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Green Synthesis, Structural Characterization and Study of Thermal Behaviour of Cu^{2+} and Co^{2+} Complexes Derived from Salicylidene-3-Amino Benzoic Acid

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Abstract

The Schiff base ligand Salicylidene-3-amino benzoic acid (SAB) was prepared by reacting salicylaldehyde with 3-amino benzoic acid. Its Cu^{2+} and Co^{2+} complexes were prepared by reacting ethanolic solutions of SAB with magnetically stirred solution of metal salts in distilled water using microwave-assisted heating for 30 min. The ligand and complexes were characterized on the basis of physical properties, FT-IR, UV-Vis, magnetic susceptibility, XRD and TGA/DTA. Unit cell dimensions obtained from XRD crystallography analysis agreed with the establishment of orthorhombic crystal structure. The spectroscopic studies revealed the presence of -C=N, -C=O, M-O, M-N, -OH and NO_3 functional groups and this showed that the ligand coordinated to metal via N and O donors. The thermal decomposition of the complexes indicates the loss of lattice of water and decomposition of the ligand as key to the interpretation of successive weight loss.

Keywords: Characterization, Coordination, Metal complexes, Salicylaldehyde, Schiff base

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INTRODUCTION

Coordination chemistry is undoubtedly the most active research area in inorganic chemistry (Anil *et al.,* 2020*;* Kadhiravansivasamy *et al.,* 2017). Thousands of coordination complexes have been synthesized and investigated during the past few decades (Fugu *et al.,* 2013; Kiran *et al.,* 2016). It has been reported that coordination compounds have wide application in food industry, dye industry, analytical chemistry, catalysis, fungicidal, agrochemical and biological activities (Zhai *et al*., 2015; Dudhat and Kurkarni, 2018; Salga *et al*., 2018). Ever since the importance of coordination phenomenon in biological processes was realized, a lot of metal containing macromolecules have been synthesized and studied to understand the mechanisms of complex biological reactions. Some metal complexes have been found to have antimicrobial properties and could be effective against diseases (Rishu *et al.,* 2013). This has led to investigations on metal-drug interactions and more studies on complexes of metal with the aim of discovering more effective chemotherapeutic agents to fight diseases. It has been discovered that the mode of action of some drugs is through chelation or by inhibitory metalloenzymes but for most of the drugs that have the potential of acting as ligands, studies are being carried out to know the effect of chelation on their biological activity (Muayed, 2012; Pallavi *et al*., 2014).

Thermogravimetric analysis of Schiff base ligands and metal complexes are useful tools as it provides information about the thermal stability and decides whether the water molecules if found are inside or outside the inner coordination sphere of the central metal ion, and also suggests the general scheme for the thermal decomposition of metal complexes (Basim *et al*., 2019).

Even though many Schiff bases derived from salicylaldehyde or substituted salicylaldehyde with amines have been reported (Chandrasekaran *et al*., 2014). Literature work on complexes formed from the condensation reaction between salicylaldehyde and 3-amino benzoic acid are scanty. Herein, we have reported the synthesis, structural characterization and study of thermal behaviour of Cu^{2+} and Co^{2+} complexes derived from salicylidene-3-amino benzoic acid.

MATERIALS AND METHODS

Reagents and Equipment

All the chemicals used were of analytical grade and purchased from Sigma-Aldrich Ltd and BDH. They were used without further purification. The infrared spectra of the ligand and complexes was carried out using DGH-9101-ISA PEC model and analyzed using KBr disc in the range of 4500-450 cm^{-1}on a Shimadzu infrared spectrophotometer. X-ray diffraction studies of the synthesized complexes were carried out using X-ray Diffractometer Thermo Scientific Model ARL X TRA X-ray 197492086.

Preparation of Salicylidene-3-amino benzoic acid

The ligand was prepared using a method described by Shamly *et al.* (2018). Salicylidene-3-amino benzoic acid was prepared by condensation of 0.01 mol (24.5 g) 3-amino benzoic acid in 10 mL of water and 0.01 mol (9 mL) of salicylaldehyde. The mixture was stirred at room temperature for 10 min. The crystals formed were filtered, washed with distilled water and dried in a desiccator.

