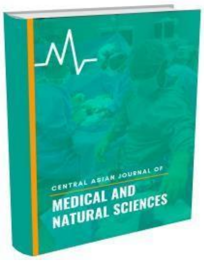

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Article

Synthesis and Study of Coordination Compounds of Copper (Ii) with N-Acetylthiourea

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Abstract: In this work, new coordination compounds of copper (II) with N-acetylthiourea (NAT) in various media (ethanol, HCl) were synthesized. The complexes of the following compositions were obtained: $[CuNAT(H_2O)_2]Cl_2$, $[Cu(NAT)_2SO_4]\cdot 2H_2O$, $[Cu(NAT)_2Br_2]\cdot H_2O$, $[CuNAT(NO_3)_2]\cdot 2H_2O$, $[CuNAT(ClO_4)_2]\cdot 3H_2O$. Their physical and chemical properties were studied using elemental analysis, IR spectroscopy, potentiometry and conductometry. It was found that N-acetylthiourea is coordinated to the central copper atom as a monodentate (via sulfur) or bidentate (via sulfur and oxygen) ligand, which is accompanied by the formation of chelate structures. IR spectroscopy data confirmed the shift of absorption bands characteristic of C=S and C=O, as well as the presence of coordinated and crystallization water. The obtained compounds demonstrate promising properties, allowing them to be considered as candidates for use in catalysis and biological systems.

Keywords: coordination compounds, copper (II), N-acetylthiourea, IR spectroscopy, chelate structures, catalysis

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1. Introduction

Copper(II) coordination compounds attract special attention in modern chemistry due to their diverse properties and wide application possibilities. Copper as a central atom in the complexes exhibits catalytic, biological and luminescent properties, which makes such compounds promising for use in medicine, biotechnology, environmental and industrial-chemical processes.

It is known from the literature that d-transition metals and some of their coordination compounds exhibit biological, catalytic and luminescent properties and have found wide practical application in various fields of industry and the national economy [1,2]. It is also known that a number of coordination compounds of zinc, copper, molybdenum, etc. are high-temperature effective catalysts and are used in organic synthesis and the oil refining industry.

In [3-10], an analysis of modern studies of thiourea and its derivatives, which represent a promising class of compounds in coordination chemistry, is carried out. Their properties, ability to complex with transition metals (Cu, Zn, Au, Re), as well as the structure and biological activity of the obtained compounds are considered. Studies show that thiourea coordinates to metals through sulfur and oxygen atoms, forming stable chelate complexes, which is confirmed by spectral methods (IR spectroscopy, X-ray diffraction analysis). Thiourea derivatives demonstrate antibacterial, antifungal and antitumor properties, especially pronounced in complexes with Au (I), Cu (II) and Zn (II) ions. These compounds are highly stable and promising for use in medicine, biotechnology, and as catalysts in organic synthesis. In addition, the possibilities of using thioureas in functional materials, such as calixarene complexes and carboxymethyl chitosan derivatives, are discussed. The use of molecular modeling and docking expands the prospects for the synthesis of new compounds with desired properties. Of particular interest are compounds involving N-acetylthiourea, which, due to its functional groups, is capable of forming stable complexes with metals. These complexes can be used as catalysts in organic synthesis, including in reduction and oxidation reactions. In addition, some copper compounds demonstrate antibacterial and antiviral activity, which is important for the development of new drugs.

Studying the structure and properties of such compounds allows not only to deepen knowledge about the chemistry of transition metals, but also to create a scientific basis for the practical application of synthesized materials in various fields, including pharmaceuticals, materials with unique optical properties and environmentally friendly technologies.

Thus, the synthesis and study of coordination compounds of copper (II) with N-acetylthiourea is an urgent task aimed at solving fundamental and applied issues of modern chemistry. In this regard, targeted synthesis and physicochemical study of thiocyanate coordination compounds of copper (II) with N-acetylthiourea and comparative analysis of the properties of the coordination compounds isolated in solid form were of interest [11].

2. Materials and Methods

For the synthesis of copper (II) coordination compounds, CuSO4·5H2O grade (chemically pure), CuCl2·2H2O grade (analytical grade), and CuBr2 grade (analytical grade) were used, which were recrystallized from the corresponding acidified aqueous solutions. N-acetylthiourea (NAT) was recrystallized twice by dissolving it in water and salting out the saturated solution with ethanol. The synthesis of copper (II) coordination compounds with N-acetylthiourea was carried out in a water-ethanol and acidic medium at a molar ratio of the initial reagents Cu:(NAT) from 1:1 to 1:6 at room temperature and with heating. The content of elements was determined according to the methods [12,13].

