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Synthesis, Characterization, and Spectrophotometric Study of Ruthenium (III) Complexes with 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone

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Abstract: -

The synthesis and characterization (FT-IR, X-RD and UV-Vis) of a novel 2-chloroquinoline-3-carbaldehyde thiosemicarbazone are reported. Its antimicrobial activity is also determined on *Klebsiella pneumoniae*. Its coordination behaviour towards Ruthenium(III) ions in solution was studied using spectrophotometry to understand its complexation properties. The study successfully identified the formation of Ruthenium(III)-2-Chloroquinoline-3-Carbaldehyde thiosemicarbazone complex and their characteristics, including probable stoichiometry and stability constants. This research offers original findings on the coordination potential of this synthesized thiosemicarbazone ligand with Ruthenium(III).

Key words:

Ruthenium (III) Complexes, 2-chloroquinoline-3-carbaldehyde thiosemicarbazone, characterization, antimicrobial activity, stoichiometry.

1. Introduction: -

The study of metal-ligand interactions in solution is fundamental to understanding the formation and properties of coordination complexes. Spectrophotometry, a powerful and versatile analytical technique, provides valuable insights into the stoichiometry, stability, and spectral characteristics of metal complexes [1]. Thiosemicarbazone ligands, with their ability to coordinate to various transition metal ions through different donor atoms, have been extensively investigated using spectrophotometric methods [2]. Quinoline and its derivatives represent an important class of heterocyclic compounds with broad applications in pharmaceuticals, agrochemicals, and materials science [3]. The introduction of chelating functionalities onto the quinoline framework can further enhance their utility in coordination chemistry. Thiosemicarbazones, known for their excellent metal-binding capabilities, when linked to quinoline moieties, can generate ligands with tailored electronic and steric properties [4]. Literature serve also reveals that Thiosemicarbazones is a versatile class of organic compounds featuring the N-C-S moiety, have garnered significant attention in coordination chemistry due to their diverse coordination modes and the remarkable properties of their metal complexes [5]. These ligands exhibit a wide range of applications in catalysis, materials science, and biological systems, often attributed to the unique electronic and structural features imparted upon metal coordination [6]. Among transition metals, Ruthenium(III) has been extensively studied for its diverse oxidation states and promising applications in catalysis, medicine and cancer treatment [7]. This study focusses on the synthesis and characterization of a novel thiosemicarbazone derivative, 2-chloroquinoline-3-carbaldehyde thiosemicarbazone and its interaction with Ruthenium(III) ions in aqueous solution. The formation and

properties of the resulting Ruthenium(III) complexes are investigated in detail using spectrophotometric techniques.

2. Experimental details:-

Synthesis of 2-Chloro-QAT, its characterization and spectral study with Ruthenium complex are included in experimentation. For the same analytical grade chemicals were purchased from Merck ltd. They were used as received. Buffer required for experiment was prepared by standard procedure [8]. Required UV Visible spectrophotometric analysis was carried on ELICO spectrophotometer models 171. IR spectra were taken on Perkin Elmer 221 IR spectrophotometer and X-Rd was taken on PW3710 diffractometer

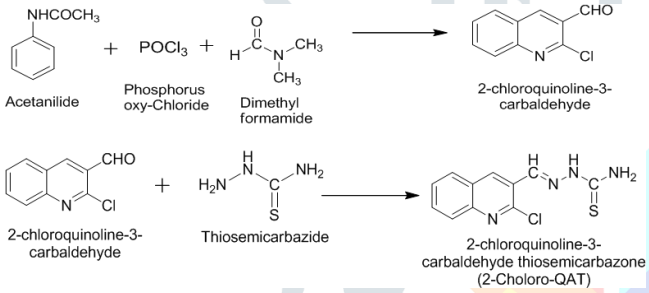
2.1.Synthesis of 2-Chloroquinoline -3- Carbaldehyde Thiosemicarbazone(2-Chloro-QAT)

2-Chloro-QAT was synthesized by refluxing equimolecular quantities of 2-Chloroquinoline thiosemicarbazide in minimum quantities of alcohol [9]. 2-Chloro-QAT formed was filtered, dried and recrystallized. It was Yellow coloured solid having melting point 225 molecular weight by formula was found to be 264.73. It was

used for further experimentation purpose. 2- Chloroquinoline- 3-Carbaldehyde required for synthesis of 2-Chloro-QAT was prepared by standard

reaction [10]. It was reaction between acetanilide and phosphorous oxy chloride in Di Methyl Formamide (DMF) as a solvent. Reaction of synthesis can be shown as below.

