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Design, Synthesis, Characterization and Spectroscopic Evaluation of an Anthraquinone-Thiophene Derived Schiff Base

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Abstract: A novel anthraquinone–thiophene Schiff base was synthesized by condensing 2-aminoanthraquinone with 2-thiophenecarboxaldehyde in ethanol under mild acidic conditions. The synthesized compound was characterized using FT-IR, X-ray diffraction (XRD) and scanning electron microscopy (SEM). FT-IR analysis confirmed the successful formation of the Schiff base with the expected functional group transformations. XRD results revealed that the compound exhibits a microcrystalline nature, while SEM images showed a rough and porous surface morphology with well-defined microcrystalline features. The antioxidant activity of the Schiff base was evaluated using the DPPH radical scavenging method, demonstrating notable free radical inhibition and indicating its potential biological importance. Overall, the structural and biological findings suggest that the synthesized Schiff base is a promising candidate for further applications in coordination chemistry, material science and medicinal chemistry.

Keywords*:-* Schiff base, Spectroscopy Microcrystalline nature, Antioxidant activity.

1. Introduction

Schiff bases constitute an important class of nitrogen-containing organic compounds formed by the condensation of primary amines with aldehydes or ketones, generating an azomethine (–C=N–) functionality that significantly influences their electronic and coordination behavior [1]. These compounds have attracted substantial attention due to their versatile applications in coordination chemistry, catalysis, medicinal chemistry, supramolecular assembly and material science [2-4]. The presence of the imine linkage enhances electron delocalization and promotes metal chelation, making Schiff bases promising ligands for transition metal complexes with diverse structural properties and functional capabilities [5].

Anthraquinone derivatives represent a privileged structural framework widely recognized for their rich π-conjugation, photochemical stability and redox-active properties [6]. Their incorporation into Schiff bases often results in new hybrid molecules with improved optical, electrochemical, and pharmacological behavior due to extended aromaticity and intramolecular charge-transfer effects [7,8]. Moreover, anthraquinone-based ligands exhibit remarkable biological activities, including antimicrobial, anticancer, anti-inflammatory and antioxidant properties, attributed to their planar aromatic core and ability to intercalate with biomolecules [9].

Thiophene and its substituted derivatives play a crucial role in modern organic chemistry and Material Science because of their high electron density, sulfur heteroatom and excellent π–π stacking capability [10]. Thiophene-containing Schiff bases often display enhanced intramolecular charge transfer, improved donor–acceptor characteristics and strong coordination potential toward various metal ions [11]. The fusion of anthraquinone and thiophene motifs within a single Schiff base framework is, therefore, expected to yield a highly conjugated ligand with superior optical, electronic and structural attributes.

The condensation of 1-aminoanthraquinone with 2-thiophenecarboxaldehyde offers an attractive route to generate a novel anthraquinone–thiophene imine system. Such hybrid Schiff bases not only provide insight into structure–property relationships but also serve as precursors for the synthesis of metal complexes with potential catalytic, sensing and biological utility [12-14]. Spectroscopic characterization including FT-IR, UV-Visible, ^{1}H and mass spectrometry provides essential information on the formation of the azomethine linkage, conjugation enhancement and structural features governing their reactivity and coordination behavior [15]. Considering the importance of heteroaromatic Schiff bases, the present work focuses on the design, synthesis and comprehensive spectroscopic evaluation of a novel Schiff base formed from 2-aminoanthraquinone and 2 thiophenecarboxaldehyde. The study aims to elucidate its structural features, electronic transitions and potential as a functional ligand for advanced chemical and biological applications [16].

2. Experimental

All the chemicals used were of AR/GR grade. Pure sample of 1-Aminoanthraquinone, molecular formula $C_{19}H_{11}NO_2S$, molecular weight 317.36 g/mol, melting point 220-230°C was obtained from Sigma Aldrich Ltd. Metal salts such as $MnCl_2.2H_2O$, $CuCl_2.2H_2O$ were of Hi-Media and Merck pharmaceuticals Ltd. Solvents used were ethanol, acetone, DMF and dimethylsulfoxide (DMSO).

