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Synthesis of octochlorosubstituted cobalt(II) and copper (II) complexes with phthalocyanine

Abstract. A modified method for the synthesis of metalloctachlorophthalocyanines and methods for their purification based on their sequential treatment with hydrochloric acid (10%) sodium hydroxide (2M), then again with hydrochloric acid (10%), pyridine (O.S.C.) in 1,2,4-trichlorobenzene as a solvent is presented. As a result, the degree of purification of copper ion complexes was achieved, 99% versus the best result using methods known in the literature 93%, for cobalt the degree of purity was 98% versus 88%. The yield of the products is also higher than in the known methods and amounted to 78, cobalt -43 for copper compounds. Physico-chemical methods have established that after the final stage of purification-pyridine treatment, impurities are removed, including cyanuric acid, the decomposition product of urea, the results of elemental analysis for carbon, hydrogen, nitrogen conducted on the ThermovomTypFlashEA 1112 analyzer complexes of cobalt (II), copper (II) with phthalocyanine, the assignment of bands of IR spectra recorded in KBr tablets on the Nicolet IR-200 FT - IR spectrophotometer, UV- the spectra of sulfuric acid solutions of metalloctachlorophthalocyanines taken on a Varian, UV - Vis/NIR spectrometer.

Keywords: phthalocyanines, metallophthalocyanines, metalloctachlorophthalocyanines, infrared spectrum.

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Introduction

Metallophthalocyanines (MPC) are endowed with exceptional thermal, light and chemical resistance for organic compounds, and good coloring properties.

MSs have a structure similar to that of natural macroheterocyclic structures - metalloporphyrins (MP) such as chlorophyll and blood hemoglobin.

The features of the structure and properties of MP and MP, especially Co(II), Cu(II) complexes, serve as the basis for their use as thermal and light stabilizers, solar energy accumulators, protein decay inhibitors, biocatalysts, in laser technology as the main coloring agent.

The high thermal and light resistance, good coloring properties, inertia with respect to acids and alkalis, and almost complete insolubility in water and organic solvents of most MP and MP with ions of the first decade of d-metals are due to their structure, namely, the presence of a chromophore - a heterocyclic macro-ring, consisting in turn of four pyrrole rings closed in a cycle through methine (-CH=) in MP or N-azo bridge (=N-) in MP and the corresponding coordination metals, leading to the formation of chelate complexes. However, insolubility in water and organic solvents does not allow widespread use of the technical and biological properties of the compounds obtained.

The literature describes in detail the methods of synthesis of MP and unsubstituted MPc, less often the synthesis of MPc having substituents in benzene rings (Figure 1).

