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SYNTHESIS AND CHARACTERIZATION OF PHENYL HYDRAZINE AND ISATIN-BASED SCHIFF BASE METAL COMPLEXES WITH IRON, COBALT AND CHROMIUM: A COMPARATIVE STUDY

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Abstract:
This study describes the synthesis and characterisation of Schiff base metal complexes generated from phenyl hydrazine and isatin ligands with iron, cobalt, and chromium ions. The Schiff bases were synthesized through the condensation reaction of phenyl hydrazine with isatin, followed by complexation with metal ions. The produced compounds were evaluated using a variety of analytical techniques, including elemental analysis, NMR, UV-Vis spectroscopy, FTIR spectroscopy, and magnetic susceptibility tests. The structural elucidation and coordination modes of the ligands with metal ions were investigated. The study aimed to understand the structural variations and potential applications in antimicrobial activity of these complexes. The results indicate the formation of stable complexes with different metal ions, providing valuable insights into their structural and spectroscopic properties.
Keywords: Phenyl hydrazine, Isatin, Schiff base, Synthesis, Characterization, Applications

Introduction
Due to wide-ranging uses in abundant domains, such as catalysis, materials science, and medicinal chemistry, Transition Metal Complexes have fascinated significant attention. Among the plethora of ligands employed for the synthesis of these complexes, Schiff bases derived from phenylhydrazine and isatin have emerged as intriguing candidates owing to their versatile coordination behaviour and potential biological activities (i, ii).
Phenylhydrazine, an aromatic hydrazine derivative, is known for its ability to form stable Schiff bases with various carbonyl compounds (iii). Isatin, on the other hand, is a bicyclic heterocyclic compound possessing a ketone group (iv). The condensation reaction of phenylhydrazine and isatin produces a Schiff base ligand, which can then coordinate with transition metal ions to create metal complexes (v).
The synthesis of Schiff base metal complexes involving phenyl hydrazine and isatin offers a wide array of possibilities for tailoring the properties and functionalities of the resulting compounds. (vi, vii) Moreover, the choice of transition metal ions, such as iron, cobalt, and

chromium, can significantly influence the physicochemical characteristics and potential applications of these complexes (viii).

Iron, cobalt, and chromium are transition metals known for their diverse coordination geometries and redox properties. Incorporating these metals into Schiff base complexes can lead to the development of novel materials with enhanced magnetic, catalytic, or biological activities (ix). Additionally, the study of their structural and electronic properties can provide valuable insights into the coordination chemistry of these metals with Schiff base ligands derived from phenylhydrazine and isatin (x).

In this research, we give a thorough investigation into the synthesis and characterisation of phenylhydrazine and isatin-based Schiff base metal complexes with iron, cobalt, and chromium.

The synthesis routes will be described in detail, highlighting the key reaction steps and optimization strategies. The structural, spectroscopic, and magnetic characteristics of the produced complexes will then be carefully studied utilizing a variety of analytical techniques, including UV-Visible spectrophotometry, FT-IR spectroscopy, NMR spectroscopy, X-ray diffraction, and magnetic susceptibility studies.

Furthermore, the potential applications of these complexes in catalysis, material science, and medicinal chemistry will be discussed, emphasizing their importance in contemporary research and technological advancements. Overall, this study aims to contribute to the expanding knowledge base in the field of coordination chemistry and provide valuable insights into the design and synthesis of functional metal complexes with phenyl hydrazine and isatin-based Schiff base ligands.

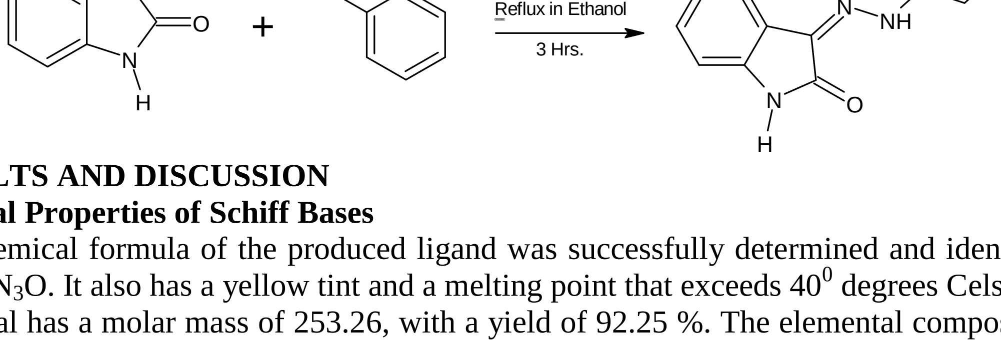
Experimental methods

Schiff base metal complexes were created using industry standard procedures. All chemicals were purchased from Merck.

Synthesis of Schiff Base and their metal complexes:

A Schiff base was synthesized by refluxing a mixture of isatin and phenyl hydrazine-based amine in ethanol. 1 millimole each of isatin and phenyl hydrazine were mixed with 10 cm^3 of ethanol and refluxed for three hours. The resulting Schiff base was recovered, recrystallized with ethanol, and dried. The ligand remained stable at room temperature and was soluble in various solvents (xi).

To form the metal complex, the prepared ligand was refluxed with metal chloride in a 2:1 mole ratio in ethanol. 2 millimoles of ligand and 1 millimole of metal chloride were used, with a few drops of weak ammonia added to maintain pH. The mixture was refluxed for 3 hours, and the precipitate of the complex was filtered, washed, and dried.