2.1 Synthesis of Schiff base

The compound was synthesized from 2-thiophenecarboxalaldehyde and 1-Aminoanthra quinone by adding 100 ml of 2-thiophenecarboxalaldehyde ethanolic solution (1.22 g; 0.01 mol) to same volume of ethanol solution/same solvent of 1-Aminoanthraquinone (0.8144 g; 0.01 mol), the mixture was refluxed for 2 hrs and kept overnight at room temperature. The resulting solution was evaporated to 20% of its original solution and the product was collected by filtration, washed several times with ethanol, recrystallized from hot ethanol and then dried. The melting point of reddish brown powder was found to be 317.36.

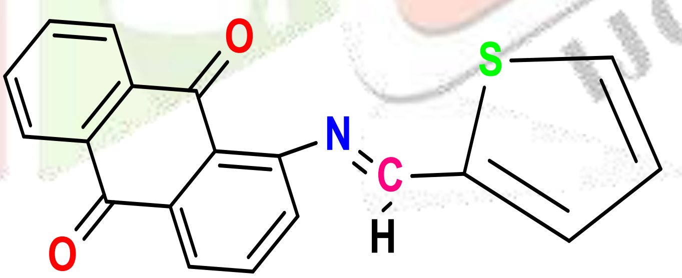


Fig.1: Structure of Ligand

2.2 Synthesis of Complexes

The solid complexes were prepared by mixing ethanolic solutions of the ligand (L) (0.37 g and 0.01 mol) with ethanolic solution of chlorides of Mn(II) (0.0809 g and 0.005 mol), Cu(II) (0.0852 g and 0.005 mol) separately. The resulting solutions were checked for pH and pH was adjusted by adding few drops of N/10 NaOH solution. The solutions were refluxed for 4 hrs and the refluxed solutions were kept for some days, solid crystalline complexes appeared in the solution which were filtered off, washed thoroughly with same solvent and finally with acetone, vacuum dried and weighed. Melting points of the complexes were recorded.

2.3 Analysis and Instrumentation

Elemental analysis was carried out on Vario MICRO V2.20 Elementar Analyse Systeme GmbH, from IIIM, Jammu. Metal contents were determined gravimetrically [16]. The infrared spectra were recorded on FT-IR Spectrophotometer Model RZX (Perkin Elmer) using KBr pellets from SAIF, Panjab University, Chandigarh. Mass were recorded at SAIF/CIL, Panjab University, Chandigarh by (LC-MS Spectrometer Model Q-TOF Micro waters). Thermogravimetric measurement were carried out at Department of Chemistry, IICT Hyderabad in nitrogen atmosphere (0.00l/min and 11/min).

3. Results and Discussion

The Schiff base ligand (L) was synthesized by the condensation of the amino group of aminoanthraquinone with 2-hydroxynaphthaldehyde. This ligand was then reacted with metal ions to yield Schiff base metal complexes. Both the ligand and the metal(II) complexes were obtained in good yields from ethanol and were isolated in pure form. The ligand appeared red brown in color, while the Mn and Cu complexes were light brown and blue green, respectively.

Elemental analyses of the complexes were consistent with a 1:2 metal-to-ligand stoichiometry, leading to the general formula $[M(L_2)]$ (M = Mn(II), Cu(II)). The complexes are air-stable solids at room temperature and do not decompose over time. They are non-hygroscopic, insoluble in water and most common organic solvents, but soluble in polar solvents such as DMF and DMSO. The molar conductance values of the complexes, measured in 10^{-3} M DMF, fall in the range of (17-19) $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$, confirming their non-electrolytic nature [17]. Magnetic studies revealed that the Mn(II) & Cu(II) complex is paramagnetic. The detailed physico-chemical characterization, analytical data and molar conductance values are summarized in Table 1 and Table 2.

Table 1: Physico-Chemical Characteristics of Ligand and its Complexes

S. No	Ligand/Complexes	Colour	%Yield	M.P °C	Molar Conductance Ω^{-1} cm^2 mol^{-1}	Magnetic Moment B.M
1	PAQ-TC	Reddish Brown	70	240	-	-
3	$[Mn(PAQ\text{-}TC)_2].2H_2O$	Light Brown	55	260	17.9	5.92
5	$[Cu(PAQ\text{-}TC)_2].2H_2O$	Blue Green	65	250	19.0	1.73