Synthesis of $[CuNAT(H_2O)_2]Cl_2$. To 10 ml of a solution of 1.26 g (0.0073 mol) $CuCl_2·2H_2O$ in 6 mol/l HCl was added in small portions with vigorous stirring 0.87 g (0.0074 mol) N-acetylthiourea dissolved in 6 mol/l HCl. The molar ratio Cu:NAT is 1:1. The resulting precipitate was stirred together with the solution for 1 h and settled at room temperature for complete crystallization. After 3 h, the precipitate was separated from the solution by filtration, washed with 6 mol/l HCl, ethanol (20 ml), ether (10 ml) and dried to constant weight in a vacuum desiccator over KOH. The yield is 77% of the theoretically calculated value. The synthesized light yellow substance is a finely crystalline powder, soluble in inorganic acids, partially in DMF and DMSO, insoluble in water, benzene, carbon tetrachloride and chloroform.

Found, %; Cu-22.02; C-12.23; H -2.00; N-9.22; S-10.76; Cl -24.04; H2O-12.16.

For $[CuNAT(H_2O)_2]Cl_2$ – $CuC_3H_{10}O_3N_2SCl_2$

calculated, %: Cu-22.15; C-12.46; H-2.07; N-9.69; S-11.07; Cl-24.57; H2O-12.46.

Taking into account the elemental analysis data, the formation of a new compound can be represented as the following reaction:

$CuCl_2·2H_2O + NAT = [CuNAT(H_2O)_2]Cl_2$

Synthesis of [Cu(NAT)2SO4]·2H2O. 2.96 g (0.0251 mol) of N-acetylthiourea were dissolved in 15 ml of 2 mol/l H2SO4. 3.12 g (0.0124 mol) of finely ground CuSO4·5H2O were added in small portions to the resulting ligand solution. (Molar ratio Cu:NAT=1:2). The resulting mixture was stirred for 2 h and left to stand at room temperature until a bright yellow precipitate formed. The precipitate was filtered off, washed with 10 ml of 2 mol/l H2SO4, water (40 ml), ethanol (30 ml), ether (25 ml) and dried to constant weight over solid KOH. Yield - 79.1% of theoretically calculated.

Found, %; Cu-14.18; C-15.95; H -3.09; N -12.11; S-21.96; H2O-8.04.

For $[Cu(NAT)_2SO_4]\cdot 2H_2O$ – $CuC_6H_{16}O_8N_4S_3$

calculated, %: Cu-14.81; C-16.67; H -3.70; N -12.96; S-22.22; H2O-8.33.

The obtained substance partially dissolves in dimethylformamide, dimethyl sulfoxide, insoluble in water, acetone, ethanol, toluene, benzene. The compound is formed according to the reaction scheme described below:

$CuSO_4\cdot 5H_2O + 2NAT = [Cu(NAT)_2SO_4]\cdot 2H_2O + 3H_2O$

Synthesis of [Cu(NAT)2Br2]·H2O. 1.24 g (0.0043 mol) of copper (II) bromide trihydrate (CuBr2·3H2O) were dissolved in 25 ml of water-ethanol mixture. 0.53 g (0.0045 mol) of N-acetylthiourea were added to the resulting solution with vigorous stirring. The molar ratio of Cu:NAT is 1:1. After stirring the reaction system for 2 hours, a yellow-orange precipitate was formed, which was left to stand at room temperature for 24 hours. The resulting orange precipitate was filtered, washed with water (25 ml), ethanol (15 ml), ether (10 ml) and dried to constant weight in a vacuum desiccator over KOH. Yield - 72-73% of theoretically calculated.

Found, %; Cu-16.10; C-8.97; H -2.42; N-7.07; S-7.93; Br-42.10; H2O-9.05.

For $[CuNAT(H_2O)_2]Br_2$ – $CuC_3H_{10}O_3N_2SBr_2$

calculated, %: Cu-16.93; C-9.52; H-2.65; N-7.41; S-8.45; Br-42.33; H2O-9.52.