The chemistry of reaction leading to the synthesis of the ligand is as presented in Equation (1)

$$C_7H_6O_2 + C_7H_7O_2N \rightarrow C_{14}H_{11}O_3N + H_2O \qquad (1)$$

Synthesis of complexes

The complexes were prepared using a procedure described by Iorungwa *et al.*, (2020) with slight modifications. Salicylidene-3-amino benzoic acid (23.2 g; 0.01 mol) was dissolved in 10 mL ethanol. 0.01 mol of the metal nitrates (Cu(II) and Co(II)) were dissolved in 10 mL of distilled water and the salicylidene-3-amino benzoic acid solution was then poured gently into the Cu(II) solution or Co(II) solution placed on a magnetic stirrer with constant stirring for 10 min. The mixture was then placed in microwave oven for 30 min. The crystals obtained were filtered, washed with distilled water and dried in a desiccator and weighed. The synthesis of the complexes was done according to Equations 2 and 3.

$$Cu(NO_3)_2.6H_2O + SAB \rightarrow [Cu(SAB)(H_2O)_2NO_3]NO_3 + 4H_2O \quad (2)$$

$$Co(NO_3)_2.6H_2O + SAB \rightarrow [Co(SAB)(H_2O)_2NO_3]NO_3 + 4H_2O \quad (3)$$

RESULTS AND DISCUSSION

Physicochemical characteristics

The physicochemical characteristics of the ligand and complexes are presented in Tables 1. The prepared compounds were crystalline, colored, have high yields and the sharp melting point shows the purity of the complexes as seen in Table 1.

Table 1: Physicochemical data of ligand and complexes

Compound	Colour	Yield	Nature of compound	M.P(°C)
SAB	Yellow	66	Powdery	174
Cu-SAB	Black	88	Crystalline	292
Co-SAB	Brown	82	Crystalline	222

Electronic Spectra and Magnetic Moment

The electronic spectral studies of the ligand SAB, and its metal complexes were recorded in methanol in the range of 190 to 1100 nm as presented in Table 2. In the SAB ligand, a sharp band was observed at 325 nm corresponding to π-π* which undergoes a blue shift to the shorter wavelength indicating complexation. The electronic spectrum of Cu-SAB shows two bands at 300 and 446 nm which can be attributed to π-π* and *d-d* transitions respectively, proper for a tetrahedral geometry. The UV/Visible spectrum of Co-SAB show two bands and these bands were assigned to π-π* and n→π* respectively.

In the complexes, there were notable changes in both frequencies and intensities in the characteristic bands of the complexes compared to free ligands. The blue shift observed in the absorption bands during complex formation indicates coordination of the ligands to the metal ion. These observations are in complete agreement with those of Vijayalakshim, (2018) and Iorungwa *et al*., (2020).

Magnetic moment was recorded at ambient temperature by suspending the powdered samples from a string using a plastic cap that was epoxy-bonded to the string *(Ejidike, 2016).*

Table 2: Electronic spectra/ Magnetic Moment data for Ligand and Complexes

Compound	λ_{max}(nm)	Assignment	M.M (B.M)	Geometry
SAB	325	π-π*	-	-
Cu-SAB	300	π-π*	2.18	Tetrahedral
	446	*d-d* transition		
Co-SAB	300	π-π*	3.89	Tetrahedral
	712	n⟶π*		

Infrared Studies

The infrared spectra of the ligand and complexes were recorded in the range of 4000-400 cm^{-1} using KBr pellets which revealed the nature of the functional groups present and presented in Table 3. The comparison of the infrared spectral of the ligand and complexes shows the binding mode of the ligand to the metal ion as observed in Figure 1. The infrared spectra result for the metal complexes are also presented in Figures 2 and 3. The free ligand exhibited a strong band at 1573 cm^{-1} which was assigned to ν(C=N). This band shifts to lower region in the Cu-SAB and higher energy region in Co-SAB. It suggests bonding through the azomethine Nitrogen (Dnyandeo *et al.,* 2015; Shamly *et al*., 2018). Another strong band was observed at 1678 cm^{-1} assignable to ν(C=O). The band position of ν(C=O) has shifted to lower frequency in the complexes on coordination of metal ions indicating the involvement of the carbonyl group in bonding to metal (Ejidike, 2016).

