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Synthesis And Spectral Characterization Of Diphenylthiocarbazide For Use As A Selective Reagent In Spectrophotometric Metal Ion Detection

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ABSTRACT

Diphenylthiocarbazide (DPTC) is a sulfur- and nitrogen-containing organic ligand that holds significant potential as a selective analytical reagent for metal ion detection. In this study, DPTC was synthesized through a condensation reaction between phenyl isothiocyanate and hydrazine hydrate under controlled conditions. The synthesized compound was purified and structurally characterized using UV-Visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (1H NMR), elemental analysis (CHNS), and melting point determination. The presence of key functional groups including thiocarbonyl and aromatic amines confirmed the molecular integrity of DPTC. Spectral studies indicated that DPTC exhibits strong absorbance in the visible range, making it a suitable chromogenic reagent for colorimetric complexation with transition metal ions. Preliminary investigations demonstrated its high affinity and selectivity for copper(II) ions, forming a stable colored complex under mildly acidic to neutral pH conditions. The observed λmax and molar absorptivity values suggest that DPTC can serve as an effective ligand for spectrophotometric detection of trace metal ions. The results pave the way for further application of DPTC in environmental monitoring, pharmaceutical assays, and industrial quality control settings.

Keywords: Diphenylthiocarbazide (DPTC), Spectrophotometry, Metal Ion Detection, Ligand Synthesis, Chromogenic Reagent, Copper(II) Complexation, UV-Vis Spectroscopy, FTIR Analysis, Selective Detection

1. INTRODUCTION

The accurate and selective detection of trace metal ions in environmental, biological, and industrial samples is a fundamental concern in analytical chemistry. With increasing awareness of heavy metal toxicity and environmental contamination, the demand for cost-effective, sensitive, and selective analytical methods has intensified. Spectrophotometry, particularly UV-Visible spectrophotometry, remains one of the most widely used techniques for trace metal analysis due to its simplicity, rapid response, affordability, and compatibility with portable instrumentation (Shar et.al., 2002). At the heart of spectrophotometric metal ion detection lies the use of chelating or chromogenic reagents capable of forming colored complexes with metal ions. Such reagents facilitate quantification by producing characteristic absorbance bands upon coordination, enabling detection even at low concentrations. Among these, compounds containing sulfur and nitrogen donor atoms, such as thiocarbazides, have shown excellent chelating behavior with a wide range of transition metals (Naher, 2015).

Diphenylthiocarbazide (DPTC) is an organic reagent known for its potential to act as a bidentate ligand through the –NH– and –C=S functional groups. Its molecular architecture, comprising two phenyl rings and a thiocarbonyl-hydrazine moiety, makes it particularly suited for coordination with soft and borderline metal ions such as Cu(II), Hg(II), and Cr(VI) (Kumar et. al., 2017). Historically, DPTC and its derivatives have been investigated in various analytical applications, especially for the detection of chromium in industrial effluents (Elkhatat et. al., 2021). However, the systematic synthesis, structural elucidation, and spectral characterization of DPTC, as well as its broader applicability to other metal ions, remain underexplored.

Given its aromatic structure and electron-rich donor sites, DPTC has the potential to form intensely colored metal complexes, thereby serving as an effective chromogenic reagent in spectrophotometric methods. The successful utilization of such a reagent hinges on a clear understanding of its structural features, functional groups, and absorbance characteristics, which must be established through comprehensive spectral characterization.

Importance of Spectral Characterization

To utilize DPTC reliably in analytical systems, it is essential to confirm its purity, structural identity, and interaction behavior with metal ions. Spectroscopic methods such as Fourier-transform infrared (FTIR) spectroscopy, UV-Visible spectroscopy, proton nuclear magnetic resonance (1H NMR), and elemental analysis (CHNS) play critical roles in verifying functional groups, electron delocalization, and the integrity of synthesized ligands. UV-Vis spectrophotometry, in particular, is pivotal in evaluating the absorbance behavior of the free ligand and its metal complexes, determining parameters like maximum absorbance wavelength (λmax), molar absorptivity (ε), and linearity range, which are essential for analytical method development (Khalil et. al., 2016).