The synthesized substance dissolves in solutions of mineral acids, slightly in DMF, DMSO and is practically insoluble in water and non-polar organic solvents.

Elemental analysis data allow us to describe the formation of a new compound in the form of the reaction described below:

$CuBr_2\cdot 3H_2O + NAT = [CuNAT(H_2O)_2]Br_2 + H_2O$

Synthesis of [CuNAT(NO3)2]·2H2O. 1.26 g (0.0107 mol) of N-acetylthiourea were dissolved in 25 ml of ethanol. 2.56 g (0.0105 mol) of crushed Cu(NO3)2·3H2O were added in small portions to the resulting solution of the organic ligand. The molar ratio of Cu:NAT was 1:1. The resulting mixture was intensively stirred on a magnetic stirrer while heating (~70 °C) until a dark gray precipitate formed. The prcipitate and solution were left to settle for 20 h and filtered, washed with water (30 ml), ethanol (20 ml), ether (20 ml), and dried at room temperature to constant weight. Yield - 78-79% of theoretically calculated

Found, %; Cu-17.94; C-9.96; H -2.10; N -15.96; S-9.18; H2O-11.08.

For $[CuNAT(NO_3)_2]\cdot 2H_2O$ – $CuC_3H_{10}O_9N_4S$

calculated, %: Cu -18.71; C -10.52; H -1.75; N -16.37; S-9.36; H2O-10.53.

The dark gray precipitate is insoluble in polar inorganic and organic solvents such as DMF, DMSO, and insoluble in water and known organic solvents. It was found that the coordination compound is formed according to the reaction:

$Cu(NO_3)_2\cdot 3H_2O + NAT = [CuNAT(NO_3)_2]\cdot 2H_2O + \cdot H_2O$

Synthesis of [CuNAT(ClO4)2]·3H2O. 2.82 g (0.049 mol) of Cu(ClO4)2·6H2O, dissolved in 20 ml of ethanol, were added with vigorous stirring to 25 ml of ethanol containing 0.76 g (0.0064 mol) of N-acetylthiourea. The molar ratio Cu:NAT = 1:1. The reaction mixture was heated (~70°C) until a dark gray precipitate formed. After settling, the formed precipitate was filtered, washed with water (30 ml), ethanol (15 ml), ether (15 ml) and dried to constant weight. Yield: 78-80.3% of theoretically calculated.

Found, %; Cu-14.17; C-8.72; H -1.43; N -5.94; S -8.05; Cl -16.62; H2O-11.41.

For $[CuNAT(ClO_4)_2]\cdot 3H_2O$ – $CuC_3H_{12}O_{12}N_2SCl_2$

calculated, %: Cu-14.71; C-8.27; H -1.38; N -6.44; S -7.35; Cl -16.32; H2O-12.41.

The obtained dark gray complex dissolves in HCl, HNO3, H2SO4, H3PO4, dimethylformamide, does not dissolve in water, alkali solutions and organic solvents. The compound is formed by the reaction:

$Cu(ClO4)2\cdot 6H_2O + NAT = [CuNAT(ClO_4)_2]\cdot 3H_2O + 3H_2O$

The composition and structure of all synthesized compounds were established based on chemical analysis data and physicochemical research methods. The table shows the analytical data of the synthesized copper (II) coordination compounds with N-acetylthiourea.

3. Results and Discussion

Coordination compounds of copper (II) with N-acetylthiourea (NAT) were isolated at a molar ratio of Cu:NAT from 1:1 to 1:6. The use of an excess amount of ligand during the syntheses, than the ratio Cu:NAT = 1:1 and Cu:NAT = 1:2, led to the precipitation of a mixture of the forming complex and the unreacted N-acetylthiourea remaining in excess. It was shown that all the synthesized compounds contain both coordinated and crystallization water, the presence of which was confirmed by chemical analysis and IR spectroscopy data. The IR spectra of some coordination compounds of copper (II) with N-acetylthiourea are shown in Fig. The interpretation of the IR spectra of the initial organic ligand and the synthesized compounds was carried out according to [14, 15].

