Vol 22, No 1 (2015): Journal of Faculty of Engineering & Technology (JFET), [Available Online]

Synthesis and spectroscopic studies of N, O containing Schiff base ligands and their metal complexes with Zn

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Abstract:

In the present work seven Schiff bases have been synthesized by the reaction of anilines and substituted anilines with benzil via condensation reaction. The selected substituted anilines were ortho and para substituted chloro anilines, ortho and para substituted methyl anilines and ortho and para substituted carboxlyic aniline. The substituted anilines were selected to observe the affect of these electron donating and withdrawing group on the Schiff base formation and consequently on the coordination behavior of these ligands with the zinc ion. These Schiff base ligands were complexed with the zinc metal ion. It was observed that all the ligands and complexes formed readily. The resulting Schiff base ligands and their coordination complexes with zinc ion were recrystallized by CH_2Cl_2/n-hexane (1:10) mixture. All the ligands and zn coordination complexes were characterized by the IR spectroscopy. The stability of these coordination complexes were observed by UV/Visible spectroscopy. Thermal stability of these complexes was observed by subjecting them to thermogravimetric analysis. Our method of preparation of the Schiff bases and the corresponding metal complexes can be used to prepare similar compounds.

Key words:

IR spectroscopy, UV visible spectroscopy, TGA: thermo-gravimetric analysis, coordination complexes, Schiff base

Introduction

Schiff bases or imines are important and largely used class of organic compounds. They are used in co-ordination chemistry and also as intermediates in various reactions. Schiff bases are useful chelators due to their ease of preparation, structural varieties, varried denticities and subtle steric and electronic control on their framework. Recently enormous interest have been developed in the synthesis and characterization of transition metal complexes containing Schiff bases ligands due to their catalytic applications for many reactions and relation to synthetic and natural oxygen carriers. Schiff bases and their complexes also have applications in pharmaceutical industries because of their biocidal effects [1,2] .

Schiff bases (R-N=C-R’) were first synthesized by the German Scientist, Hugo Schiff and so named. Condensation reaction of aldehyde or ketone with primary amine leads to the production of Schiff bases [3]. Taking into account the availability of different types of amines and carbonyl compounds, Schiff bases exhibiting diverse structural features can be prepared [4]. Schiff bases are of importance because of their anticancer, antibacterial, antifungal, antiviral and anti-parasitic agents. Some medicinal chemists renewed and used salicylidenebenzylamine based Schiff bases as starting material to synthesize therapeutic products because of their antimicrobial, antifungal and antitumor activities [5]. Ease of preparation of Schiff bases together with their chelation capability and the ability to change the chemical surrounding of the C=N make them an important ligand of coordination chemistry [6]. The synthetic model complexes, based on Schiff bases, of metalloproteases and other enzymes, contributed immensely for the development of medicinal chemistry, radio immunotherapy, cancer diagnosis and treatment of tumor [7,8]. Schiff base complexes containing N and O donors find applications as catalysts for a wide variety of reaction types both in organic and inorganic chemistry.

Bidentate Schiff bases that can be used as metal ligands mostly contain donor set in form of N and O. These types of ligands commonly act as chelating mono anions [9]. Sacconi and the coworkers reported that the hydroxyl oxygen can act as a tridentate ligand favoring the formation of the binuclear complexes [10]. Bidentate ligands derived from β-diketones bind to Zn (II) through the oxygen atom only with intra molecular hydrogen bonding [11,12].

With modern technology at hand the research in Schiff base coordination chemistry is propagating rapidly. The importance of Schiff base complexes for bioinorganic chemistry, biomedical applications, supramolecular chemistry, catalysis and material science, separation and encapsulation processes, and formation of compounds with unusual properties and structures has been well recognized and reviewed [13].

In the present we describe preparation of Schiff bases and their metal complexes, and presents a series of new Schiff bases resulting from the condensation of benzil with aniline and substituted anilines.

Experimental Techniques:

Reagents:

All the chemicals used were of maximum purity and were purchased from Merck.

Preparation of Schiff bases:-

Solution of aniline was prepared by dissolving in spirit (0.1M) and benzil in acetone (0.1M). Both solutions were mixed thoroughly by adding slowly aniline solution into benzil solution in 1:1 ratio. Then few drops of pH 5.0 solution (NaOH + HCl) were added in it. The reaction mixture was then stirred and refluxed for half an hour. After refluxing, it was allowed to cool down slowly. Precipitation began after cooling. The resulting precipitates were washed with water, filtered off by suction and dried using vacuum desiccators. The dried precipitates were recrystallized from a CH_2Cl_2/n-hexane (1:10) mixture.

