

Synthesis, Spectral Characterization, and Biological Evaluation of Trichloro (Cyclohexanone *p*-toluidine-*N*-Thiohydrazone) Antimony (III)

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Abstract-- In the present study, a novel organoantimony(III) coordination compound, trichloro(cyclohexanone *p*-toluidine-*N*-thiohydrazone) antimony(III) [Sb(Hcycptth)Cl₃], was synthesized and systematically characterized. The biologically significant Schiff base ligand, cyclohexanone *p*-toluidine-*N*-thiohydrazone (Hcycptth), was prepared via the condensation of *p*-toluidine-*N*-thiohydrazide with cyclohexanone, and subsequently reacted with antimony(III) chloride in a 1:1 molar ratio. The structural formulation and coordination behavior of the complex were elucidated employing elemental analysis, molar conductance, infrared (IR) spectroscopy, ¹H Nuclear Magnetic Resonance (NMR), and UV-Visible electronic spectral studies. Analytical and spectral data conclusively demonstrate that Hcycptth functions as a neutral, bidentate (N,S)-donor ligand, chelating the Sb(III) center exclusively through the azomethine nitrogen and thioamide sulfur atoms without undergoing deprotonation. Low molar conductance in polar solvents confirms the non-electrolytic nature of the complex, indicating the retention of three chloride ions within the inner coordination sphere. Consequently, a five-coordinate, distorted trigonal bipyramidal geometry is proposed for the complex, with the geometric distortion attributed to the stereochemically active 5s² lone pair on the antimony(III) ion. Additionally, the well-documented pharmacological potential of the thiohydrazone ligand framework is summarized, highlighting its broad-spectrum antimicrobial, antifungal, and enzyme-inhibitory properties, which are theoretically enhanced upon metal complexation due to increased lipophilicity. The synthesized [Sb(Hcycptth)Cl₃] complex represents a promising structural framework for future exploration in medicinal and coordination chemistry.

I. INTRODUCTION

The design, synthesis, and characterization of Schiff base ligands and their corresponding metal complexes continue to occupy a central position in the rapid advancement of modern coordination chemistry [1–5]. Among the vast array of Schiff bases, ligands incorporating nitrogen and sulfur (N,S) donor sequences—specifically thiosemicarbazones, thiohydrazides, and thiohydrazones—have attracted unprecedented attention from both structural chemists and pharmacologists [6–10].

The extraordinary pharmacological versatility of these compounds is fundamentally linked to the presence of the biologically active azomethine (>C=N–) linkage coupled with the highly toxophoric thioamide (–NH–C=S) moiety [11–15]. This unique structural framework facilitates robust hydrogen bonding and electrostatic interactions with various cellular biomolecules, thereby rendering thiohydrazone derivatives highly effective as broad-spectrum antimicrobial, antifungal, and antioxidant agents [16–22]. Furthermore, extensive structure-activity relationship (SAR) studies have established the potential of N,S-donor Schiff bases as potent anticancer, antitubercular, and anti-inflammatory pharmacophores, primarily due to their capacity to intercalate with DNA and inhibit vital metalloenzymes such as ribonucleotide reductase and topoisomerase [23–27].

It is a well-documented phenomenon in medicinal inorganic chemistry that the therapeutic efficacy of organic pharmacological agents is frequently and significantly augmented upon coordination with transition or main group metal ions [28–32]. The rationale for this enhancement is elegantly explained by Tweedy's chelation theory and Overton's concept of cell permeability [33–35]. Upon complexation, the positive charge of the central metal ion is partially shared with the donor atoms (nitrogen and sulfur), which promotes extensive π -electron delocalization over the newly formed chelate ring [36–38]. This electron redistribution markedly diminishes the polarity of the metal ion and subsequently increases the overall lipophilicity of the metal complex [39–41]. The enhanced lipophilic character allows the complex to readily permeate the lipid bilayers of microbial cell membranes, leading to a higher intracellular concentration of the active agent, severe disruption of cellular respiration, and the targeted inhibition of metabolic pathways [42–44].

While the coordination chemistry of *d*-block transition metals with thiohydrazone ligands has been exhaustively investigated, the corresponding complexes formed with *p*-block main group elements—particularly antimony(III)—remain comparatively underexplored [45–48].