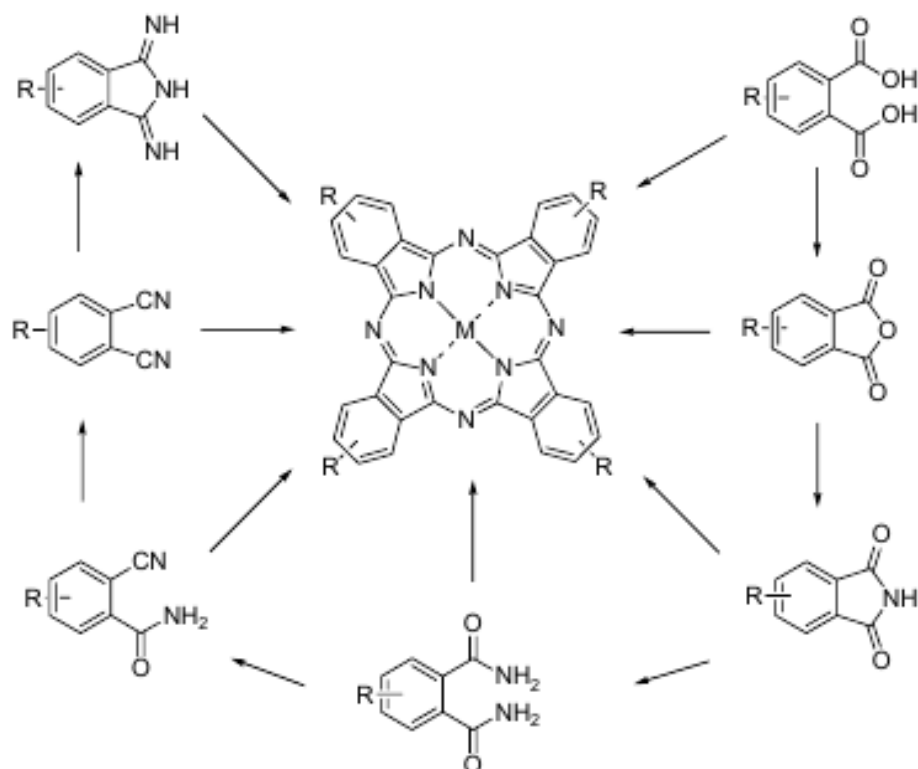
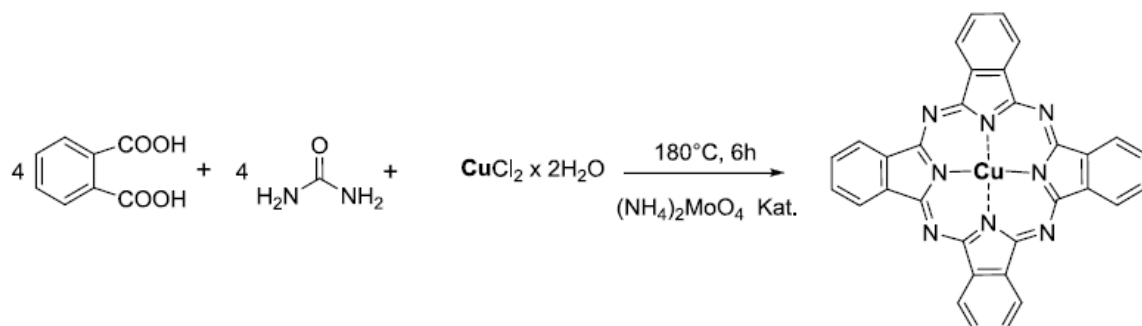


Figure 1. Scheme of synthesis of metallophthalocyanines [1-4].

Experimental work

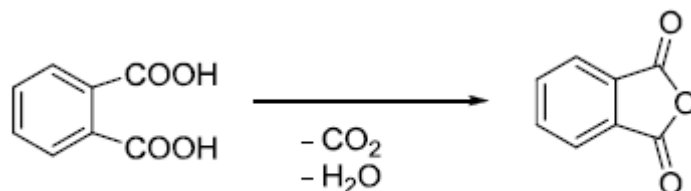
We synthesized and identified by elemental analysis, UV and IR spectroscopy phthalocyanine complexes of cobalt(II), copper(II) obtained by solid-phase synthesis [5], as well as chlorine-substituted phthalocyanine complexes of the same metals in the same oxidation states in the presence of solvent 1,2,4-trichlorobenzene $C_6H_3Cl_3$.

The scheme of the general technique of solid-phase synthesis of phthalocyanine complexes, described by us in [5], can be described by the following equation of the synthesis of CuPc:

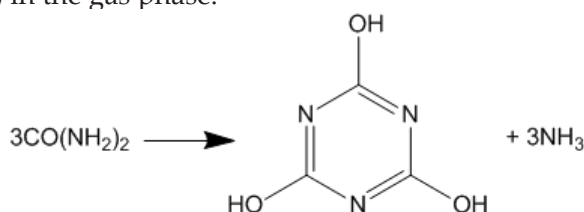


The method of synthesis of chlorosubstituted phthalocyanine complexes of the above metals in the presence of a solvent - 1,2,4-trichlorobenzene - is generally identical to the method of synthesis of MPc.

