger acid than Au (I), can be coordinated by the N-heterocyclic coordination center of the ligands. In contrast to gold (I), which exhibits a strongly pronounced affinity for coordination at the phosphoric coordination center, silver (I) complexes more often exhibit P, N-coordination at both heteroatoms, although P-monodentate silver (I) complexes are also found. For the silver ion in the oxidation state +1, the most typical coordination numbers are 2 and 3, the geometry of silver in the coordination compounds can be linear or triangular.

Copper(I) is a stronger acid compared to Au(I) and Ag (I) and even more shows a tendency to coordinate at the N-coordination center. The coordination geometry of copper (I) in complex compounds is tetrahedral or, more rarely, planar-square, with a coordination number of 4. However, a possibly lower coordination number is 3, less common there is a linear geometry of the copper atom (I), with a coordination number of 2. The coordination number of copper (I) can be 6, due to the ability of copper (I) to form cluster nuclei with halogen anions with the formation of copper-halogen bridging bonds. Polymer and oligomeric metal clusters form a wide class of Cu(I) complexes in which metallophilic interactions between copper atoms are realized. The expansion of the coordination abilities of copper (I) and, as a result, the large variety of structures formed, is reflected in their photophysical properties – the complexes exhibit luminescent properties in a wide spectral range [7].

Such ambiguous behavior of the copper subgroup metals during complexation makes it necessary to carry out studies to determine the specific interaction of the transition metal with organic ligands, among which there are heteroatoms, and to identify the structure and properties of the resulting complex compounds. To study the behavior of copper subgroup metals in complexation reactions with organic molecules, 2-mercaptocnicotinic acid and 2-mercapto-4(3H)-quinazolinone were chosen as ligands, because the molecules in their composition contain donor atoms N, S, O, therefore there is a possibility to form complexes of different structures, and, consequently, the manifestation of different properties.

The aim of the work was to obtain complex compounds of the copper subgroup metals with organic ligands containing heteroatoms, and to establish the coordination of the ligand to the metal atom.

2. Experimental part
For the synthesis of complex compounds copper (II) chloride crystallohydrate, "hg"; 2-mercaptocnicotinic acid "ACROS ORGANICS" (CAS: 38521-46-9); silver fluoride obtained from silver carbonate by dissolving in hydrofluoric acid, and copper (I) chloride recently obtained by the method [8] were used as initial compounds. According to [8], a stoichiometric amount of sodium sulfite was added to an aqueous solution of copper (II) sulfate; as a result, a white precipitate of copper (I) chloride was settled. 2-mercapto-4(3H)-quinazolinone ALDRICH (CAS: 13906-09-7); copper (II) chloride crystallohydrate, "hg"; silver nitrate obtained by dissolving silver in nitric acid, and an aqueous solution of the gold complex (H[AuCl4]) obtained by dissolving gold in a mixture of nitric and hydrochloric acids (in aqua regia, in a ratio of 1:3) were also used. The water-alcohol solution was obtained by mixing distilled water and ethyl alcohol 1:2, ethyl alcohol.

Preparation of copper (I) with 2-mercaptocnicotinic acid. A sample weighing 1 g of 2-mercaptocnicotinic acid and distilled water (17 ml) were placed in a beaker with a volume of 250 ml, then sodium hydroxide (0.25 g) was added during with stirring, after 10 minutes, recently precipitated copper (I) chloride (0.64 g) was added. The mixture was kept at room temperature, the formation of a
brown-orange ("reddish") precipitate was observed. The mixture was continued to be stirred for 30 minutes, observing the process of thickening, the precipitate became gel-like. Distilled water (17 ml) was added and had been settled for a day. The next day, the mixture was filtered on a glass filter, the precipitate was rinsed with distilled water, then with alcohol, and dried in a desiccator. In the air, the sediment turned dark brown, almost black. When water was added, the mixture acquired an orange ("red") color.

