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SYNTHESIS, CHARACTERIZATION, THERMAL AND PHOTOLUMINESCENT STUDIES OF NEWLY SYNTHESIZED METAL COMPLEXES SULPHANLIC ACID-THIOUREA-FORMALDEHYDE Cu(II), -Ni(II)

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ABSTRACT
Using 2 M HCl as a catalyst, the copolymer was synthesized by condensation of sulphanilic acid (SA), thiourea (T), and formaldehyde (F) in a 1:1:2 monomer ratio. Metal complexes were synthesized by employing this terpolymer as a ligand with two transition metal ions, Cu(II) and Ni(II), in a 2:1 molar ratio. The reaction was run for three hours at 60 °C with effective reflux. UV-visible spectroscopy, NMR, FTIR, SEM, and XRD were used to analyze the resulting metal complexes. The elemental composition of the SATF-I-M copolymeric metal complexes was examined using elemental analysis. The thermal durability of the terpolymer ligand metal complexes was assessed using thermogravimetric analysis (TGA), and the activation energy was calculated using the Freeman–Carroll and Sharp–Wentworth techniques based on TGA data. The RF-501 (PC) S CE (LVD) MODEL PL spectrometer was used to measure the spectra of complexes containing the two transition metal ions in order to study the photoluminescence characteristics of the newly generated copolymeric metal complexes. The main goal of this study is to create new polymeric metal complexes and investigate their photoluminescent properties, while recognizing the important contributions of current researchers in the area.
Keywords: terpolymer, metalcomplex, characterization, thermal degradation, morphology, photoluminescence.

INTRODUCTION
The synthesis of coordination polymers has attracted a lot of attention lately because of their exceptional qualities, which include photoluminescence, thermal endurance, catalytic capabilities, and the capacity to bind hazardous metal ions [1–4]. Researchers have been especially interested in making use of polymer–metal complexes due to their excellent antibacterial activity and thermal reliability. Numerous studies have explored the various organic components in different proportions used to create distinct terpolymers, each with unique characteristics, properties, and applications [4–5]. W. B. Gurnule, Kiran S. Vajpai, R. V. Mankar, and C. G. Kohad et al. have examined the photoluminescent investigations of copolymer–metal complexes generated from copolymers with 8-hydroxyquinoline, hexamethylenediamine, and formaldehyde [6]. Azarudeen et al. created novel metal chelates

and terpolymer ligands from anthranilic acid, aminopyridine, formaldehyde, and phenyl hydrazine. The complexes were examined for antibacterial activity and thermal stability. All of the complexes were found to be more effective antibacterial agents and more thermally stable than their equivalent ligands, according to the data [7, 8]. Using Cu(II), Ni(II), and Zn(II), D. Shedmake et al. developed metallic complexes that were further investigated by various spectroscopic and physicochemical techniques. They also investigated the antibacterial and thermodynamic properties of the synthesized copolymer–metal complexes [9].

A few divalent complexes with transition metals of 8-hydroxyquinoline have been created, and their antibacterial and thermal stability were reported [10]. Currently, novel terpolymer–metal complexes are being synthesized. Additionally, the structures of the copolymer–metal complexes were verified using several physical and spectroscopic techniques. Similarly, Rahagandale et al. synthesized resorcinol–melamine–formaldehyde and tested its antibacterial properties, showing effectiveness against *Staphylococcus aureus*, *Escherichia coli*, *Aspergillus niger*, and *Candida albicans* [11].

MATERIALS AND METHODS

Materials

Central Scientific Company, Nagpur, India, was the source of A.R. grade sulfuric acid. Thiourea, formaldehyde, nickel nitrate, and copper nitrate were the compounds employed in the current research. SATF-I terpolymer ligand was synthesized in a 1:1:2 ratio, obtained, and employed following distillation in DMF and DMSO. Additionally, ethyl alcohol was utilized for the terpolymer, such as sulphanilic acid–thiourea–formaldehyde–(Cu and Ni).

Method of Synthesis of SATF-I-Cu, Ni complexes:

The produced terpolymers have been employed as ligands with a small number of transition metal ions, such as Cu^{2+} and Ni^{2+} ions, to form the terpolymer complexes of transition metals [12]. For the complex formation reaction, the transition metal ions (Cu^{2+} and Ni^{2+}) were taken at 1 M and the terpolymer at 2 M. To allow it to swell for two hours, two grams of the sulphanilic acid–thiourea–formaldehyde terpolymer were added to a round-bottom (RB) flask and submerged in ethanol solution. After dissolving 1 g of cupric nitrate (or nickel nitrate) in ethanol solution, the mixture was transferred into a round-bottom flask fitted with a reflux condenser and a mechanical stirrer. For three hours, the reaction was conducted at 60 °C with efficient reflux. Once the colloidal precipitate was observed in the flask, it was separated. To remove contaminants, the product was filtered and washed with ethanol and ether. The purification process was carried out several times to obtain the refined product. The final purified sample was air-dried, ground into a powder, and stored with silica gel in a vacuum desiccator. The SATF-I terpolymer complexes with Ni^{2+} metal ions were prepared using the same process. The scheme illustrates how the SATF-I metal complex is produced using Cu(II) and Ni(II) metal ions.