The broad band absorptions in the region 3437-3379 cm^{-1} in the complexes are ascribed to phenolic hydroxyl group (Salawu and Aliyu, 2012). In the IR spectra of complexes, a very intense band appears at 1307-1388 cm^{-1} which indicates the existence of free nitrate group in the coordination sphere (Lekha*,* 2014). The absence of these bands in the ligands further confirms that coordination has taken place. In the region 548-447 cm^{-1} range, bands associated to ν(M-N) and ν(M-O) have been assigned and are in good agreement with data found in the literature (Rishu *et al*., 2013; Asep *et al*., 2019).

Table 3: IR bands of ligands and their complexes

Compound	ν(C=N)	ν(C=O)	ν(M-O)	ν(M-N)	ν(OH)	ν(NO_3)
SAB	1573	1678	-	-	-	-
CuSAB	1550	1550	451	548	3437	1388
CoSAB	1573	1678	447	548	3379	1307

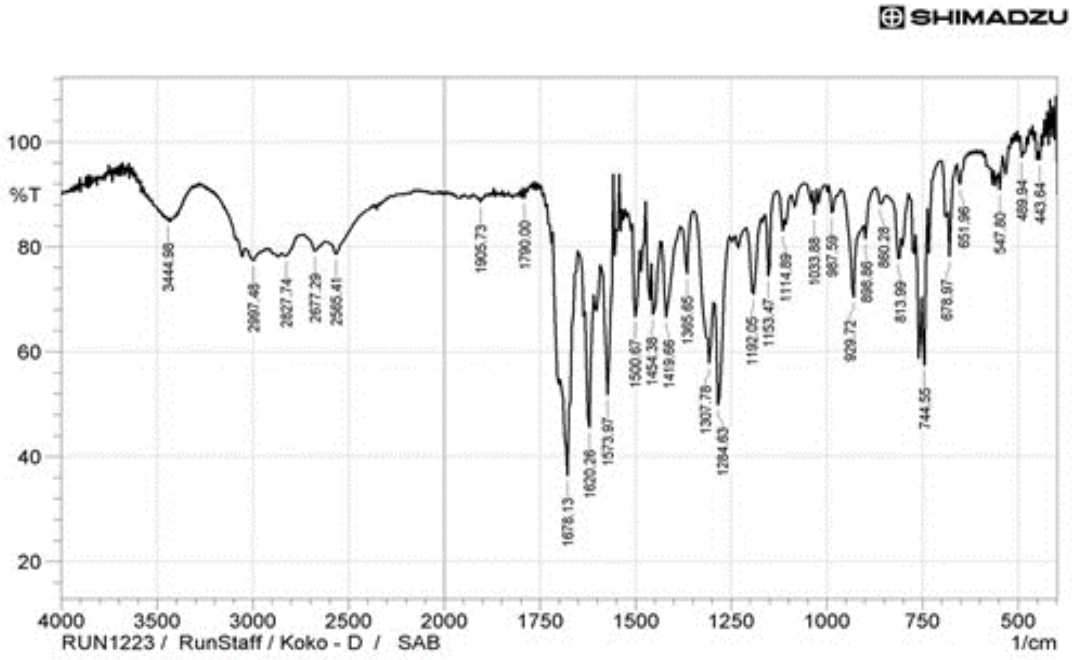


Figure 1: FTIR spectrum of SAB

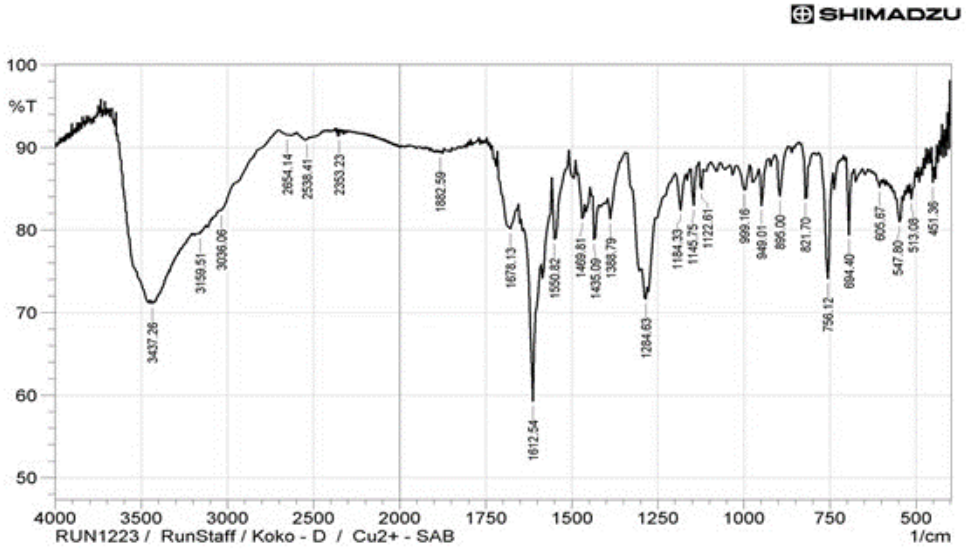


Figure 2: FTIR spectrum of Cu-SAB

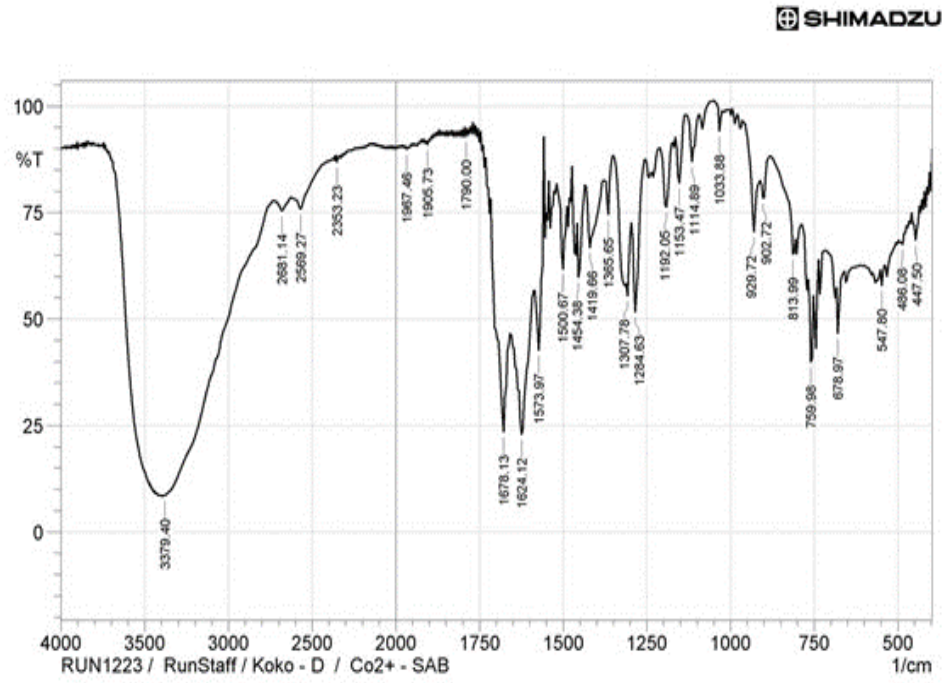


Figure 3: FTIR spectrum of Co-SAB

X-ray Diffraction (XRD) Studies

The X-ray diffraction studies was carried out to determine the type of crystal system lattice parameters and the cell volume as presented in Table 4-6 and their spectral patterns are in Figures 4 and 5 for the complexes.