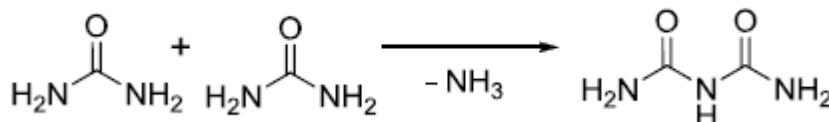
The general methodology for the synthesis of chlorosubstituted phthalocyanines in the presence of 1,2,4-trichlorobenzene is as follows: ≈ 7.05 g of 4,5 dichlorophthalic acid is ground with ≈ 2.39 g (depending on the metal weight may vary) $MCl_2 \cdot nH_2O$, 25 g of urea and 50 mg of ammonium molybdate as a catalyst, the resulting mixture is crushed to a homogeneous mass in a mortar and 100 ml of solvent is added. The mixture is transferred to a round-bottomed flask and heated in an oil bath, depending on the nature of the metal, from 10 to 27 hours. At a temperature of $120^\circ C$, the litmus paper test shows an acidic reaction of the gas phase, which indicates the release of carbon monoxide (IV):



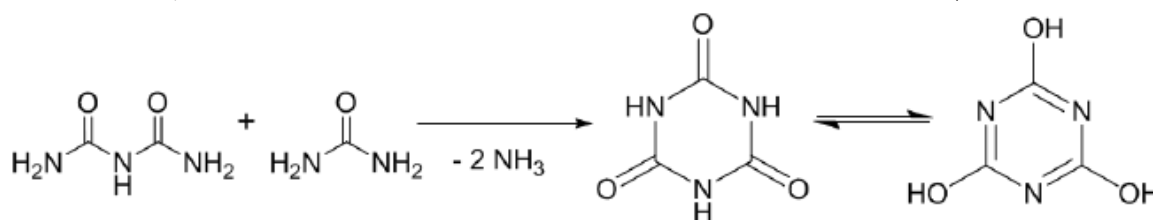
At $135^\circ C$, the evaporation of urea begins with the formation of cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine $C_3H_3N_3O_3$) in the gas phase:



At the same time, at this temperature, the formation of a biuret $C_2H_5N_3O_2$ occurs, accompanied by the release of ammonia:



At $175^\circ C$, the reaction of biuret and urea occurs with the formation of cyanuric acid:



The synthesis was continued until the pH of the reaction medium was approximately equal to 7, at this value of the acidity of the medium, the formation of cyanuric acid as a by-product ends.

The subsequent stages of synthesis involve work in a hydrochloric acid medium. Since cyanuric acid is insoluble in 6N hydrochloric acid, the precipitate separated by filtration and pre-crushed was washed with dichloromethane, extracted with ethanol, then acetone to remove cyanuric acid from the final product. The purity of the final product was confirmed by its IR spectrum, in which there were no bands characteristic of cyanuric acid.

Further, the synthesis was continued in accordance with the methodology given in [5].

Methods of analyzing the results obtained

Elemental analysis for carbon, hydrogen, nitrogen was carried out on a Thermovom Typ Flash EA 1112 analyzer (table 1, table 2).

UV spectra of sulfuric acid solutions of metallophthalocyanines were taken on a Varian, UV-Vis/NIR spectrometer.

IR spectra were recorded in KBr tablets on a Nicolet IR200 FT-IR spectrophotometer (fig.1, fig.2, fig.3).

Table 1. Results of elemental analysis of chloro-substituted phthalocyanine complexes of cobalt(II), copper(II) obtained by solid-phase synthesis

Connection	Elemental composition, %, calculated	Elemental composition, %, according to the results of analyses	Product Output
CoPcCl₈ C ₃₂ H ₈ CoN ₈ Cl ₈ (847.024 g.mol ⁻¹)	C: 45,37 H: 1,00 N: 13,23	C: 45,21 H, 1,06 N, 13,64	3,5280 (0,014 mmol)
CuPcCl₈ C ₃₂ H ₈ CuN ₈ Cl ₈ (851.636 g.mol ⁻¹)	C: 45,13 H: 0,95 N: 13,15	C: 44,73 H: 1,21 N: 13,25	3,1714 (0,018 mmol)