Table 2: Analytical Data of Ligand and its Complexes

S. No	Molecular Formula (Molecular Weight)	Elemental Analysis (%) Found (Calculated)				
		C	H	N	S	Metal
1	$C_{19}H_{11}NO_2S$ (317.36)	71.90 (71.82)	3.49 (3.46)	4.41 (4.41)	10.10 (10.10)	- -
3	$C_{36}H_{26}N_2O_6S_2Mn$ (701.67)	61.62 (61.56)	3.73 (3.70)	3.99 (3.99)	9.13 (9.63)	7.82 (7.82)
5	$C_{36}H_{26}N_2O_6S_2Cu$ (710.28)	60.87 (60.78)	3.68 (3.65)	3.94 (3.93)	9.13 (9.02)	8.94 (8.94)

3.1 Magnetic Measurements

The Mn(II) complex showed a value of 5.40 B.M., which is slightly lower than the spin only value of 5.92 B.M. for high spin octahedral Mn(II) complexes [18]. Cu(II) complex showed magnetic moment value of 1.73 B.M., slightly higher than the spin only (2.83 B.M.) value, indicating an octahedral environment around Cu(II) ion [19-20].

3.2 IR Spectra

The ligand shows a characteristic azomethine stretching band at 1610 cm^{-1}, which shifts to 1649–1629 cm^{-1} in the Mn(II) and Cu(II) complexes, confirming coordination through the azomethine nitrogen. The phenolic $\upsilon_{C–O}$ band at 1266 cm^{-1} shifts to 1281-1269 cm^{-1}, indicating bonding through phenolic oxygen after deprotonation. A noticeable shift in the $\upsilon_{C=O}$ band from 1672 cm^{-1} in the ligand to 1684–1688 cm^{-1} in the complexes suggests involvement of the carbonyl oxygen in coordination, while remaining largely intact structurally. The $\upsilon_{C–S}$ stretching band also shifts from 675 cm^{-1} to 648–652 cm^{-1}, supporting participation of sulfur in metal binding. New bands observed at 550–553 cm^{-1} $\upsilon_{(M–S)}$ and 625–626 cm^{-1} $\upsilon_{(M–O)}$ confirm metal-sulfur and metal-oxygen bond formation. These spectral changes collectively indicate that the ligand acts as a tridentate N, O, S donor, forming stable metal complexes [21–22].

Table 3: IR Spectral Bands (cm^{-1}) of Ligand and its Metal Complexes

S.NO	Group	PAQ-TC	[Mn(PAQ-TC)$_2$].2H$_2$O	[Cu(PAQ-TC)$_2$]. 2H$_2$O
1	$\upsilon_{(HC=N)}$	1610 s	1649 s	1629 m
2	$\upsilon_{(Phenolic)\ CO}$	1266 s	1281 s	1269 s
3	$\upsilon_{C-H\ (AA)\ Str.}$	30475 s	3136 b	3141 b
4	υ_{C-N}	1187 s	1184 s	1190 s
5	$\upsilon_{C-H\ Str.}$	2890 w	3100 s	3093 m
6	υ_{M-O}		625 s	626 s
7	$\upsilon_{C=O}$	1672	1684 s	1688 s
8	υ_{S-M}	-	550 w	553 s
9	υ_{C-S}	675	648	652

3.3 X-Ray diffraction studies

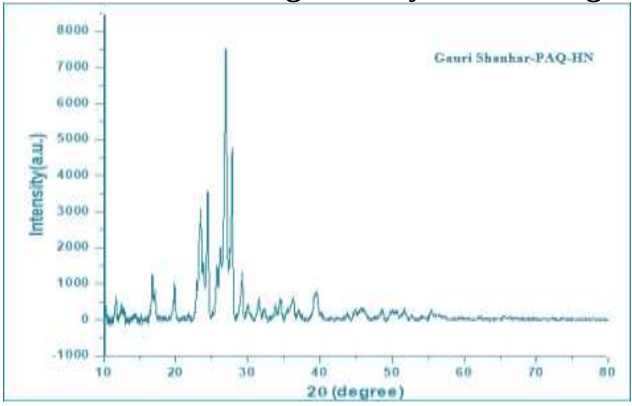
X-ray powder diffraction pattern is a set of lines or peaks, each of the different intensity and position (d-spacing or Bragg angle, θ) on either a strip of photographic film or on a length of chart paper. For a particular substance, the line positions are essentially fixed and are characteristic of that substance [23]. Each crystalline substance has its own characteristic powder diffraction pattern which may be used for its identification. Standard patterns are given in the powder diffraction file known as the JCDPDS file or formally as the ASTM file [24].