Preparation of metal complexes:-

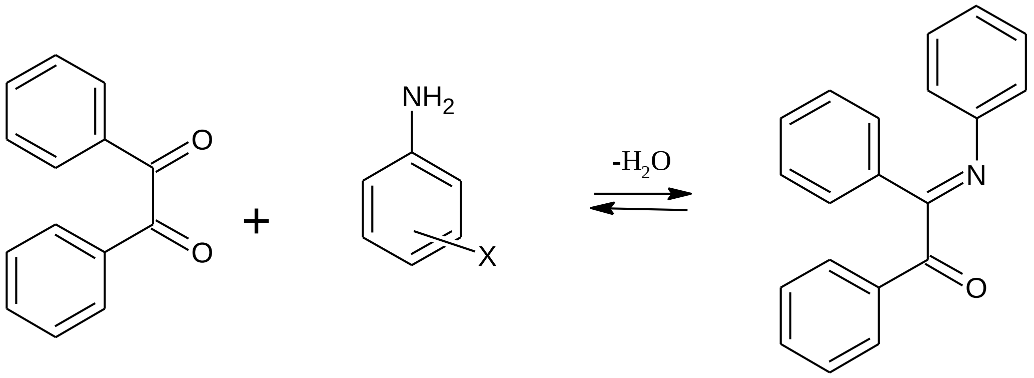
Solution of $Zncl_2$ (0.05M) in a 50% spirit/water mixture was taken in a flask fitted with reflux condenser and magnetically stirring hot plate. To this solution, 0.1M benzil in acetone and 0.1M aniline solution were added. The resulting mixture was then stirred and refluxed for one hour. Precipitation occurred immediately. The reaction mixture was allowed to cool and the resulting precipitates were washed with water, filtered off by suction and dried using vacuum desiccators. The dried precipitates were recrystallized from a CH_2Cl_2/n-hexane (1:10) mixture.

Physical measurements*:*

The synthesized Schiff bases and their metal complexes were analyzed by UV spectroscopy by applying UV spectrophotometer Perkin Elmer Model 2S. IR spectras were recorded as KBr pellets on IR spectrophotometer, Hitachi Tokyo JP, 270-30/60 scanned at full wavelength range 4000-250cm^{-1}. Thermogravimetric analysis was carried out by using thermal analyzer TGA-7 Perkin Elmer.

Results and discussions:

The general reaction scheme for the preparation of Schiff bases (Table 1), is outlined below.



The coordination complexes were prepared by direct reaction between the metal ions, benzyl, aniline and substituted anilines. Nucleophilic attack of the amine on the carbonyl group is enhanced by polarization of the carbonyl group by coordination of the oxygen atom to the metal ion (Table 2). The reaction scheme for the preparation of complexes is given below