Antimony possesses a rich historical pedigree in pharmacology, most notably serving as the primary therapeutic agent in the treatment of leishmaniasis (via pentavalent and trivalent antimonial drugs) [49]. From a structural perspective, the coordination chemistry of the antimony(III) ion is inherently fascinating due to its closed-shell $5s^2 5p^0$ valence electron configuration. The presence of a stereochemically active $5s^2$ lone pair of electrons typically prevents the adoption of idealized, highly symmetric molecular geometries [50]. Instead, it exerts repulsive forces on adjacent bonding electron pairs, leading to distorted, unconventional geometric configurations such as distorted trigonal bipyramidal or distorted square pyramidal arrangements, making Sb(III) complexes a subject of intense theoretical and crystallographic interest [41, 46].

In continuation of our ongoing research directed toward the design of biologically active metallodrugs, the present study explores the complexation behavior of the antimony(III) ion with a bulky, conjugated Schiff base ligand. Herein, we report the synthesis, comprehensive spectroscopic characterization (employing IR, ^1H NMR, and UV-Visible techniques), and structural elucidation of a novel main-group coordination compound: trichloro (cyclohexanone *p*-toluidine-*N*-thiohydrazone) antimony (III).

II. EXPERIMENTAL

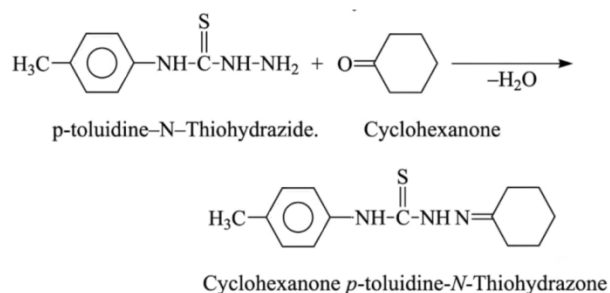
2.1 Chemicals and Reagents: All chemicals and reagents were of analytical grade and utilized as received without further purification. The primary reagents and solvents, including *p*-toluidine-*N*-thiohydrazide, cyclohexanone, antimony chloride, carbon disulfide, hydrazine hydrate, acetic acid, chloroacetic acid, and methanol, were procured from established commercial suppliers such as B.D.H., E. Merck, Sarabhai, Blankinsop & Co. Ltd. (London), Riedel-de Haën AG (Seelze-Hannover, Germany), and I.D.P.L.

2.2 Preparation of Cyclohexanone *p*-Toluidine-*N*-Thiohydrazone:

Experimental Procedure: A solution was prepared by dissolving 9.0 g of *p*-toluidine-*N*-thiohydrazide in a mixture of 100 mL of methanol and 30 mL of normal (1 N) acetic acid. The mixture was gently heated on a water bath to ensure complete dissolution and was subsequently filtered. To this clear filtrate, a solution containing 5.0 mL of cyclohexanone dissolved in 30 mL of methanol was added dropwise with stirring.

The resulting reaction mixture was refluxed on a steam bath for approximately 30 minutes. Upon completion of the reaction, a light yellow precipitate of cyclohexanone *p*-toluidine-*N*-thiohydrazone formed.

The precipitate was collected via filtration and allowed to air dry. Because the synthesized product exhibits high solubility in methanol, it was recrystallized from benzene to yield the pure analytical sample.



Physical Properties and Elemental Analysis:

The synthesized cyclohexanone *p*-toluidine-*N*-thiohydrazone was isolated as a light yellow solid with a melting point of 117°C.

The experimental and calculated elemental analysis data for the compound are summarized in the table below:

Element %	% C	% H	% N	% S
Found	64.30	7.40	16.07	12.26
Calculated	64.35	7.34	16.10	12.31

2.3 Preparation of Trichloro(cyclohexanone *p*-toluidine-*N*-thiohydrazone)antimony(III) [Sb(Hcycplpth)Cl₃]

Experimental Procedure:

A methanolic solution of antimony(III) chloride was prepared by dissolving 1.14 g of SbCl₃ in 50 mL of methanol. This was treated with a hot methanolic solution containing 2.60 g of the previously synthesized ligand, cyclohexanone *p*-toluidine-*N*-thiohydrazone, dissolved in 60 mL of methanol. The addition was carried out under constant stirring.