X-ray diffraction of the Schiff bases and metal complexes derived from these Schiff bases are entirely different (Fig. 2 and Table 4). All the reflections in the complexes are new ones and the patterns are also new ones and fairly strong which suggests that there is a complete conversion of reactants into products [25-28].

Table 4: Diffraction Patterns Ligand

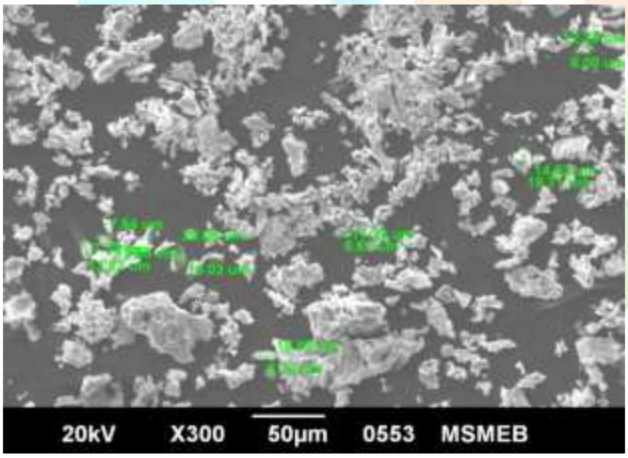
2theta(θ)	FWHM
17.9115	0.39952
19.8436	0.44642
23.50463	0.46998
26.97911	0.45044
31.86619	0.14912
34.53599	0.4217
39.57571	0.60965
45.61009	0.39219

Fig.2: X-ray diffraction graph



3.4 Scanning Electron Microscopic studies

The surface morphology of the ligand and its metal complexes was studied using SEM. The Schiff base ligand displayed a rock-like, irregular surface with several patchy regions, indicating its amorphous nature. In contrast, the metal complexes showed well-defined microcrystalline features with rough, pitted surfaces. The micrographs revealed distinct morphological patterns such as cauliflower-, bead-, rock-, and root-like structures, depending on the metal ion. The complexes exhibited crystal growth from small particles (<100 nm) into larger agglomerates, confirming nanoscale to microscale aggregation behavior. The absence of any surface shadowing by metal ions suggests uniform complex formation. Overall, the SEM images clearly indicate that complexation significantly alters the morphology of the parent ligand, reducing particle size and promoting the formation of more ordered crystalline aggregates [29-31].



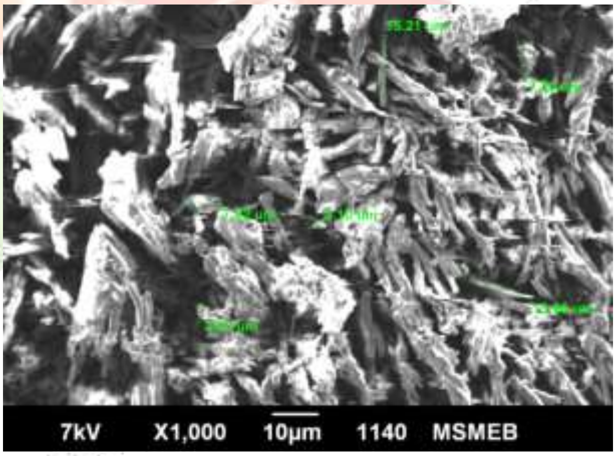


Fig.3: SEM of PAQ-TC Schiff Base

Fig.4: SEM of PAQ-TC-Mn Complex

3.5 Antioxidant Activities

In vitro free radical scavenging activity of different concentrations DPPH radicals i-e 20, 40, 60, 80 and 100 (µg/ml's) was determined. Being stable radical, it is neutralized by molecules which donate H atoms. The absorbance at 517nm reveals the scavenging effect of DPPH radicals [32-33]. The tested compounds with electron donor groups (N, S) can act as radical scavengers and are able to resist oxidative challenges. It can be seen from the table that derived complexes revealed highest scavenging potential against DPPH, while the complexes derived from Schiff bases with Mn(II) and Cu(II) ions revealed moderate scavenging effect against DPPH.