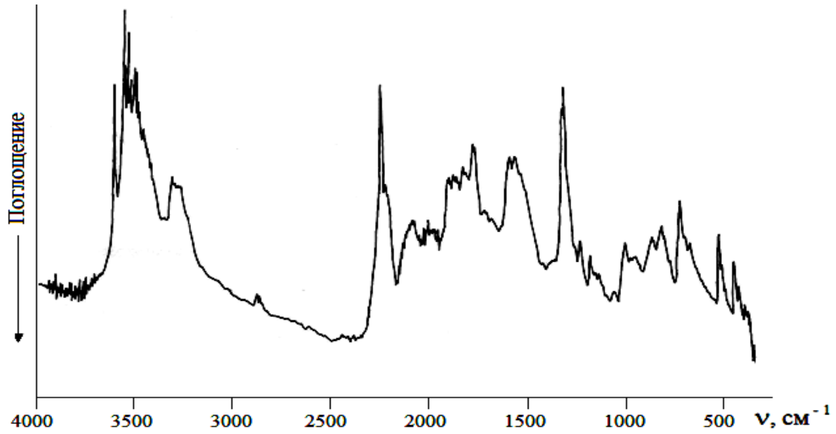
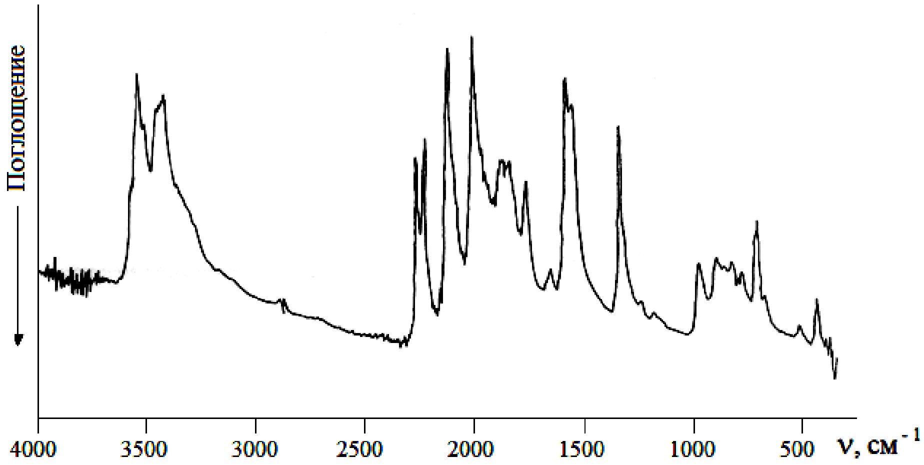


Fig. 1. IR spectra of N-acetylthiourea

It was revealed that the spectrum of uncoordinated N-acetylthiourea contains intense and medium absorption bands (ν, cm-1) in the region of 485-595 (w), 821-917 (w), 1043-1184 (m), 1242-2283 (m), 1401-1432, 1611-1624, 2406-2604 and 3231-3482. The appearance of absorption bands at 677 and 821 cm-1 in the spectra of N-acetylthiourea (Fig. 1) and a medium-intensity band at 770 cm-1 indicate that in the solid state the specified ligand can exist in the form of two tautomeric formione and thiol.



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The analysis of IR spectra of N-acetylthiourea and the above coordination compounds shows that in the region of 400-4000 cm-1 in their spectra there are many absorption bands responsible for various vibrations of bonds (C=S), (NH), (NH2), chlorine, bromine, nitrate, sulfate, thiocyanate and also water molecules. For example, in the spectra of coordination compounds $[Cu(NAT)_2(H_2O)_2]Cl_2$ and $[Cu(NAT)_2Br_2]\cdot 2H_2O$ there are weak absorption bands in the region of 1100-1140 cm-1 and at 625-825 cm-1, which are shifted to the low-frequency region. According to [4], the bands at 1110, 735 and 623 cm-1 are related to the ◎(C=S) bond of the coordinated N-acetylthiourea molecules via the sulfur atom of the thiol group.

Comparison of the IR spectra of the coordination compounds with the spectrum of the free ligand shows that the spectra of all the coordination compounds exhibit bands of deformation vibrations of the (C=S) bond. At 572-580 cm-1 It was found that in the spectrum of the coordination compound of the composition $[Cu(NAT)_2Br_2]\cdot 2H_2O$, the ◎(C=S) absorption band with low intensity appears at 535 cm-1, and in the spectrum of $[Cu(NAT)_2(H_2O)_2]Br_2$ at 527 cm-1, respectively.