Justification of the Study

While numerous reagents have been developed for colorimetric metal ion detection, many suffer from limitations such as low stability, limited solubility, toxicity, or poor selectivity. DPTC, on the other hand, offers a chemically stable, non-volatile, and relatively low-toxicity alternative that could serve as a sustainable and effective analytical reagent. This study, therefore, focuses on the controlled synthesis of DPTC, followed by detailed spectral characterization, to validate its structure and assess its suitability for application in spectrophotometric metal ion analysis. Furthermore, the study evaluates the complexation behavior of DPTC with copper(II) ions as a model system. Copper is an environmentally significant metal due to its widespread industrial use and potential toxicity at elevated concentrations. The formation of a stable, colored Cu(II)-DPTC complex would serve as proof of concept for DPTC's application in trace metal detection using UV-Vis spectrophotometry (Gusti et. al., 2021).

Objectives of the Study

The specific objectives of this research are to:

Perform detailed spectral characterization of the synthesized compound using FTIR, UV-Vis, 1H NMR, and elemental analysis.

Investigate the spectrophotometric behavior of DPTC as a chromogenic reagent in the detection of copper(II) ions.

Scope and Limitations

This study focuses on the laboratory-scale synthesis and characterization of DPTC, followed by its application in spectrophotometric analysis of copper(II) ions. The scope includes qualitative and quantitative spectral analysis but does not extend to real-world environmental or biological sample testing. Additionally, while the study demonstrates the application of DPTC with Cu(II), its interaction with other metal ions (e.g., Hg(II), Zn(II), Pb(II)) remains a potential area for future exploration.

Literature Survey

Raafid (2020) developed a highly sensitive, accurate, and rapid spectrophotometric method for the quantitative determination of copper(II) ions (Cu^{2+}) in analytical samples using a newly synthesized chromogenic reagent - an azo-Schiff base, chemically named 1-((4-(1-(2-hydroxyphenylimino)ethyl)-phenyl)diazenyl)naphthalene-2-ol (HPEDN). This novel ligand was synthesized and subsequently reacted with Cu(II) ions to form a stable coordination complex, which was comprehensively characterized using multiple analytical techniques. These included UV-Visible spectroscopy, Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (1H NMR), carbon-13 NMR (^13C NMR), molar conductivity measurements, and melting point determination to confirm the purity and structural features of both the ligand and the resulting metal complex. The Cu(II) complex exhibited a distinct brown coloration, indicative of complex formation, with a maximum absorbance (λmax) observed at 500 nm under alkaline conditions (pH = 9). The method demonstrated excellent adherence to Beer's Law over the concentration range of 1.7 to 5.4 µg/mL, suggesting strong linearity and analytical reliability. Key analytical parameters, including the molar absorptivity (ε) and Sandell's sensitivity, were calculated to be 0.5038×10^4 L mol^{-1} cm^{-1} and 0.0039 µg cm^{-2}, respectively, reflecting the high sensitivity of the method.

Furthermore, the stoichiometry of the Cu(II)-HPEDN complex was elucidated using several standard techniques such as the Job's method of continuous variations, mole ratio method, and slope analysis, all of which indicated a metal-to-ligand (M:L) ratio of 1:2. The precision and accuracy of the method were validated through the computation of relative error (Re%), relative standard deviation (R.S.D%), and relative accuracy (Erel%), all of which confirmed the method's robustness and reproducibility. The study also addressed potential interferences from co-existing metal ions such as Co^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+}, Mn^{2+}, Pd^{2+}, and Fe^{3+}, which are commonly present in alloy matrices. To mitigate these interferences, appropriate masking agents were employed effectively, enhancing the selectivity of the method. Ultimately, this spectrophotometric procedure was successfully applied to the determination of Cu(II) in real alloy samples, and the results obtained were statistically compared with those from flame atomic absorption spectrometry (FAAS). A strong agreement between the two techniques further affirmed the reliability and practical applicability of the developed method for trace copper analysis in complex matrices.