Table 5: Percent inhibition data of DPPH of free radical scavenging assay

Concentration (μg/mL)	% Inhibition of PAQ-TC-Mn	% Inhibition of PAQ-TC-Cu	% Inhibition of Ascorbic Acid
20	7.94±0.0011	8.94±0.0013	13.20±0.0010
40	9.00±0.0014	12.00±0.0007	24.51±0.0008
60	19.17±0.0010	18.17±0.0001	39.59±0.0009
80	24.41±0.0017	25.41±0.0010	45.46±0.0013
100	35.47±0.0020	36.47±0.0005	65.32±0.0006
IC50	85.2	82.6	45.1

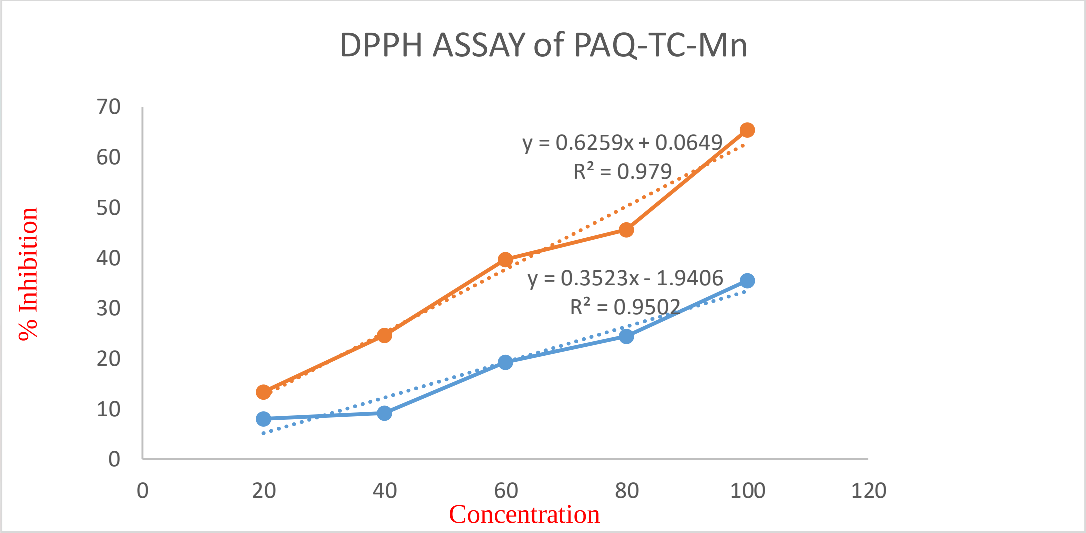


Fig.5: Line graph showing antioxidant activity of PAQ-TC-Mn complex

4. Conclusion

In this work, the anthraquinone–thiophene Schiff base (PAQ-TC) was successfully synthesized and confirmed through spectral and analytical techniques. FT-IR, XRD and SEM data verified the formation of stable Mn(II) and Cu(II) complexes with tridentate N, O, S coordination. XRD and SEM studies showed clear structural and morphological changes after complexation. Magnetic measurements supported octahedral geometries for both metal complexes. Antioxidant studies revealed moderate DPPH scavenging activity, with Cu(II) complexes showing slightly higher efficiency. Overall, the results suggest that PAQ-TC and its complexes possess promising structural and biological properties for future applications.

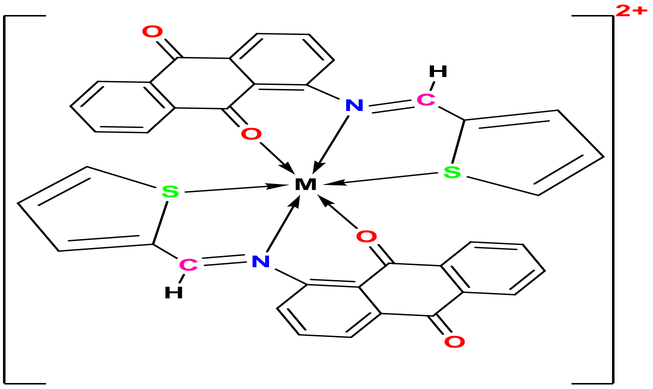


Fig.6: M= Mn(II) and Cu(II)

5. Acknowledgement

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