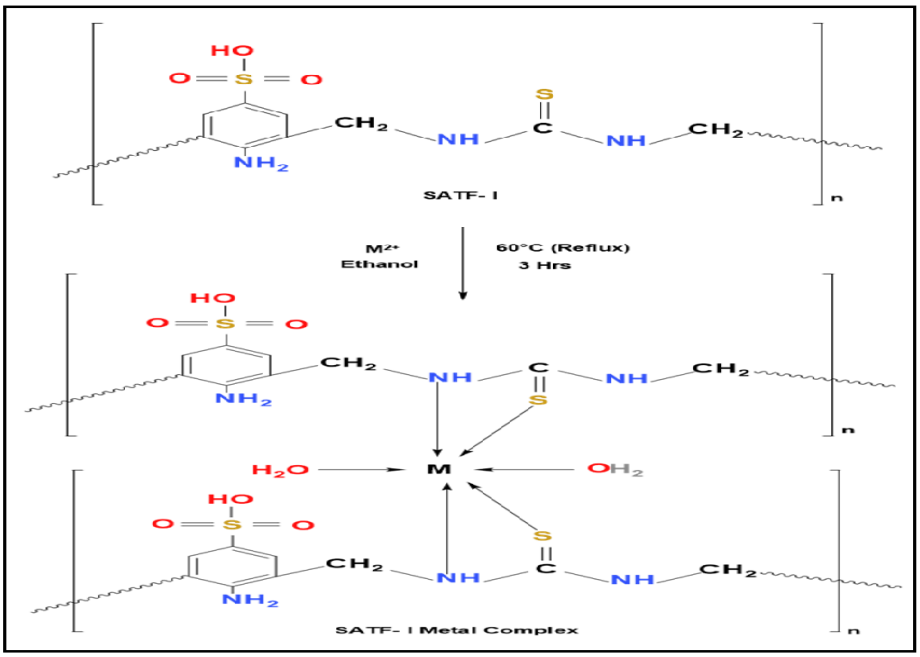

Fig. 1: Synthesis of SATF-I Metal complexes [M= Cu, Ni]

Results and Discussion

(Result obtained from STIC Sophisticated Test and instrumental Centre, Kochi)

Physico-chemical and Analytical Data

1. **Elemental analysis**

The SATF-I terpolymer ligand and its complexes of metals with Cu^{2+} and Ni^{2+} ions are shown in Table 1 along with their physical and analytical data.

Table 1. Analysis of elements and empirical formula of SATF-I metal complexes

Compounds	% of C Observed Found (Cal.)	% of H Observed Found (Cal.)	% of N Observed Found (Cal.)	% of S Observed Found (Cal.)	% of M Observed Found (Cal.)	Empirical Formula of Repeated Unit	Empirical Formula Weight
SATF-I	38.38 (39.87)	3.83(4.02)	14.72(15.37)	22.62 (23.47)	-	C9H11N3O3S2	273.13
SATF-I-Cu	33.05 (33.46)	3.13 (3.40)	12.72 (13)	19.37 (19.85)	9.41 (9.83)	C18H22N6O6S4Cu.2H2O	645.98
SATF-I-Ni	32.98 (33.71)	3.32 (3.43)	12.79 (13.10)	19.88 (20)	8.87 (9.15)	C18H22N6O6S4Ni.2H2O	641.13

2. **SPECTRAL ANALYSIS**

UV-Visible

Figure 2 displays the UV–visible spectra of the SATF-I terpolymer and its metal complxes. At a scanning rate of 100 nm min^{-1}, the UV–visible spectra were recorded in pure DMSO over the range of 200–700 nm.

Compound	Band I (λmax) (230–250 nm)	Band II (λmax) (280–300 nm)	Electronic Transitions	Chromophoric Group (Assignment)
SATF-I	230	282	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$	Aromatic Ring (Benzene), C=S (Thiourea)
SATF-I-Ni	236	287	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, LMCT	Metal-Ligand Coordination (Ni → O/N/S)
SATF-I-Cu	236	285	$\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, LMCT	Metal-Ligand Coordination (Cu →O/N/S)

