NEW PYRIDINE DERIVED HYDRAZONES AS OPTICAL SENSORS FOR METAL CATIONS

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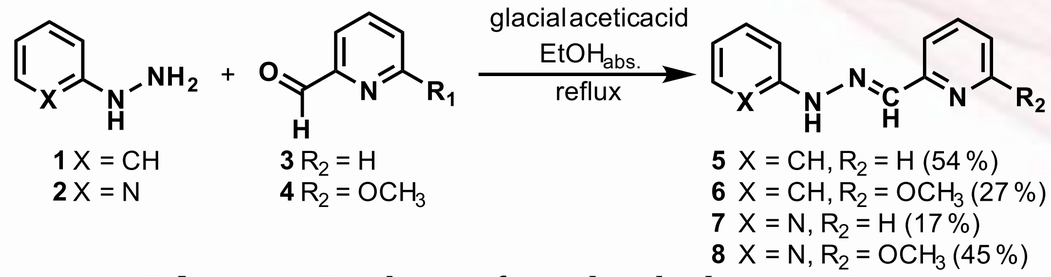
INTRODUCTION

Hydrazone derivatives and their metal complexes have attracted considerable scientific interest due to their versatile chemical properties and broad range of potential applications. Owing to the presence of nitrogen, hydrazones can act as efficient chelating ligands and readily coordinate various metal ions, forming stable metal complexes with diverse structural and physicochemical properties. Hydrazone ligands and their metal complexes have been extensively investigated for their biological and pharmacological activities, including antimicrobial, antioxidant, anticancer, and anti-inflammatory effects. [1, 2] Metal coordination can significantly influence the electronic and structural properties of hydrazone ligands and may enhance or modify their biological activity. Their pronounced chromogenic and fluorogenic properties enable their use as sensitive molecular probes for the selective detection and quantitative determination of trace metal ions by spectroscopic methods. Changes in absorption or fluorescence properties upon metal coordination provide a convenient approach for the development of highly sensitive metal-ion sensing systems. [3]

SYNTHESIS

The hydrazone derivatives were synthesized via an acid-catalyzed condensation reaction between the corresponding hydrazine derivatives and pyridine-based aldehydes in absolute ethanol under reflux. The reaction proceeds through nucleophilic addition to the aldehyde carbonyl group, followed by dehydration to afford the characteristic azomethine (C=N) bond.



Scheme 1. Synthesis of pyridine hydrazones **5**–**8**

UV/Vis SPECTROSCOPIC CHARACTERIZATION

Metals such as K, Zn, Co, Cu and Fe, as essential biogenic elements, play vital roles in the human body, and their deficiency or excess can lead to various pathological effects. [4] UV/Vis spectroscopic characterization in several organic solvents with different polarity and titrations with aqueous solutions of chosen metal cations (K^+, Co^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+}) were performed to evaluate the potential applicability of the synthesized hydrazones for metal ion sensing purposes. [5]

