

Preparation, Spectroscopic Investigation and Biological Activity of New Mixed Ligand Chelates

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Summary: Preparation and investigation of new Co(II), Ni(II), Zn(II) and Cr(III) chelates with mixed ligands including Schiff base (L¹) formed from the condensation of 4-dimethylaminobenzaldehyde with 2-aminophenol and anthranilic acid (L²) were studied. The obtained Schiff base and mixed ligand chelates were subjected to several physiochemical techniques, in terms of CHN elemental analyses, molar conductivity, magnetic moment measurements, infrared, proton nuclear magnetic resonance, electronic and mass spectra. The analytical data showed the formation of the Schiff base compound and the ratio of metal to ligands of the chelates are 1:1:1[M:L¹:L²]. The infrared spectral data exhibited that the used ligands behaving as bidentate ligands towards the metal ions. The proton nuclear magnetic resonance spectral data showed the signals of the active groups in the ligands which entered in chelation with Zn(II) metal ion. The electronic spectral results showed the existence of $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ (C=N) of the ligands and suggested the geometrical structures of the chelates. Meanwhile, the mass spectral data revealed the fragmentations of the Schiff base, anthranilic acid and their Ni(II) mixed ligand chelate has been preformed the only chelate conducted for justification. All the prepared mixed chelates were non-electrolyte in nature. The antibacterial activity of the Schiff base, anthranilic acid, metal salts and mixed ligand chelates were studied and found to be that mixed ligand chelates have the most biological activity in comparison to the free ligands and salts.

Keywords: Schiff base, 4-dimethylaminobenzaldehyde, 2-aminophenol, Anthranilic acid, Mixed ligand chelates, Physiochemical techniques and Antibacterial activity.

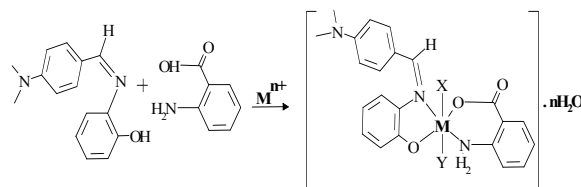
Introduction

Schiff bases are significant class of ligands in coordination chemistry and found in extensive purpose in different fields [1]. The rapid development of these ligands in enhanced research activity in the field of coordination chemistry lead to very interesting conclusions [2]. Cobalt(II) chelates of mixed Schiff base derived from 2-amino-N-salicylidine-4-nitrophenol with some amino acids were prepared and investigated by using different physiochemical techniques. A geometrical structure was proposed for all Co(II) mixed ligand chelates [3]. Also the antifungal activity of the ligands and their complexes has been studied. The mixed ligand chelates of Co(II), Ni(II) and Zn(II) ions with Schiff bases; N-(2-hydroxy)-1-naphthylamine and N-(2-hydroxybenzylidene)-2,3-dimethylaniline have been prepared and characterized by using different tools; such as, CHN elemental analyses, molar conductivity, magnetic moment measurements, thermogravimetric analysis and spectroscopic techniques. An octahedral geometry was proposed for all complexes. The antibacterial activity of the Schiff bases and their mixed ligand complexes were screened and found to be that the activity of the chelates have higher effect than free Schiff bases.[4]

The present study aims to prepare and investigate some new mixed ligand chelates containing Schiff base derived from [4-dimethylamino- benzaldehyde with 2-aminophenol] and anthranilic acid with Cr(III), Co(II), Ni(II) and Zn(II) ions. Also to study their antibacterial activity on some pathogenic bacteria.

Results and Discussion

The reaction between the Schiff base(L1) , anthranilic acid (L2) and metal ion is shown below:



In case of M= Zn²⁺, Ni²⁺, Co²⁺, X, Y= H₂O

In case of M= Cr³⁺, X= H₂O, Y= OH

n = 1 in case of Ni chelate and 6 in case of Cr, Co and Zn chelate

Fig. 1: Reaction between the ligands and metal ions.

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Physicochemical Analysis and Molar Conductivity

The elemental analysis data of the prepared mixed ligand chelates as shown in Table-1 exhibit the formation of 1:1:1[M:L¹:L²] ratio. It was found that the theoretical values are in a good agreement with the found data. The purity of the Schiff base and mixed ligand chelates were tested by, melting points, TLC and CHN elemental analyses. The molar conductivity measurements of the prepared mixed ligand chelates were carried out in DMF solvent and the obtained values which shown in Table-1, were taken as a good evidence for the presence of non-electrolytic nature [5].

Infrared Spectra

The infrared spectral data of the ligands and their mixed ligand chelates were listed in Table-2 and their spectra were given in Fig. 1. The infrared spectra of the prepared mixed ligand chelates exhibited bands in the range of 3407-3414cm⁻¹ corresponding to the existence of water molecule as hydrated and coordinated [6]. Meanwhile, the same spectra showed bands in the range of 1594-1600 cm⁻¹ attributed to $\nu(\text{HC}=\text{N})$ vibration, the lowering of these bands to low frequency comparing to the Schiff base (L¹) confirmed the participation of this group in chelation through nitrogen atom [7]. The other coordination sites of which can take a part in coordination are -NH₂ and -COO groups, the strong evidence of sharing of these groups can be seen from the position of the bands at 3373 and 3067cm⁻¹, respectively in the spectrum of anthranilic acid (L²).