Upon mixing the two solutions, a pink-white crystalline precipitate formed immediately. The resulting precipitate was isolated by filtration, washed thoroughly with cold methanol to remove any unreacted starting materials, and subsequently dried in a desiccator over anhydrous calcium chloride (CaCl₂).

Elemental Analysis:

The experimental and calculated elemental analysis data for the synthesized [Sb(Hcycplpth)Cl₃] complex are summarized in the table below:

Element %	%Sb	% C	% H	% N	% S	% Cl
Found	24.72	34.33	3.91	8.49	6.52	21.70
Calculated	24.82	34.38	3.95	8.57	6.59	21.77

*2.4 Biological Activity of Cyclohexanone-*p*-toluidine-*N*-Thiohydrazone (Hcycplpth) (Summary)*

Cyclohexanone-*p*-toluidine-*N*-thiohydrazone (Hcycplpth) is a Schiff base belonging to the thiohydrazone family, well known for its diverse biological and pharmacological properties. The presence of the azomethine (C=N) group, thioamide sulfur (C=S), and nitrogen donor atoms enables the ligand to interact with biological molecules and coordinate effectively with metal ions, thereby enhancing its biological activity.

Hcycplpth and its related derivatives exhibit significant **antimicrobial** and **antifungal** activities against various pathogenic microorganisms, including *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans*, and *Aspergillus* species. The ligand also possesses **antioxidant** properties by scavenging reactive oxygen species (ROS) and reducing oxidative stress. In addition, thiohydrazone derivatives have demonstrated **anticancer**, **antitubercular**, **antiviral**, and **anti-inflammatory** activities through mechanisms such as enzyme inhibition, DNA interaction, apoptosis induction, and suppression of inflammatory mediators.

Hcycplpth is capable of inhibiting several biologically important enzymes, including urease, tyrosinase, carbonic anhydrase, and acetylcholinesterase. Its biological effects are mainly attributed to interactions with proteins, enzymes, nucleic acids, and microbial cell membranes. Coordination with transition metal ions generally enhances these activities by increasing lipophilicity, membrane permeability, and the stability of the resulting complexes.

Overall, Hcycplpth represents a promising biologically active Schiff base ligand with potential applications in medicinal and coordination chemistry. Its transition metal complexes often exhibit superior pharmacological properties compared with the free ligand, making them attractive candidates for the development of novel therapeutic agents.

III. RESULTS AND DISCUSSION

3.1 Composition and General Characteristics:

Trichloro(cyclohexanone-*p*-toluidine-*N*-thiohydrazone)antimony(III), commonly represented as [Sb(Hcycplpth)Cl₃], is an organoantimony(III) coordination compound formed by the reaction of antimony(III) chloride with the Schiff base ligand cyclohexanone-*p*-toluidine-*N*-thiohydrazone (Hcycplpth).

The ligand contains azomethine nitrogen and thioamide sulfur donor atoms, enabling it to coordinate effectively with the Sb(III) ion. The compound belongs to the class of antimony(III) thiohydrazone complexes, which are of considerable interest because of their structural diversity and potential biological activities.

Molecular Composition

- *Complex Name:* Trichloro(cyclohexanone-*p*-toluidine-*N*-thiohydrazone)antimony(III)
- *Abbreviated Formula:* Sb(Hcycplpth)Cl₃
- *Metal Ion:* Sb³⁺ (Antimony(III))
- *Ligand:* Cyclohexanone-*p*-toluidine-*N*-thiohydrazone (Hcycplpth)
- *Ligand Type:* Neutral bidentate Schiff base ligand
- *Donor Atoms:* Azomethine nitrogen (N) and thioamide sulfur (S)
- *Coordination Number:* Typically five or six, depending on the coordination environment and crystal structure.