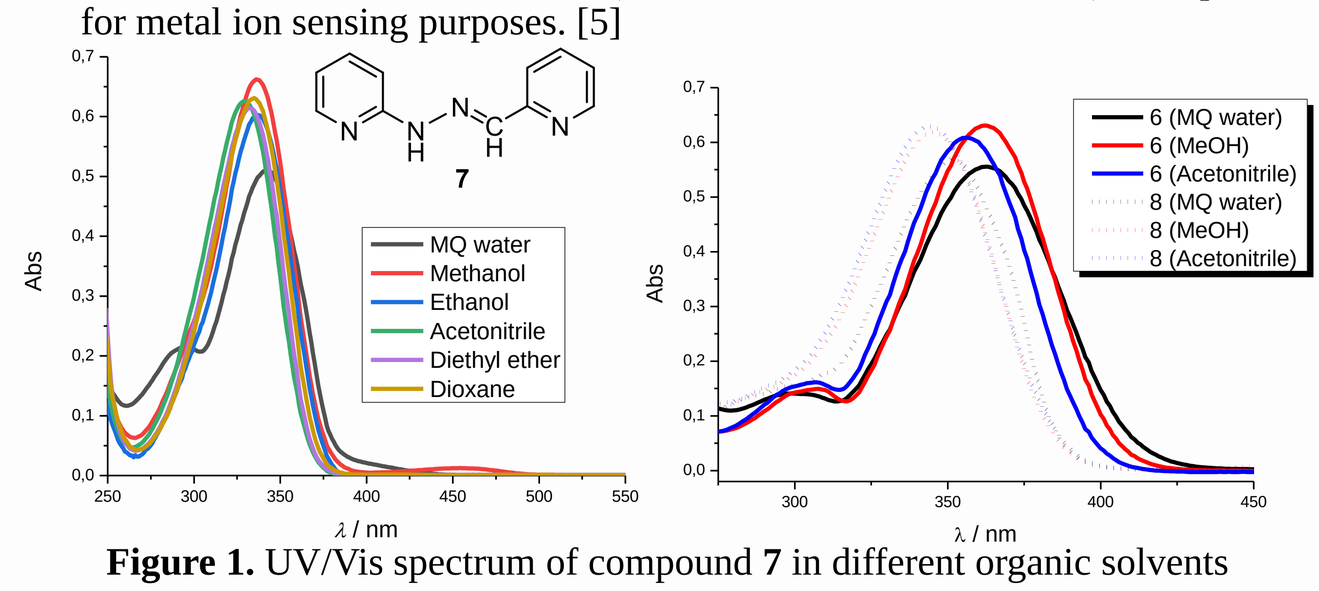


Figure 1. UV/Vis spectrum of compound **7** in different organic solvents and comparable spectrum of **6** and **8**.

Synthesized hydrazones showed variations in λ_{max} depending on the type of organic solvent. Comparison of compounds **6** and **8** revealed a pronounced influence of the additional pyridine nitrogen on their UV/Vis absorption properties. Compound **8**, which contains two pyridine moieties, showed a hypsochromic shift of the main absorption band in all tested solvents. This indicates that the replacement of the phenyl ring with a pyridine ring significantly affects the electronic distribution and solute-solvent interactions within the hydrazone system. (Figure 1.)

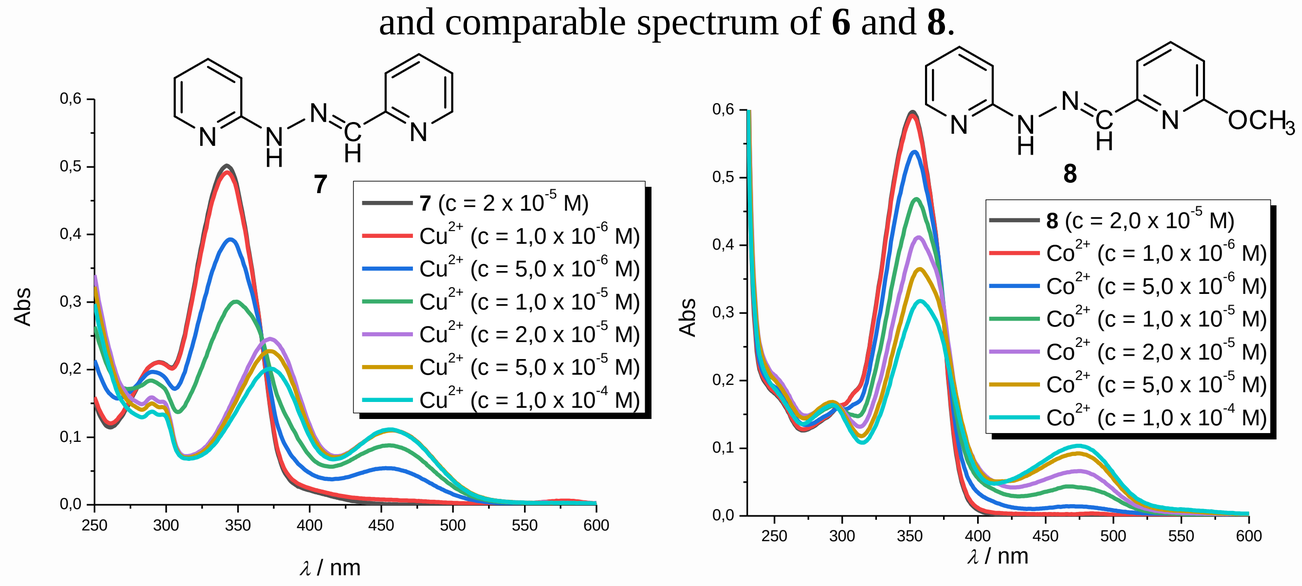


Figure 2. UV/Vis titrations of compound **7** with titrations with aqueous solution of Cu^{2+} and **8** with aqueous solution of Co^{2+}.

