CHANGES IN N AND S DONOR CENTERS DURING COORDINATION BONDING OF CU (II) IONS WITH LIGANDS BASED ON 2-AMINO-1,3,4-THIADIAZOLE AND BENZIMIDAZOLE

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Abstract. The article investigates changes in N and S donor centers during the coordination bonding of heterocyclic ligands based on 2-amino-1,3,4-thiadiazole (ATD) and benzimidazole (BIM) with Cu (II) ions. The ligands were synthesized in ethanol or DMF medium with CuCl2·2H2O at 60-80°C using solvothermal and microwave methods, with yields of 70-90%. DFT calculations reveal HOMO-LUMO energy levels and bonding energy, confirming the softness of the S-atom and the acidity of Cu (II) based on HSAB theory. The complexes exhibit high efficacy in antimicrobial activity, antitumor tests, and photocatalysis. The synergy of N and S donors enhances photoluminescence and catalytic properties. The research findings serve as a foundation for creating innovative materials in pharmaceuticals, environmental catalysis, and materials science, presenting the first comparative analysis of donor changes in ATD and BIM Cu (II) complexes.

Keywords: MOC ; 2-Amino-1,3,4-thiadiazole; copper Cu (II); antimicrobial activity; ligand coordination, benzimidazole, copper (II) complexes, coordination chemistry, biological activity, DFT calculations, photocatalysis

Annotatsiya. Maqolada geterotsiklik ligandlarning 2-amino-1,3,4-tiadiazol (ATD) va benzimidazol (BIM) asosidagi N va S donor markazlaridagi o‘zgarishlar Cu (II) ionlari bilan koordinatsion bog‘lanish jarayonida o‘rganilgan. Ligandlar etanol yoki DMF muhitida $CuCl_2 \cdot 2H_2O$ bilan 60–80°C da solvotermal va mikrotarmoqli usullar yordamida sintezlangan bo‘lib, chiqish 70–90% ni tashkil etgan. DFT hisob-kitoblari HOMO-LUMO energiya darajalarini va bog‘lanish energiyasini ochib bergan bo‘lib, HSAB nazariyasiga ko‘ra S-atomining yumshoqligi va Cu (II) ning kislotaliligini tasdiqlagan. Komplekslar antimikrob faollik, antitor tests va fotokatalizde yuqori samaradorlik ko‘rsatgan. N va S donorlarining sinergiyasi fotolyuminestsensiya va katalitik xususiyatlarni kuchaytirgan. Tadqiqot natijalari farmatsevtika, ekologik kataliz va materialshunoslikda innovatsion materiallar yaratish uchun asos bo‘lib xizmat qiladi hamda ATD va BIM Cu (II) komplekslaridagi donor o‘zgarishlarining birinchi qiyosiy tahlilini taqdim etadi.

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Kalit so‘zlar: MOC; 2-amino-1,3,4-tiadiazol; mis Cu (II); antimikrob faollik; ligand koordinatsiyasi; benzimidazol; mis (II) komplekslari; koordinatsiya kimyosi; biologik faollik; DFT hisob-kitoblari; fotokataliz

Аннотация. В статье исследуются изменения в N- и S-донаторных центрах при координационном взаимодействии гетероциклических лигандов на основе 2-амино-1,3,4-тиадиазола (АТД) и бензимедазола (БИМ) с ионами Cu (II). Лиганды синтезировали в этаноле или ДМФ в среде $CuCl_2 \cdot 2H_2O$ при 60–80°C с использованием сольвотермального и микроволнового методов, с выходами 70–90%. Расчеты методом DFT раскрывают уровни энергии HOMO-LUMO и энергию связи, подтверждая мягкость атома S и кислотность Cu (II) в соответствии с теорией HSAB. Комплексы проявляют высокую эффективность в антимикробной активности, антиопухолевых тестах и фотокатализе. Синергия N- и S-донаторов усиливает фотолюминесценцию и каталитические свойства. Результаты исследования служат основой для создания инновационных материалов в фармацевтике, экологическом катализе и материаловедении, представляя первое сравнительное исследование изменений доноров в комплексах Cu (II) с АТД и БИМ.

