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YNTHESIS AND X-RAY DIFFRACTION ANALYSIS OF A HIGH-INTENSITY COPPER PHTHALOCYANINE PIGMENT CONTAINING NITROGEN AND SULFUR

Yusupov Muzafar [1], ***Mukxlisa Robiddinova*** [1], ***Doniyor Sherkuziyev*** [1]

[1] Department of Chemical Engineering, Namangan State Technical
University, Republic of Uzbekistan, Namangan region

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Abstract

The synthesis and characterization of a novel high-intensity copper phthalocyanine (CuPc) pigment incorporating nitrogen and sulfur within its molecular framework are presented in this study. The pigment is distinguished by the formation of chelate complexes that contribute to the stabilization of the macroheterocyclic structure and enhance its optical performance. The synthetic approach employed a carefully controlled process, ensuring the incorporation of heteroatoms into the phthalocyanine ring system.

Comprehensive structural analysis was conducted using advanced physicochemical methods, with a particular focus on X-ray diffraction (XRD) techniques. The diffraction peak profiles revealed well-defined crystalline features, accompanied by amorphous domains, confirming both the successful integration of heteroatoms and the composite nature of the synthesized pigment. These findings indicate that nitrogen and sulfur substitution significantly influences the crystallographic arrangement and electronic distribution within the macrocyclic lattice.

The study further highlighted the contribution of organic components that coexist within the pigment, providing insight into their role in stability and spectral behavior. The presence of nitrogen- and sulfur-containing moieties was shown to play a pivotal role in modulating the electronic transitions, as supported by spectroscopic evaluations. These structural modifications have a direct impact on the pigment's optical intensity, chemical stability, and potential multifunctionality.

Overall, this work not only advances the understanding of copper phthalocyanine derivatives but also opens new perspectives for their practical use in high-performance functional materials. Potential applications include optoelectronic devices, heterogeneous catalysis, photovoltaic systems, and advanced pigment technologies, where enhanced structural integrity and tunable electronic properties are of critical importance.

Keywords: *copper phthalocyanine, nitrogen-sulfur pigments, chelate complexes, X-ray diffraction, optical properties, functional materials*

Introduction

Colorants, including dyes and pigments, have been utilized extensively since ancient times for decorative, protective, and functional purposes. Their application spans a wide range of fields, from art and textiles to construction and industrial manufacturing. In recent decades, the demand for paints and coatings has grown substantially in response to the rapid pace of construction and infrastructural development both worldwide and within our Republic. This increasing demand has consequently intensified the need for high-quality raw materials, particularly pigments, which serve as the essential coloring agents in paint and coating formulations (Yusupov M., Kayumjanov O., 2024).

Pigments play a crucial role not only in imparting color but also in enhancing the durability, weather resistance, and overall performance of paint products. The advancement of pigment chemistry has allowed for the creation of materials with improved optical properties, higher stability, and multifunctionality, thus expanding their role in modern coating technologies. As the construction industry continues to expand, the strategic importance of developing efficient, sustainable, and cost-effective pigment systems becomes increasingly evident (Yusupov, M., & Kadirkhanov, J., 2023).

Phthalocyanines (Pcs) are planar, highly conjugated macroheterocyclic compounds that exhibit strong structural and functional resemblance to porphyrins. Their discovery in the early 20th century revolutionized the pigment industry, and since then, phthalocyanines have been established as one of the most stable classes of synthetic dyes (Lever, A. B. P., 1990). The unique physicochemical properties of these molecules-such as intense absorption in the visible region (Q-band), high molar extinction coefficients, and remarkable thermal and chemical stability – have positioned them as versatile candidates in both traditional and emerging technological domains (Linstead, R. P., 1934; Kadish, K. M., & Smith, K. M. (Eds.). 2003).

Among metallophthalocyanines, copper phthalocyanines (CuPcs) stand out as industrially significant pigments due to their vivid blue-green coloration and resistance to photobleaching. Beyond their conventional use in paints, inks, and coatings, CuPcs have attracted growing interest in advanced applications, including organic photovoltaics, gas sensing, and electrocatalysis (Bottari, G., et al., 2010). Recent advances in coordination chemistry and synthetic design have facilitated the incorporation of heteroatoms such as nitrogen and sulfur into the phthalocyanine macrocycle. These modifications have been shown to profoundly influence the electronic distribution within the macrocycle, enhancing intermolecular π–π stacking, tuning HOMO–LUMO energy levels, and improving solubility and processability (Dini, D., & Hanack, M., 2006; Han, J., et al., 2024).