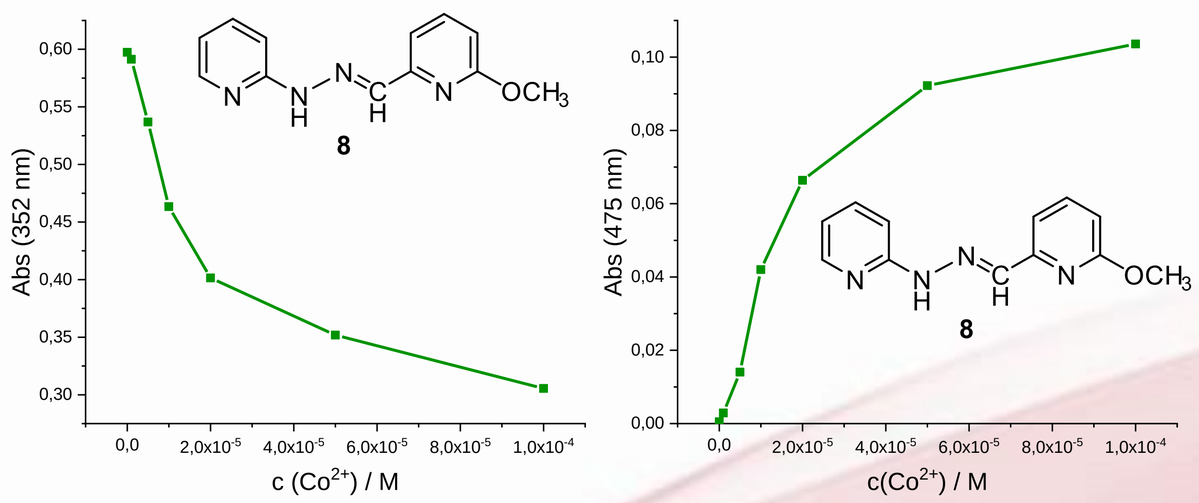


Figure 3. Dependence of the absorbance of compound **8** on the [Co^{2+}] at the absorption maxima of 352 and 475 nm.

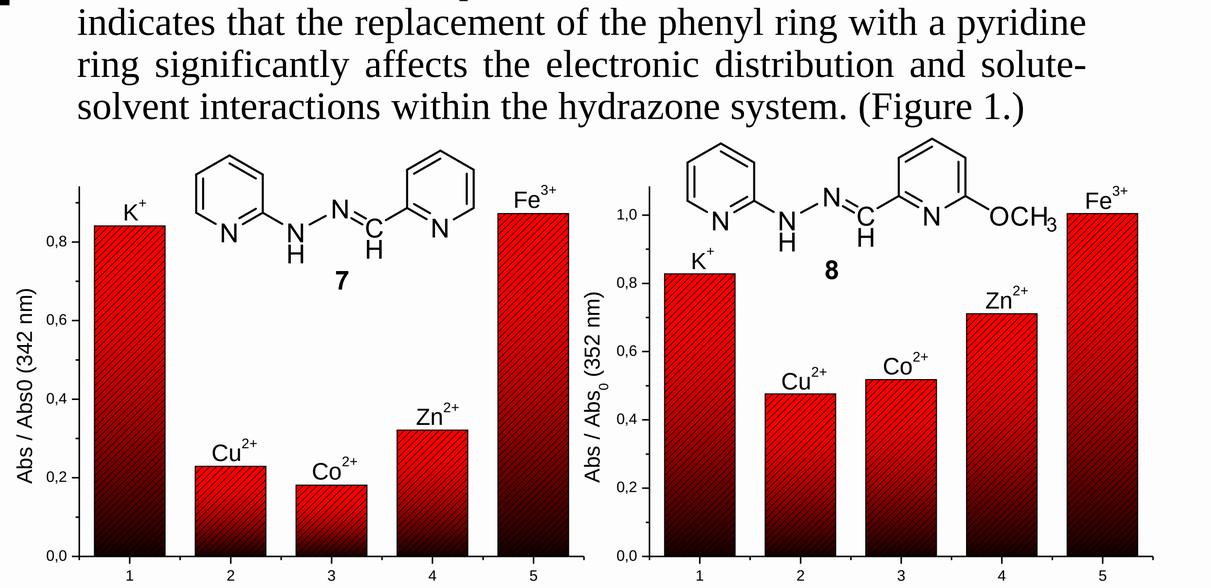


Figure 6. The selectivity of compounds **7** and **8** towards different cations.

