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SYNTHESIS AND STRUCTURE OF *bis*-[3-(FLUOROPHENYL-AZO-PENTADIENE-2,4)ETHYLENEDIIMINES] AND THE STUDY OF COMPLEX FORMATION WITH COPPER(II) ION

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Based on acetylacetone a new organic reagent was synthesized. Its crystal structure was studied. Its complexation with copper was studied by spectrophotometric method. The effect of the third component on the complexation of Cu–R was considered. The composition of the reactants was studied by different physico-chemical methods. The effect of foreign ions on complexation was studied. The technique was applied to the determination of trace amounts of copper in natural objects.

Keywords: extraction-photometric analysis, β -diketones, copper(II), complexation β -diketones, 3-(fluorophenylazo-pentadiene-2,4), *bis*[3-(fluorophenylazo-pentadiene-2,4)]ethylene diimine, X-ray structural analysis.

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Azo-compounds take a particular place among these reagents. In order to reduce the limit of analytical reactions and increase the selectivity they are passed through from binary to three-component systems. Therefore, the development of sensitive, selective, high-precision and rapid methods for the determination of copper(II) using azo compounds– modified forms of azo derivatives with β -diketones is an important task of analytical chemistry. It is known from literature that β -diketones and their derivatives are used for photometric and extraction-photometric determination of a number of metals [1–6]. These reagents are highly selective for the determination of Cu^{2+} , Fe^{3+} and they are also used for group concentration of metals [7–12].

Therefore, the synthesis of new derivatives of β -diketones, the study their analytical capabilities are of great interest.

In this work, based on 3-(fluorophenylazo-pentadiene-2,4) a new reagent *bis*[3-(fluorophenylazo-pentadiene-2,4)]ethylenediimine was synthesized. Its crystal structure was determined.

Its complex compounds with copper(II) ion were investigated by spectrophotometric method.

Experimental part

Equipment. The optical density of the solutions was measured on a Lambda- 40 spectrophotometer (Perkin Elmer) and a KFK-2 photocolormeter in a cuvette with thickness of a layer 1 cm. The pH of the solutions was controlled using a pH-25 ionomer calibrated by standard buffer solutions.

X-ray diffraction analysis was performed on a Bruker SMART APEX II CCD automatic diffractometer (M_0K_α -radiation, $\lambda = 0.71073 \text{ \AA}$ – on a graphite monochromator, φ and ω – scanning).

Solutions and reagents. The initial reagent 3-(4-fluoro-pentadiene-2,4) was synthesized according to a known method [13, 14]. *bis*[3-(Fluorophenylazo-pentadiene-2,4)]ethylenediimine was synthesized according to the following scheme.

The reagent was synthesized according to the following procedure. 0.2 M *bis*[3-(fluorophenylazo-pentadiene-2,4)] dissolved in 60 ml of ethanol was transferred into a conical flask and 0.1 M ethylenediamine dissolved in 10 ml of ethanol was added. The flask is attached to the reflux condenser. The mixture is stirred for 2 hours at 60°C. The solution is left at room temperature. After a week, needle-shaped red color crystals fall out from solution. The yield was 73%.

The initial ($1 \cdot 10^{-3}$ M) copper solution was prepared by dissolving the exact weighting of the analytical grade copper in concentrated HCl at heating [15]. Working solutions with a lower copper content were prepared by diluting the stock solution with distilled water. The reagent is highly soluble in ethanol. $1 \cdot 10^{-3}$ M reagent solution dissolved in ethanol, water-ethanol solution of $1 \cdot 10^{-2}$ M phenanthroline, 2,2-dipyridyl and aqueous solution of ethylene diamine were used in the work.

Results and discussion

The structure of this compound was determined by X-ray diffraction analysis. The crystals are obtained with an orthorhombic structure: $a = 18.9757$ (10) Å, $b = 10.7254$ (6) Å, $c = 22.2875$ (12) Å³, $Z = 8$, Sp.g. P_2/n (Figure 1).

Fig. 1. The structure of the copper(II) complex.

The complex formation of copper with this reagent was studied by spectrophotometric method. Studied reagent formed a colored complex compound with copper ion. The maximum

yield of the complex is observed at pH 3, the optimal wavelength tape at 432 nm. Under these conditions, the maximum light absorption of the reagent is observed at 348 nm.

In the presence of the third component (2,2'-dipyridyl, α,α' -phenanthroline, ethylenediamine) different ligand complexes of Cu(II)-R-T/k are formed, while bathochromic shifts are observed in the absorption spectra. Absorption of mixed ligand complexes Cu(II)-R-2,2'-dipyridyl, Cu(II)-R-phen, Cu(II)-R-ED is maximum at 444, 441 and 450 nm, respectively. The study of the dependence of optical density on the pH of the solution showed that all the complexes are formed in an acidic medium at pH=2. With the formation of mixed-ligand complexes, the output shifts into an acidic medium compared with the corresponding binary complexes (Figure 2). The color of the reagent and complexes depends on the pH of the medium, therefore, the absorption spectra under complexation were studied against the background of the control experiment. It was established that the optical density of binary mixed-ligand copper complexes is maximum at 440 nm (Figure 3).