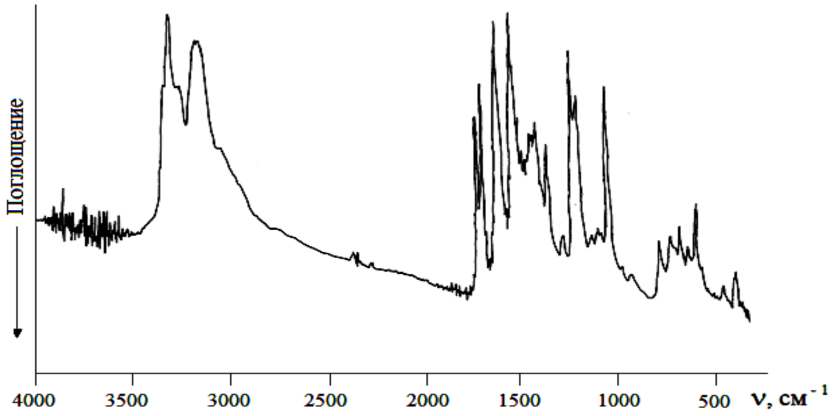

Fig. 3. $[Cu(NAT)_2Br2]\cdot 2H_2O$

According to literature data, the absorption bands in the region of 812–1033 cm-1, 1167–1184 cm-1, 1421–1452 cm-1, 1613–1634 cm-1 and 3232–3258 cm-1 are responsible for the stretching-deformation vibrations υ(C=S), υ(CH3), υ(NH) υ(NH2) and υ(C–N) bonds of the ligand molecule [16]. Comparison of the IR spectra of coordination compounds of the following compositions: $[Cu(NAT)_2Cl_2]\cdot 2H_2O$, $[Cu(NAT)2Br_2]\cdot 2H_2O$, $[Cu(NAT)_2(SCN)_2]\cdot H_2O$, $[CuNAT(H_2O)_2]SO_4$, $[CuNAT(SO_4)]\cdot 2H_2O$ with the spectra of N-acetylthiourea shows that in the spectra of the complexes, some of these bands are retained with minor changes.

Thus, based on the IR spectroscopic studies of the shift of the absorption bands of the stretching (νS) and deformation (νδ) vibrations of the functional groups C=S, C=O and -C-NH-NH2 of the hydrazine fragment of the N-acetylthiourea molecule, it was established that the organic ligand in disubstituted copper (II) coordination compounds obtained in an acidic medium is mainly coordinated monodentately, via a sulfur atom, and in monosubstituted compounds isolated both in neutral and acidic media, it is coordinated bidentately, via donor sulfur atoms of the thiol and oxygen of the carbonyl group. Such coordination of the N-acetylthiourea molecule to the central ion is accompanied by the formation of five-membered chelate metallocycles. It has been established that monosubstituted complexes are poorly soluble polycrystalline compounds, compared to disubstituted ones, and have a higher melting point than the latter, which is indirect evidence of the formation of chelate coordination compounds and confirmation of elemental analysis and IR spectroscopic data.

4. Conclusion

As a result of the work, new coordination compounds of copper (II) with N-acetylthiourea were synthesized: $[CuNAT(H_2O)_2]Cl_2$, $[Cu(NAT)_2SO_4]\cdot 2H_2O$, $[Cu(NAT)_2Br_2]\cdot H_2O$, $[CuNAT(NO_3)_2]\cdot 2H_2O$, $[CuNAT(ClO_4)_2]\cdot 3H_2O$. The yield of the products was 72–80% of the theoretical one, which confirms the high efficiency of the synthesis.

It was established that N-acetylthiourea is coordinated to copper (II) as a monodentate ligand through the sulfur atom of the thio group or as a bidentate ligand through the sulfur and oxygen atoms of the carbonyl group.

Analysis of IR spectroscopy data showed a shift in the absorption bands of C=S, NH and C=O, indicating the formation of chelate structures in disubstituted compounds. The presence of coordinated and crystallization water is confirmed by bands in the region of 3200-3600 cm-1.

Disubstituted complexes ($[Cu(NAT)_2SO_4]\cdot 2H_2O$ and $[Cu(NAT)_2Br_2]\cdot H_2O$) have a higher melting point and low solubility, which confirms their stability compared to monosubstituted complexes ($[CuNAT(H_2O)_2]Cl_2$).

The results obtained complement the existing knowledge of the chemistry of copper (II) coordination compounds and open up new areas for their use in the chemical and biotechnological industries.

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