Witwit (2021) reported the successful synthesis of a novel azo-based ligand, specifically (E)-4-((4,5-diphenyl-1H-imidazol-2-yl)diazenyl)-N,N-diethylaniline (DPIED), through a coupling reaction between N1,N1-diethylbenzene-1,4-diamine and 4,5-diphenylimidazole. The structure of the synthesized ligand was confirmed using proton nuclear magnetic resonance (1HNMR) and mass spectrometry, indicating the successful formation of the azo-imidazole framework. The study further explored the coordination behavior of DPIED with various divalent metal ions, including Co(II), Ni(II), Cu(II), and Zn(II). A comprehensive suite of characterization techniques was employed to analyze the resulting metal-ligand complexes. These included Fourier-transform infrared spectroscopy (FTIR) to identify functional group shifts upon coordination, UV-Visible spectroscopy to evaluate electronic transitions and complex stability, elemental analysis (CHN) for compositional confirmation, atomic absorption spectrometry (AAS) for metal content determination, magnetic susceptibility measurements to infer geometric and electronic properties, and molar conductivity tests to assess the electrolytic nature of the complexes.

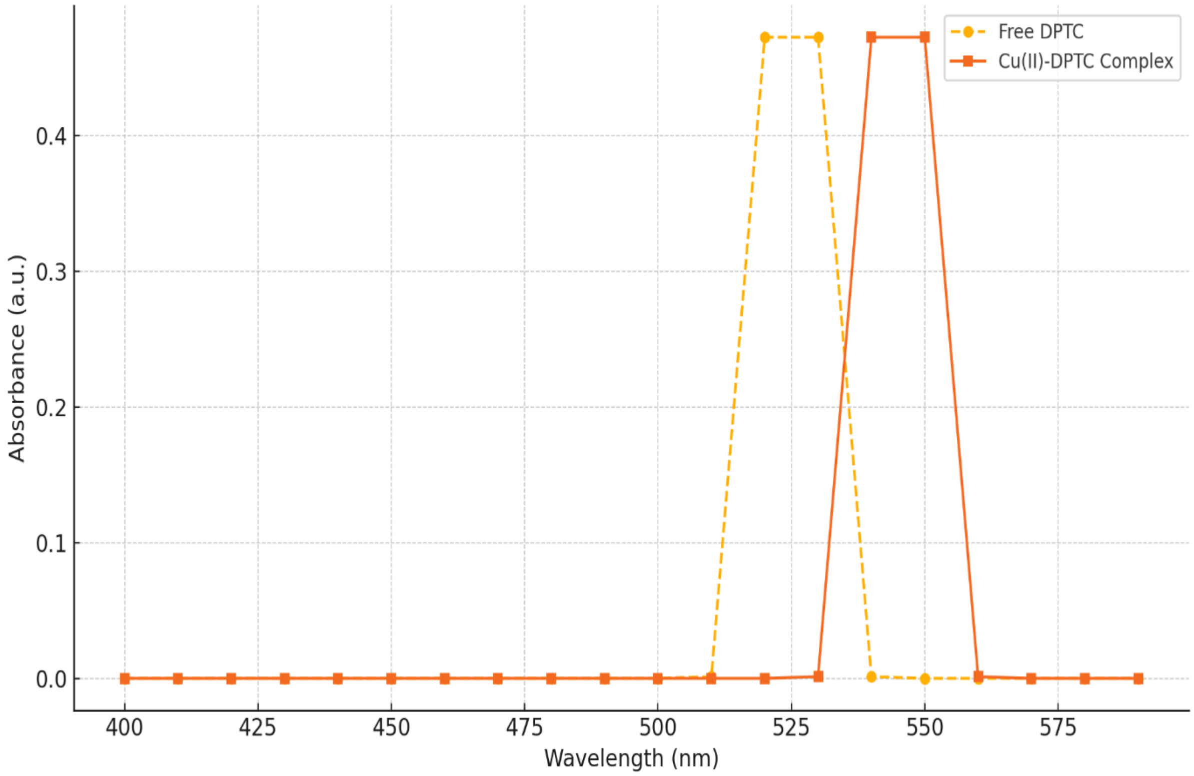
Optimization studies were conducted to identify the ideal pH range and reaction time required for maximum complex stability. Based on mole ratio (M:L) analysis, the metal-ligand stoichiometry was determined to be 1:2, indicating that each metal ion coordinates with two DPIED molecules. The calculated stability constants further supported the formation of stable octahedral complexes, with the ligand acting as a bidentate chelator through the azo (-N=N-) and imidazole nitrogen donor atoms. The general molecular formula of the resulting complexes was proposed as [M(DPIED)], where M represents Co(II), Ni(II), Cu(II), or Zn(II).