The shifting of the -NH₂ group band to lower frequency in the spectra of the mixed ligand chelates suggest the involvement of this group in complexation via nitrogen atom[8]. The disappearance of -COO group band of the anthranilic acid in the spectra of the mixed ligand chelates indicates the participation of this group in bonding with the metal ions [9]. New bands in the range of 620-642 and 439-460 cm⁻¹ which are not present in the free ligands are assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibration bands and the appearance of these bands supports involvement of oxygen and nitrogen atoms of the azomethine and OH groups of the free ligands in chelation process[10].

Proton Nuclear Magnetic Resonance Spectra

The ¹H-NMR spectra of the ligands and Zn(II) mixed ligand chelate of the formula [Zn(L¹L²)(H₂O)₂].6H₂O showed signals in the range 2.50-8.65ppm. The singlet obtained at 8.50 ppm due to HC=N group in the spectrum of L¹[11]. The singlets in the range of 6.76-7.16 ppm are assigned to the presence of protons of the phenyl rings. The signal at 8.70 ppm attributed to O-H group of the Schiff base. The methyl and DMSO solvent appeared at 2.50 and 2.01 ppm. The signals at 3.60 and 8.40 ppm assigned for -COO and NH₂ groups of the anthranilic acid ligand. The shifting of the signals of -COO, NH₂, -OH and HC=N groups during the complexation process indicates their participation in bonding with metal ions, Fig. 2.

Table-1: CHN elemental analyses, magnetic moments and conductivity of the mixed ligand chelates.

Ligand/Chelates	M.Wt	colour	Yield (%)	C%		%H		%N		μ BM	Λ^*
				Calc.	Exp.	Calc.	Exp.	Calc.	Exp.		
Schiff base (L ¹)	240	Yellow	92.98	75.00	75.76	6.60	5.84	11.67	12.77	-	-
[Co(L ¹ L ² (H ₂ O) ₂].6H ₂ O	506	Light brown	70.50	47.40	46.26	4.15	3.68	8.30	9.88	4.20	4.06
[Ni(L ¹ L ² (H ₂ O) ₂].H ₂ O	487	Pale green	75.51	49.28	48.02	4.20	3.22	8.40	9.62	3.38	7.25
[Zn(L ¹ L ² (H ₂ O) ₂].6H ₂ O	499	Yellow	86.85	48.02	48.10	4.20	3.72	8.42	8.85	0.00	0.00
[Cr(L ¹ L ² (OH)(H ₂ O))].6H ₂ O	571	Deep brown	65.14	42.03	41.06	3.67	3.93	7.35	7.02	4.78	0.06

$\Lambda^* = \text{oh}^{-1} \text{cm}^2 \text{mol}^{-1}$, BM= Bohr magneton

Table-2: Infrared and electronic spectral data of Schiff base, anthranilic acid and their mixed ligand chelates

Ligand / Chelate	νCOO^-	νOH	νNH_2	$\nu\text{C}=\text{N}$	$\nu\text{M}-\text{O}$	$\nu\text{M}-\text{N}$	nm (cm ⁻¹)
Schiff Base (L ¹)	-	3337	-	1588	-	-	375(26666)
Anthranilic acid	3076	-	3373	-	-	-	333(30030)
[Co(L ¹ L ² (H ₂ O) ₂].6H ₂ O	-	3407	3308	1594	620	439	310(32258), 330(30303), 762(13123)
[Ni(L ¹ L ² (H ₂ O) ₂].H ₂ O	-	3410	3313	1598	642	439	298(33557), 339(29498)
[Zn(L ¹ L ² (H ₂ O) ₂].6H ₂ O	-	3413	3300	1595	642	469	344(42553)
[Cr(L ¹ L ² (OH)(H ₂ O))].6H ₂ O	-	3408	-	1600	640	460	339(29498).

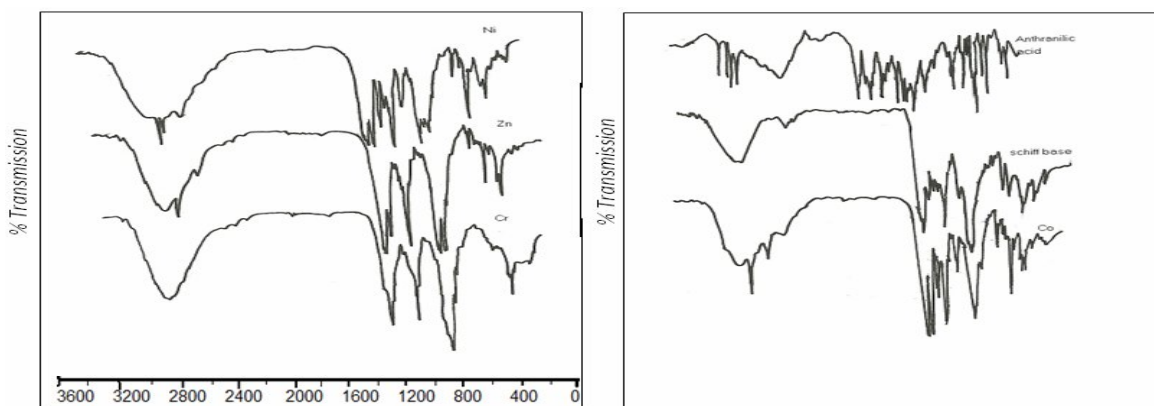


Fig. 1: Infrared spectra of anthranilic acid, Schiff base and their mixed ligand chelates.