Table 2. Results of elemental analysis of chloro-substituted phthalocyanine complexes of cobalt(II), copper(II) obtained in a solvent medium

Connection	Elemental composition, %, calculated	Elemental composition, %, according to the results of analyses	Product Output
CoPcCl₈ C ₃₂ H ₈ CoN ₈ Cl ₈ (847.024 g.mol ⁻¹)	C: 45,37 H: 1,00 N: 13,23	C: 46,09 H, 1,04 N, 12,85	6,0731 g
CuPcCl₈ C ₃₂ H ₈ CuN ₈ Cl ₈ (851.636 g.mol ⁻¹)	C: 45,13 H: 0,95 N: 13,15	C: 45,98 H: 1,09 N: 12,78	5,7183 g (0,0067 mol)

The following are the band assignments in the IR spectra of substituted phthalocyanine complexes of cobalt(II), copper(II) obtained in a solvent medium:

CoPcCl₈. IR (KBr): ν , cm⁻¹ 1595, 1506, 1410, 1385, 1320, 1275, 1196, 1129, 1085, 964, 875, 775, 745.

CuPcCl₈. IR (KBr): ν , cm⁻¹ 1590, 1495, 1404, 1375, 1327, 1285, 1194, 1120, 1078, 951, 880, 772, 741.

Results and their discussions

The spectra of cobalt(II) and copper(II) complexes are graphically presented.

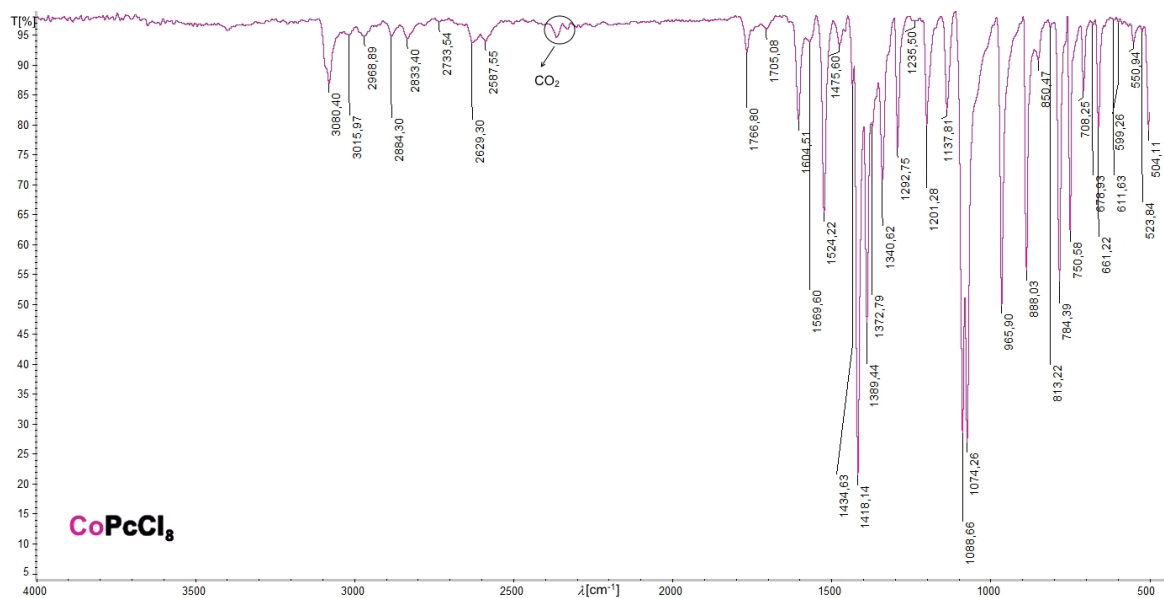


Fig.1. IR spectrum of cobalt(II) complex with chloro-substituted phthalocyanine obtained in 1,2,4-trichlorobenzene medium