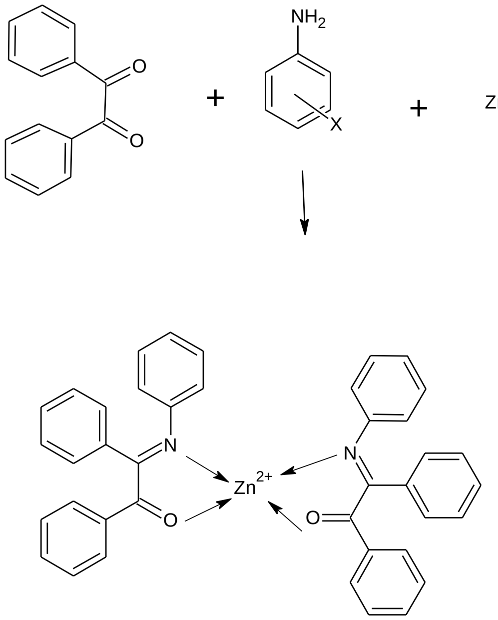


Table 1: List of Schiff bases prepared in this work

Abbreviations used: Ben; Benzil, A: Aniline

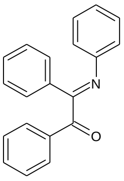
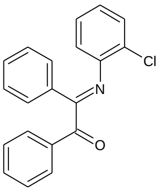
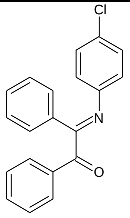
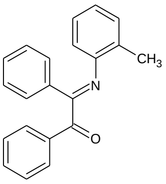
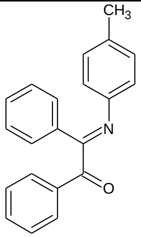
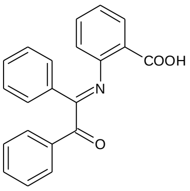
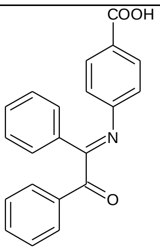
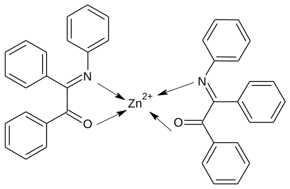
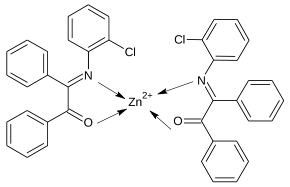
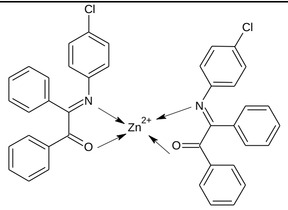
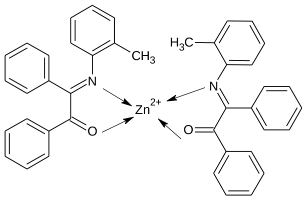
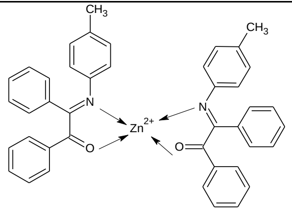
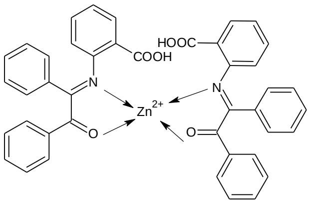
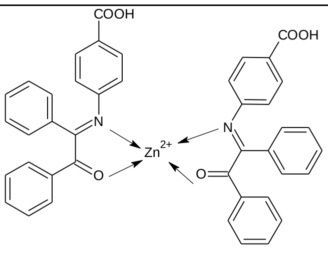
Sr.No	Structural formula	Molecular formula	Abbreviations used
1		$C_{20}H_{15}NO$	Ben.A
2		$C_{20}H_{14}NOCl$	Ben.2(Cl).A
3		$C_{20}H_{14}NOCl$	Ben.4(Cl).A
4		$C_{21}H_{17}NO$	Ben.2(CH_3).A
5		$C_{21}H_{17}NO$	Ben.4(CH_3).A
6		$C_{21}H_{15}NO_3$	Ben.2(COOH).A
7		$C_{21}H_{15}NO_3$	Ben.4(COOH).A

Table 2: List of Coordination complexes prepared in this work

Sr.No	Structural formula	Molecular formula	Abbreviations used
1		$C_{40}H_{30}N_{2}O_{2}Zn^{2+}$	$[Ben.(A)]_{2}Zn^{2+}$
2		$C_{40}H_{28}N_{2}O_{2}Cl_{2}Zn^{2+}$	$[Ben.2(Cl).A]_{2}Zn^{2+}$
3		$C_{40}H_{28}N_{2}O_{2}Cl_{2}Zn^{2+}$	$[Ben.4(Cl).A]_{2}Zn^{2+}$
4		$C_{42}H_{34}N_{2}O_{2}Zn^{2+}$	$[Ben.2(CH_{3}).A]_{2}Zn^{2+}$
5		$C_{42}H_{34}N_{2}O_{2}Zn^{2+}$	$[Ben.4(CH_{3}).A]_{2}Zn^{2+}$
6		$C_{42}H_{3}0N_{2}O_{6}Zn^{2+}$	$[Ben.2(COOH).A]_{2}Zn^{2+}$
7		$C_{42}H_{3}0N_{2}O_{6}Zn^{2+}$	$[Ben.4(COOH).A]_{2}Zn^{2+}$

Infrared spectra:

IR spectra of all the compounds was recorded as KBr pellets on IR spectrophotometer, Hitachi Limited Tokyo JP, 270-30/60 scanned at full wavelength range 4000-250cm^{-1}. Tentative assignments have been made on the basis of earlier publications [13,14]. Table 3 shows infrared absorption frequencies of various functional groups present in the compound. The IR spectra of the ligand shows strong absorption bands at 1580 and 1660cm^{-1}due to C=N and C=O groups. These bands have been shifted to low frequency region because of the presence of extensive conjugation. Bands due to =C-H stretch, =C stretch and =C-H (oop) bend appears at 3060, 1440 and 870cm^{-1}.