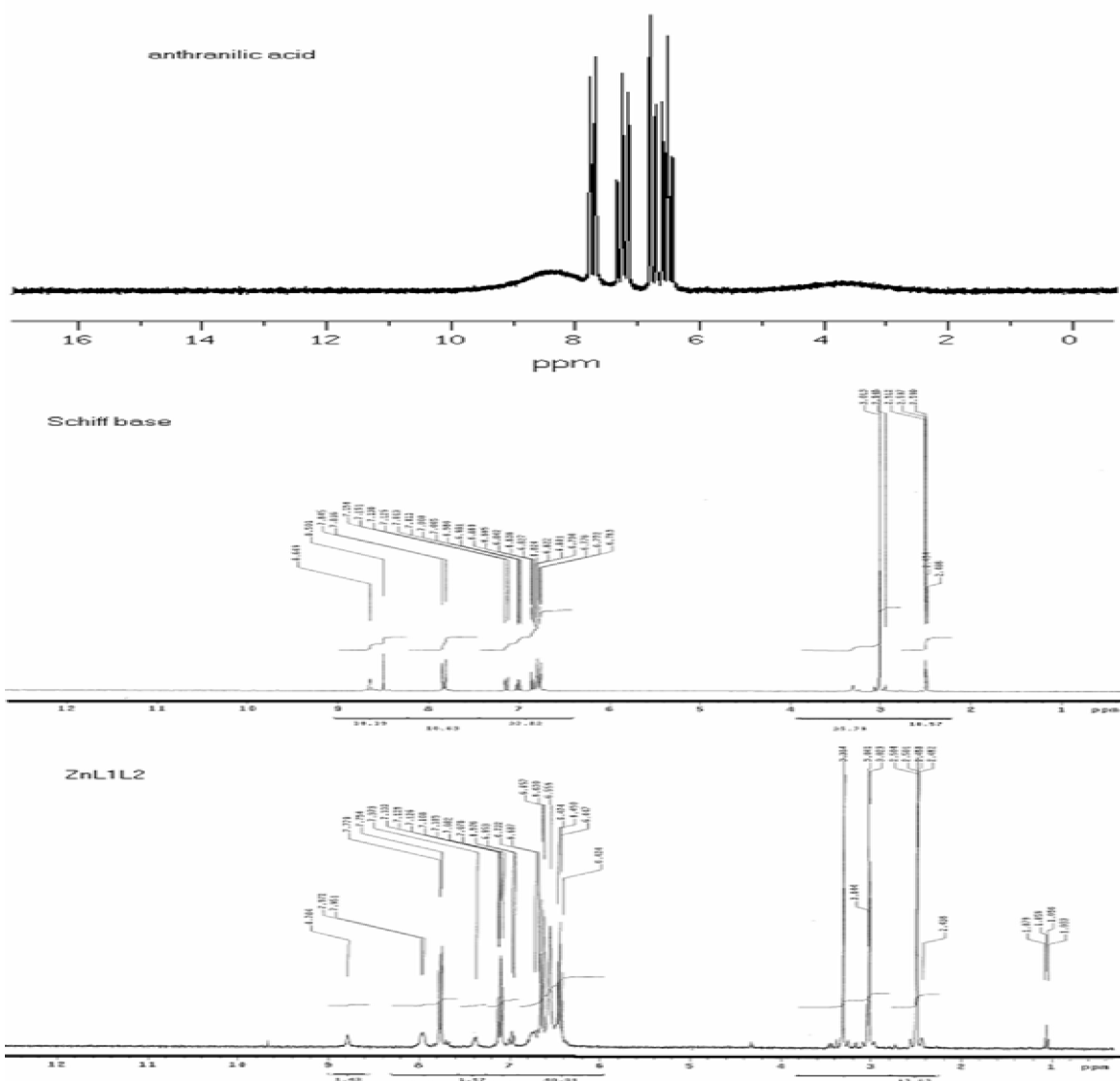


Fig. 2 : ¹H-NMR of ligands and Zn(II) mixed ligand chelate.