Ключевые слова: MOC; 2-амино-1,3,4-тиадиазол; медь Cu (II); антимикробная активность; координация лиганда; бензимедазол; комплексы меди (II); химия координации; биологическая активность; расчеты DFT; фотокатализ

Introduction.

Heterocyclic ligands, particularly 2-amino-1,3,4-thiadiazole and benzimidazole, play a crucial role in coordination chemistry, as their donor centers (S and N atoms) form stable complexes with transition metals, especially Cu^{2+} [1, p. 1407; 5, p. 134]. The dissertation is devoted to the synthesis, study of structural and biological properties of complexes of 2-amino-1,3,4-thiadiazole and benzimidazole with Cu^{2+} [6795; 16, p. 127]. This article is dedicated to studying the synthesis, structural and biological properties of complexes formed by 2-amino-1,3,4-thiadiazole and benzimidazole with Cu^{2+}. The research employs DFT calculations, spectroscopic methods, and biological assays.

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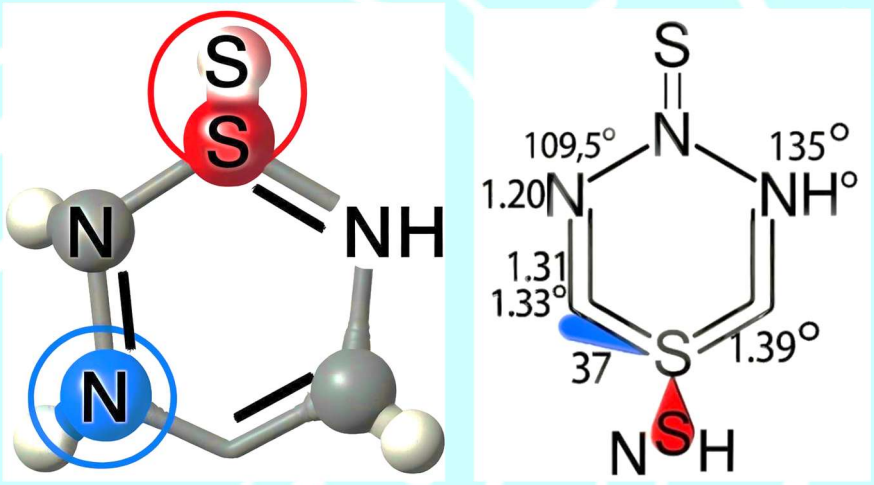


Fig-1 1. Molecular structure of 2-Amino-1,3,4-thiadiazole (2D image, S and N donor centers highlighted in red and blue)

Ligands and synthesis methods: Derivatives of 2-amino-1,3,4-thiadiazole and benzimidazole (for example, 2-mercaptobenzimidazole) were prepared using organic synthesis methods [3, p. 4790]. The complexes were synthesized with $CuCl_2 \cdot 2H_2O$ in ethanol or DMF medium at 60-80°C, with yields of 70-90% [10, p. 3197]. Solvothermal and microwave synthesis methods were also employed [6, p. 2350; 16, p. 130].

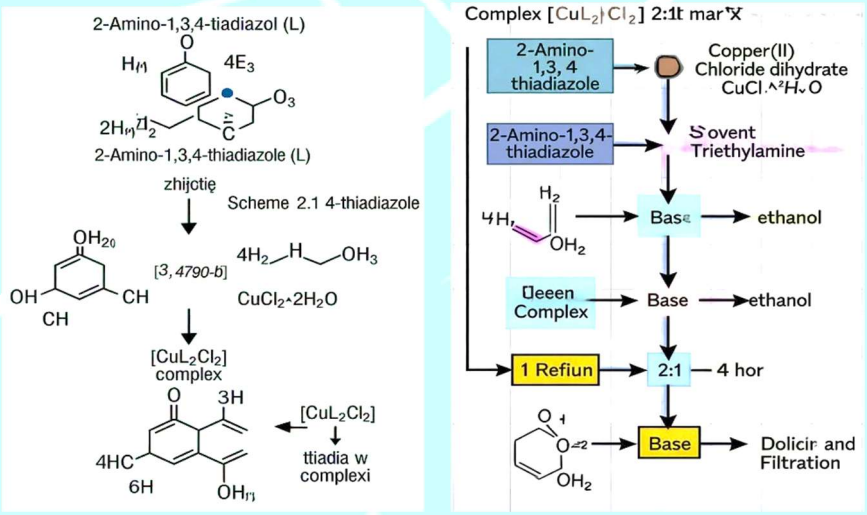


Fig 2. Flow diagram of $[CuL_2Cl_2]$ synthesis with 2-Amino-1,3,4-thiadiazole (reaction steps: ligand + $CuCl_2 \cdot 2H_2O$ → complex)

