IN THE CONDITIONS OF COVID-19,SYNTHESIS AND ANALYSIS OF COORDINATION COMPOUNDS OF COPPER (II) CHLORIDE WITH MONOETHANOLAMINE AND P-NITROBENZOIC ACID

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Abstract: The article highlights the study of the synthesis of a complex combination of p-nitrobenzoic acid with $Cu^{2+}$from aromatic carbonic acid derivatives. Influencing factors on the synthesis of complex compounds in the room were studied. Specifically, the time dependence of the reaction, the effect of temperature, the concentration dependence wasobserved in practice. The synthesized complex was evaluated by means of IR-Fourier spectrometry, elemental analysis, mass spectrometry, TG-DSK and X-ray structural analysis to determine its chemical structure, as well as to justify that the new complex is thermally and chemically steady.

Keywords: p-nitrobenzoic acid, copper (II) chloride, monoethanolamine, complex compound, metal complex, X-ray structural analysis, elemental analysis, antimicrobial, single crystals.

Introduction

Nearly at all stages of human development, one of the pressing issues was to provide the population with a variety of food products. In this process, one of the key factors is the rational protection of plants from harmful organisms (pests, diseases and weeds). Protection of plants from pests is very crucial in the

cultivation of grain products, potatoes, fruits, vegetables and other crops, as well as, breeding livestock in our country. The main reason for this is that the conditions of Uzbekistan (hot climate, its geographical location and soil conditions) are very favorable for the development of pests. They find plenty of food and a comfortable place to live in fields, which in turn causes more damage to crops. It should be noted that in Uzbekistan one of the main pests in cotton fields is spider mite(Tetranychidae), which gives up to 18-20 generations, while caradrina 4-6, bollworm 3-4, plant lice 16-17 and in potato growing areas Colorado worm 3-4 generations. Therefore, in our conditions, the development and effective use of specific methods of pest control is one of the most important measures to increase productivity [1].

In this regard, in the fight against plant pests include simple monocycles of benzoic acid - all types of isomers of nitro-, amino- and hydroxybenzoic acids (primary ligand), and auxiliary ligands to obtain mono, di and tri ethanolamines with similar bioactivity. It is advisable to use complex compounds that form them with biometals such as Cu, Co, Mn, Mo and Ni. Because these newly synthesized complexes have antimicrobial and stimulant properties.

This work is also devoted to the synthesis and study of complex compounds of antimicrobial and stimulant substances: copper (II) chloride with monoethanolamine and p-nitrobenzoic acid.

Theaim of the work is to develop a method for the synthesis of a complex of Cu (II) chloride with p-nitrobenzoic acid and to study the composition and structure of the synthesized complex by modern physicochemical methods.

Literature Review

Researches on the synthesis of complexes of carbonic acids with biometals, their spatial structure, "bioactivity-structure" relationship have conducted by leading research centers and universities around the world, including the Delhi Institute of Pharmaceutical Sciences and Research (India), Institute of Inorganic Chemistry in the University of Aachen (Germany), Institute of General and Inorganic Chemistry, Moscow State University (Russia), University of Tokyo (Japan), Royal Institute of London (UK), Institute of Engineering (China), Jagiellonian University (Poland), General and Inorganic Institute of Chemistry (Uzbekistan).

World researches on the structure of carboxylic acid complexes with biometals and their biological activity have yielded a number of scientific results, including: synthesis of chelated complexes of metals, their spatial structure and charge density were identified (Institute of Inorganic Chemistry, University of Aachen, Germany); mixed ligand coordination compounds in the presence of carboxylates were synthesized (Institute of General and Inorganic Chemistry, Moscow State University, Russia); complexes based on biometals were synthesized, molecular and crystalline structures as well as bioactivity were determined (Royal Institute of London, UK); polymer-type coordination compounds of carbonic acids were obtained (Engineering Institute, China); complexes of metals with phenoxyacetic acid derivatives were obtained and

their types of mutual coordination were determined (Jagiellonian University, Poland); micronutrients, urea, carbonic acids and monoethanolamine-based plant growth stimulants were identified (Institute of General and Inorganic Chemistry, Uzbekistan).