The XRD pattern indicated a crystalline nature for the ligand and its metal complexes. Indexing of the diffraction pattern was performed with the aid of the trial and error method. The Miller indices (*hkl*) along with observed and calculated 2θ angles, the observed and calculated d values are shown in Tables 5-6. From the data, it was found that the ligand and its complexes have orthorhombic structure. The crystal structures of similar type of samples were reported as orthorhombic (Kiran *et al.*, 2019). Again, using the diffraction data, the mean crystallite sizes of the ligands and complexes D was determined. The average crystallites sizes of all the samples were found to be (7.28 nm) as presented in Table 4-6.

Table 4: Unit Cell Parameters for Ligand and Complexes

Compound	Unit cell parameters a(Å) b(Å) c(Å)	Cell Volume	Crystallite Size	Crystal Structure
SAB	5.97 5.43 6.13	198.72	2.11	Orthorhombic
Cu-SAB	0.085 5.13 7.10	3.10	4.83	Orthorhombic
Co-SAB	2.40 2.38 2.39	13.71	10.42	Orthorhombic

Table 5: X-Ray Diffraction Data of Cu-SAB

	d-Spacing (Å)		2θ values		Δ2θ	*hkl*
	Observed	Calculated	Observed	Calculated		
1	6.3735	6.3730	6.9390	6.9369	0.0005	100
2	8.6390	8.6385	5.1281	5.1265	0.0005	010
3	9.5555	9.5495	4.6400	4.6385	0.006	011
4	11.5360	11.5311	3.8518	3.8520	0.0049	111
5	14.6940	14.6906	3.0368	3.0351	0.0034	221
6	19.0105	19.0019	2.3647	2.3641	0.0086	003
7	22.1150	22.1109	2.0459	2.0452	0.0041	222

Table 6: X-Ray Diffraction Data of Co-SAB

	d-Spacing (Å)		2θ values		Δ2θ	*Hkl*
	Observed	Calculated	Observed	Calculated		
1	2.4139	2.4130	18.6095	18.6025	0.007	100
2	2.1847	2.3869	20.6455	20.6403	0.0052	010
3	1.6841	1.6834	27.219	27.2066	0.0124	110
4	1.6728	1.6728	27.42	27.4065	0.0135	002

Thermo gravimetric Analysis

The Thermal Gravimetric Analysis (TGA) was carried out on the complexes to determine their thermal stability. The thermal behaviors of all the complexes were studied in the

temperature range of 30-950 °C. Thermal analysis plays an important role in studying the stability, melting point, structure and decomposition properties of the metal complexes (Palanimurugan *et al.*, 2016).The thermo gravimetric analysis of the metal complexes has been studied to establish different decomposition process and confirm the proposed stoichiometry (Rahman, 2022).

It also provides information about thermal stability of the complexes and decides whether the water molecules are inside or outside the inner coordination sphere of the central metal ion. The results of the thermal behavior of the synthesized metal complexes are presented in Table 4. The result indicated a reasonable correlation between the calculated and found weight loss values.

The Cu-SAB complex indicate a total weight loss of 4.2 % (cal. 4 %) observed in the temperature range of 30-225 °C with the DTA value of 25 °C which is attributed to the loss of 2 molecules of water. The second stage of the decomposition suffers the loss of $C_{14}11ON_2$ with the total weight loss of 88.5 % (cal. 85.7 %) in the range of 226-560 °C. The CuO residue decomposed at a temperature above 561 °C with the total weight loss of 2.5 % (cal. 2.2 %) which agrees with the theoretical value.

The TGA curve of Co-SAB complex follows a four-stage decomposition process. The first stage decomposition is obtained in the temperature range of 30-150 °C with the percentage weight of 7.0 % (cal. 7.2 %) which correspond to the dehydration of 3 moles of water. The second stage decomposition corresponds to the loss of C_6H_5ON with the total weight loss of 35.5 % (cal. 35 %). The third stage decomposition range is obtained at 381-480 °C with the total mass loss 38.5 % (cal. 37.3 %) attributed to the loss of C_8H_5O. The CoO decomposed in the fourth stage in the temperature range above 481 °C. The total weight loss corresponding to this decomposition is 20.8 % (cal. 20.5 %).