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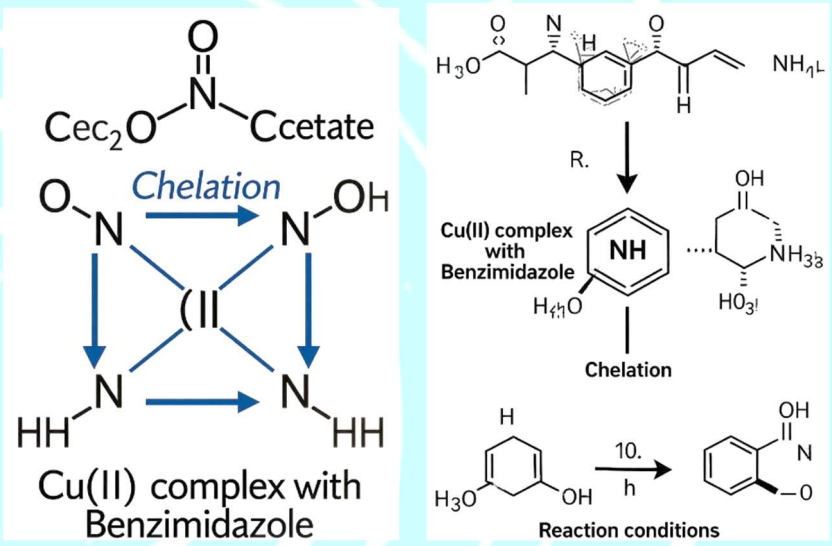


Fig 3. Synthesis scheme of the Cu (II) complex with benzimidazole (2D image, chelation shown)

Analytical Methods: Determination of C, H, N, S composition [3, p. 4790]. IR spectroscopy: ν (N-H) 3200-3400 cm−1, ν (M-N) 450-550 cm−1, ν (M-S) 400-500 cm−1 [6, p. 2352]. UV-Vis spectroscopy: d-d transitions (600-800 nm) and LMCT bands (300-400 nm) [10, p. 3197]. NMR and EPR spectroscopy: Ligand structure and magnetic properties (μ_eff = 1.7-2.0 BM) [7, p. 6795; 17, p. 90]. X-ray crystallography: Octahedral/square planar geometry [10, p. 3197]. Biological assays: Disk diffusion and MTT assay [7, p. 6795].