In the spectra of the complexes, characteristic absorptions occurred at 460-599 and 320-340 cm^{-1} for Zn←N and Zn←O respectively. Other characteristic bands due to C=O, C=N, C=C, =C-H stretch, and =C-H (oop) bend occur almost in the same region as for the ligand.

From the IR data it was concluded that C=N bond has been formed and Schiff bases have complexed with Zn metal. There is no observable shifting of peaks due to the electron withdrawing and electron donating groups present on the benzene ring of the complex. The IR spectrum of coordination compound 2 is given in Fig 1.

Table 3: Infrared spectra of complexes

All values are in wave number (cm-1)

Sr. No	**Compound**	**C=N- (s)**	**C=O (s)**	**Zn←N (w)**	**Zn←O (w)**	**C-Cl (m)**	**-OH (m)**	**-CH$_3$ Bend (m)**	**-CH$_3$ Stretch (s)**	**Ar-C=C (s)**	**Ar=C-H stretch (s)**	**Ar=C-H OOP Bend (m)**
1	Ben.A	1580	1660	---	---	---	---	---	---	1440	3060	870
2	[Ben.(A)]$_2$Zn	1575	1660	340	525	---	---	---	---	1450	3050	870
3	[Ben.2(Cl).A]$_2$Zn	1580	1660	340	460	640	---	---	---	1440	3050	870
4	[Ben.4(Cl).A]$_2$Zn	1580	1660	320	460	640	---	---	---	1440	3050	870
5	[Ben.2(CH$_3$).A]$_2$Zn	1580	1660	340	460	---	---	1320	2910	1450	3050	870
6	[Ben.4(CH$_3$).A]$_2$Zn	1580	1660	340	460	---	---	1320	2920	1450	3050	870
7	[Ben.2(COOH).A]$_2$Zn	1580	1660	340	460	---	3300	---	---	1400	3050	870
8	[Ben.4(COOH).A]$_2$Zn	1595	1660	340	500	---	3220	---	---	1410	3050	870

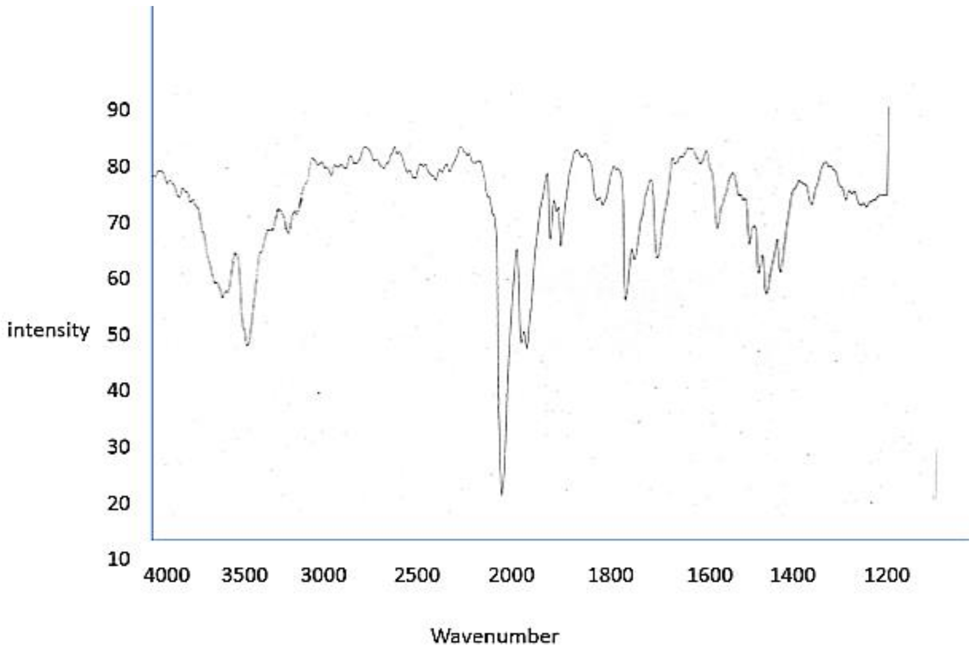


Figure 1: IR spectrum of compound 2

Electronic spectra:

The λmax of the compounds No 1, 3, 5 and 7 were taken on the UV spectrophotometer Perkin Elmer Model 2S. It was observed that substituents present on the benzene ring shifts λmax to higher wavelength. The UV scans of 0.1% solutions of the compounds in ethanol or acetone over five days showed that the compounds are stable.