Mass spectra

The mass spectral fragmentations of the Schiff base (SB), anthranilic acid and their Zn(II) mixed ligand chelate are shown in Table-3, scheme-1 and Fig. 3. The peak at $m/e^+ = 238$ analogous to $C_{15}H_{14}N_2O^+$ meanwhile, another peak at $m/e^+ = 195$ is equal the formula $C_{13}H_9NO^+$. The structure $C_{12}H_7O^+$ is analogous to peak at $m/e^+ = 167$. Meanwhile, the last peak at $m/e^+ = 64$ is attributing this formula $C_5H_4^+$. The base peak of anthranilic acid at $m/e^+ = 137$ attributed to the original molecular weight. The peak at $m/e^+ = 119$ is analogous to the loss of oxygen and two hydrogen atoms from the

compound. The loss of one carbon, three hydrogen, nitrogen and one oxygen atoms give a peak at $m/e^+ = 92$. The peak at $m/e^+ = 68$ due to loss of two carbon atoms. The same spectrum shows a peak at $m/e^+ = 39$ corresponding to loss of carbon, hydrogen and oxygen atoms from the free compound. A peak at $m/e^+ = 27$ is attributed to loss of carbon atom. The mass spectrum of the nickel mixed ligand chelate showed a molecular ion peak at $m/e^+ = 355$, which is corresponding to $[Ni(C_{16}H_{16}N_2O_3)]^+$. Meanwhile, the peak at $m/e^+ = 315$ analogues to $[Ni(C_{11}H_{10}N_2O_2)]^+$. The peak at $m/e^+ = 137$ analogues to anthranilic acid $C_7H_7NO_2$. The final peak appeared at $m/e^+ = 55$ due to $C_4H_7^+$

Table-3: Mass spectral fragmentation of Schiff base, anthranilic acid and their Ni(II) mixed ligand chelate.

Compound	Fragmented ions	m/z values
$C_{15}H_{16}N_2O$ (S.B); (L^1)	$C_{15}H_{16}N_2O$	240
	$C_{15}H_{14}N_2O^+$	238
	$C_{13}H_9NO^+$	195
	$C_{12}H_7O^+$	167
	$C_5H_4^+$	64
	$C_7H_7NO_2$	137
	$C_7H_5NO^+$	119
$C_7H_7NO_2$ (L^2)	$C_6H_4O^+$	92
	$C_4H_4O^+$	68
	$C_3H_3^+$	39
	$C_2H_3^+$	27
	$[Ni(C_{15}H_{16}N_2O)(C_7H_7NO_2)(H_2O)_2]H_2O$	487
$[Ni(L^1 L^2)(H_2O)_2]H_2O$	$[Ni(C_{16}H_{16}N_2O_3)]^+$	355
	$[Ni(C_{11}H_{10}N_2O_2)]^+$	315
	$C_7H_7NO_2^+$	137
	$C_4H_7^+$	55