RESULTS AND DISCUSSION

Physical Properties of Schiff Bases

The chemical formula of the produced ligand was successfully determined and identified as $C_{14}H_{11}N_3O$. It also has a yellow tint and a melting point that exceeds 40^0 degrees Celsius. The chemical has a molar mass of 253.26, with a yield of 92.25 %. The elemental composition of sample was examined using analytical methods, showing the existence of carbon (C) at a relative abundance of 55.7%, hydrogen (H) at 4.9%, nitrogen (N) at 8.6%, oxygen (O) at 19.81%, and sulfur (S) at 9.9%.

Complex	**Wavelength (cm^{-1})**			
	V (Metal-Oxygen)	**V (Carbon-Oxygen)**	**V (Metal-Nitrogen)**	**V (Carbon=Nitrogen)**
Ligand	---------	1617.43	---------	1685.89
Cr-L	627.51	1617.21	690.08	1684.67
Co-L	627.11	1617.43	689.77	1685.86
Fe-L	664.63	1617.33	689.77	1685.69

The synthesized Schiff Base exhibits a distinctive -C=N- (azomethine) stretch band at 1685.89 cm^{-1} in its infrared spectrum, indicating the condensation process between Phenyl hydrazine's amino cluster and the ketonic group of the Schiff base from isatin. In the Co complex, a similar band at approximately 1685.86 cm^{-1} suggests the presence of azomethine in electron donation to Co^{2+}, facilitating complex formation. The shift in the IR band to 1684.67 cm^{-1} in the Co complex further supports this electron transfer. Similarly, the Fe complex displays an absorption band at 1685.69 cm^{-1}, indicating the contribution of azomethine to Fe^{2+} complex formation within the Schiff base structure (xii, xiii).

NMR Spectral analysis

7.81, 7.26, 7.50 and 7.86 ppm are the peaks of protons present on aromatic ring of 2-indolinone part of Schiff base and 7.35, 7.20 and 6.81ppm are the peaks of protons present on aromatic ring of phenyl hydrazine part of Schiff base.

8.00 ppm is a peak for proton which present on nitrogen of 2- indolinone part here little deshielding effect observed when compare it with NMR peaks of 2- indolinone.

7.00 is a peak for proton which is present on nitrogen of phenyl hydrazine part here little shielding effect observed when compare it with NMR peaks of phenyl hydrazine (xiv, xv, xvi).

Conductivity, Electronic Absorption Spectroscopy, and Magnetic Characteristics.

Sr. no.	Complex	Conductance $\Omega^{-1}cm^2mol^1$	Magnetic moments (B.M.)	Raccah Parameter (cm-1) (E/B)	Absorption Maxima cm^{-1} (nm)	Transition.	Expected Geometry
1.	Co-L	35.2	3.87	0.07382	270, 360, 400	$^4T_{1g}$ $4T_{2g}$ $^4T_{1g}$ $^4T_{1g(P)}$ $^4T_{1g}$ ^{4A2g}	Trigonal bipyramidal
2.	Cr-L	33.1	4.8989	0.0454	280	$^5T_{2g}$ ^5E_g ^5E_g $^5T_{2g}$	Tetrahedral
3.	Fe-L	26.3	diamagnetic	-------	320	$^1T_{2g}$ $^1A_{2g}$ $^1T2g^1A1g$	Octahedral

Above table indicates the value of Conductivity, Magnetic moment, Racah parameter and Absorption maxima. Through the absorption value transitions of electrons are determined and with the help of all values Geometry are determined. In Cobalt complex, one chloride ion is and in Iron complex, two chloride ions are supposed to get attached to metal ions (xvii, xviii).

Stability constants

Sr. no.	Complexes	Stability complex value 10^{-3} KJ/Mol
I.	Co-L	3.134
II.	Cr-L	2.764
III.	Fe-L	24.01

Antimicrobial studies:

Sample preparation:

The synthesized chemical was produced as stock solutions in ethanol at a concentration of 1 mg/ml (Sigma Aldrich). Next, 100ug/ml concentrations of several materials were tested for antibacterial activity.

Test organisms:

Six bacteria were utilized in the study: three Gram-positive (Bacillus cereus, Bacillus subtilis, and Staphylococcus aureus) and three Gram-negative (Proteus vulgaris, Escherichia coli, and Pseudomonas aeruginosa). The modified agar well diffusion method assessed the antibacterial activity of crude extracts and wine against these bacterial strains. Pathogens were spread on Muller and Hinton agar plates, followed by the creation of agar wells. Test samples were added to each well and allowed to diffuse before incubation at 37°C for 24 hours.

Results:

This study suggests that synthesized metal complex show good antimicrobial activity. Cobalt based metal complex shows broad-spectrum antimicrobial activity means it inhibits the growth of all 6 pathogens. On the other hand, Ligand molecule shows antimicrobial activity against only Gram-positive bacteria, *S.aureus*. While other compounds show mixed antimicrobial activity against tested pathogens. Chromium based metal complex is inactive against *B. cerus* and *P.aeruginosa* while Iron based metal complex is inactive against *S.aureus* and *P.aeruginosa* (xix, xx).

Sr. No	Test organisms	Zone of inhibition of respective nanoparticles in mm			
		Ligand	Co-L	Cr-L	Fe-L
1	***B.cerus***	00	20	00	17
2	***S.aureus***	12	21	17	00
3	***B.subtilis***	00	21	18	19
4	***E. coli***	00	18	16	14
5	***P.aeruginosa***	00	19	00	00
6	***P. vulgaris***	00	20	13	18

Conclusion

The metal complex synthesized have good stability. Cobalt metal complex have trigonal bipyramidal geometry and have good stability constant value. It shows good antimicrobial activity against all microbes. Chromium metal complex have tetrahedral geometry and have good stability constant value. It shows good antimicrobial activity against all microbes except *B.cerus* and *P.aeruginosa.* Iron metal complex have octahedral geometry and high good stability constant value. It shows good antimicrobial activity against all microbes except *S.aureus* and *P.aeruginosa.*

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