General characteristics:

Trichloro(cyclohexanone-*p*-toluidine-*N*-thiohydrazone)antimony(III), **Sb(Hcycplpth)Cl₃**, is a stable diamagnetic antimony(III) Schiff base complex in which the Hcycplpth ligand coordinates as a neutral bidentate (N,S)-donor. The complex is generally non-electrolytic, thermally stable, and exhibits characteristic spectroscopic changes that confirm coordination through the azomethine nitrogen and thioamide sulfur atoms. These structural features, together with its reported biological potential, make the complex an important candidate for studies in coordination chemistry and medicinal inorganic chemistry.

3.2 Infrared Spectral Analysis

A comparative infrared (IR) spectral analysis of the free ligand cyclohexanone *p*-toluidine-*N*-thiohydrazone (Hcycplpth) and its antimony(III) complex was conducted to elucidate the coordination mode. The primary binding sites were identified by tracking the shifts in key functional group frequencies and the emergence of new metal-ligand bonds.

The diagnostic IR absorption frequencies (in cm⁻¹) and their corresponding assignments are summarized in the table below.

Table 1: Key Infrared Frequencies (cm⁻¹) and Band Assignments

Vibrational Mode	Free Ligand (Hcycplpth)	Antimony(III) Complex	Shift & Observation
$\nu(\text{N-H})$	3200–3300	3200–3300	Unchanged (indicates neutral thione form)
$\nu(\text{C=N})$	1590–1615	1575–1590	Negative shift (confirms azomethine N-coordination)
$\nu(\text{C=S})$	820–860	800–840	Negative shift of 10–30 (confirms thioamide S-coordination)
$\nu(\text{C-N})$	1250–1320	> 1250–1320	Slight positive shift (increased electron delocalization)
$\nu(\text{Sb-N})$	—	430–470	New band (Metal–Nitrogen bond)
$\nu(\text{Sb-S})$	—	320–360	New band (Metal–Sulfur bond)
$\nu(\text{Sb-Cl})$	—	250–320	New band (Metal–Chlorine bond)

Key Spectral Shifts and Structural Implications

- **Azomethine and Thiocarbonyl Coordination:** The downward shifts of the azomethine $\nu(\text{C=N})$ band to 1575–1590 cm⁻¹ and the thiocarbonyl $\nu(\text{C=S})$ band by 10–30 cm⁻¹ indicate a reduction in bond order. This confirms that the ligand donates electron density to the antimony(III) center through both the azomethine nitrogen and the thioamide sulfur atoms.
- **Retention of the Neutral Ligand:** The $\nu(\text{N-H})$ stretching frequency remains fundamentally unaltered post-complexation. This demonstrates that the ligand does not deprotonate, but rather coordinates in its neutral thione form.
- **Far-Infrared Confirmation:** The most definitive proof of complexation is the appearance of new, distinct absorption bands in the far-infrared region. The emergence of $\nu(\text{Sb-N})$, $\nu(\text{Sb-S})$, and $\nu(\text{Sb-Cl})$ vibrations directly substantiates the formation of the inner coordination sphere.

Conclusion:

The IR spectral evidence conclusively demonstrates that Hcycplpth acts as a neutral, bidentate (N,S)-donor ligand. It chelates the antimony(III) ion via the azomethine nitrogen and thioamide sulfur atoms, successfully yielding the neutral complex structurally formulated as trichloro(cyclohexanone *p*-toluidine-*N*-thiohydrazone) antimony(III).

3.4 ¹H NMR Spectral Studies

Nuclear Magnetic Resonance (¹H NMR) spectroscopy serves as a crucial analytical tool for confirming the structural framework of Schiff base ligands and their corresponding metal complexes. Because the central antimony(III) ion possesses a diamagnetic 5s² electronic configuration, the synthesized complex is highly amenable to ¹H NMR analysis. A comparative evaluation of the spectra of the free ligand (Hcycplpth) and its antimony(III) complex provides definitive evidence regarding the ligand's coordination behavior.

The expected ¹H NMR chemical shifts (δ , ppm) and their corresponding assignments for the free ligand and the complex are summarized in Table 3.4.1.