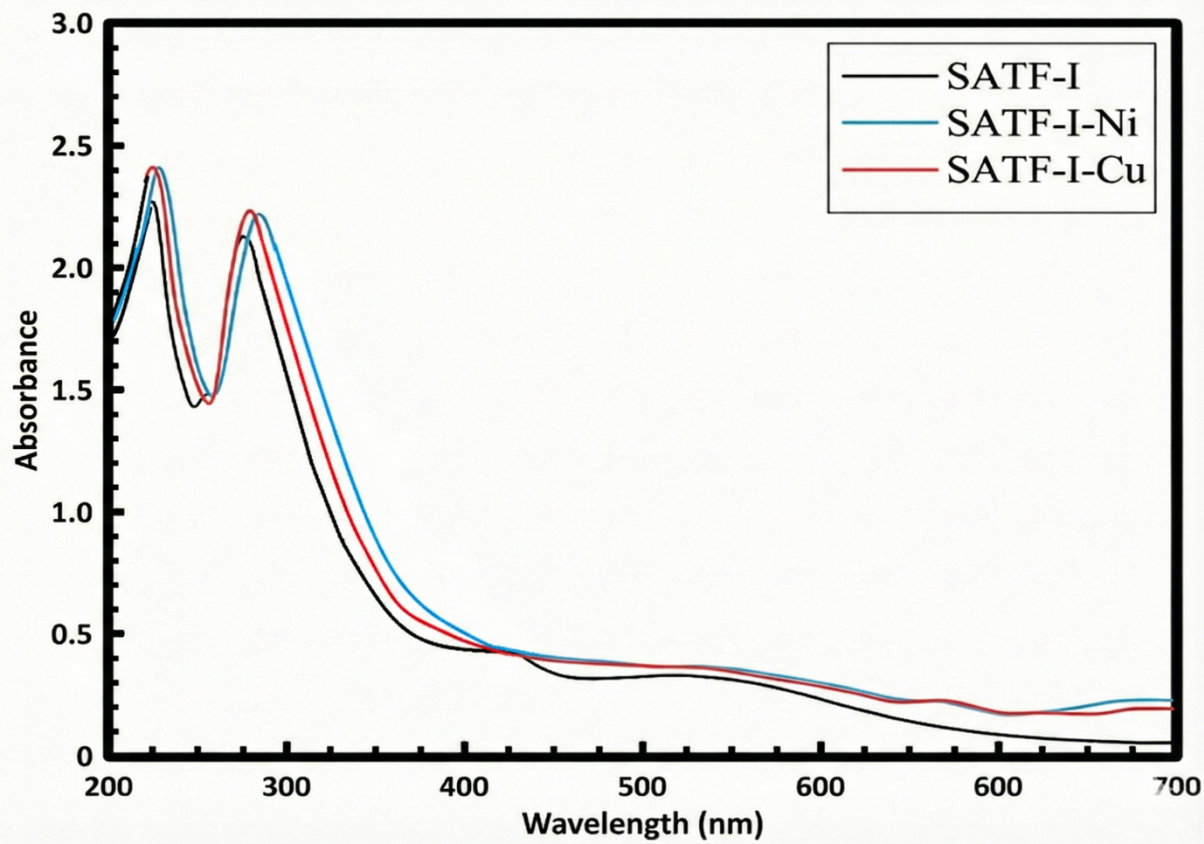

Fig.2: UV-Visible spectra of (a) SATF-I terpolymer (b)SATF-I-Cu (c)SATF-I-Ni

Fourier transform infrared spectra

Significant changes in the important functional group frequencies are visible in the infrared spectrum data of SATF-I and its metal complexes, SATF-I–Cu and SATF-I–Ni, demonstrating that the ligand and metal ions have successfully coordinated.

Table. 2: Infrared spectra of SATF-Iterpolymer resin and its metal complexes

Compound	ObservedFrequencies(cm^{-1})

	SATF-I	SATF-I–Cu	SATF-I–Ni
Aryl -NH Stretching	3313.85	3435.8	3334.1
Aryl C-H Stretching	3033.71	3050.9	3048.4
N-H bridge Stretching	2922.32	2925.6	2924.7
C=S Stretching	1709.26	1685	1702.2
Ar-stretching	1533.81	1620	1612.8
-CH2 Bending(wagging and twisting),	1033.71	1030	1023
>CH2 methylene bridge Stretching	1324.69-1266.61	1360.2-1195	1333-1265.5
=S-M	-	520	516
-N-M	-	418	420