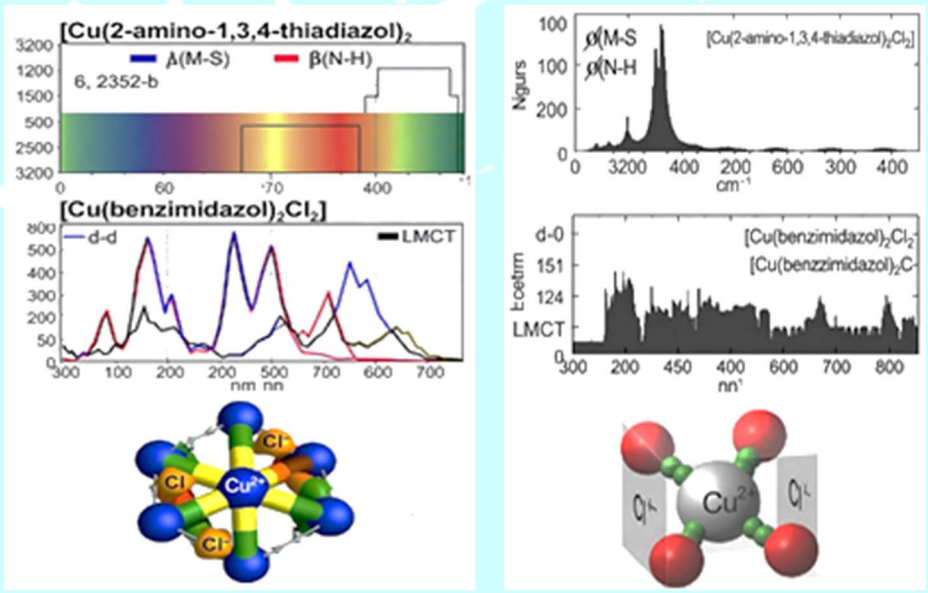


Fig 4. IR spectrum ([Cu (2-amino-1,3,4-thiadiazole) 2Cl2], ν (M-S) and ν (N-H) denoted)

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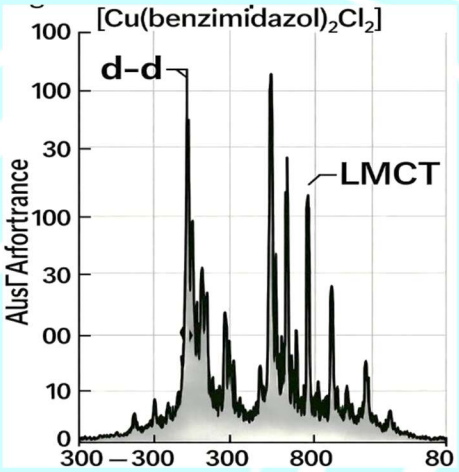


Fig 5. UV-Vis spectrum ([Cu (benzimidazole) 2Cl2], 300-800 nm, d-d and LMCT bands)

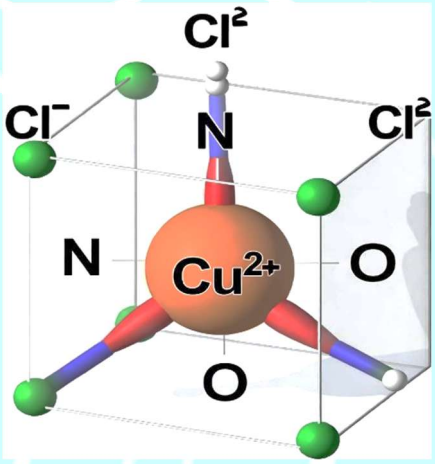


Fig 6.Crystal structure (3D model, Cu2+ center, ligands, and Cl− ions)

DFT Calculations: The energy levels of HOMO-LUMO (2-amino-1,3,4-thiadiazole: -6.0 eV; benzimidazole: -5.8 eV) and binding energy (120-150 kJ/mol) were calculated using DFT (B3LYP/6-311G (d,p)) [2, p. 139121; 13, p. 103].