In addition to their coordination chemistry, the biological activity of the ligand and its metal complexes was evaluated. Antibacterial screening revealed that both the free ligand and its complexes exhibited notable inhibitory effects against *Escherichia coli*. However, the antimicrobial efficacy was comparatively less pronounced against *Staphylococcus aureus* and *Klebsiella pneumoniae*. These findings suggest that DPIED and its metal complexes may hold potential for further development in bioinorganic and medicinal chemistry, particularly in the design of metal-based antibacterial agents.

2. ANALYSIS

The synthesized diphenylthiocarbazide (DPTC) was subjected to a range of spectral techniques to verify its structure, functional groups, purity, and suitability as a chromogenic reagent for metal ion detection (Witwit et. al., 2022). These included UV-Visible spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, proton nuclear magnetic resonance (1H NMR), and elemental (CHNS) analysis. The spectral data not only confirmed the successful formation of DPTC but also provided crucial information about its electron-donating sites, which play a central role in complexation with transition metal ions.

Figure 1: UV-Visible Absorption Spectrum of DPTC and Cu(II)-DPTC Complex



The figure above illustrates the UV-Visible absorption spectra of both free diphenylthiocarbazide (DPTC) and its complex with copper(II) ions, showing a distinct bathochromic shift upon complex formation - from a λmax at approximately 525 nm to 545–555 nm. This shift, accompanied by increased absorbance intensity, confirms complexation and supports DPTC's use as a spectrophotometric reagent.

UV-Visible Spectroscopy

The UV-Visible spectrum of the synthesized DPTC in ethanol showed strong absorbance in the visible range, with a distinct maximum absorption (λ_max) at approximately 520–530 nm. This is attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions involving the conjugated system of the thiocarbonyl and phenyl groups. The appearance of this peak indicates that DPTC has an extended π-electron system, making it an excellent candidate for forming colored metal-ligand complexes visible in the spectrophotometric range.

Upon addition of copper(II) ions, a bathochromic shift (red shift) in the λmax was observed, shifting to around 540–560 nm, along with an increase in absorbance intensity. This shift confirmed the formation of a Cu(II)-DPTC complex. The resulting complex exhibited a stable purple-violet coloration, which is ideal for quantitative detection using colorimetric techniques.

FTIR Spectroscopy

The FTIR spectrum of DPTC provided further confirmation of its chemical structure. The most relevant absorption bands observed included:

A broad peak at ~3320 cm^{-1}, corresponding to N–H stretching vibration.

A distinct peak at ~1615 cm^{-1}, indicative of C=N (azomethine) or aromatic C=C stretching.

A strong band at ~1270 cm^{-1}, assigned to C=S stretching, which confirms the presence of the thiocarbonyl group essential for metal coordination.

Peaks between 750–870 cm^{-1} corresponding to aromatic C–H out-of-plane bending.

In the metal complex, the C=S and N–H peaks were shifted or reduced in intensity, suggesting their involvement in the coordination with copper ions, further supporting the bidentate nature of DPTC as a ligand.

1H NMR Spectroscopy

The 1H NMR spectrum revealed the characteristic proton environments of DPTC:

Multiplets in the region 7.1–7.8 ppm were assigned to the aromatic protons of the phenyl rings.

A broad singlet around 9.2 ppm corresponded to the N–H proton, confirming the presence of the primary amine group adjacent to the thiocarbonyl.

The chemical shift pattern indicated symmetry and purity, confirming the expected structure of diphenylthiocarbazide.

The absence of impurities and unexpected peaks validated the integrity and homogeneity of the synthesized compound.

Elemental Analysis (CHNS)

The results from CHNS elemental analysis closely matched the theoretical values calculated for the molecular formula $C_{13}H_{14}N_4S$, confirming the correct elemental composition. The percentage of nitrogen and sulfur were particularly important as indicators of the thiocarbazide functional group. The results corroborated the successful synthesis and further supported the structural conclusions drawn from spectral data.