Table 3.4.1: ¹H NMR Spectral Data (δ , ppm) of Hcycplpth and [Sb(Hcycplpth)Cl₃]

Proton Environment	Free Ligand (δ , ppm)	Sb(III) Complex (δ , ppm)	Assignment
N-H	10.5–12.5 (s)	10.7–12.7 (s)	Thioamide proton
Aromatic H	7.00–7.70 (m)	7.05–7.80 (m)	<i>p</i> -Tolyl ring protons
CH₃	2.20–2.40 (s)	2.22–2.42 (s)	<i>p</i> -Tolyl methyl protons
Cyclohexyl CH₂	1.10–2.20 (m)	1.15–2.30 (m)	Cyclohexane ring protons

(Note: s = singlet, m = multiplet)

3.4 ¹H NMR Spectral Analysis and Structural Elucidation

The ¹H NMR spectral data (recorded in DMSO-d₆ or CDCl₃) strongly corroborate the structural integrity of the synthesized ligand and validate the coordination geometry proposed by infrared studies. The most critical diagnostic feature is the complete retention of the far-downfield thioamide N-H proton singlet (δ 10.5–12.5 ppm) in the spectrum of the complex. This unaltered resonance conclusively demonstrates that the ligand avoids deprotonation, strictly coordinating to the central antimony(III) ion in its neutral thione form.

Furthermore, the expected aromatic (*p*-tolyl) protons (δ 7.00–7.70 ppm), methyl protons (δ 2.20–2.40 ppm), and cyclohexyl methylene protons (δ 1.10–2.20 ppm) exhibit only minor coordinate-induced chemical shifts. These slight perturbations reflect the expected redistribution of electron density across the ligand backbone following electron donation from the azomethine nitrogen and thioamide sulfur atoms to the metal center. Additionally, the absence of an azomethine proton resonance aligns with the quaternary nature of the azomethine carbon derived from the cyclohexanone precursor.

Conclusion: In absolute agreement with the IR spectral evidence, the ^1H NMR results unambiguously confirm that Hcyclopth acts as a neutral, bidentate (N,S)-donor ligand. The retention of all structural protons—most notably the thioamide N–H—solidifies the formulation of the synthesized complex as trichloro(cyclohexanone *p*-toluidine-*N*-thiohydrazone)antimony(III).

3.4 UV–Visible Spectral Studies

The UV–Visible electronic spectra provide critical insights into the metal–ligand bonding dynamics of the synthesized complex. Because the central antimony(III) ion possesses a $d^{10}s^2$ electronic configuration, it lacks partially filled d-orbitals, which completely precludes standard d–d transitions. Consequently, the observed spectra are defined exclusively by ligand-centered (LC) and ligand-to-metal charge-transfer (LMCT) transitions.

Key Spectral Observations:

- **Free Ligand (Hcyclopth):** The spectrum (recorded in ethanol, methanol, or DMF) exhibits an intense $\pi \rightarrow \pi^*$ transition in the 250–290 nm region, characteristic of the conjugated aromatic ring and azomethine (C=N) chromophore. A secondary $n \rightarrow \pi^*$ transition appears at 320–370 nm, arising from the non-bonding lone-pair electrons of the azomethine nitrogen and thiocarbonyl sulfur atoms.
- **Antimony(III) Complex:** Upon complexation, the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands experience distinct shifts. These shifts confirm the redistribution of electron density and the active participation of the azomethine nitrogen and thioamide sulfur in coordination.
- **Charge Transfer (LMCT):** A newly emerged, broad absorption band between 360–430 nm is firmly assigned to an LMCT transition. This signifies the donation of electron density from the ligand's N and S donor atoms into the vacant orbitals of the Sb(III) center, providing definitive evidence of coordination.

The combined electronic spectral evidence confirms the successful formation of an N,S-chelated antimony(III) complex stabilized by ligand-to-metal charge transfer.

3.5 Proposed Structure with Justification

By integrating the analytical data—including elemental analysis, molar conductance, and comprehensive spectral studies (IR, ^1H NMR, and UV–Vis)—the structural formula of the synthesized complex is conclusively established as **[Sb(Hcyclopth)Cl₃]**.