Reaction



2.2. Characterization of 2-Chloroquinoline-3- Carbaldehyde Thiosemicarbazone[11]

Synthesised 2-Chloro-QAT was characterized by various parameters like

elemental analysis, IR spectra and X-RD . Elemental analysis was carried by standard method [12]. UV-Visible spectra of 2-Chloro-QAT was taken at different wavelength in UV-Visible range and IR spectra in the range of 4000-700 cm^{-1}. The characteristic bands observed is shown in fig.1. Expected functional groups are shown in Table2. To determine type of structure of 2-Chloro-QAT, X-RD spectra of 2-Chloro-QAT was taken on diffractometer type PW 3710 based with tube anode Cu and wavelength 1.54. It is shown in fig.2. Antimicrobial activity of 2-Chloro-QAT was carried on gram negative bacteria- *Klebsiella pneumoniae*. It was conducted by disc diffusion method and was measured in term of zone of inhibition. [13].

2.3.Spectrophotometric Study of Ruthenium(III) Complexes:

Preparation of Solutions:

2-Chloro-QAT was recrystallised in ethanol and used for preparation of its Standard

solution. It was prepared in DMF:Water (1:1) and used for further study with Ruthenium, while equimolar solution of Ruthenium was prepared in water. For the same $RuCl_3.3H_2O$ of A.R. grade was used. Concentration of both the solution was 9.890 x 10^{-4} M. Phosphate buffer was prepared using Na_2HPO_4 and Citric acid of A.R. grade. Optimum pH (pH 3)was maintained for further experiments. Absorption spectra, extinction coefficient, effect of time on absorbance, effect of pH, effect of reagent concentration, stability, validity of Beers law, stoichiometry of complex by Jobs method & mole ratio method and diverse ion effect on Ruthenium - 2-Chloro-QAT were studied.

3. Resullt and discussion

3.1 Characterisation of 2-Chloro-QAT-

Elemental analysis of 2-Chloro-QAT revealed that it contains Carbon, Hydrogen, Nitrogen, Sulphur and chlorine and their percentage were 49.80,03.20,21.8,12.00 and 13.20 respectively (Table 1). It shows antimicrobial activity against *Klebsiella pneumoniae* in terms of zone of inhibition. It shows λ_{max} at 260 nm, while its Molar extension coefficient was found to be 1.297x 10^4 L Mol $^{-1}$ Cm^{-1} It means it has absorption in UV range. IR spectra shown in fig. 1 reveals various functional group present in 2-Chloro-QAT. It is shown in Table 2 X-RD of 2-Chloro-QAT is shown in fig. 2 From X-RD it reveals structure of 2-Chloro-QAT is Orthorhombic.

Table 1

Sr. No.	Chemical Analysis	Percentage found	Expected percentage
1	Carbon	49.80	49.90
2	Hydrogen	03.20	03.40
3	Nitrogen	21.80	21.17
4	Sulphur	12.00	12.10
5	Chloride	13.20	13.42

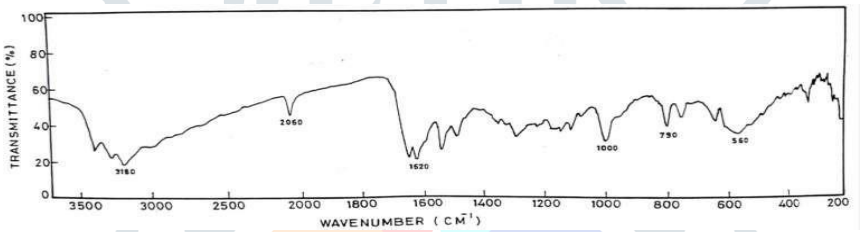


Fig 1 IR Spectra of 2-Chloroquinoline-3-Carbaldehyde Thiosemicarbazone

Table 2-Frequencies and corresponding functional groups

Sr. No.	Frequencies, Wave Number	Expected elements or Functional groups
1	3400	Simple H bonded –NH_2, -NH_3
2	3380	-C=N stretch
3	3290	-OH, C=CH_2, -CHO weakly
4	2200	-N-C=S stretch
5	1700	Aldehyde- > C = Ostrech
6	1600	Pyridine, Quinoline etc
7	1540	-C=S, -NH Medium
8	1480	-C=S, -NH, Pyridine
9	1280	-C=S Strong
10	1140	Other olefin ≡ C − HMedium
11	1110	Other olefin ≡ C − H Medium
12	800	Five adjacent aromatic –C-H
13	750	≡ C − Cl

