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DISPLACED LIGAND COPPER(II) COMPLEXES WITH QUINAZOLONE-4 AND ITS DERIVATIVES

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ABSTRACT

One of the important areas of modern coordination chemistry is the synthesis and study of complex compounds of transition metals with biologically active ligands. The development of new highly effective biologically active drugs is one of the tasks of modern medicine and agriculture. The directed synthesis of coordination compounds of biometals with physiologically active organic compounds can be of great help in solving this problem.

***Keywords:** transferable ligand complexes, coordination, anisotropic spectrum, g-factor, quaternary metallocycles, bidentate coordination.*

АННОТАЦИЯ

Одним из важных направлений современной координационной химии является синтез и исследование комплексных соединений переходных металлов с биологически активными лигандами. Разработка новых высокоэффективных биологически активных препаратов является одной из задач современной медицины и сельского хозяйства. Большую помощь в решении этой проблемы может оказать направленный синтез координационных соединений биометаллов с физиологически активными органическими соединениями.

***Ключевые слова:** переносимые лигандные комплексы, координация, анизотропный спектр, g-фактор, четвертичные металлоциклы, бидентатная координация.*

INTRODUCTION

Determination of synthesis conditions, determination of the composition and structure of copper (II) coordination compounds with quinazolone-4 and derivatives. Determination of the method of coordination of ligands and the dependence of the physicochemical properties of the synthesized compounds on their structure. Methods for the synthesis of copper (II) coordination compounds with quinazolone-4 and its derivatives were first developed. Their identities were verified. Based on chemical analysis, IR, EPR spectroscopy, their structure in solid state and in solution was determined. Conclusions are drawn on the mode of coordination of ligands in quinazolone-4 derivatives and the competitive coordination of donor atoms. Received information. The composition of the synthesized compounds was determined by elemental analysis. Copper (II) ions with quinazolone-4 have been shown to form 1: 1, 1: 2, and 1: 3 complexes. The quinazolone-4 anion was found to be involved in bilateral coordination with the metal either by oxygen in position 4 or by nitrogen in position 3 or simultaneously by these atoms. Ionic contact with the metal is mainly carried out by oxygen, rarely by nitrogen. In position 1, the coordination ability of nitrogen was not found. Studies have shown that quinazolone-4 is the most active complexing agent. It was found to extract 2-oxo-, -thioxo-, -amino- and -methoxycarbonylaminoquinazolones-4 from copper (II) complexes[6-7].

Features:

- ligand complexes of copper (II) mixed with quinazolone-4 and its derivatives were obtained.
- The individuality of the synthesized complexes is proved on the basis of chemical analysis, IR, EPR spectroscopy. One of the important directions of modern coordination chemistry is the synthesis and study of complex compounds of transition metals with biologically active ligands. The development of new highly effective biologically active drugs is one of the challenges of modern medicine and agriculture. Targeted synthesis of coordination compounds of biometals with physiologically active organic compounds can be of great help in solving this problem.

It is known that the inclusion of vital metals in biologically active drugs not only reduces their harmfulness, but in many cases increases the biological activity of the drug, and often reveals new biological properties[6-8]..

DISCUSSION AND RESULTS

There are many different ligands in coordination chemistry that differ greatly in their properties and structure. One of the important classes of such compounds is quinazolone-4 and its derivatives, which are very common in plant and biological objects. Among them were identified drugs with herbicides, fungicides, bactericides, growth regulators, pharmacological and other properties. The purpose of this work is to determine the conditions of synthesis, to determine the composition and structure of copper (II) coordination compounds with quinazolone-4 and its 2-oxo-, -thioxo-, -amino- and -methoxycarbonylamino derivatives. To determine the method of coordination of ligands and the dependence of the physicochemical properties of the synthesized compounds on their structure. Methods and materials. Element analysis, IR spectroscopy, EPR spectroscopy. To determine the chemical composition, the synthesized compounds were analyzed for metal content (cobalt, copper and zinc) by trilonometric titration, carbon, hydrogen and nitrogen in a helium stream on a ChN-1 element analyzer (1 mg sample). IR absorption spectra of ligands and complexes were recorded on a UR-20 spectrophotometer in the range of 400–4000 cm-1 by pressing the sample with KBr or grinding in Vaseline oil. The recording of the EPR spectra of the mixtures was performed on a radiospectrometer with an EPR OZ of 9.3 MHz. Results and discussion[8]. When a methanolic solution of the potassium salt quinazolone-4 (KHz) is added to the suspension of the $CuXHz.2H_2O$ complex (X = NO_3, CH_3COO), the Cu (Hz) 2,$3H_2O$ complex is separated from the solution, viz. the nitrate ion is replaced by another quinazolone-4 molecule. These data suggest that metal complexes with quinazolones can replace one anion with another heterocyclic ligand that differs from the parent compound. We therefore decided to use this opportunity to synthesize displaced ligand complexes that are unknown in the literature for the cinema series[6]..