A graph of absorbance vs. Time is shown in Fig. 2. The curves show an increase in absorbance for first 24-38 hours showing the solubility in progress and then become constant, which confirms that the compounds are stable.

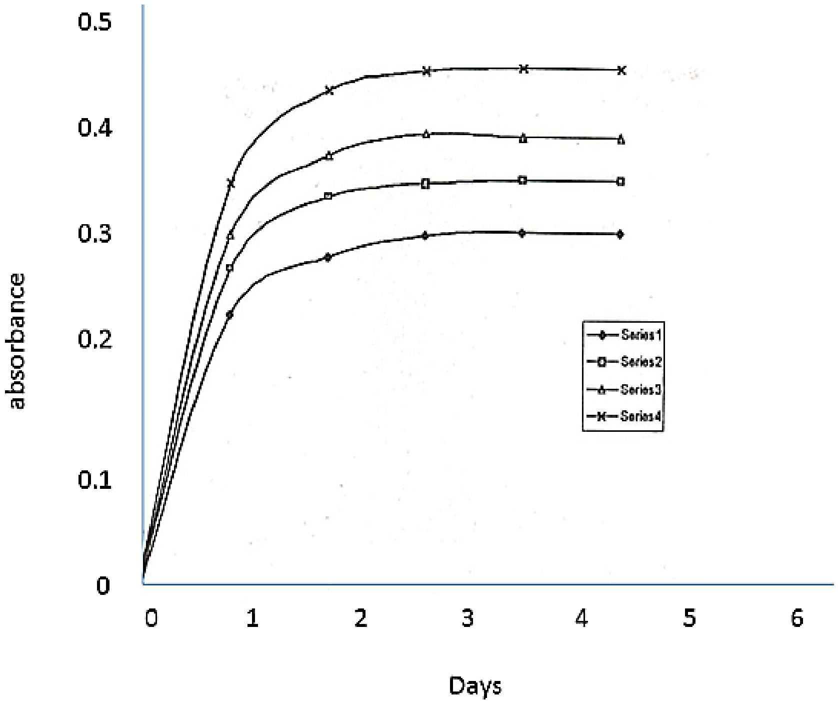


Figure 2: Stability study of the compounds with UV spectroscopy

Thermogravimetric analysis:

The samples were subjected to thermogravimetric analysis on thermal analyzer TGA-7 Perkin Elmer. The TGA was conducted under inert atmosphere at a heating rate of 20°C/min. The results are shown in Table-4.

The TGA of ligand was carried out from 50-350°C. The compound is stable up to 150°C and then shows a sharp and complete decomposition over a narrow temperature range 150-260°C. The DTG curve also shows a single change. The thermo gram of compound number (2) shows that the compound is thermally stable up to 145.490°C and then it shows the loss of one ligand at 270°C. It is completely decomposed beyond 700°C. The thermogram of compound number (2) is given in Fig.3.

It can be concluded from the results of TGA that the ligand and the complexes decomposed almost at the same temperature. So we can say that the complexation does not add to the thermal stability of the complexes. It can also be concluded that there is no systematic effect of electron donating and electron withdrawing groups present on the complex.