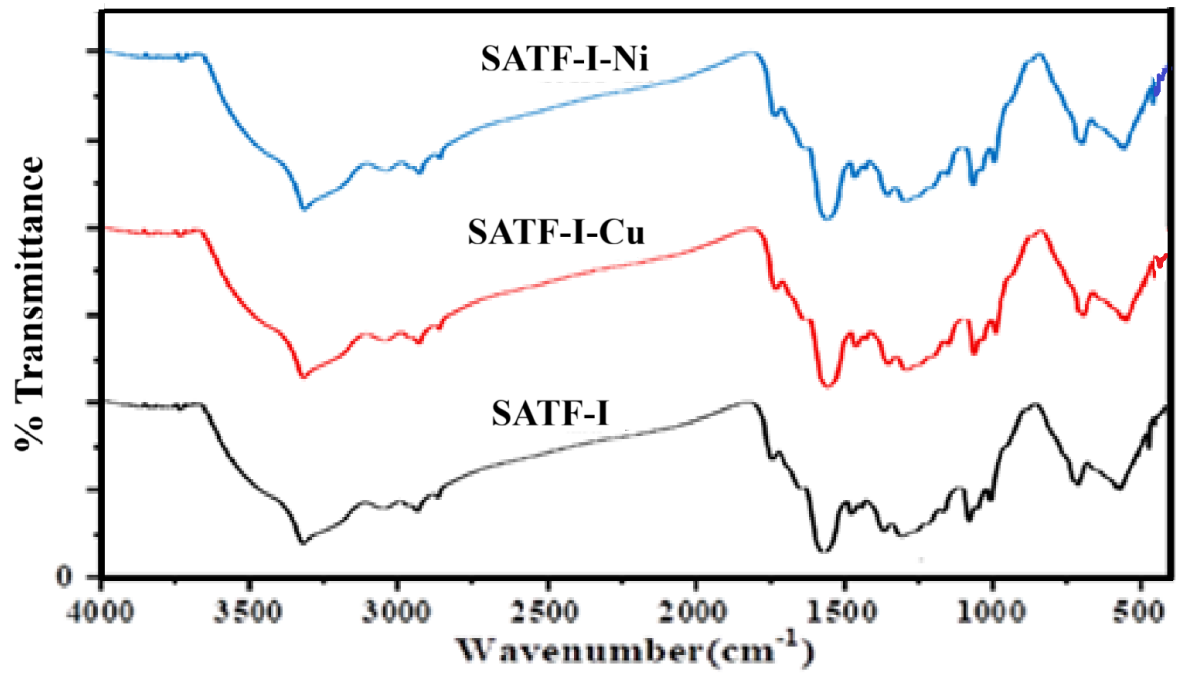

Fig. 3:(a)FTIR spectra of SATF-I-M complexes

H^1 NMR

The observed chemical shift data for SATF-I and its metal complexes SATF-I–Cu and SATF-I–Ni indicate shifts in proton environments due to coordination with metal ions.

Table 3. H^1 NMR Spectral data of SATF-I and its metal complexes

Obsereved chemical shift (δ) ppm			Nature of proton assigned
SATF-I	SATF-I-Cu	SATF-I-Ni	
10.02	10.0	10.01	**Proton of -SO3H group**
9.01	9.02	9.03	**Proton of Thioura amide group**
5.05	5.06	5.04	**proton of Ar-NH2 linkage**

6.8	6.91	6.89	**Aromatic proton (unsymm. Pattern)**
3.84	3.82	3.83	**Methylene proton of Ar - CH_2 - N - linkage**
2.5	2.39	2.41	**Residual solvent or moisture solvent**