The percentage weight loss in all the complexes is in agreement with the calculated values (Grace *et al.* 2015). The nature of the thermographs and percentage weight loss in all the complexes correspond to [ML].$2H_2O$, [ML].$3H_2O$ for Cu-SAB and Co-SAB respectively. These observations are in agreement with previous works (Aswathy *et al.,* 2020). The percentage loss in all the complexes is in agreement with all the calculated values. Similar findings were reported by Fugu *et al.* (2013). The absence of weight loss at higher temperatures indicated that there is no hydrated water molecule in the crystalline solid (Anil

et al., 2015). The thermogravimetric curves for the complexes are presented in Figures 6 and 7.

Table 7: Thermo Analytical Results for SAB Complexes

Compound	TGA (˚C)	DTA (˚C)	Stage	Mass loss		Assignment
				Found	Calculated	
Cu-SAB	30-225	25	I	4.2	4.0	Dehydration of 2 moles of water
	226-560	400	II	88.5	85.7	$C_{14}H_{10}O_2N$
	>561	560	III	2.5	2.2	CuO Residue
Co-SAB	30-150	50	I	7.0	7.2	Dehydration of 2 moles of water
	151-380	160	II	35.5	35.0	C_6H_5ON
	381-480	360	III	38.5	37.3	C_8H_5O
	>481	615	IV	20.8	20.5	Co Residue