To select the optimal conditions the effect of concentrations of initial substances, temperature and time on the formation of binary and mixed-ligand complexes has been studied. The output of the complexes $8 \cdot 10^{-5}$ M MR; Cu(II)-R-Phen $8 \cdot 10^{-5}$ M MR and $4 \cdot 10^{-5}$ M MR Phen, Cu(II)-R-2,2'-dip., $8 \cdot 10^{-5}$ M R and $4 \cdot 8 \cdot 10^{-5}$ M MR-2,2'-dip, Cu-R-ED $8 \cdot 10^{-5}$ M R and $4 \cdot 10^{-5}$ M ED. All complexes are formed immediately after mixing the solutions of the components and differ in their stability. So if binary complexes are stable for two hours and when heated to 60°C, then mixed-ligand complexes are stable for more than a day and when heated to 80°C.

The ratio of components in the composition of the resulting complexes was established by the methods of isomolar series, the relative yield of the Starik-Barbanel, and the equilibrium shift.

The molar absorption coefficients of the complexes are calculated from the saturation curves. Concentration intervals have been established where Beer's law [16] is observed (Table 1).

Fig. 2. Dependence of optical density of copper(II) solution complexes on pH in the presence and absence of third components at λ_{opt} on the background experience: 1 – Cu–R; 2 – Cu–R–Phen; 3 – Cu–R–2,2-dip; 4 – Cu–R–Ed. $C_{\text{Cu}} = 4 \cdot 10^{-5} \text{ M}$, $C_{\text{R}} = 8 \cdot 10^{-3} \text{ M}$, $C_{\text{Phen,2,2-dip}} = 8 \cdot 10^{-5} \text{ M}$, $C_{\text{Ed}} = 8 \cdot 10^{-4} \text{ M}$, $l = 1 \text{ cm}$.

Fig. 3. Absorption spectra of copper(II) complexes: 1 – Cu–R, 2 – Cu–R–Phen, 3 – Cu–R–2,2-dip, 4 – Cu–R–ETD. $C_{\text{Cu}} = 4 \cdot 10^{-5} \text{ M}$, $C_{\text{R}} = 8 \cdot 10^{-3} \text{ M}$, $C_{\text{Phen,2,2-dip}} = 8 \cdot 10^{-5} \text{ M}$, $C_{\text{Ed}} = 8 \cdot 10^{-4} \text{ M}$, $l = 1 \text{ cm}$.

Table 1. The main characteristics of the photometric method determination of the copper(II) complexes

Complex	λ_{max} , nm	Me:R	pH_{opt}	$\epsilon_{\text{max}} \cdot 10^{-4}$	Submission to the law of Beer Cu mg /ml
Cu–R	442	1:1	3	0.42	2.0–24
Cu–R–Phen	444	1:1:1	2	0.48	2.0–25.6
Cu–R–2,2'-dip	447	1:1:1	2	0.47	1.8–25.6
Cu–R–ETD	452	1:1:1	2	0.51	1.8–25.6
OHT+anilin [9]	660	–	3.6–5.4	0.28	0.2–20

The study of the influence of foreign ions and masking substances on the complexation of copper in the form of binary and mixed-ligand complexes showed that in the presence of the third component, the selectivity of the reaction increases (Table 2).

The developed technique was applied to determine copper in copper-based alloys.

The course of the analysis. 0.2 g of the alloy is dissolved in 15 ml of HNO_3 (1:1) when heated. The solution is transferred to a flask with a capacity of 100 ml and diluted with distilled water to the mark. An aliquot portion of the solution is transferred to a 25 ml flask, 2 ml of $1 \cdot 10^{-3} \text{ M R}$ and 1 ml of $1 \cdot 10^{-2} \text{ M R}$ of phenanthroline are added, diluted to the mark with

buffer pH 2. The optical density of the solution is measured on a KFK-2 spectrophotometer at $\lambda = 440 \text{ nm}$ in cuvettes with a layer thickness of $l = 1 \text{ cm}$. The results of the study are shown in Table 2.

Table 2. Copper definitions in copper based alloys ($n = 5$, $P = 0.95$)

Standard sample	According to passport, %	Found%		S_r
		By electrogravimetric method	R-Phenantr.	
972	64.90	64.85	64.81	0.004
973	64.01	63.94	63.95	0.003
974	65.95	65.90	65.88	0.03
975	61.52	61.50	61.47	0.04

With large quantities of iron(III) (more than 30 mg) when determining copper it is masked with 5 ml of 5% NH_4F . The remaining elements contained in the alloy do not interfere to the definition.

As can be seen from the Table 3, alkaline, alkaline-earth elements, REE(III), Co(II), Cr(III), Cd(II), Th(IV), Zn(II), Pb(II), Bi(III), Be(II), Al(III), U(VI), Mn(II), halides, rhodanides, sulfates, sulfosalicylic and ascorbic acids practically do not interfere to the determination of copper.