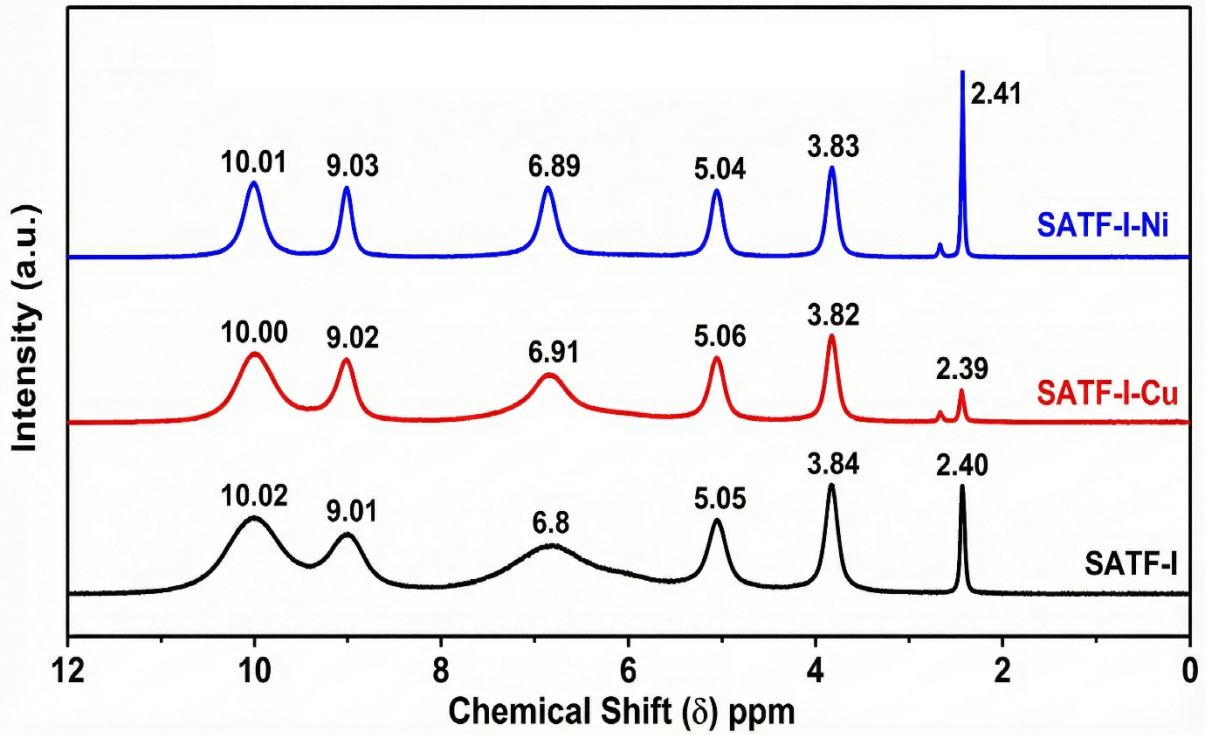

Fig. 4(a): H^1 NMR spectra of SATF-I-M complexes

SURFACE ANALYSIS

SEM

Upon coordination with metal ions, the surface morphology undergoes distinct transformations, imaged at a magnification of X500 to observe the bulk particle distribution. The comparative morphological order between the ligand and its complexes is Amorphous/Globular (Ligand) →Granular/Microspherical (Cu-Complex) →Crystalline/Faceted (Ni-Complex). The SATF-I-Cu complex exhibits a highly defined microspherical or bead-like morphology, appearing more discrete and uniform than the parent ligand, which suggests that Copper(II) ions promote a regular, granular assembly of the polymer particles. Conversely, the SATF-I-Ni complex is characterized by large, angular, and faceted crystalline blocks. The presence of these sharp-edged structures aligns with the XRD data, confirming that the Nickel ions induce a highly ordered, rigid lattice arrangement, effectively increasing the crystallinity and altering the packing density of the polymer upon

complexation.

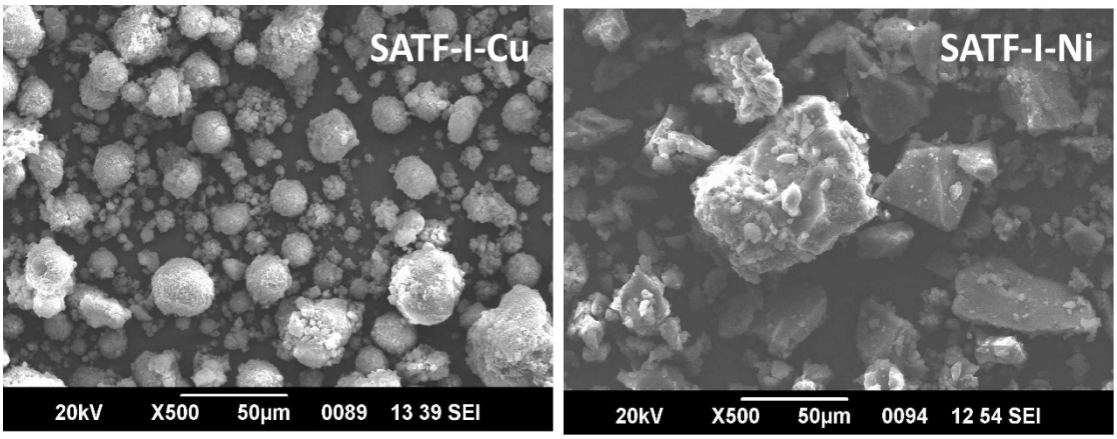

Fig. 5. SEM Micrographs of (a)SATF-I-Cu, (b)SATF-I-Ni

XRD

The X-ray diffraction patterns of the metal complexes, SATF-I-Cu and SATF-I-Ni, exhibit new, sharper, and more intense reflections compared to the ligand, particularly in the regions $2\theta \approx 18°, 32°, and\ 37°$. The appearance of these crystalline peaks indicates that the degree of crystallinity increases upon coordination. This phenomenon is attributed to the chelation of metal ions with the functional groups (-NH and C=S) of the polymer chain. The metal ions act as cross-linking agents, bridging adjacent polymer chains and restricting segmental motion, which facilitates a more ordered, compact packing of the polymer layers. Specifically, the SATF-I-Ni complex displays the most pronounced sharp peaks, suggesting that nickel ions induce a highly ordered lattice arrangement compared to the copper complex**.**