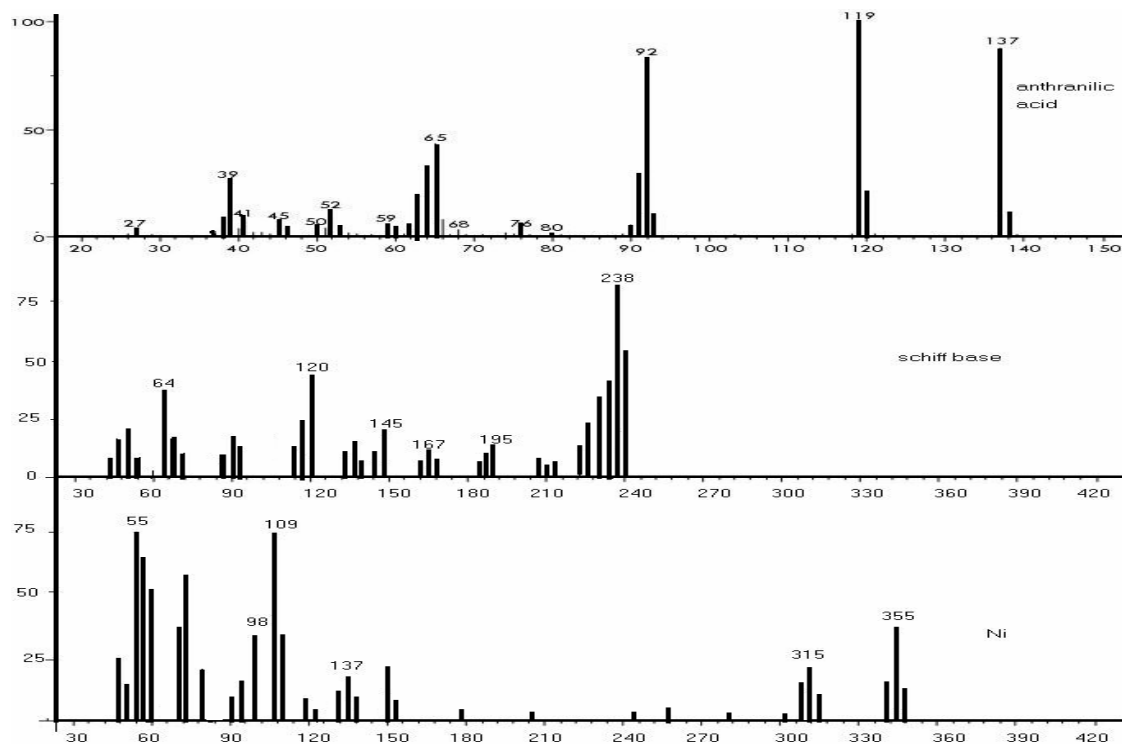
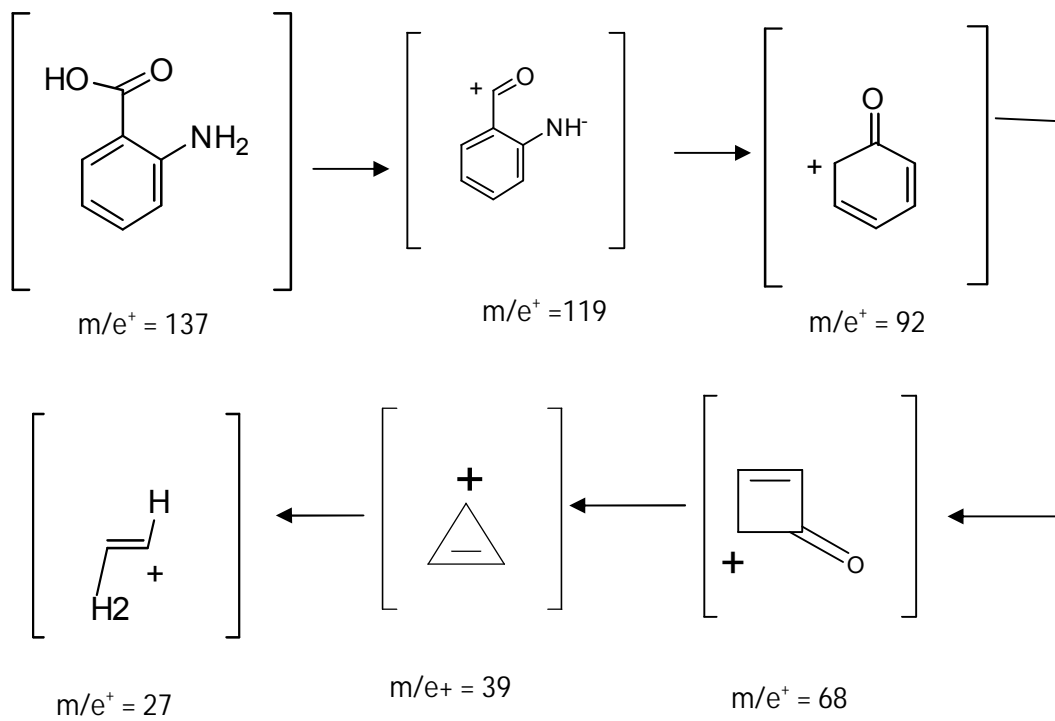
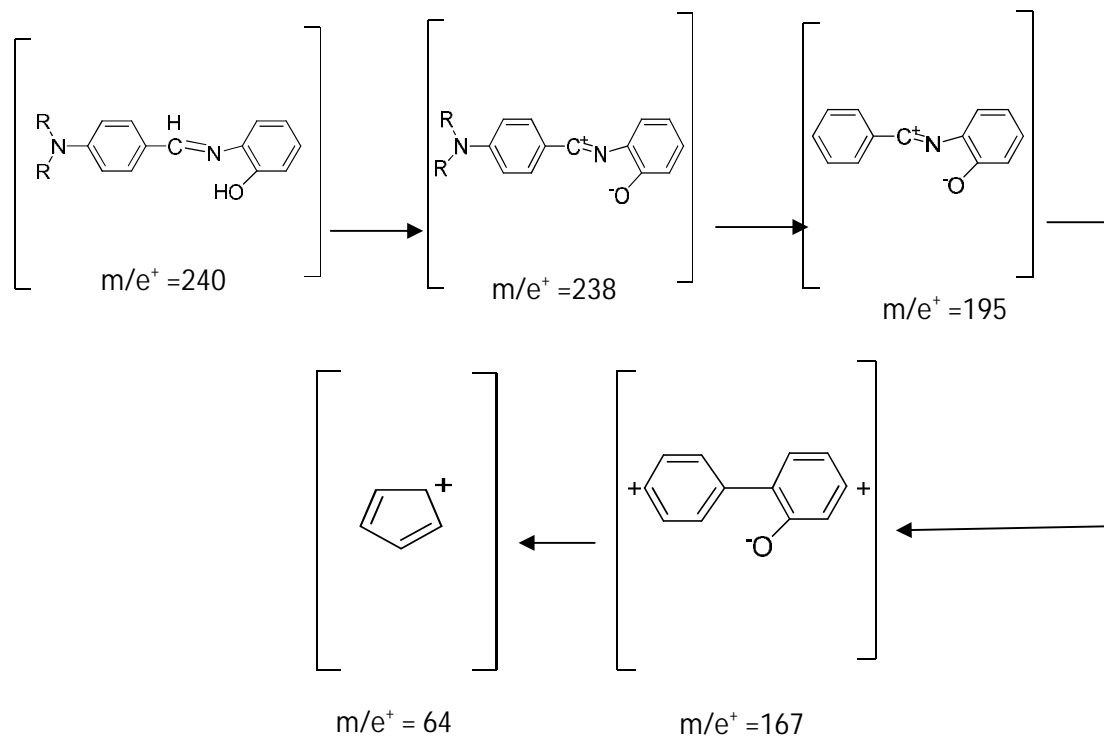
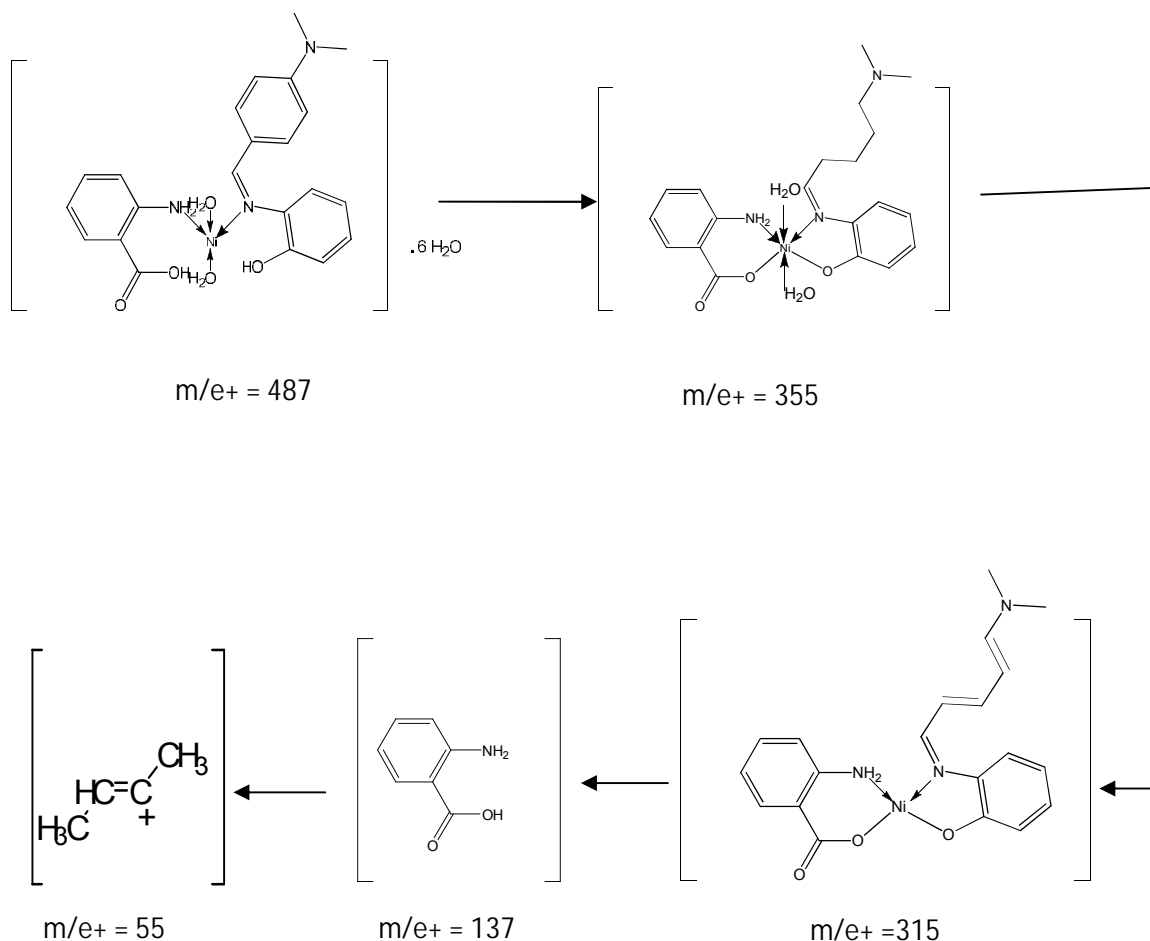