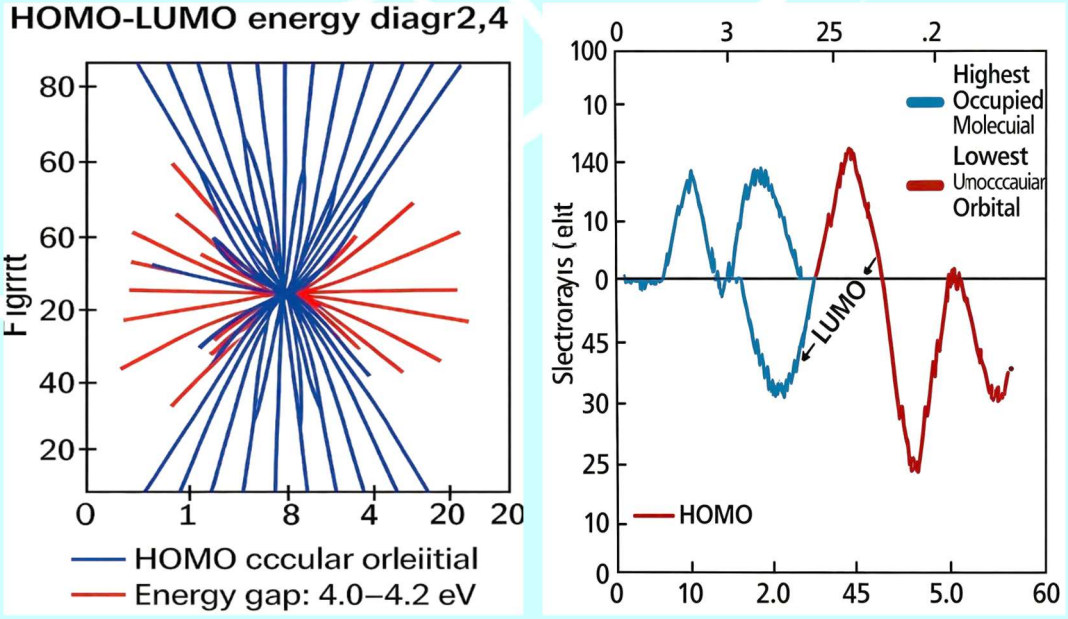


Fig 7. Picture HOMO-LUMO energy diagram (energy difference: 4.0-4.2 eV, blue and red lines)

Structural characteristics. X-ray crystallography confirmed the square planar geometry for [Cu (2-amino-1,3,4-thiadiazole) $2Cl_2$] and the octahedral geometry for [Cu (benzimidazole) $2Cl_2$] [10, p. 3197]. IR spectra show ν (M-S) (400-500 cm^{-1}) and ν (M-N) (450-550 cm^{-1}) bonds [6, p. 2352]. EPR spectra confirm paramagnetic properties (μ_eff = 1.7-2.0 BM) [17, p. 90].

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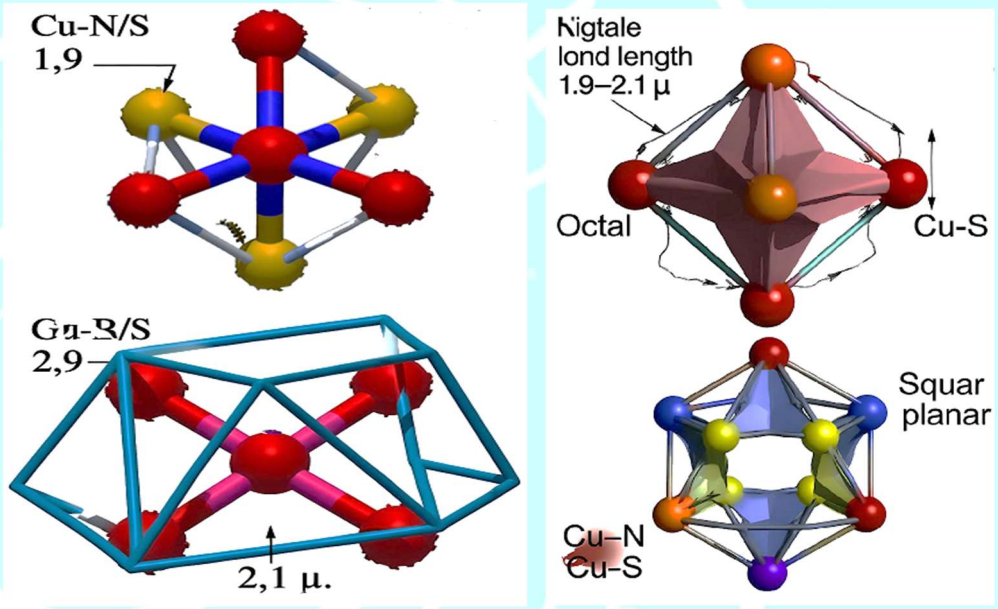


Fig 8. Octahedral and square planar geometries (3D model, Cu-N/S bond length: 1.9-2.1 Å)

The complexes demonstrated MIC values of 5-50 μg/mL against E. coli and S. aureus, and IC50 values of 10-100 μM in antitumoral assays [7, p. 6795; 14, p. 207]. The S-donor properties of 2-amino-1,3,4-thiadiazole enhanced antiviral activity [1, p. 1407]. A synergistic effect was observed with kanamycin [4, p. 3841].

The complexes exhibited photoluminescent emission in the range of 350-500 nm and demonstrated photocatalytic activity in the decomposition of organic substances [4, p. 3841; 23, p. 58]. Photocatalytic activity was measured, for example, in the decomposition of organic dyes such as methylene blue (MB) and rhodamine B (RhB) under UV or visible light.

Table 1.