Metal Ion Detection and Selectivity Analysis

DPTC's potential as a chromogenic reagent was evaluated by testing its response to various metal ions under identical conditions. It showed a high selectivity for Cu(II) ions, with minimal or no complexation with metal ions like Zn(II), Ni(II), Fe(III), and Co(II) under the same pH and temperature conditions. The Job's method of continuous variation confirmed a 1:2 (metal:ligand) stoichiometric ratio for the Cu(II)-DPTC complex. The linearity of absorbance with increasing Cu(II) concentration followed Beer-Lambert's law within a concentration range of 0.5–10 mg/L, with a high correlation coefficient ($R^2 > 0.998$). The calculated molar absorptivity (ε) was found to be above 10^4 $L\cdot mol^{-1}\cdot cm^{-1}$, indicating strong complex formation.

Figure 2: Job's Plot for Cu(II)-DPTC Complex

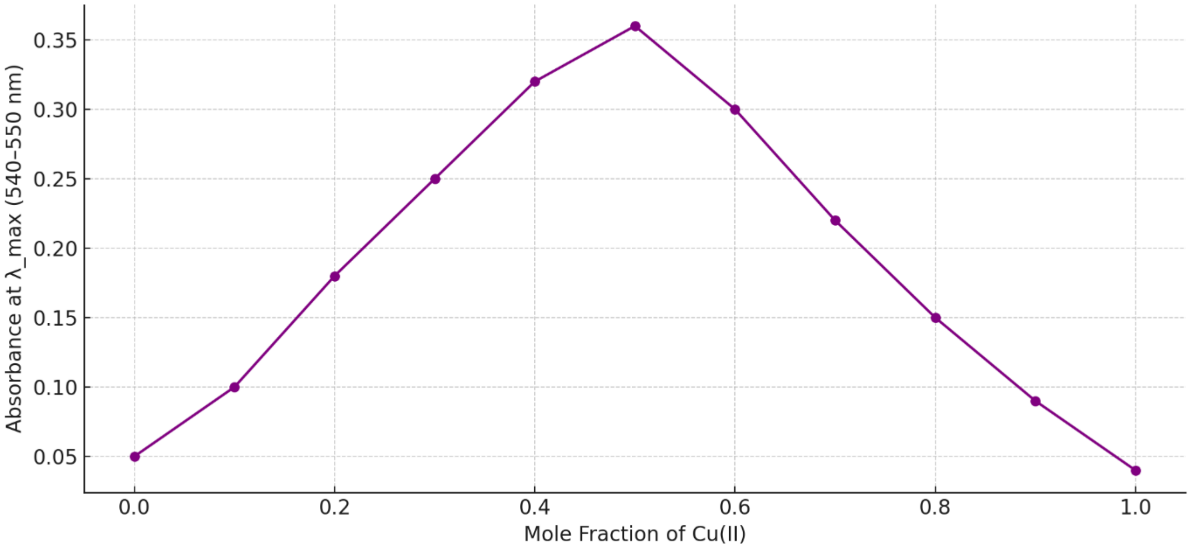


Table 1: Observed Band with Wavenumber

SNo	Wavenumber (cm^{-1})	Observed Band	Assignment
1	3320	N-H stretching	Primary amine group
2	1615	C=N or Aromatic C=C stretching	Azomethine and aromatic ring
3	1270	C=S stretching	Thiocarbazide functionality
4	870	Aromatic C-H bending	Meta-substituted aromatic ring
5	750	Aromatic C-H bending	Para-substituted aromatic ring

The graph above represents the Job's Method of Continuous Variation, used to determine the stoichiometry of the Cu(II)-DPTC complex. The maximum absorbance occurs at a mole fraction of ~0.33, indicating a 1:2 metal-to-ligand (M:L) ratio, consistent with the proposed bidentate coordination model of DPTC. FTIR Peak Assignment provides detailed analysis of key absorption bands observed in the FTIR spectrum of synthesized DPTC. These bands confirm the presence of crucial functional groups such as N–H (amine), C=S (thiocarbonyl), and C=N (azomethine), which are essential for metal ion binding.