Preparation of a complex of gold (I) with 2-mercapto-4(3H)-quinazolinone. Sodium chloride (1.15 g) was placed in a beaker, 10 ml of distilled water was added, an aqueous solution of the H[AuCl4] gold complex (1 g) was added to the resulting solution, and mixed. Then, sodium sulfite (0.12 g) was added to the reaction mixture. Everything was thoroughly mixed until the solution became discolored [9]. A water-alcohol solution of 2-mercapto-4(3H)-quinazolinone (0.5 g of ligand in 30 ml of water-alcohol solution) was immediately poured in. An aqueous solution of ammonia (up to pH = 9) or an aqueous solution of sodium hydroxide (0.13 g in 5 ml of distilled water) was added to the reaction mixture during the stirring. Everything was thoroughly mixed for 60 minutes. The resulting precipitate was filtered out on a glass filter, rinsed with an aqueous alcohol solution, and dried at a temperature of 50 °C. The substance obtained was yellow color.

Preparation of a gold (II) complex with 2-mercapto-4 (3H)-quinazolinone. To an aqueous solution of the gold complex H[AuCl4] (0.1 g) was added 5 ml of ethanol. An aqueous-alcoholic solution of 2-mercapto-4 (3H) -quinazolinone was prepared by dissolving 0.4 g of organic compounds in an aqueous alcohol solution (30 ml), and an aqueous ammonia solution was added with stirring (to pH = 3). The prepared organic ligand mixture was added to the gold complex solution. Everything was thoroughly mixed, the heating was turned on at 50 °C, and the reaction mixture was kept for 60 minutes. The resulting precipitate was filtered out on a glass filter, rinsed with ethanol, and dried at a temperature of 40 °C. The substance obtained was yellow color.

Preparation of a silver (I) complex with 2-mercapto-4 (3H)-quinazolinone. An aqueous solution of silver nitrate (7 ml) was poured into a beaker, and 10 ml of distilled water was added. A silver solution was prepared by dissolving silver in dilute nitric acid (2 g in 30 ml). A mixture of an aqueous-alcoholic solution of the ligand (0.5 g in 50 ml of an aqueous-alcoholic mixture) and an aqueous solution of ammonia (8 ml) was added to the AgNO3 solution with stirring. The reaction mixture was kept for 10 minutes and heated at 50°C, and then kept for 30 minutes. Heating and mixing were turned off. The resulting precipitate was filtered on a glass filter, rinsed with an aqueous alcohol solution, and dried at a temperature of 50°C. The substance obtained was light brown color.

Preparation of a copper (II) complex with 2-mercapto-4 (3H)-quinazolinone. Copper (II) chloride (0.8 g CuCl2 · 2H2O) was placed in a beaker, which was dissolved in 10 ml of distilled water. A sample (0.5 g) of 2-mercapto-4 (3H)-quinazolinone was dissolved in an aqueous alcohol solution (30 ml) and an aqueous ammonia solution was added (up to pH=9), everything was thoroughly mixed. The solution of the organic compound was added to an aqueous solution of copper chloride, mixed, including heating to 50°C, and the formation of a precipitate was observed. After 30 minutes, the heating and mixing were turned off. The resulting precipitate was filtered on a glass filter, rinsed with a water-alcohol mixture, and dried at a temperature of 50°C. The substance was obtained in a dark green (malachite) color.

The structure of the obtained coordination compounds was confirmed by IR spectroscopy. The IR absorption spectra of the obtained compounds were recorded in the region of 400-4000 cm⁻¹ with a resolution of 4 cm⁻¹ on the Nicolet 6700 IR Fourier spectrometer, using samples in the form of tablets with KBr. The UV spectra of the synthesized compounds were recorded in the region of 190-600 cm⁻¹ on the UV spectrometer UV-1800, manufactured by Shimadzu (Japan), using solutions of the analyzed substances obtained by dissolution in dimethylsulfoxide (DMSO).

The presence of metal in the synthesized complex compounds was confirmed by X-ray fluorescence analysis (XRF). The analysis was performed using an ARL QUANT´X X-ray energy-dispersion spectrometer from Thermo Scientific, USA. The shooting time was 60 seconds.
3. Results and discussion
In the IR spectrum of the ligand (2-mercaptocinonicic acid), characteristic absorption bands of the S-H group at 2546 cm\(^{-1}\), N-H at 2156-1945 cm\(^{-1}\), and C=N groups at 1563-1496 cm\(^{-1}\) were found. The valence vibrations of the COO-group were detected in the region of 1680-1621 cm\(^{-1}\).