The structural elucidation of such heteroatom-modified CuPcs often relies on X-ray diffraction (XRD), which provides critical insights into crystallinity, molecular packing, and polymorphic phases. For example, nitrogen-substituted phthalocyanines typically adopt more ordered packing arrangements, whereas sulfur-substituted analogues introduce distortions that modulate intermolecular interactions and lead to changes in optical and catalytic properties (Claessens, C. G., et al., 2002). Complementary spectroscopic techniques such as infrared (IR) spectroscopy and UV–Vis absorption further confirm the presence of characteristic functional groups and conjugated electronic systems (Dinçer, H. A., et al., 2007).

Several studies have emphasized the synergistic role of nitrogen and sulfur atoms in improving both the optical intensity and the structural rigidity of copper phthalocyanines. Zhan et al. (2014) demonstrated that simultaneous substitution of these heteroatoms significantly enhances the material's applicability in optoelectronic devices, owing to improved electron mobility and tailored absorption profiles (Zhan, R., et al., 2014). Moreover, Claessens et al. (2002) highlighted that such structural modifications not only enrich the optical features but also contribute to catalytic activity in redox reactions, making these pigments multifunctional materials.

Despite these advancements, gaps remain in fully understanding the correlation between structural modifications and functional performance. While nitrogen and sulfur substitution has been proven to alter crystallinity and intermolecular interactions, systematic studies linking these modifications to large-scale performance in device applications are still scarce. Hence, further exploration of the structure–property relationship in heteroatom-containing copper phthalocyanines is essential for advancing their practical utility in optoelectronics, catalysis, and next-generation pigment technologies (Abbaspour, A., et al., 2013).

Research method

For the high-temperature synthesis, 1 mol of phthalic anhydride and 5 mol of urea were placed into a 250 mL heat-resistant beaker and heated in an HP-550-S electric furnace under a fume hood at approximately 140 °C until complete melting occurred. Subsequently, 1 mol of copper(I) chloride was added at the same temperature. Upon stirring, the mixture changed its color to light blue. Continuous stirring was maintained, followed by the addition of 1 mol of ammonium sulfate and ammonium heptamolybdate as a catalyst. The reaction mixture was thoroughly homogenized with a glass rod and heated until a uniform mass was obtained.

Initially, the reagents fully liquefied and then transformed into a viscous mass. The reaction was interrupted, cooled to room temperature, and then maintained in a SNOL furnace for 3 h at a temperature up to 260 °C. This treatment yielded a dark-blue porous powder. Concentrated sulfuric acid (<90%) was gradually added at 80 °C under a fume hood until a paste-like consistency was achieved. During this stage, irritating and suffocating gaseous by-products were released, at which point the process was halted and hot water was carefully introduced. As a result, unreacted starting materials and intermediate products were transferred into the aqueous phase.

After standing, a dark bluish precipitate together with a partially blue solution was observed. The precipitate was collected into a larger vessel, and the acidic medium was neutralized with distilled water. The pigment was then filtered through a Büchner funnel and dried at 80 °C in a ШС-8001 ШСУ dryer.

Results analysis

Thus, the exothermic reaction leading to the formation of the phthalocyanine pigment containing nitrogen, sulfur, and copper (CuSPc) was completed. The target pigment was synthesized with a theoretical yield of 69.3%. Single-crystal X-ray diffraction (SCXRD) is a powerful and widely applied analytical technique for determining the three-dimensional atomic structure of crystalline materials. This method has become indispensable across multiple disciplines, including chemistry, biology, physics, and materials science, due to its ability to reveal the precise atomic arrangement within molecules, minerals, metals, and complex biological macromolecules such as proteins and DNA.