Fig. 3: Mass spectra of Schiff base, anthranilic acid and Ni(II) mixed ligand chelate.





Scheme -1 : Mass fragmentations of ligands and Ni(II) mixed ligand chelate.

Electronic spectra and magnetic moment

The electronic spectral results of the ligands and their mixed ligand chelates are shown in Table-2. The electronic spectral studies of the mixed ligand chelates of Co(II), Ni(II), Zn(II) and Cr(III) with Schiff base (L^1) and anthranilic acid (L^2) ligands were carried out in DMSO solvent. The electronic spectra of the Schiff base and anthranilic acid show $\pi \rightarrow \pi^*$ (phenyl rings) and $\pi \rightarrow \pi^*$ (HCN) transitions as shown in Table-2 [12]. The electronic spectral results of Co(II) chelate exhibit two bands at 330 nm (30303 cm^{-1}) and 762 nm (13123 cm^{-1}) assigned to $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions, respectively, in octahedral field. The intensity of the obtained band and the magnetic moment value (4.20 BM) support the structure. [13] The electronic spectrum of Ni(II) chelate displays two bands at

298 nm (33557 cm^{-1}) and 339 nm (29498 cm^{-1}) corresponding to $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$ transitions. The nature of the bands and the magnetic moment of the chelate (3.38 B.M) confirm the existence of an octahedral geometry [14]. The spectrum of Zn(II) chelate shows a band at 344 nm (42553 cm^{-1}) due to the presence of charge transfer transitions, and the intensity of the bands and diamagnetic character of the chelate also suggest the octahedral structure. [15] For Cr(III) chelate of the formula $[\text{Cr}(L^1L^2)(\text{OH})(\text{H}_2\text{O})] 6\text{H}_2\text{O}$, the spectrum exhibits a band at 339 nm (29498 cm^{-1}) analogous to $^4A_{2g}(F) \rightarrow ^4T_{2g}(F)$, transitions. Based on the magnetic moment value (4.78 B.M) and the nature of the bands, an octahedral structure was proposed for this chelate [16].