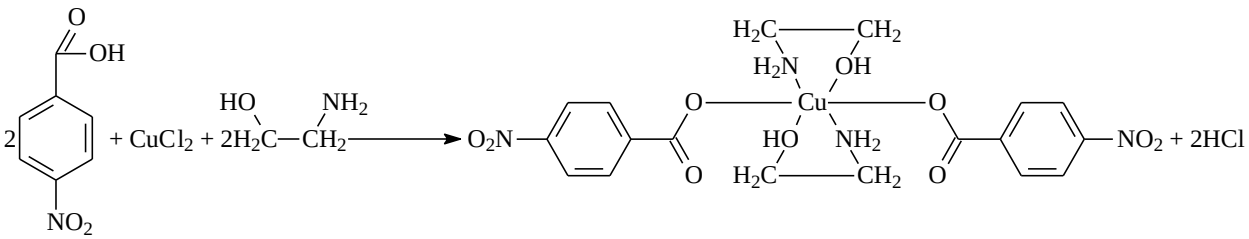
A number of scientific works were dedicated to the study ofthe synthesis and physicochemical analysis of complex compounds of 3d metals and p-nitrobenzoic acid in solutions by Imanakunov B.I., Sulaymonkulov K.S., Tsivadze G.V., Tsintsadze G.V., Kharitonov Yu.A., B.Kol, M.Kholt, Hamilton V.S., Kozlova I.A., Savinkin Ye.V., Kuzmin N.E., Palkin K.K., Penland R.B., Rau T.F., Dursun A.K. and others.

A number of biologically active coordination compounds used in medicine and other sectors of the economy have been synthesized by leading scientists of our state, such as Parpiev N.A., Khodjaev O.F., Khakimov H.H., Ibragimov B.T., Sharipov K.T., Azizov T.A., Azizov M.A., Kadirova Sh.K., Kadirova Z.Ch. and by their students. The technology of obtaining complex compounds of various salts of metals with organic ligands has been developed, the processes of formation of coordination compounds in solutions and solid phases have been studied. Physicochemical properties of synthesized compounds were analyzed. Although there are many experimental materials for the study of complexes of metal salts with substances containing the nitro group and carboxyl group, the synthesis of ligand metal complexes of copper (II) chloride mixed with p-nitrobenzoic acid from these 3d-metal salts has not been studied enough. There is also no information about the structure of the coordination node of this class of connections.

Research Methodology

The complex was synthesized according to the following method: 0.002 mol of p-nitrobenzoic acid was dissolved in 20 ml of hot methanol and it was placed in a round three-mouth-the bottom-flask and fixed on a tripod on a mixer. A thermometer is attached to the left mouth of the flask, a return cooler is attached to the center mouth, and a drip funnel is attached to the right mouth. The reaction temperature was controlled using a thermometer (optimal reaction temperature t = 45-50 ^{o}C). The time to start the reaction was clearly set. A solution of 0.001 mol of copper (II) chloride in 30 ml of water was then added to a 5 ml solution of ligand in a flask every 30 minutes using a dropper funnel.

Two hours after the start of the reaction, a 1:30 alcohol solution of monoethanolamine was added to the mixture. The mixture was stirred at 45-50^{o}C in a MS-H280-Pro brand magnetic stirrer for 3 hours. The reaction mixture was then left to crystallize at room temperature. After 7–8 days, the blue complex precipitate formed was separated, washed in methanol, and dried in the open air. Reaction of mixed ligand complex:



$2C_7H_5NO_4$ $+CH_3OH+CuCl_2*2H_2O+H_2O+2MEA$ $=[Cu((PNBA)_2(MEA)_2)]+2HCl$

Product yield 75%. T_{liquid}= 293ºC.

Analysis and results

The amount of metal in the synthesized complex was determined on the Novaa 300 apparatus of Analytic Jena (Germany), and the analysis of carbon, hydrogen and nitrogen elements was determined on the "EA 1108" apparatus of Carlo-Erba (Italy) (Table 1). The IR spectra of the compound were obtained, in the area of 400-4000 $cm^{-1}$by IRAffinity-1S spectrophotometer of the firm Shimadzu (Japan) samples were prepared with KBr tablets with a diameter of 7 mm. X-ray structural analysis was obtained on an Xcalibur ROxford Diffraction automatic diffractometer at a temperature of 293 K (Cu Karadiation, k = 1.54184 Å, xscan mode, graphite monochromator).