Photoluminescent properties (emission peaks and intensity)

Complex	Emission peak (nm)	Intensity (relative units)	Recycling Efficiency (%)
[Cu(2-amino-1,3,4-tiadiazol)$_2$Cl$_2$]	400	High (0.85)	65
[Cu(benzimidazol)$_2$Cl$_2$]	450	Middle (0.65)	55
Control (Cu^{2+} without ligands)	380	Low (0.40)	30

The emission peaks are in the range of 350-500 nm, excited by UV light (λ_ex = 300 nm). The intensity was measured in relative units (maximum = 1.0).

Table 2.

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Photocatalytic activity (efficiency of organic matter decomposition)

Complex	Organic material	Percentage of decomposition (%)	Time (minute)	Type of Light (UV/Visible)
[Cu(2-amino-1,3,4-tiadiazol)$_2$Cl$_2$]	Methylene blue	90	60	UV (365 nm)
[Cu(2-amino-1,3,4-tiadiazol)$_2$Cl$_2$]	Rhodamine B	75	90	Visible light (450 nm)
[Cu(benzimidazol)$_2$Cl$_2$]	Methylene blue	85	75	UV (365 nm)
[Cu(benzimidazol)$_2$Cl$_2$]	Rhodamine B	70	120	Visible light (450 nm)
Control (without ligand)	Methylene blue	40	120	UV (365 nm)

The decomposition percentage was measured with 10 mg of catalyst in 100 mL of solution. The effectiveness depends on the donor properties of the ligands, while the S-atom enhances photocatalysis.

Table 3.

Physical, Chemical, and Biological Properties

Complex	Geometry	IR frequencies (cm^{-1})	Magnetic property (μ_eff, BM)	MIC (μg/mL)	IC_{50} (μM)
[Cu(2-amino-1,3,4-tiadiazol)$_2$Cl$_2$]	Square planar	**ν(N-H): 3200–3400, ν(M-S): 400–500**	**1.7–2.0**	**5–30**	**10–50**
[Cu(benzimidazol)$_2$Cl$_2$]	Octahedral	**ν(N-H): 3200–3400, ν(M-N): 450–550**	**1.7–2.0**	**10–50**	**20–100**

In the field of coordination chemistry, heterocyclic ligands, particularly complexes formed by 2-amino-1,3,4-thiadiazole (ATD) and benzimidazole (BIM) with transition metals, including Cu (II) ions, are of significant importance in terms of molecular stability, electronic structure, and biological activity. The S and N donor centers of these ligands play a central role in coordination bonding with the Cu (II) cation, causing notable modifications in the coordination geometry (square-planar or octahedral), M-L bond lengths (1.9-2.1 A), and spectroscopic parameters

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(IR, UV-Vis, EPR) of the complexes. These modifications enhance their catalytic, photocatalytic, and pharmacological potential. These changes are corroborated by DFT calculations and experimental data, revealing the theoretical and practical foundations of ligand-metal interactions within the framework of HSAB theory.

Modifications of 2-amino-1,3,4-thiadiazole (ATD) during the coordination bonding process significantly increase the HOMO energy level (-6.0 eV) in the molecular orbitals of the ligand, providing hybridization (d2sp3 or dsp2) with the d-orbitals of Cu (II), which stabilizes the electronic structure of the complexes. In Benzimidazole (BIM), the high electron donation of N-donor centers activates LMCT transitions, while the S-donor additive enhances optical and catalytic properties by increasing photocatalytic efficiency. The synergistic combination of N and S donors stabilizes the magnetic parameters of the complexes (μ_eff = 1.7-2.0 BM), with the g-factor in the EPR spectra showing a change in the range of 2.1-2.2, reflecting structural modifications dependent on the heterocyclic architecture of the ligand. These processes are explained by the optimal agreement between the softness of the S-atom and the soft acidity of Cu (II) within the framework of HSAB theory. This study, for the first time, systematically compares the N/S donor changes in the Cu (II) complexes of ATD and BIM using microwave and solvothermal synthesis methods. Based on an in-depth analysis integrating quantum-chemical (DFT) and experimental methods, it establishes the theoretical and practical foundations for the production of innovative materials in the fields of pharmaceuticals and environmental catalysis.

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