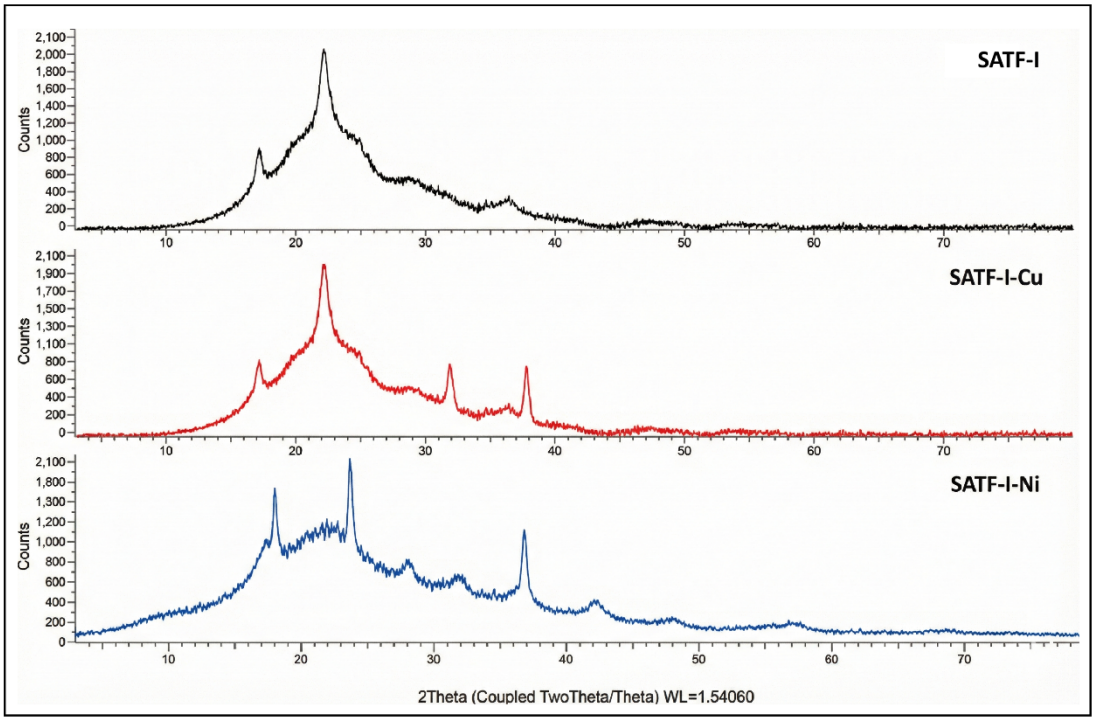

Fig. 6:(a): X-ray diffraction of SATF-I -Cu (b) SATF-I -Ni terpolymer metal complex

THERMAL STUDIES

The thermal endurance of the SATF-I terpolymer and the associated metal complexes has

been investigated using thermogravimetric evaluation. The temperature-dependent properties of the terpolymer and its corresponding metal complexes are shown in Figure 7, and the percentage of weight loss at various temperatures is reported in the table below.

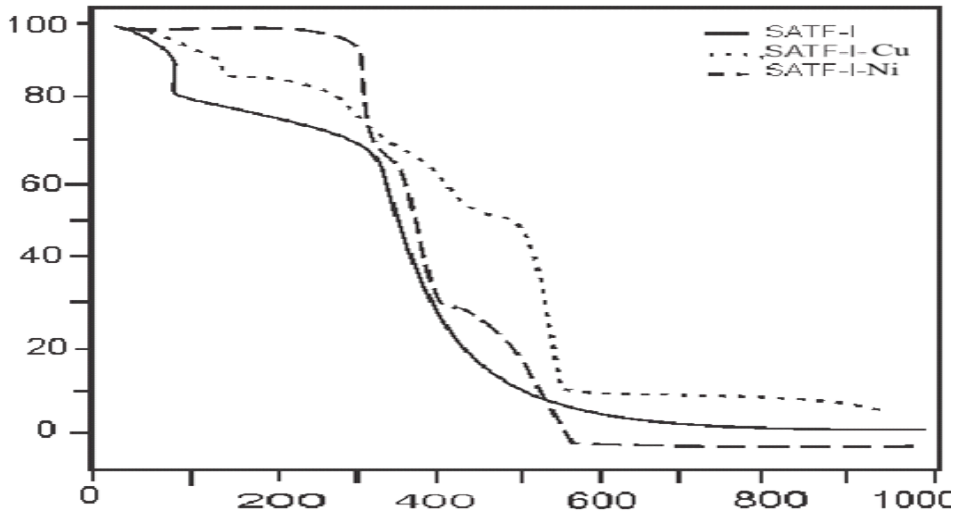

Fig:7: Thermogram of SATF-I metal complxes of Cu and Ni

The thermal examination of the SATF-I terpolymer and its metal complexes reveals that the copolymer complexes are marginally more stable than the SATF-I terpolymer due to metal ion coordination. The thermal stability of the SATF-I polymer and its complexes was found to follow the sequence: SATF-I–Cu(II) > SATF-I–Ni(II) > SATF-I–ligand. The increased stability of the metal complexes might be attributed to their coordination, better cross-linking properties, and crowding effect. In the case of the Cu(II) complex, degradation occurred at a significantly lower temperature than that of the ligand, which may be attributed to polymer oxidation caused by the catalytic action of metal ions.

Table no. 4: Thermogravimetric Analysis of SATF-I-Cu, Ni and Zn Metal Complexes.