Table 3. Valid ratios of foreign ions on copper(II) at determination of it in the form of mono- and mixed-ligand complexes ($C_{Cu}=2 \cdot 10^{-5}$, error 5%).

Ion or substance	R	R-2,2'dip	R-phen	R-ED	Pikramin epsilon [7]	bis(acetylacetonate)ethylenediamine [8]
Na(I)	2000	2450	2500			1796
K(I)						3046
Ca(II)	380	700	760	780	20	312
Ba(II)	800	1450	1465	1510		642
Zn(II)	710	1220	1250	1305	1500	508
Cd(II)	920	1560	1560	1590	1000	875
Mn(II)	90	120	120	140		43
Ni(II)	550	725	720	730	50	461
Co(II)	380	450	465	476	100	276
Al(III)	205	230	230	245	10	126
Fe(III)	12	16	18	18		9
Ga(III)	88	110	125	120	60	
In(III)	130	135	138	143		
Sn(V)	70	85	85	92		
Ti(IV)	110	125	130	130		
Mo(IV)	460	485	480	485	3	450
W(VI)	430	480	498	505	100	
$C_2O_4^{2-}$	140	170	185	180		121
ЭДТА	10	15	15	15		
F	60	75	80	80		58
Thiourea	180	205	210	220		
Citric acid	350	1600	1610	1610		
Na_2HPO_4	1500	1720	1740	1730		
Wine acid	1700					

Conclusions

1. To determine copper(II) by the photometric method, the azo-derivatives of β -diketones and their modified forms were used. The structure of the reagents was studied by NMR and IR spectroscopy, and the purity was verified by paper chromatography.

2. The structure of this compound was determined by the method of X-ray structural analysis.

3. Complex compounds of copper(II) with reagents were investigated by the spectrophotometric method, the optimal conditions of complexation and the characteristics of the complexes were determined (pH_{opt} , λ_{opt} , molar absorption coefficients, the composition of the complexes, the interval of subordination to Beer's law, stability constant).

4. The effect of amines on the complex compounds of copper(II) with reagents was determined. It was determined that in the presence of the third component some analytical parameters of the reaction increase.

5. The effect of foreign ions and masking substances on complexation reactions was studied. It has been established that reactions with modified forms of reagents are characterized by higher selectivity.

6. The developed technique is applied to the determination of trace amounts of copper in natural objects.

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bis[3-(FLÜORFENİL AZO-PENTADIEN-2,4)] ETİLENDİİMİNİN SİNTEZİ VƏ QURULUŞU, MİS İONLARI İLƏ KOMPLEKSƏMƏLƏGƏLMƏNİN ÖYRƏNİLMƏSİ

F.S.Əliyeva, F.O.Məmmədova, Y.E.Yusifov, F.M.Çıraqov

Asetilaseton əsasında yeni üzvi reagent sintez edilmişdir. Onların kristal quruluşları öyrənilmişdir. Spektrofotometrik metodla onların mislə kompleksəmələgətirməsi öyrənilmişdir. Cu–R kompleksəmələgətirməsinə üçüncü komponentlərin təsiri öyrənilmişdir. Fiziki-kimyəvi metodlarla reaksiyaya girən maddələrin tərkibi müəyyənəşdirilmişdir. Kompleksəmələgəlməyə kənar ionların təsiri öyrənilmişdir. İşlənilib hazırlanmış metodika mis saxlayan obyektlərdə misin mikromiqdarlarının təyini üçün tətbiq edilə bilər.

Açar sözlər: ekstraksiya-fotometrik analiz, mis(II), β -diketonlar, 3-(flüorfenilazo-pentadien-2,4), bis[3-(flüorfenilazo-pentadien-2,4)]etilendiimin, rentgen struktur analiz.

СИНТЕЗ И СТРОЕНИЕ бис[3-(ФТОРФЕНИЛАЗО-ПЕНТАДИЕН-2,4) ЭТИЛЕНДИИМИНОВ] И ИЗУЧЕНИЕ КОМПЛЕКСООБРАЗОВАНИЕ С ИОНОМ МЕДИ(II)

Ф.С.Алиева, Ф.О.Мамедова, Ю.Е.Юсифов, Ф.М.Чырагов

На основе ацетилацетона синтезирован новый органический реагент. Изучена его кристаллическая структура. Спектрофотометрическим методом изучено его комплексообразование с Cu(II) ионом. Рассмотрено влияние третьего компонента на комплексообразование Cu–R. Разными физикохимическими методами изучен состав полученного вещества. Показано влияние посторонних ионов на комплексообразование. Разработанная методика рекомендована для определения микроколичеств меди в медьсодержащих объектах.

Ключевые слова: экстракционно-фотометрический анализ, медь(II), β -дикетоны, 3-(фторфенилазопентадие-2,4), бис[3-(фторфенилазо-пентадие-2,4)]этилендиимин, рентгеноструктурный анализ.