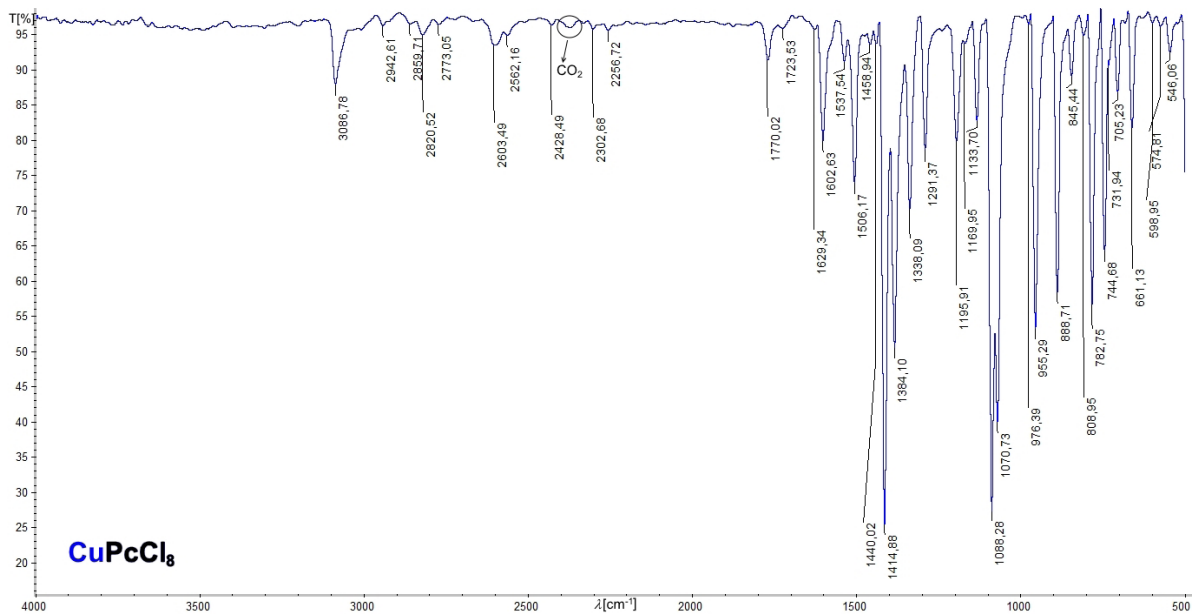


Fig.2. IR spectrum of copper (II) complex with chloro-substituted phthalocyanine obtained in 1,2,4-trichlorobenzene medium