Copolymer	Half Decomposition Temp. (T)	Activation Energy Ea (KJ)/mol	
		SW	FC
SATF-I	479	7.32	7.49
SATF-I-Cu	550	2.07	2.92
SATF-I-Ni	490	2.34	2.51

Kinetics of Thermal Degradation

Formulas for Calculating Kinetic Parameters

(i) Entropy Change (ΔS)
The intercept can be expressed as:
Intercept = log (KR/h ϕ E) + ΔS/2.303R
where:
- K = 1.380 x 10^-16 erg/deg/mole-
- R = 1.987 cal/deg/mole (or 8.314 J/K/mol)
- h = 6.625 x 10^-27 erg sec
- U = 0.166
- ΔS = change in entropy
- E = activation energy derived from the graph.
(ii) Free Energy Change (ΔF)
The free energy change can be calculated using the formula:
ΔF = ΔH - TΔS
where:
- ΔH = enthalpy change (activation energy)
- T = temperature in Kelvin
(iii) Frequency Factor (Z)
The frequency factor can be derived from:

$B_{2/3} = \log ZE_a/R$□

$B_{2/3} = \log 3 + \log[1 - 3\sqrt{(1-$□$)}] - \log p(x))$

where:
- Z = frequency factor
- log p(x) = calculated using Doyle's table related to activation energy
- □ = degree of transformation, defined as a = w/Wc.
(iv) Apparent Entropy (S*)
The apparent entropy can be calculated as:
S* = 2.303 R log (Zh/RT)
where:
- Z = Frequency factor
-T* = half decomposition temperature.

Sharp–Wentworth and Freeman–Carroll Method
The expressions to calculate the kinetic and thermodynamic parameters are presented in Table 5 and the results in Table 6.
Table no. 5:Kinetic and Thermodynamic Parameters of SATF-I Ligand and its metal complexes

Copolymer Ligands and its metal complexes	Entropy Change ΔS(J)	Free Energy Change ΔF (KJ)	Frequency factor Z (S^{-1})	Apparent Entropy Change (S*)	Order reaction
SATF-I	-240.00	130.31	1258	-25.14	0.99
SATF-I-Cu	-220.04	121.02	1273	-26.11	1.05
SATF-I-Ni	-212.66	115.35	1276	-26.12	1.01