Table-1

Results of elemental analysis of a complex compound of copper (II) chloride with monoethanolamine and p-nitrobenzoic acid

Compound	Cu %		C, %		H, %		N, %	
	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated
$Cu((PNBA)_2(MEA)_2)$	12,35	12,67	41,69	42,54	4,24	5,16	10,81	11,2

Indeed, at the centers of inversion, Cu (II) ions in crystals are located. They coordinate the two molecules of MEA through the nitrogen and oxygen atoms to form chelate. (Figure 1).

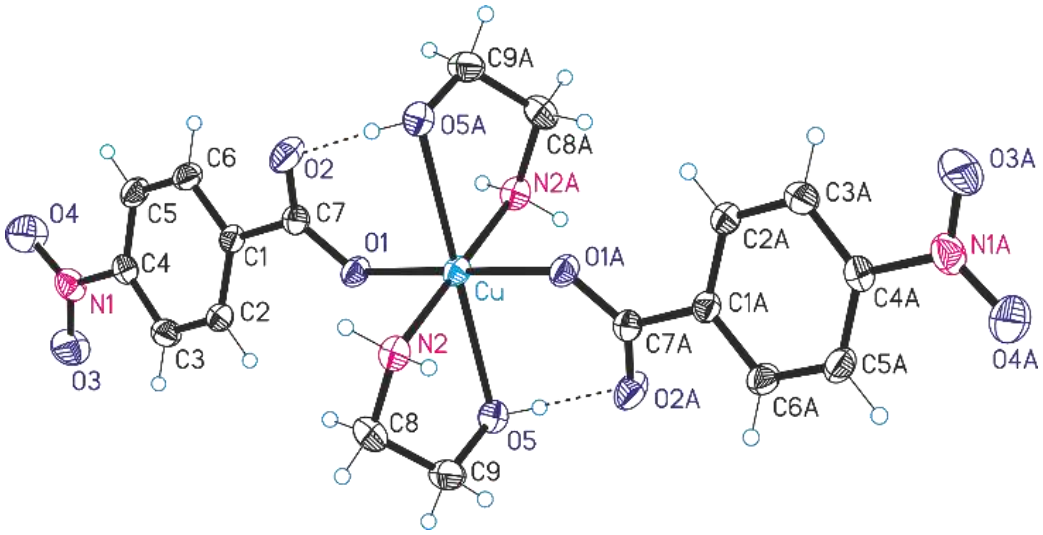


Figure 1.The structure of a complex molecule in the compound [Cu (PNBA)$_2$ (MEA)$_2$]

Two molecules of PNBA are attached by a monodentate through an oxygen atom of the carboxyl group, which is in the form of a carboxylate to compensate for the positive charge of the copper ion. The carboxylate group is not covered with the benzene cycle - the corresponding dielectric angle is 25.28º, the nitro group deviated 11.51º relative to the aromatic core.

The copper ion coordination polyhedron is in the form of a strongly broken octahedron due to the Yan-Teller effect. In the equatorial plane, the oxygen atom of PNBA and the nitrogen atoms of MEA are located at a bond length of 2,000 ± 0.03Å, while the oxygen atoms of MEA occupy apical positions with a bond length of 2,552 (4) Å. The largest deviations from 90º correspond to angles O5-Cu-N2 (76.20 (13)) and O5-Cu-N2 (1-x, 1-y, -z) (103.80 (13) Å).

The bond lengths and valence angles analyzed in the MOGUL program integrated into the MERCURY complex show that there are no unusual geometric parameters.

Table-2

Bond lengths and valence angles of metal atoms in the compound [Cu (PNBA) $_2$ (MEA) $_2$]

Compound	
[Cu(PNBA)$_2$(MEA)$_2$]	
Bond	Bond length, Å
Cu-O1	2.024(4)
Cu-N2	1.969(4)

Cu-O5	2.552(4)
Cu-O1_a	2.024(4)
Cu-O5_a	2.552(4)
Cu-N2_a	1.969(4)
Angle	Value of angle, degree.
O1-Cu-O5	88.15(11)
O1-Cu-N2	88.64(14)
O5-Cu-N2	76.20(13)
O1-Cu-O5_a	91.86(11)
O1-Cu-N2_a	91.36(14)
O5-Cu-N2_a	103.80(13)
Symmetry: (a) 1-x,1-y,-z	

There is an intramolecular strong hydrogen bond between the uncoordinated oxygen atom of the carboxylate group of PNBA and the hydroxyl group of the coordinated MEA, which closes the graph-set six-membered cycle $C^1_1(6)$.