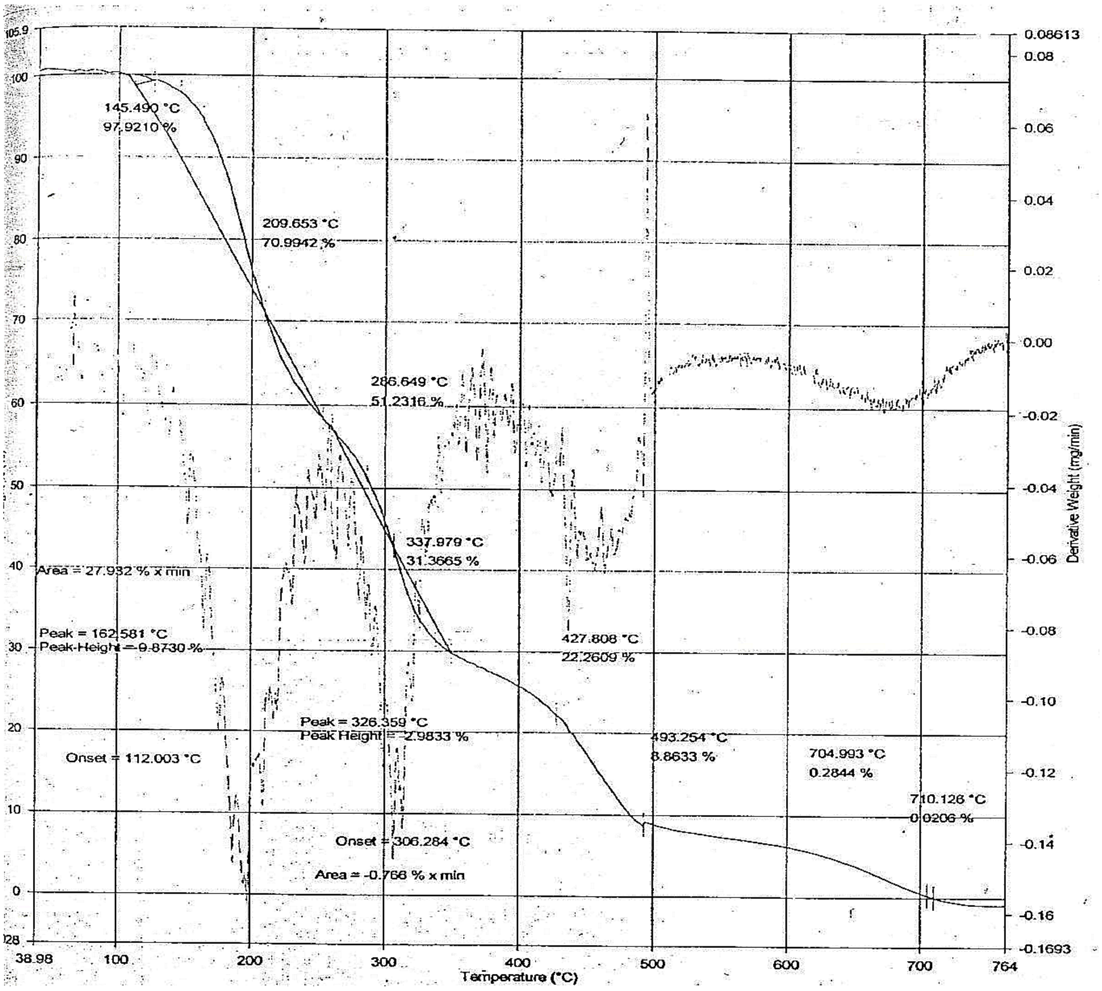


Figure 3: TGA of compound 2

Table 4: TGA data of selected Shiff bases and complexes

Sr.No	**Compound**	**Temp(^{o}C) Thermal step**	**% Loss Actual (calculated)**	**Assignments**
1	Ben.A	Up to 150	---	Thermally stable
		150-260	---	Complete decomposition
2	[Ben.(A)]$_2$Zn	Up to 145.49	---	Thermally stable
		145.490-270	43.77(44.9)	Loss of one ligand
		270-710.126	---	Complete decomposition
3	[Ben.4(Cl).A]$_2$Zn	Up to 145.49	---	Thermally stable
		145.49-286.649	---	Complete decomposition
4	[Ben.4(CH_3).A]$_2$Zn	Up to 130.195	---	Thermally stable
		130.195-360	45.09 (45.1)	Loss of one ligand
		<800	---	Complete decomposition
5	[Ben.4(COOH).A]$_2$ Zn	Up to 146.64	---	Thermally stable
		146.64-161	4.9 (4.7)	Loss of two lattice water molecules
		161-395.372	46.05 (45.5)	Loss of one ligand
		<700	---	Complete decomposition

Conclusion:

The ligands and their complexes were prepared in good yield. The results of IR are consistent with the proposed structure. The IR shows no observable shifting of peaks due to electron withdrawing and electron donating groups present on the benzene ring of the complex. The complexes are stable as shown by the UV studies. Thermal analysis shows that the complexes are stable up to 145^{o}C and decompose in a complex pattern.

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