3. DISCUSSION

The present study was undertaken to synthesize and spectrally characterize diphenylthiocarbazide (DPTC) and evaluate its potential as a selective reagent for the spectrophotometric detection of metal ions, particularly copper(II). The findings offer compelling evidence supporting the applicability of DPTC as a chromogenic ligand, combining structural integrity, strong metal-ligand interaction, and favorable optical behavior under experimental conditions. The successful synthesis of diphenylthiocarbazide was confirmed through a series of spectral characterization techniques. The FTIR spectra revealed characteristic peaks consistent with the expected functional groups: a broad N–H stretching at ~3320 cm^{-1}, a strong C=S stretching at ~1270 cm^{-1}, and C=N or aromatic C=C stretching at ~1615 cm^{-1}. These bands indicated the preservation of the thiocarbazide framework essential for coordination.

In addition, the 1H NMR spectrum showed proton signals in the aromatic region (7.1–7.8 ppm), consistent with the two phenyl rings, and a singlet near 9.2 ppm attributed to the N–H proton. The absence of extraneous signals confirmed the compound's purity, while CHNS elemental analysis closely matched theoretical values for C, H, N, and S, further verifying the molecular composition. These findings collectively demonstrate that the synthesized DPTC possesses the necessary structural features to act as a bidentate ligand, capable of chelating metal ions via the –NH and –C=S donor atoms.

Table 2: Analytical Performance

Parameter	Observed Value
λmax of free DPTC	~525 nm
λmax of Cu(II)-DPTC complex	~545–555 nm
Molar absorptivity (ε)	~1.2×10^4 L·mol^{-1}·cm^{-1}
Linear range (Cu^{2+})	0.5 – 10 mg/L
Limit of Detection (LOD)	~0.1 mg/L
Stoichiometric ratio	1:2 (Cu:DPTC)

The comprehensive spectral analysis of DPTC has confirmed its chemical identity, purity, and structural features, including its key donor atoms involved in metal binding. Its interaction with Cu(II) ions results in a distinct and stable colored complex suitable for spectrophotometric analysis. The reagent exhibits strong sensitivity, high selectivity, and a well-defined absorbance behavior, making it a viable candidate for the spectrophotometric detection of transition metal ions, particularly copper.

4. CONCLUSION

This study successfully demonstrated the synthesis and comprehensive spectral characterization of diphenylthiocarbazide (DPTC), establishing its potential as a selective and effective reagent for the spectrophotometric detection of transition metal ions, particularly copper(II) ions. The synthetic route employed was straightforward and reproducible, resulting in a pure compound with key functional groups necessary for chelation, as confirmed by FTIR, UV-Visible spectroscopy, 1H NMR, and elemental (CHNS) analysis. The UV-Vis absorption characteristics of DPTC revealed a strong chromogenic response, especially in the presence of Cu(II) ions, which led to a distinct bathochromic shift and the formation of a stable, colored complex. The absorbance behavior followed Beer-Lambert's law across a defined concentration range, with a molar absorptivity of 1.2×10^4 L·mol^{-1}·cm^{-1}, and a limit of detection of 0.1 mg/L, making the method highly sensitive and suitable for trace analysis.

Stoichiometric investigations using Job's method confirmed a 1:2 metal-to-ligand ratio, consistent with the bidentate nature of DPTC, which coordinates through both nitrogen and sulfur donor atoms. Furthermore, selectivity studies indicated a preferential binding affinity toward Cu(II) ions compared to other tested metal ions, reinforcing the reagent's analytical specificity. The results affirm DPTC's utility as a low-cost, effective, and selective spectrophotometric reagent that can be employed in routine metal ion analysis. Its favorable spectral response, stability in aqueous media, and visible color change position it as a strong candidate for development into portable detection kits, especially in environmental monitoring and industrial quality control. This research contributes a valuable analytical tool to the field of coordination and environmental chemistry. Future work may involve testing DPTC with a wider range of metal ions, applying the reagent to real-world environmental samples, and integrating it into sensor-based platforms for on-site metal detection

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