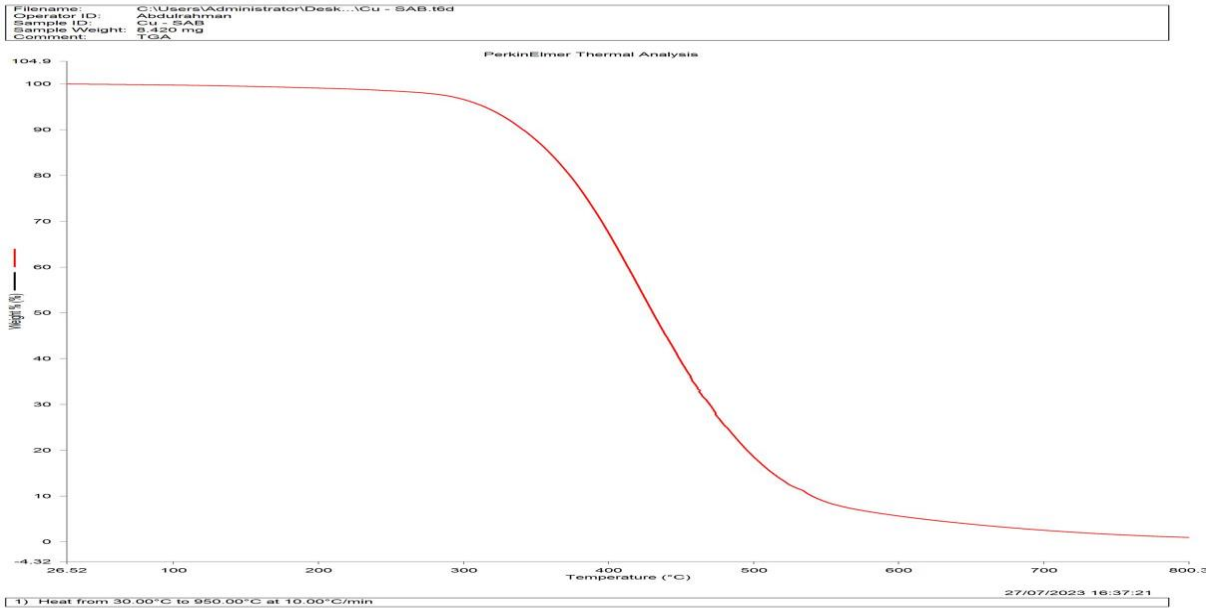


Figure 4: XRD Measurement of Cu-SAB

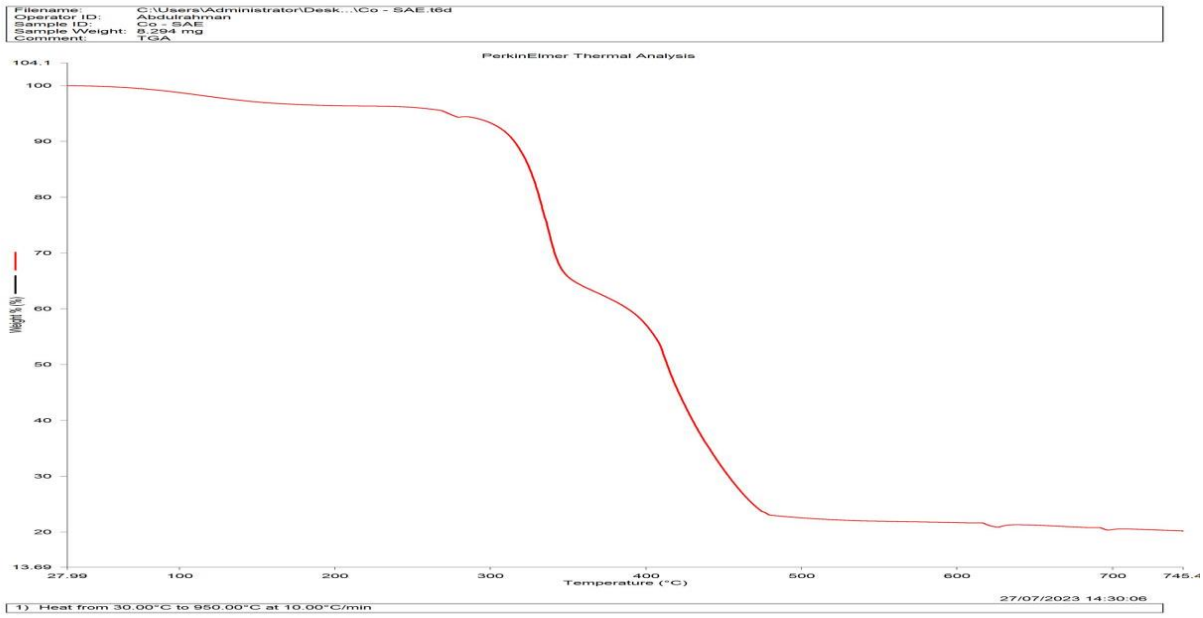


Figure 5: XRD Measurement of Co-SAB

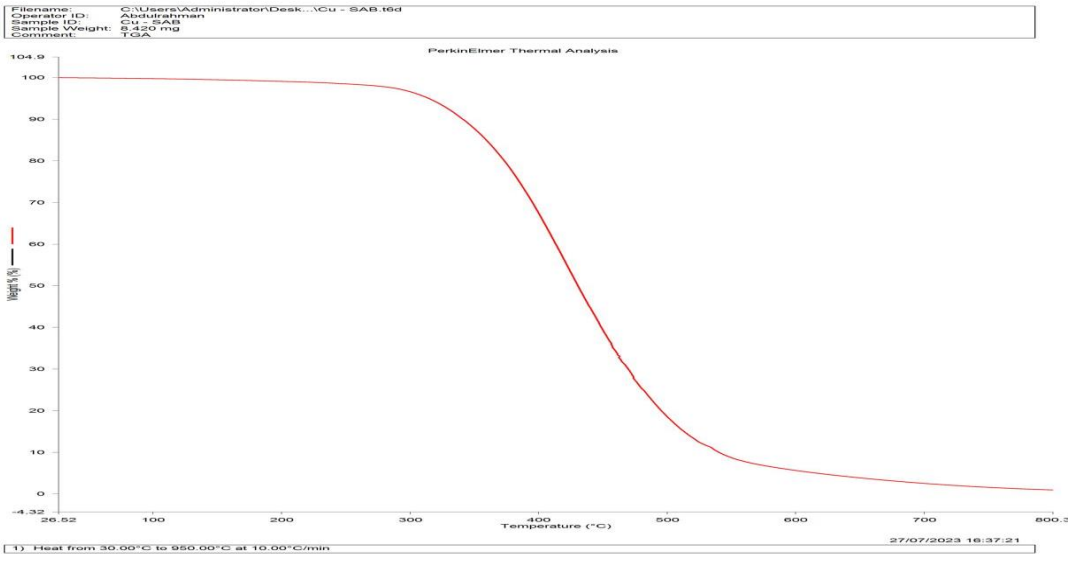


Figure 6: Thermogravimetric curve for Cu-SAB Complex

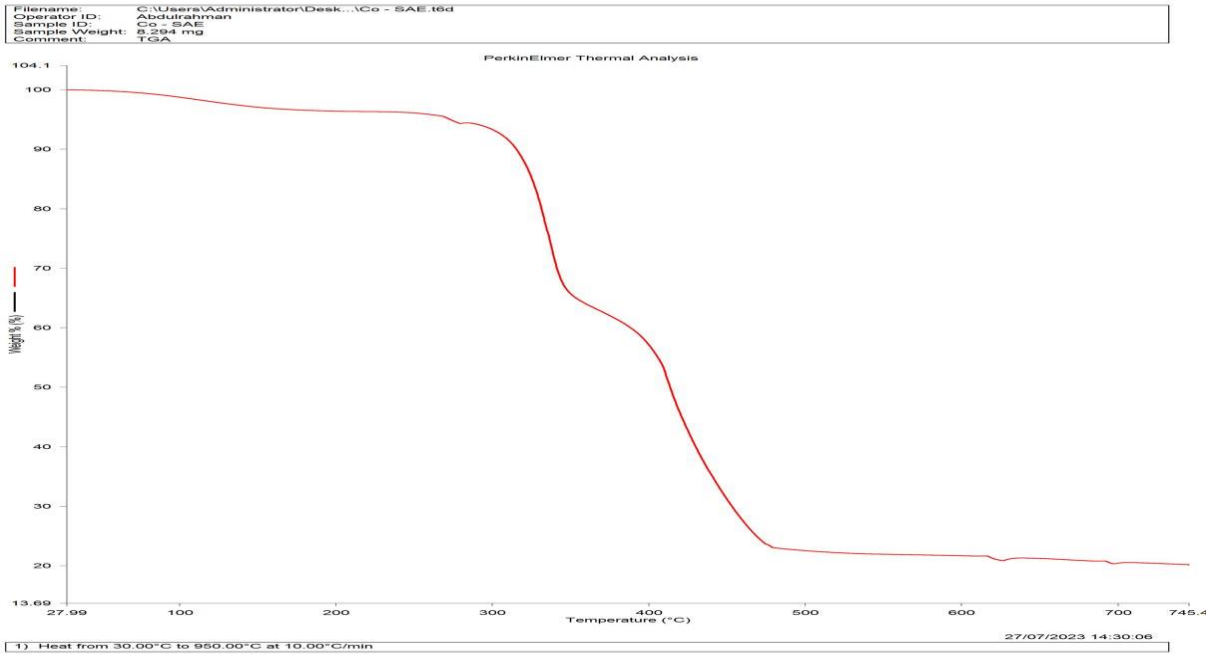


Figure 7: Thermogravimetric curve for Co-SAB Complex

CONCLUSION

The synthesis of complexes of azomethine linkages have been extensively studied, and it is an area of research with great potentials in new drug design. The present work describes the synthesis of Cu^{2+} and Fe^{2+} Schiff base complexes derived from the condensation reaction of 3-amino benzoic acid with salicyaldehyde. The physical and spectral data (XRD, FT-IR, UV-vis, molar conductance, solubility, magnetic susceptibility measurement and thermal gravimetric analysis) for the complexes provides clear evidence that the Schiff base is coordinated to the metal ion through the phenolic and azomethine linkage. The thermogravimetric analysis affirms the stability of the complexes and the position of the water molecule in the coordination sphere of the complexes.

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