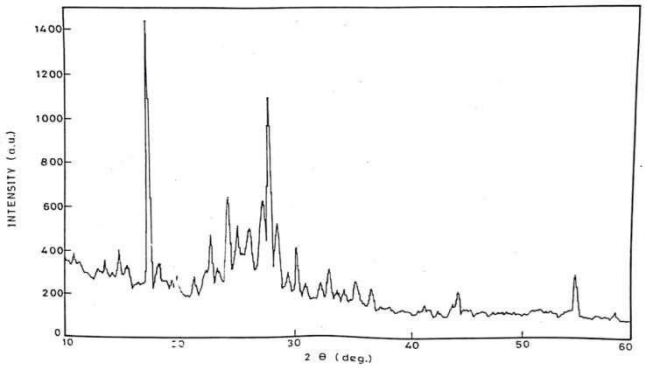
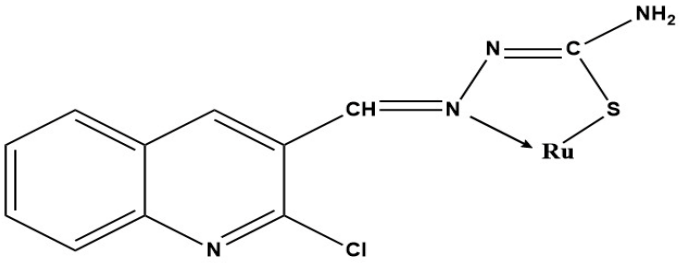


Fig 2 X-RD of 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone

3.2 Characterisation of Ruthenium -2-Chloro-QAT complex.

Experimentally, it has been proved that Ruthenium forms coloured complex with 2-Chloro-QAT and its λ_{max} was found to be 400nm. Mean molar extension coefficient at 400 nm was 3.433 x 10^4 L Mol $^{-1}$ Cm^{-1}. As λ_{max} was changed from 260 to 400 nm, it confirms formation of Ru (III)- 2-Chloro-QAT complex. For further experimentation, absorbance was measured at 400nm. Optimum pH was experimentally found to be 3. Ru (III)- 2-Chloro-QAT complex was found to be stable for several hours (up to 72 hrs). Neither the colour nor absorbance was changed during testing time-24,36,48 &72 hrs. Effect of reagent concentration was studied by keeping different amount of reagent and same amount of Metal in optimum condition. 3.0 mL reagent was found to be suitable for complex formation. Validity of Beers law was studied keeping different amount of Ruthenium and same amount of reagent in optimum condition. It obeys in between 4.95 x 10^{-6} M to 2.47x10^{-5} M. For stoichiometry of Ru (III)- 2-Chloro-QAT, Jobs method of continuous variation was used and it was confirmed by Mole ratio method. From both the methods, complex was found to be in 1:1 ratio. Hence its probable structure can be-



Effect of diverse ion was studied and found that interference of salicylate and thiocyanide ions was strong, hence they must be absent in a solution, while interference of Fe^{2+}, Cd^{2+} Co^{2+}, Hg^{2+}, Mg^{2+}, Sn^{2+}, Ni^{2+} was negligible. Hence their presence to some extent is tolerable.