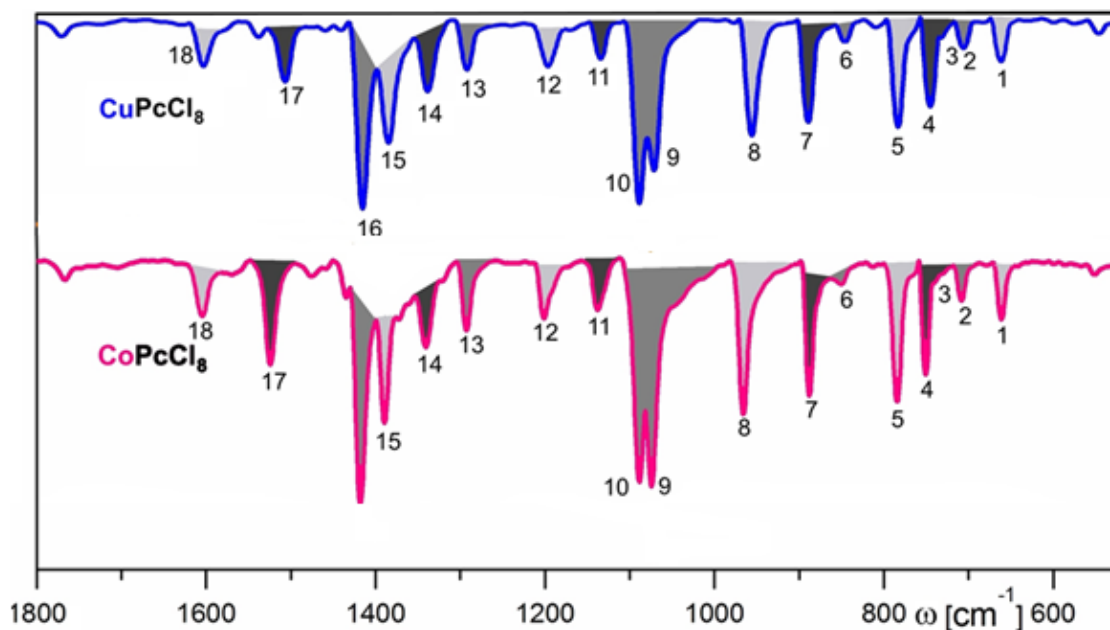


Fig.3. Combined spectrum of CuPcCl_8 and CoPcCl_8 compounds in the range from 500 to 1800 cm^{-1}

A detailed assignment of the bands of valence and deformation vibrations in the IR spectra of unsubstituted phthalocyanine complexes of cobalt(II), copper(II) obtained by solid-phase synthesis was done by us in (fig.3) [5]. The IR spectra of chloro-substituted metallophthalocyanine complexes of the same metals in the same oxidation states obtained in the presence of 1,2,4-trichlorobenzene have minor differences, since the IR spectra of substituted metallophthalocyanines consist of bands belonging to the phthalocyanine part of the molecule and bands of chloride ions. Due to the fact that these bands partially overlap, the interpretation of the spectra was carried out on the basis of a comparative analysis with the spectra of chloro-substituted methylphthalocyanines and their unsubstituted metallophthalocyanines.

In the spectra of synthesized compounds in the region of 1650-1500 cm^{-1} there are bands of valence vibrations of C-C benzene rings, the interpretation of spectra in the region of 1400-750 cm^{-1} is complicated due to the overlap of bands related to both the vibrations of phthalocyanine fragments and fragments of chloride ions.

Table 3. Attributions in the IR spectra of metalloctachlorophthalocyanines complexes of MPcCl_8

Attributions	Connection	
	CuPcCl_8	CoPcCl_8
valence vibrations of C-H bonds (weak intensity)	3080 3086	3080
fluctuations of C-C bonds	1629	1604
β -oscillations of C-H bonds	1506 1500	1522 1524
Fluctuations of groupings -C=C-N=	1384 1415	1389 1418
β - fluctuations C-H-bonds under plane deformation	1071	1088 1074
of C-C-bonds vibrations in the aromatic ring	955 889	966 888

of C-N-bonds vibrations	783 745	784 751
γ - oscillations of out-of-plane deformation C-H - bonds	744 732 661	750 708 661

Based on the results of spectral studies of the compounds presented by us, the substitution of chlorine atoms in benzene rings leads to a bathochromic shift of all absorption bands, the intensity of long-wavelength bands when comparing the MPc spectra with MPcCl8 spectra gradually decreases.

The bathochromic band shift is associated with electronic transitions in the macrocycle. This process can be explained by the expansion of the conjugated phthalocyanine system due to the inclusion of the p-electrons of the chlorine atom in the π -electron system of benzene rings and macro rings. The expansion of the conjugate system and the corresponding effect are noticeable with the manifestation of 8 chlorine atoms, in this case, despite the sufficiently high autonomy of the benzene rings of macrocyclical chromophores, the π -electrons of chlorine atoms lead, in all probability, to a significant increase in the π -electron density of the macrocircle.

The coupling effect of the chlorine atom is associated with its specific and powerful auxochromic effect on isolated chromophores of benzene phthalocyanine. Short-wave bands associated with transitions in benzene rings of protonated phthalocyanine experience a shift under the influence of bathochromic substitution.