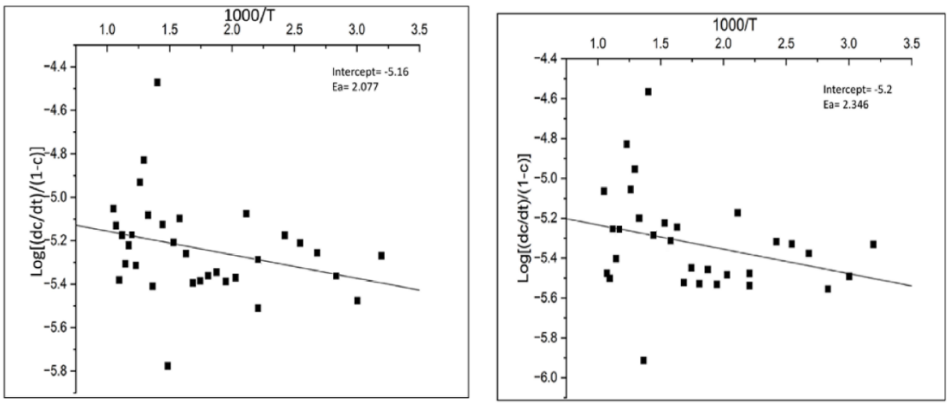

Fig8(a): Sharp–WentworthplotsofaSATF-I-Cu(b)aSATF-I-Ni

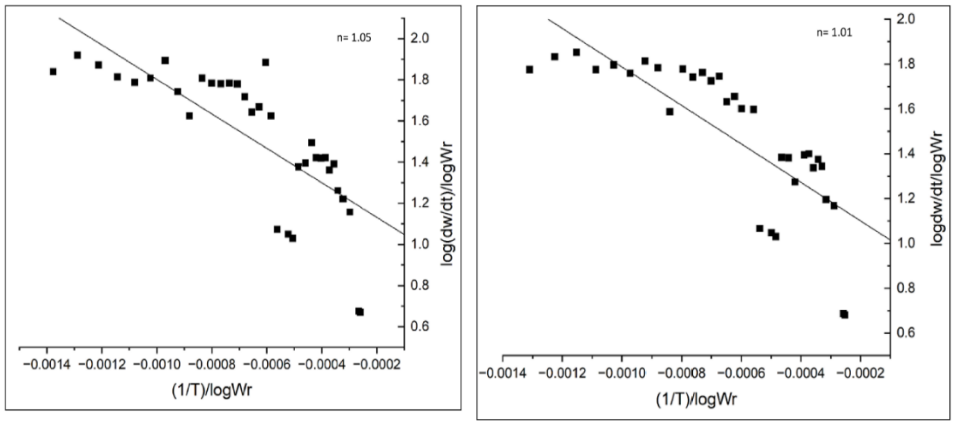

Fig9(a):Freeman-CarrollPlotofSATF-I-Cu(b)SATF-I-Ni

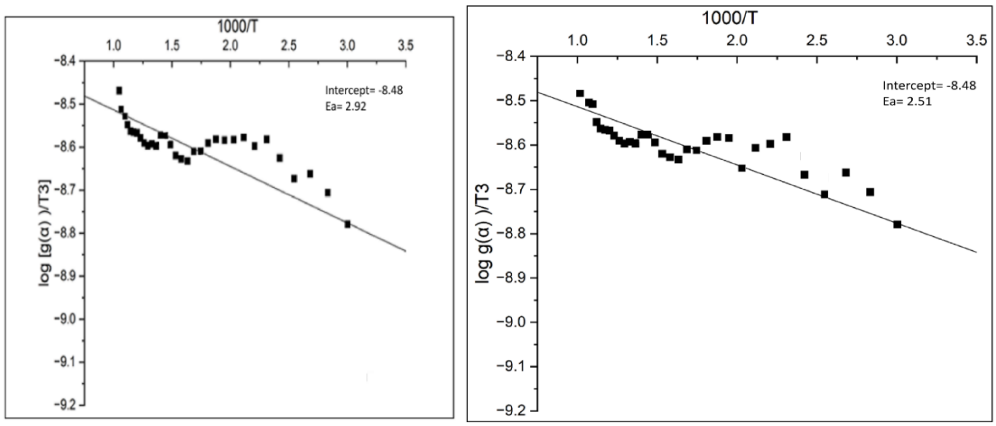

Fig10(a).Activation Energy (E_a) By Freeman-CarrollPlot of (a)SATF-I-Cu(b)SATF-I-NiComplexes

Photoluminescent properties

The PL spectra of SATF-I–Cu and SATF-I–Ni both show strong blue-region emissions with major peaks at approximately 435 nm, 450 nm, and 465 nm, but their intensities differ notably. SATF-I–Cu displays higher emission strengths, with its dominant peak at 450 nm reaching ~660–680 a.u., compared to the Ni complex which reaches only ~630–650 a.u. at the same wavelength, while the peaks at 435 nm (~480 a.u. for Cu; ~420 a.u. for Ni) and 465 nm (~420 a.u. for Cu; ~350 a.u. for Ni) also show this same trend. Emission for both complexes begins near 410 nm and gradually tapers off beyond 500–600 nm, but the Cu complex consistently maintains greater relative intensity, indicating fewer non-radiative losses. Overall, the higher peak intensities across all wavelengths confirm that SATF-I–Cu exhibits superior photoluminescent efficiency compared to SATF-I–Ni.

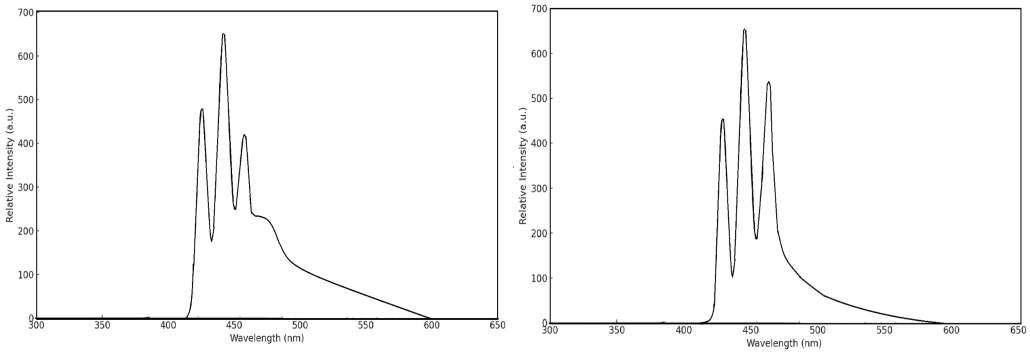

Fig.11:(a) PL Spectra SATF-I–Cu(b) SATF-I–Ni Complex

CONCLUSION

The SATF-Icopolymer metal complexes of Cu(II) and Ni(II)has been synthesized using the condensation polymerization of formaldehyde, thiourea, and sulphanilic acid in the appearance of an acid catalyst. The SATF-I copolymer metal complexes suggested structure has been established using FT-IR, 1H NMR, XRD and UV-visible spectrum investigations. The spectral studies have facilitated an assessment of the SATF-I-M purity, validating its composition as per the expected ratios of the constituent monomers. The found physicochemical characteristics have direct consequences for the prospective uses of SATF-I-Cu and Ni. SEM methods have been used to get a deep knowledge of molecular structure.

This structural information is essential for predicting the behaviour of terpolymer metal complexes in a wide range of situations and applications. The metal complexes have higher thermal stability than their terpolymer ligands. This TGA data provides crucial insights into the thermal properties of the copolymer and its metal complexes, indicating that the addition of copper and nickel increases the material's overall thermal resistance.

The photoluminescence study suggests that SATF-I copolymer metal complexes of Cu and Ni are effective photoluminescent materials.They have the capacity to act as supporting materials and beginning components for a wide range of light-emitting and semiconductor devices.

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