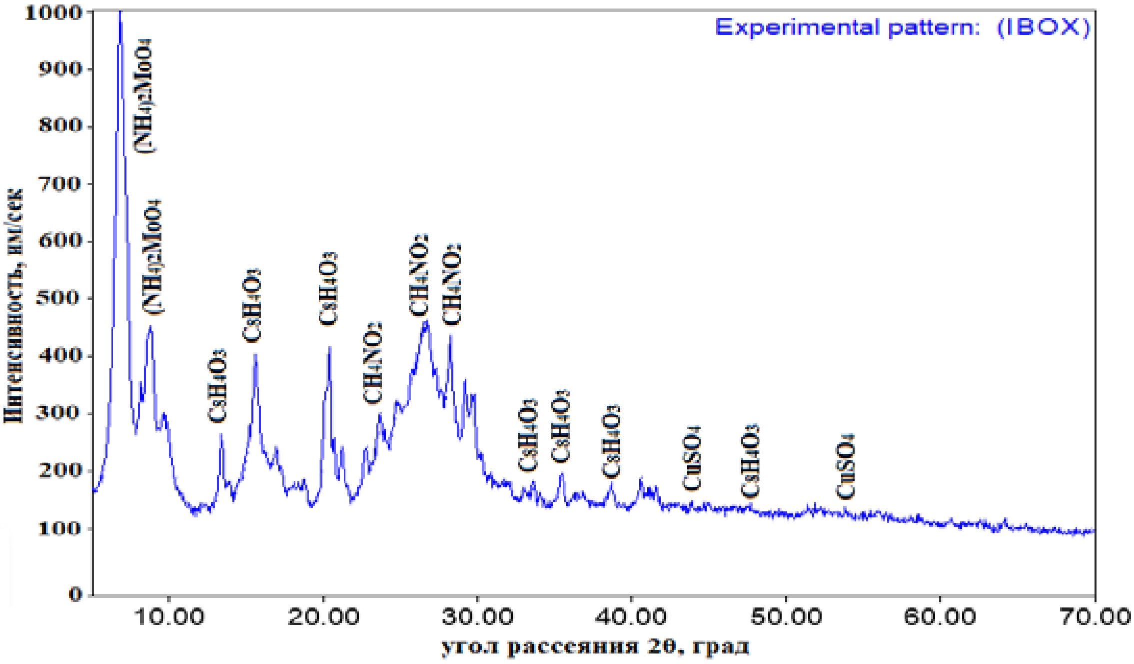
The primary strength of X-ray crystallography lies in its ability to provide accurate structural information at the atomic scale. This makes the technique essential not only for molecular characterization but also for the discovery and development of new compounds. The principle of the method is based on the diffraction of X-rays by the periodic array of atoms within a crystal lattice. The diffraction pattern produced carries detailed information about the internal crystal structure. Through mathematical modeling and computer-assisted analysis, the atomic positions can be precisely determined. Figure 1 presents the results of the X-ray analysis, showing the presence of functional groups in the structure of the synthesized copper phthalocyanine pigment.

The diffractogram displays several distinct peaks corresponding to both the target product and residual secondary phases.

At lower diffraction angles (7–10°), intense peaks corresponding to ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$ were observed, indicating the partial retention of the catalyst within the pigment matrix. In the region between 15–40°, characteristic reflections assigned to intermediate organic compounds such as $C_8H_{10}O_3$ and $CH_4N_2O_2$ were detected. These signals suggest that certain organic precursors or by-products were not fully decomposed during the synthesis.

At higher angles (>40°), diffraction peaks corresponding to copper sulfate ($CuSO_4$) were identified, together with minor contributions from residual organic species. The presence of $CuSO_4$ implies that a portion of copper remained bonded in the form of sulfate salts rather than being completely integrated into the phthalocyanine framework.

Figure 1. *X-ray diffraction (XRD) analysis of the synthesized copper phthalocyanine pigment (CuSPc)*



Overall, the XRD results confirm the successful formation of copper phthalocyanine (CuPc) pigment, as evidenced by the dominant crystalline features associated with phthalocyanine derivatives. However, the detection of catalyst residues $(NH_4)_6Mo_7O_{24}$, unreacted intermediates, and CuSO4 side phases indicates that the reaction did not proceed to full completion under the applied conditions. Optimization of synthesis parameters, particularly temperature control and purification steps, may further improve the phase purity of the final pigment.

Conclusion (discussion)

The X-ray diffraction (XRD) analysis of the synthesized copper phthalocyanine pigment (CuSPc) clearly demonstrates the successful formation of the target crystalline phase, confirming the efficiency of the applied synthesis approach. Nevertheless, the diffractogram also revealed the presence of several secondary phases, including residual ammonium heptamolybdate, partially undecomposed organic intermediates, and copper sulfate. These findings indicate that the catalytic agent was not completely eliminated, and a fraction of the organic precursors and copper salts persisted in the final product, suggesting that the reaction did not reach full completion under the current experimental conditions.

The coexistence of the desired CuSPc phase with secondary by-products may negatively affect the pigment's structural homogeneity and potentially influence its optical, electronic, and chemical stability characteristics. Therefore, to achieve higher phase purity and enhanced performance, further optimization of the synthesis parameters is required. Particular attention should be directed toward more precise temperature control, extended reaction time, and improved purification protocols. Such refinements are expected to not only eliminate unwanted residues but also promote the complete incorporation of copper into the phthalocyanine framework, thereby ensuring superior functional properties of the resulting pigment for advanced material applications.

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Contact: muz.yusupov90@gmail.com; robiddinovamuhlisa@gmail.com;
doniyor_8184@mail.ru