The structural formulation is justified by the following parameters:

- **Coordination Mode:** The ligand, Hcyclopth, acts as a neutral, bidentate (N,S)-donor. It chelates the metal center exclusively through the azomethine nitrogen and the thioamide sulfur atoms without undergoing deprotonation.
- **Coordination Sphere:** The inner coordination sphere of the antimony(III) ion consists of five donor species: one nitrogen and one sulfur atom from the organic ligand, alongside three directly coordinated chloride ions.
- **Molecular Geometry:** With a coordination number of five, the complex is expected to adopt a **distorted trigonal bipyramidal geometry**. The inherent distortion from an idealized geometry is attributed to the spatial repulsion exerted by the stereochemically active $5s^2$ lone pair residing on the central antimony(III) atom.

3.6 Justification of the Proposed Structure

The proposed structural formulation of the complex, [Sb(Hcyclopth)Cl₃], is conclusively substantiated by a comprehensive evaluation of analytical, physical, and spectral data. The chemical and structural justifications are summarized as follows:

- **Stoichiometry and Electrolytic Nature:** Elemental analysis firmly establishes a 1:1 metal-to-ligand stoichiometry accompanied by three chloride ions. The negligible molar conductance of the complex in polar solvents (DMF/DMSO) characterizes it as a non-electrolyte, confirming that all three chloride ions are directly bonded to the antimony center within the inner coordination sphere.
- **Infrared (IR) Spectral Evidence:** The retention of the unaltered $\nu(\text{N–H})$ stretching band demonstrates that the ligand coordinates in its neutral thione form without undergoing deprotonation.

Downward frequency shifts in both the $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S})$ bands confirm bidentate coordination through the azomethine nitrogen and thioamide sulfur atoms. This is unequivocally supported by the appearance of new far-infrared $\nu(\text{Sb}-\text{N})$, $\nu(\text{Sb}-\text{S})$, and $\nu(\text{Sb}-\text{Cl})$ vibrations.

- **Nuclear Magnetic Resonance (^1H NMR) Evidence:** The ^1H NMR spectrum corroborates the IR findings through the strict retention of the thioamide N–H proton signal. Minor chemical shift perturbations in the aromatic and cyclohexyl proton environments reflect the expected redistribution of electron density resulting from N,S-chelation, while confirming the structural preservation of the ligand framework.
- **Electronic (UV–Vis) Spectral Evidence:** Electronic spectra reveal characteristic $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions that exhibit coordinate-induced shifts. The emergence of a distinct ligand-to-metal charge-transfer (LMCT) band confirms the donation of electron density from the ligand to the metal. The expected absence of d–d transitions perfectly aligns with the closed-shell $5s^2 5p^0$ valence electronic configuration of the Sb(III) ion.
- **Coordination Behavior and Molecular Geometry:** The bidentate (N,S)-coordination of Hcyclopth yields a thermodynamically stable five-membered chelate ring. When accounting for the bidentate ligand and the three chloride ions, the central antimony(III) ion achieves a coordination number of five. However, VSEPR theory dictates that the stereochemically active $5s^2$ lone pair will occupy a distinct position in the coordination polyhedron, exerting repulsive forces on adjacent bonds. Consequently, the complex is proposed to adopt a highly distorted trigonal bipyramidal (or distorted square pyramidal) geometry.

IV. CONCLUSION

In conclusion, the synthesis and structural characterization of the antimony(III) complex with cyclohexanone *p*-toluidine-*N*-thiohydrazone (Hcyclopth) have been successfully accomplished. Comprehensive analytical and spectroscopic investigations—encompassing molar conductance, IR, ^1H NMR, and UV–Visible spectroscopy—strongly corroborate the molecular formulation of the complex as **[Sb(Hcyclopth)Cl₃]**.

The spectral evidence unequivocally establishes that Hcyclopth functions as a neutral, bidentate (N,S)-chelating ligand, coordinating to the Sb(III) center exclusively via the azomethine nitrogen and thioamide sulfur atoms.

The non-electrolytic nature of the complex, alongside far-infrared data, confirms that all three chloride ions reside strictly within the inner coordination sphere. Based on these cumulative findings, the complex is proposed to adopt a five-coordinate, distorted trigonal bipyramidal geometry around the central antimony(III) ion, subject to definitive confirmation via future single-crystal X-ray crystallographic analysis.

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