4. Conclusion:

In this study, the ligand 2-Chloroquinoline-3-carbaldehyde thiosemicarbazone was successfully synthesized and characterized using UV-Vis, IR, XRD techniques and elemental analysis. The IR spectrum confirmed the presence of functional groups pertinent to coordination, while the XRD analysis revealed that the ligand crystallizes in an orthorhombic structure. The ligand exhibited promising antimicrobial activity against *Klebsiella pneumoniae*, demonstrating its potential for biological applications. The Ruthenium (III) complex with the synthesized ligand was formed and studied in solution. UV-Vis spectrophotometric analysis showed a maximum absorption at 400 nm, with a high molar extinction coefficient (3.437×10^4 $L \cdot mol^{-1} \cdot cm^{-1}$), indicating strong complex formation. The complex obeyed Beer's Law in between 4.95 x 10^{-6} to 2.47 x 10^{-5} and its stoichiometry was determined to be 1:1 by both Job's and mole ratio methods. The optimum pH for the complex formation was found to be 3.0, and the ideal reagent volume was 3 mL. The complex exhibited excellent analytical sensitivity, with a Sandell's sensitivity of 3.433×10^{-4} $\mu g \cdot cm^{-2}$, a low dissociation constant (1.793×10^{-9}), and a high stability constant (5.576×10^8), indicating strong complex stability. The effect of diverse ions was also investigated, highlighting the selectivity of the complexation under optimized conditions.

Overall, the synthesized ligand and its ruthenium (III) complex demonstrate significant analytical and biological potential, making them promising note for further development in coordination chemistry and antimicrobial applications.

5. References:-

1. Lumfr Sommer, Marie Langová &Gerhard Ackermann, Spectrophotometric Methods for the Investigation of Metal Complex Formation, C R C Critical Reviews in Analytical Chemistry, Volume 19, 1988 (2008)- Issue 3, p 225-269, https://doi.org/10.1080/10408348808542812
2. Subhash Padhyé, George B. Kauffman, Transition metal complexes of semicarbazones and thiosemicarbazones, Coordination Chemistry Reviews,Volume 63, April 1985, Pages 127-160.
3. Divya Utreja, Riddhi Salotra, Gurbir Kaur, Shivali Sharma and Sonia Kaushal Current Organic Chemistry, Volume 26, Issue 20, Oct 2022, p. 1895 - 1913 https://doi.org/10.2174/1385272827666221219101902
4. Maciej Serda , Danuta S. Kalinowski , Anna Mrozek-Wilczkiewicz , Robert Musiol , Agnieszka Szurko , Alicja Ratuszna , Namfon Pantarat , Zaklina Kovacevic , Angelica M. Merlot , Des R. Richardson , Jaroslaw Polanski, Synthesis and characterization of quinoline-based thiosemicarbazones and correlation of cellular iron-binding efficacy to anti-tumor efficacy, Bioorganic & Medicinal Chemistry Letters,Volume 22, Issue 17, 1 September 2012, Pages 5527-5531, https://doi.org/10.1016/j.bmcl.2012.07.030
5. Carmela Bonaccorso, Tiziano Marzo and Diego La Mendola, Biological Applications of Thiocarbohydrazones and Their Metal Complexes: A Perspective Review, *Pharmaceuticals* 2020, *13*(1), 4; https://doi.org/10.3390/ph13010004
6. Arora, Shefali,Agarwal, Shilpi,Singhal, Shailey, Anticancer Activities of Thiosemicarbazides/Thiosemicarbazones: A Review, International Journal of Pharmacy and Pharmaceutical Sciences, Vol 6, Issue 9, 2014, http://hdl.handle.net/123456789/1903
7. Richard D. Gerardi, Neil W. Barnett, Simon W. Lewis, Analytical applications of tris(2,2′-bipyridyl)ruthenium(III) as a chemiluminescent reagent, Analytica Chimica Acta,Volume 378, Issues 1–3, 4 January 1999, Pages 1-41, https://doi.org/10.1016/S0003-2670(98)00545-5
8. Vogel A. I., Text book of practical Organic Chemistry, longman group ltd, 802.
9. Vogel A. I.,Text book of practical Organic Chemistry, longman group ltd,1112-1129
10. Otto Meth-Cohn, Brahma Marine Brain Taarnawaski, 1981,Perkin J,C.S.,15,1920.
11. Omprakash Tukaram Sangule, Synthesis characterisation and analytical applications of 2-Chloro quinoline-3-Carbaldehyde thiosemicarbazone,International journal of Current advanced Research, vol 10,issue 05, may 2021,pages 24417-24421
12. S.K.Jain, Introduction to metallurgical analysis, 1982, 201
13. C. Perez, M. Paul, and P. Bazerque, An Antibiotic assay by the agar well-diffusion method, Acta Biologiae et Medicinae Experimentalis, 15, 1990,113–115.