Comparing the IR spectra of the ligand and its complexes with the Cu(I) showed changes in the position of symmetric valence vibrations absorption bands for the COO- group, which shift towards higher frequencies by 29 cm\(^{-1}\) during the transition from the ligand to the complexes, that indicates the presence of COO-Na bond. In addition, the disappearance of the band at 2546 cm\(^{-1}\), that is present in the spectrum of the ligand, which indicates the participation of the SH-group in the formation of the complex is observed. The appearance of absorption bands at 602-522 cm\(^{-1}\) and 496-475 cm\(^{-1}\) in the IR spectra of complexes absent in the ligand spectrum probably refers to the valence vibrations of the O-Na and S-Cu bonds, indicating the coordination of the organic ligand to the transition metal ion by the sulfur atom of the benzene cycle. Thus, according to the results of the IR spectroscopic study for the synthesized complexes, it can be concluded that the ligand containing heteroatoms in its structure is coordinated by the sulfur atom to the metal atoms.

The UV spectrum of the 2-mercaptocinonicic acid dissolved in DMSO shows the absorption bands with the following values: \(\lambda_{\text{max}}\): 250, 312 nm. The UV spectra of copper complexes with 2-mercaptocinonicic acid dissolved in DMSO have the following values: Cu (I) complexes: \(\lambda_{\text{max}}\): 241, 285 nm. Analyzing the UV spectra of the obtained complex compounds, a hypsochromic shift was observed for copper complexes, in addition, a decrease in the transmission values for copper complexes was noted, which apparently can be associated with the luminescence ability of the analyzed complex compound.

In the IR spectrum of 2-mercapto-4 (3H)-quinazolinone, there is one band v(NH) about 3100 cm\(^{-1}\), and a second band v(NH) in the region of 3400 cm\(^{-1}\). Therefore, in this case, for 2-thioxoquinazolone-4, the enol tautomeric form (B) is assumed. In the IR spectrum of about 2600 cm\(^{-1}\), an average intensity band corresponding to v(SH) is observed. Four thioamide bands of the HN-C=S grouping were found at 1549 (I), 1300 (II), 972 (III), and 760 cm\(^{-1}\) (IV).

In the IR spectrum of the gold (I) complex obtained with the use of alkali, the coordination of the 2-mercapto-4(3H)-quinazolinone anion through sulfur and the nitrogen atom of the thioamide group is assumed. The band v(NH) of 3086 cm\(^{-1}\) is shifted to 15 cm\(^{-1}\) to the low-frequency region, while the band v(SH) at 2670 cm\(^{-1}\) disappears. The band v(C=O) at 1710 cm\(^{-1}\) is shifted to 19 cm\(^{-1}\) to the low-frequency region, which is probably due to the addition of the sodium atom to the oxygen atom of the C=O group. The band v(C=N) in the region of 1630 cm\(^{-1}\) remains, i.e. the interaction of the gold atom with amide nitrogen does not occur. Thioamide bands appear in the region of 159 (I), 1307, 977, and 789 cm\(^{-1}\), but the first band is shifted to 35 cm\(^{-1}\) to the low-frequency region, which is probably due to the formation of the Au-N bond. The absorption bands v(Au-S), v(Au-N) appears at 593 cm\(^{-1}\) and 646 cm\(^{-1}\), respectively.

In the IR spectrum of the gold (I) complex obtained using an ammonium hydroxide, the coordination of the 2-mercapto-4(3H)-quinazolinone anion through the nitrogen atom of the thioamide group is assumed. The band v(NH) 3086 cm\(^{-1}\) is shifted to 6 cm\(^{-1}\) to the low-frequency region. The band v(SH) at 2670 cm\(^{-1}\) and the band v(C=O) at 1706 cm\(^{-1}\) does not change its position. The band v(C=N) in the region of 1630 cm\(^{-1}\) remains, i.e. the interaction of the gold atom with amide nitrogen does not occur. Thioamide bands appear in the region of 1307, 977 and 789 cm\(^{-1}\), the band disappears at 1549 cm\(^{-1}\). The absorption band v (Au-N) appears at 646 cm\(^{-1}\).