IR-spectrum, mass spectrometer and thermal analysis of the obtained new complex form the following spectrum:

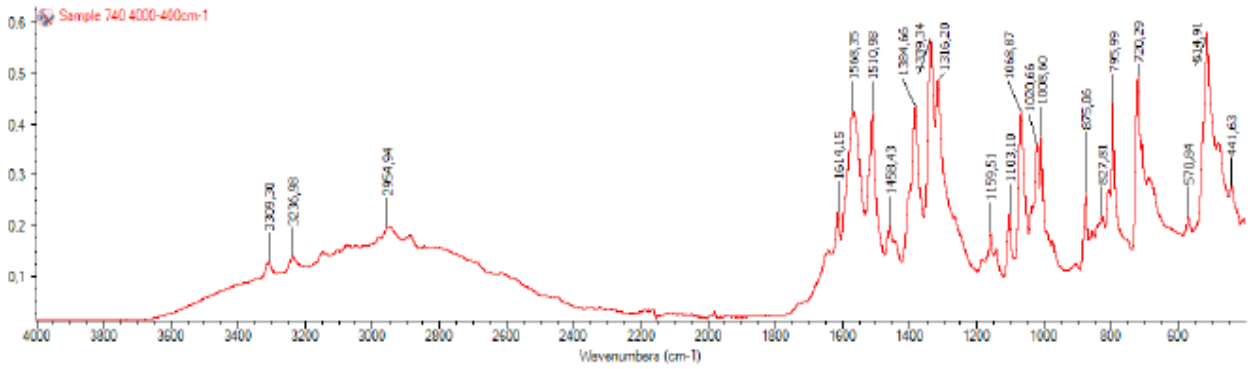


Figure 2.IR spectra of the compound [Cu $(PNBA)_2(MEA)_2$]

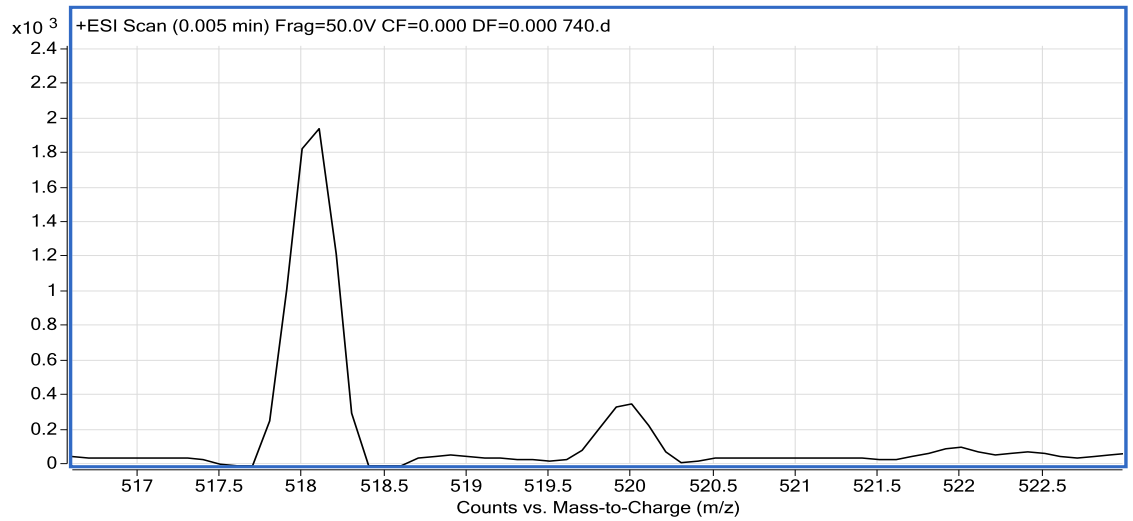


Figure 3.Mass spectra of compounds[Cu $(PNBA)_2(MEA)_2$]