The interaction of the potassium salt of 2-oxo- (OHz), -thioxo- (THz), -amino- (AHz) and methoxycarbonylaminoquinazole-4 (MKAHz) on the suspension of the $CuNO_3Hz.2H_2O$ complex in methanol yields a shifted ligand. complexes. According to the results of chemical analysis, the complexes do not contain nitrate ions, which is confirmed by the disappearance of the characteristic absorption zones of nitrate ions in the region in the IR spectra of shifted-ligand complexes. 1390 and 835 cm-1. It therefore mixes with OHz, THz, AHz and MKAHz anions. In this case, the coordinated quinazolone molecule (Hz) remains in the complex (Figure 1). The characteristic absorption zones of coordinated quinazolone in the IR spectra of the complexes change little. New absorption zones appear that correspond to other derivatives of kinazolone. Thus, in the spectrum of the Cu (Hz) (OHz) .2H2O complex, n (NH) OHz disappears in the region of 3060 cm-1 and n (C = O) in the region of 1715 cm-1. At 1675 cm-1, which is characteristic of the carbonyl group in position 2, the second n (C = O) band passes into the low-frequency region at 15 cm-1 (Fig. 1).

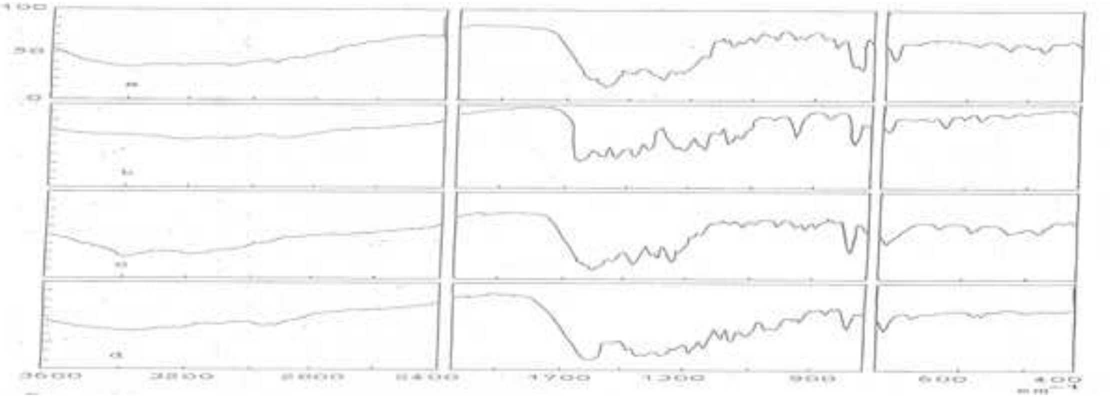
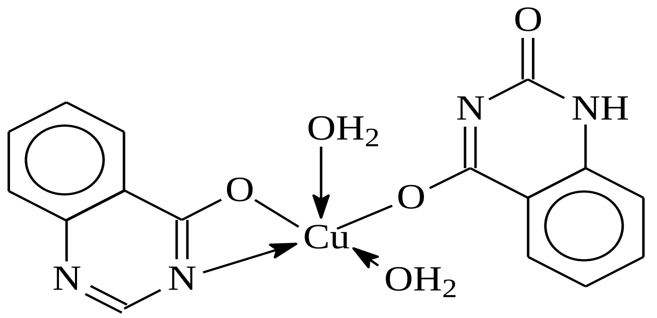


Figure-1. IR spectra OHz and Cu (Hz) (OHz) .2H2O (a), Cu (Hz) (THz) .H2O (b), Cu (Hz) (AHz) .H2O (c) and Cu (Hz) (MKAHz) (d).

Such an image is found in the spectrum of the Co (OHz) 2.4H2O complex, where the monodentate coordination of the OHz anion is established by means of oxygen in state 4. Based on this, the following structure can be estimated for Cu (Hz). (OHz) .2H2O complex:

The complex in the polycrystalline state has a well-dissolved anisotropic EPR spectrum in the parallel direction, which is characteristic of copper (II) compounds whose basic state is dx2-y2. Some parameters: gII = 2,280, A = 178 Oe, g1 = 2,043 and B = 18 Oe differ from the EPR parameters of the $CuNO_3Hz.2H_2O$ and Cu (Hz) 2,3H2O complex. The increase in factor g relative to the latter and the decrease in the HFI constant are explained by the change in the coordinate position of Cu (NO4) to Cu (O5) [1, 2].