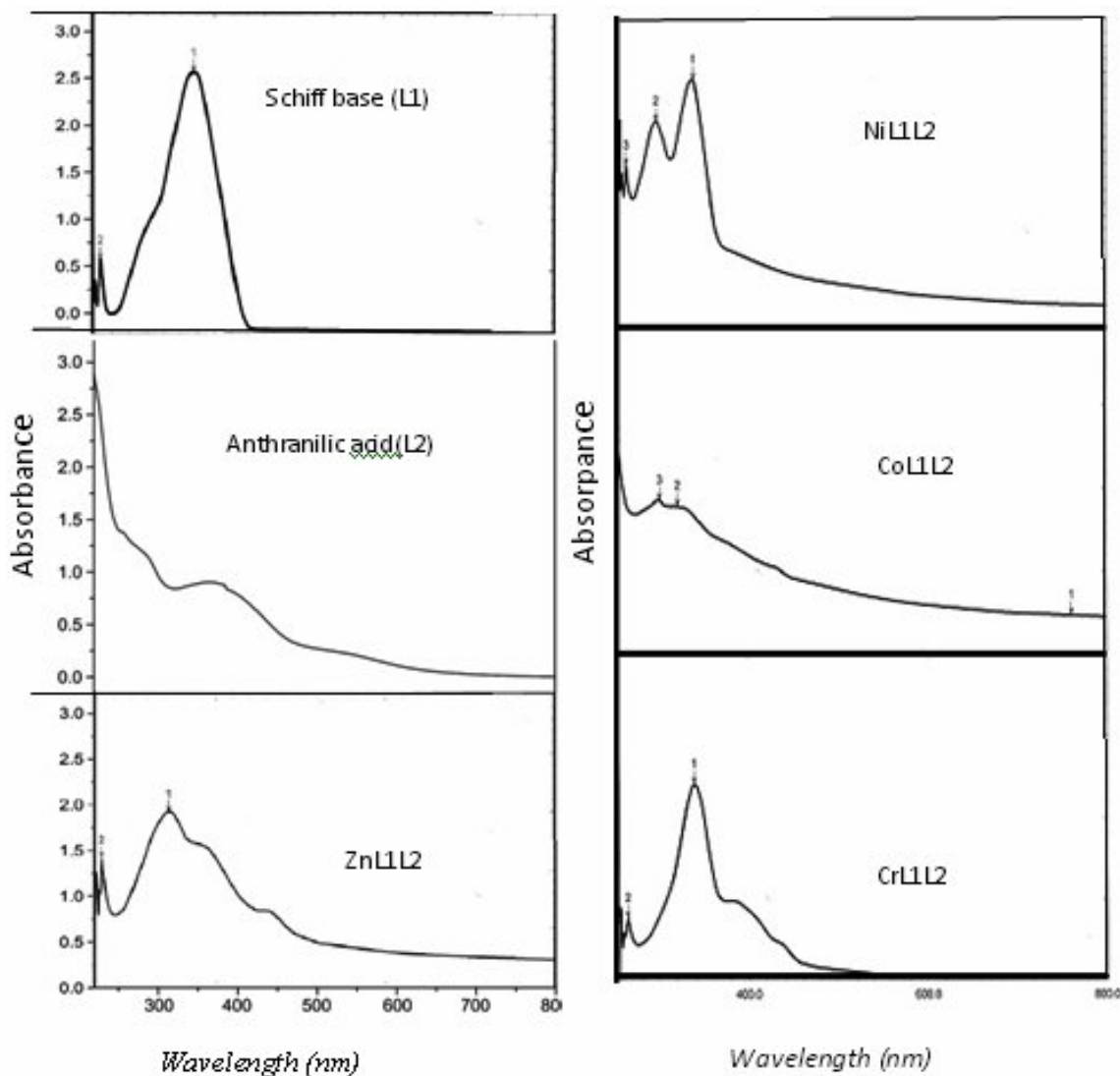


Fig. 4: Electronic spectra of Schiff base, anthranilic acid and their mixed ligand chelates

Biological Activity

The ligands, salts and mixed ligand Co(II), Ni(II), Zn(II) and Cr(III) chelates were screened for their antibacterial activity against *Acinetobacter SP*, *Enterococcus faecalis*, *Escherichia coli*, *Pseudomonas aeruginosa* and *staphylococcus aureus*. The antibacterial activity results, presented in Table-4. The maximum inhibitory concentrations of all the compounds have been given in 15mg. The results show that all the metal salts of Co(II), Ni(II), Zn(II) and Cr(III) have different antibacterial activity against the tested bacteria. The mixed ligand chelates were more effective than their parent ligands against the same bacteria tested. The highest rate of antibacterial activity was observed by $[\text{Ni}(\text{L}^1\text{L}^2)(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ chelate against *Enterococcus*

faecalis and *staphylococcus aureus* as shown in Table-4. In contrast the $[\text{Co}(\text{L}^1\text{L}^2)(\text{H}_2\text{O})_2]\cdot 6\text{H}_2\text{O}$ chelate was slightly activity against all bacteria tested. The antibacterial activity of the mixed-ligand chelates may be due to the effect of the metal ion on the normal cell.