CONCLUSION

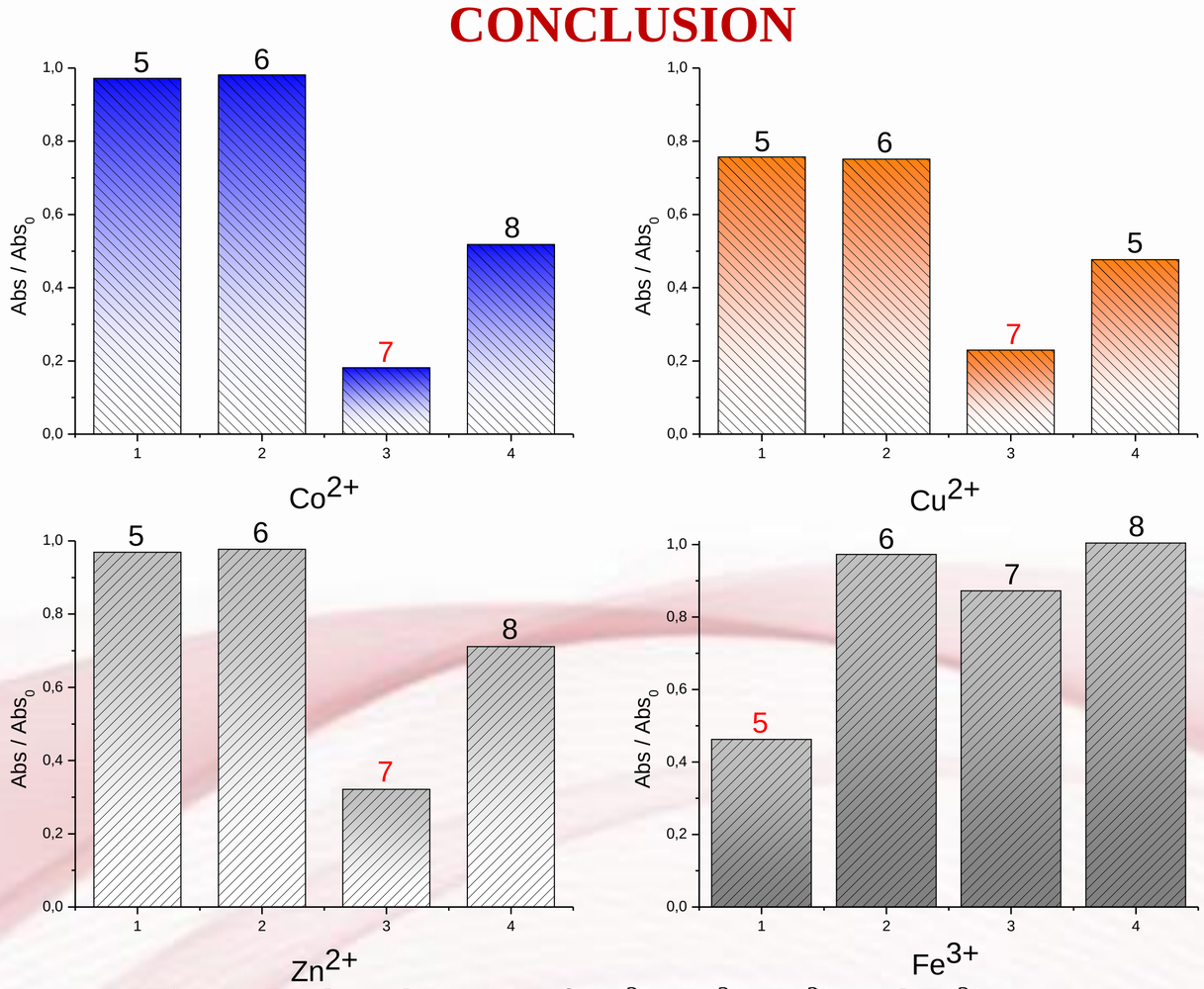


Figure 7. The selectivity of Co^{2+}, Cu^{2+}, Zn^{2+}, and Fe^{3+} cations towards compounds **5-8**.

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