Each of the methods of synthesis of chloro-substituted phthalocyanine complexes of cobalt(II), copper(II) - the method of solid-phase synthesis and the method using 1,2,4-trichlorobenzene as a solvent - has certain advantages and disadvantages.

The advantage of the solid-phase synthesis method is that it is less time-consuming (6-8 hours), and the resulting product does not require additional purification.

The synthesis process in the 1,2,4-trichlorobenzene medium is complicated by the need for constant monitoring of the pH of the medium. The synthesis time is significantly increased compared to the solid-phase method - from 10-27 hours to 3 days. To a noticeable extent, cyanuric acid is formed, which requires a significant amount of time to clean the final product. The advantage of the solvent-based method is a slight increase in the yield and degree of purity of the final product.

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Кобальт (II) және мыс (II) фтаоцианинмен октохлоралмастырылған кешендерінің синтезі

Аңдатпа. Кобальт(II) және мыс(II)-нің октохлорорынбасқанфталоцианиндермен түзетін комплекстерінің синтезінің модифицирленген әдістері келтірілген және оларды тұз қышқылымен (10%), натрий гидроксидімен (2м), содан кейін қайтадан тұз қышқылымен (10%) тазартқаннан кейін, еріткіш ретінде 1,2,4-трихлорбензолдағы пиридинмен өңдеуге негізделген тазарту әдістері келтірілген. Нәтижесінде Cu(II) тазарту дәрежесіне 99%қол жеткізілді әдебиетте белгілі әдістерді қолданған кезде ең жақсы нәтижеге қарсы 93%, Co(II) үшін тазалық дәрежесі 88%-ға қарсы 98% құрады. Өнімнің шығымдылығы сипатталған белгілі әдістерге қарағанда жоғары және Co(II) 78, Cu(II) 43 құрады. Пиридинмен өңдеудің соңғы кезеңінен кейін біз физика-химиялық әдістермен анықтадық, өнімнің құрамынан қоспалар, соның ішінде цианур қышқылы, мочевианың ыдырау жойылады, және thermovomturflashea 1112 анализаторында жүргізілген көміртекке, сутекке, азотқа элементтік талдау нәтижелері жойылатыны анықталды. Nicolet IR-200, УК- спектрофотометріндегі KBr таблеткаларында жазылған, күкірт қышқылындағы - октахлорметаллфталоцианин ерітінділерінің ультракүлгін спектрлері Varian UV-VIS / Nir спектрометрінде түсірілген.

Түйін сөздер: фталоцианиндер, металлофталоцианиндер, инфрақызыл спектрлер.

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Синтез октохлорзамещенных комплексов кобальта(II) и меди (II) с фталоцианином

Аннотация. Приведены модифицированная методика синтеза октахлорометаллофталоцианинов и способы их очистки, основанные на их последовательной обработке соляной кислотой (10%), гидроксидом натрия (2М), затем снова соляной кислотой (10%), пиридином в 1,2,4-трихлорбензоле в качестве растворителя. В результате была достигнута степень очистки комплексов ионов Cu(II) 99% против наилучшего результата при использовании известных в литературе способов 93%, для Co(II) степень чистоты составила 98% против 88%. Выход продуктов также выше, чем при описанных известных способах, и составил Co(II) 78, Cu(II) 43. Физико-химическими методами установлено, что после заключительной стадии очистки - обработки пиридином удаляются примеси, в том числе циануровая кислота, продукт разложения мочевины, результаты элементного анализа на углерод, водород, азот, проведенного на анализаторе ThermovomTurFlashEA 1112 комплексы кобальта (II), меди (II) с фталоцианин, назначение полос ИК-спектров, записанных в таблетках KBr на спектрофотометре Nicolet IR-200 FT - IR, УФ-спектры растворов металлооктахлорфталоцианинов в серной кислоте, снятые на спектрометре Varian UV - Vis/NIR.

Ключевые слова: фталоцианины, металлофталоцианины, инфракрасный спектр.

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