Experimental

Chemicals

All chemicals and reagents used in this investigation are of pure grade (BDH or Aldrich), they include; 4-dimethylamino benzaldehyde, 2-aminophenol, anthranilic acid, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, ZnCl_2 , $\text{CrCl}_3\cdot 6\text{H}_2\text{O}$, DMSO, DMF, NH_4OH , ethanol and double distilled water.

Table-4: Maximum inhibitory weight (15mg) for ligands, salts and mixed ligand Chelates.

Inhibition Zone (mm)					Compound	No.
<i>S. aureus</i>	<i>P. aeruginosa</i>	<i>E. faecalis</i>	<i>E. coli</i>	<i>Acineto</i>		
0	0	0	0	0	Schiff base (L ¹)	1
8	14	12	10	11	anthranilic acid (L ²)	2
25	16	11	34	18	CoCl ₂ .6H ₂ O	3
28	13	9	29	8	NiCl ₂ .6H ₂ O	4
20	17	7	20	19	ZnCl ₂	5
21	19	22	21	20	CrCl ₃ .6H ₂ O	6
0	2	8	0	0	[Co(L ¹ L ²)(H ₂ O) ₂].6H ₂ O	7
43	4	37	24	7	[Ni(L ¹ L ²)(H ₂ O) ₂].H ₂ O	8
0	3	30	16	0	[Zn(L ¹ L ²)(H ₂ O) ₂].6H ₂ O	9
30	3	21	22	4	[Cr(L ¹ L ²)(OH)(H ₂ O)].6H ₂ O	10

Preparation of the Schiff Base

The Schiff base was synthesized by dissolving 4-dimethylaminobenzaldehyde (0.01 mol; 1.49g) and same moles of 2-aminophenol in 50ml of ethanol. The mixture was stirred magnetically at 60°C for two hours. Yellow crystals will form then filtered, washed, dried and recrystallized from hot methanol to give pure yellow crystals in excellent yield of 85%.

Preparation of Mixed Ligand Chelates

A general procedure has been adopted for the preparation of chelates in basic media. Solutions of 0.01 mole of the salts [CoCl₂.6H₂O; 2.38 g, NiCl₂.6H₂O; 2.37 g, ZnCl₂; 1.36 g and CrCl₃.6H₂O; 2.67 g] in 25 mL ethanol, were added to the same volume of solutions of 0.01 mole of Schiff base and anthranilic acid respectively. The chelates were prepared by adding ammonium hydroxide(10%) until pH of the solutions becomes 8. The mixtures were refluxed for three hours then allowed to stand then cooled. The obtained chelates of characteristic colours were filtered off, washed several times with hot ethanol and dried.

Physical Measurements

The melting points of the synthesized mixed ligand chelates were not recorded. The Schiff base and its chelates were subjected to elemental analysis using 2400 CHN elemental analyzer. The molar conductivity of the chelates was measured in DMSO solvent using digital conductivity meter CMD-650, at chemistry department, Benghazi University, Benghazi, Libya. The infrared spectra of the Schiff base and its mixed ligand chelates were carried out applying KBr disc technique using IFS-25 DPUS/IR spectrometer. The electronic spectra of the Schiff base and its mixed ligand chelates were measured in CHCl₃ solvent by using a Perkin-Elmer lambda 4β spectrophotometer. The mass spectra were carried out by using Shimadzu QP-2010 Plus. Elemental

analysis, infrared, electronic and mass spectra were done at micro-analytical centre, Cairo University, Giza, Egypt.

Biological Activity Investigation

Five types of human pathogenic bacteria were used to test to the biological effects of the present mixed ligand chelates. All bacteria were obtained and identified from Benghazi medical center, Benghazi, Libya. The bacteria used were *Enterococcus faecalis*, *Escherichia coli*, *Pseudomonas aeruginosa*, *staphylococcus aureus* and *Acinetobacter SP*. The five species of bacteria were streaked on nutrient agar OXID England) plates, so that the streaking covered the surface of the plates. The chelates were applied on the streaked nutrient agar plates as a powder (5, 10 and 15 mg), taking an area not more than 6 mm (Size of an antibiotic paper disc) and leaving enough distances between them. The plates were incubated at 37°C for 24hrs. The inhibition zones were then measured in millimeters and recorded.

Conclusion

The obtained Co(II), Ni(II), Zn(II) and Cr(III) mixed ligand were prepared and characterized by using several physiochemical tools, in terms CHN elemental analyses, molar conductivity, magnetic moments, infrared, proton nuclear magnetic resonance, electronic and mass spectroscopies. All the experimental data confirm an octahedral geometry for all chelates. The antibacterial activity results show the presence of an effect for the ligands and chelates on the tested bacteria. Based on the physiochemical data. The geometrical structures as shown in the chemical equation-1 agreed with the result data cited in the text.

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