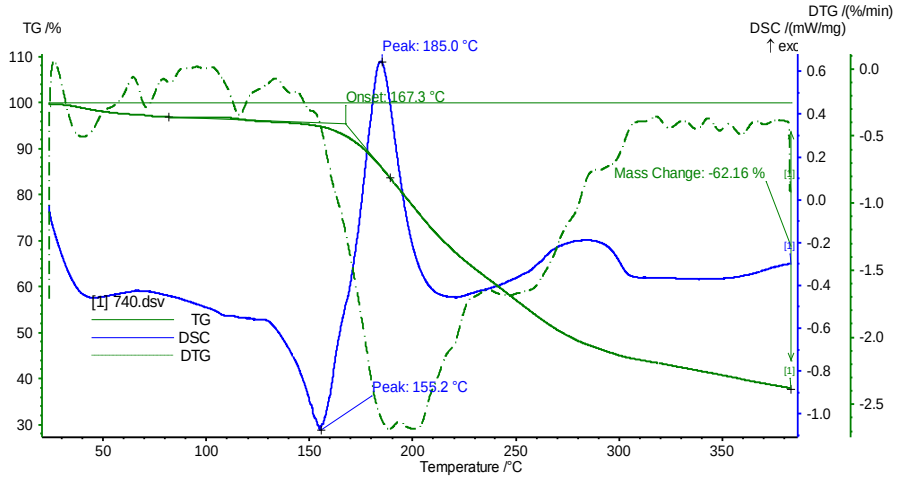


Figure 4. Thermograms of compounds[Cu $(PNBA)_2(MEA)_2$]

Conclusion

The [Cu ($(PNBA)_2$ $(MEA)_2$)] complex consists of Cu (II), PNBA, and MEAs and is a 1: 2: 2 containingligand compound. The complex molecule contains O5-H- and N2-H_2-groups that can act as donors in hydrogen bonds. When the hydroxyl group only participates as a donor in the internal hydrogen bond, the two hydrogen atoms of nitrogen in the MEA form intermolecular hydrogen bonds with the O1 and O5 atoms, leading to the formation of x-axis-oriented columns. Oxygen atoms of the nitro group do not participate in the formation of hydrogen bonds. The relatively large distance between the centroids of the parallel aromatic nuclei indicates that there is no significant stacking effect of 4,781 Å. Therefore, only a pair of hydrogen bonds of the amino group MEA are involved in the formation of the crystal structure and form columns oriented along the x-axis. [2].

The structure of the obtained compound was analyzed by X-ray and it was determined that it has the following structure (Fig. 5).

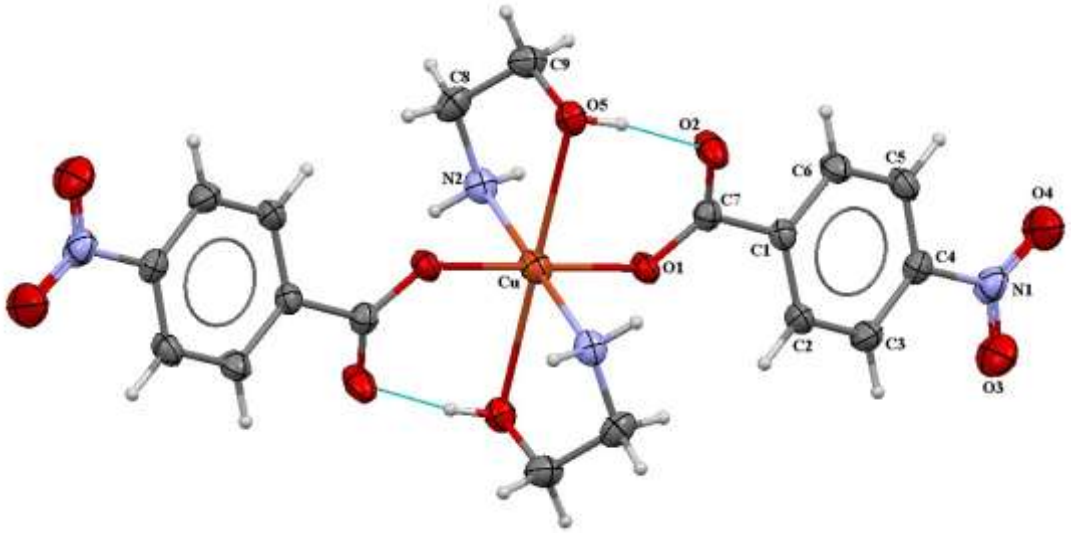


Figure 5. Spatial structure of the synthesized complex compound

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