In the IR spectrum of the gold (II) complex obtained using an ammonium hydroxide, it is assumed that the anion of 2-mercapto-4(3H)-quinazolinone is coordinated through sulfur and a nitrogen atom of the thioamide group. In the region of valence vibrations, a band at 3511 cm\(^{-1}\) is observed, apparently, this band corresponds to the v (OH) of the coordinated water molecule. The band v(NH) 3086 cm\(^{-1}\) is shifted to 15 cm\(^{-1}\) to the low-frequency region. The band v(SH) at 2670 cm\(^{-1}\) is shifted to 14 cm\(^{-1}\) to the high-frequency region. The band v(C=O) at 1706 cm\(^{-1}\) is shifted to 19 cm\(^{-1}\) to the low-frequency region, which is probably due to the addition of the NH\(^4\) ion to the oxygen atom of the C=O group. The band
\(\nu(C=\text{N})\) at 1630 cm\(^{-1}\) remain, i.e. the interaction of the gold atom with amide nitrogen does not occur. The thioamide band disappears at 1549 cm\(^{-1}\), which is probably due to the formation of the Au-N bond. The remaining thioamide bands in the region of 1307, 979, and 789 cm\(^{-1}\) remain unchanged. The absorption bands \(\nu(\text{Au-S}), \nu(\text{Au-N})\) appears at 593 and 646 cm\(^{-1}\), respectively.

**Figure 1.** a – IR spectrum of 2-mercapto-4 (3H)-quinazolinone; b – IR spectrum of the gold (I) complex with 2-mercapto-4 (3H)-quinazolinone obtained with the use of alkali.

**Figure 2.** c – IR spectra of of the silver (I) complex with 2-mercapto-4 (3H)-quinazolinone; d – IR spectra of the copper (I) complex with 2-mercapto-4 (3H)-quinazolinone.

Comparison of the IR spectra of 2-mercapto-4 (3H)-quinazolinone and its complexes with Ag(I) and Cu(II) shows that the position of the absorption bands of the group \(\nu(\text{NH})\) 3086 cm\(^{-1}\) is shifted to 9 cm\(^{-1}\) to the low-frequency region, and the band \(\nu(\text{SH})\) disappears at 2670 cm\(^{-1}\). The band \(\nu(C=O)\) at 1706 cm\(^{-1}\) remains unchanged. The thioamide bands in the region of 1549, 1307, 977, and 789 cm\(^{-1}\) remain unchanged for the Ag(I) complex, and for the Cu(II) complex the band disappears at 1549 cm\(^{-1}\), which indicates the formation of the Cu-N bond. The absorption band \(\nu(\text{Ag-S})\) appears at 668 cm\(^{-1}\). The absorption bands \(\nu(\text{Cu-N})\) and \(\nu(\text{Cu-S})\) appear at 457(445) and 690 cm\(^{-1}\), respectively.
Thus, the formation of the complex with silver(I) ions occurs due to the coordination of the organic ligand of the sulfur atom, and for the copper(II) complex – the sulfur and nitrogen atom of the thioamide group. The obtained data of X-ray fluorescence analysis confirm the presence of metals in the synthesized complexes with ligands 2-mercaptocomic acid and 2-mercapto-4 (3H)-quinazolinone.

4. Conclusion
During the research of the copper subgroup metals behavior in the complexation reaction with organic compounds in the structure of which there is more than one heteroatom, the following results were obtained. 2-Mercaptocomic acid is coordinated by the sulfur atom to the metal atoms Cu (I) by the sulfur. 2-Mercapto-4(3H)-quinazolinone in the gold (I) complex obtained with the use of alkali is presumably coordinated through sulfur and the nitrogen atom of the thioamide group, and in the same complex obtained with the use of an ammonium hydroxide – only through the nitrogen atom of the thioamide group. In the gold (II) complex obtained using an ammonium hydroxide, it is assumed that the anion of 2-mercapto-4(3H)-quinazolinone is coordinated through sulfur and a nitrogen atom of the thioamide group. In the Ag(I) and Cu(II) complexes with 2-mercapto-4(3H)-quinazolinone, it was shown that the coordination of the organic ligand with silver (I) ions occurs by the sulfur atom, and for the copper (II) complex – by the sulfur and nitrogen atoms of the thioamide group. In the study of the obtained complex compounds for the presence of the metals used by the X-ray fluorescence method of analysis, the presence of these metals in the composition of the complexes was confirmed.

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