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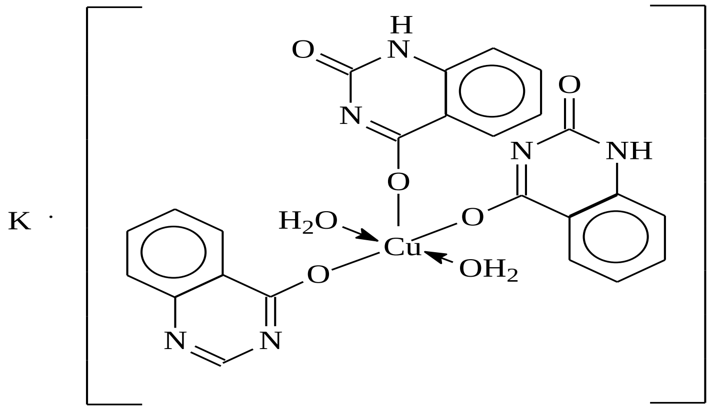
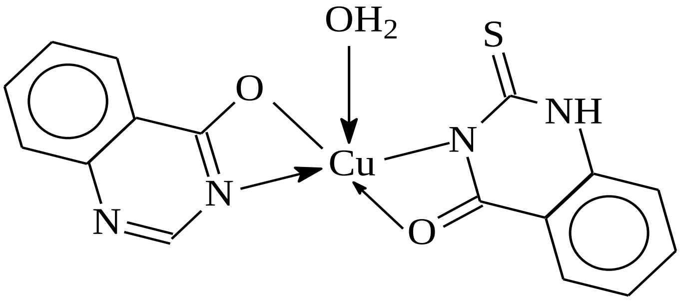
The OHz and CuNO3Hz.2H2O complex also form a purple complex containing K [Cu (Hz) (OHz) $2,2H_2O$], which is readily soluble in methanol [2]. In a frozen solution, the anisotropic EPR spectrum dissolves well in parallel and perpendicular directions. In region G, the lines differ in two directions gx and gy. EPR parameters: gz = 2.395, A = 195 Oe, gy = 2.073, B = 15.7 Oe, gx = 2.035 and C = 16.7 Oe indicate the exchange of coordinated nitrogen with oxygen. On this basis, ligands (Hz, OHz) in this complex are coordinated by oxygen, apparently monodentate, occupying three coordination sites.



The complex parameters in the polycrystalline state at room temperature have an asymmetric single EPR signal with g = 2,085 and line width ΔH = 225 Oe = -1 / 2 and -3/2. When the solution freezes, the typical anisotropic EPR spectrum is observed with a well-resolved parallel orientation, while the lines in the perpendicular orientation are not defined: gII = 2,324, A = 150 Oe, g1 = 2,075 (Fig. 2).



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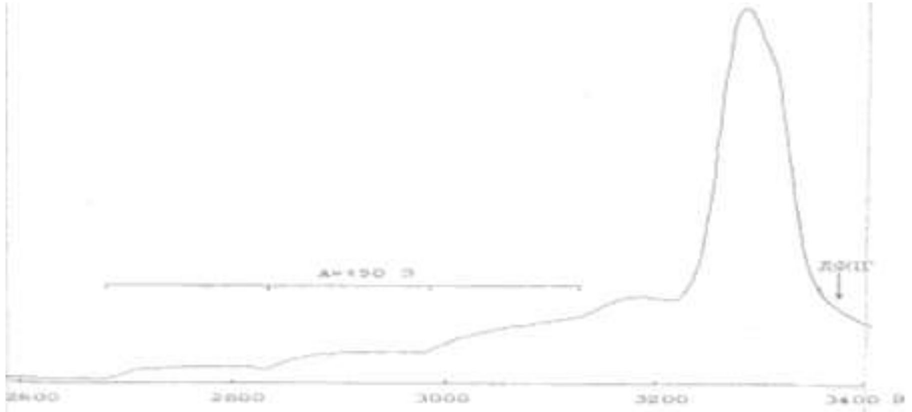

Figure-2. Cu (Xz) (TXz) at 77 K in DMSO. EPR spectra of H2O.

Cu (Hz) (AHz). In the IR spectrum of the H2O complex, 3060 n (NH) AHz and 1695 cm-1 have no n (C = O), n (3410 cm-1 range corresponding to. NH). 1 and new lines n (NH2) and ns (NH2) are found at 3080 and 3170 cm-1, respectively [3]. They shift to a lower frequency range of 120–130 cm-1 relative to the ligand spectrum. In the region 1595–1620 cm – 1, a broad band corresponding to n (S = N) and n (S = S) of the aromatic ring is observed [4]. The n (S-O) zone is not clearly observed because there are 1390 and 835 cm-1 ranges corresponding to the n3 and n2 elongation oscillations of the coordinated nitrate ion in this region. The remaining bands of the $CuNO_3Hz.2H_2O$ complex and the coordinated AHs remain unchanged.

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