Synthesis, Spectroscopic and biological activity Studies of Azo-Schiff base and Metal Complexes derived from 5-Methyltryptamine

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ABSTRACT

A novel Azo-Schiff base ligand L 2-[1.5-Dimethyl-3-[2-(5-methyl-1H-indol-3-yl) - ethylimino] - 2 - phenyl - 2,3 - dihydro - 1H - pyrazol - 4 - ylazo] - 5-hydroxy -benzoic acid has been synthesized from reaction 1.5-Dimethyl-3-[2-(5-methyl- 1H - indol - 3 - yl) - ethylimino] - 2 - phenyl - 2.3 - dihydro - 1H - pyrazol - 4 - ylamine (A) with m-hydroxy benzoic acid. Then, its Zn(II), Cd(II) and Hg(II) complexes were synthesized with the general formula [ML$_1$Cl] where M = Zn(II), Cd(II) and Hg(II) are reported. The ligand and its metal complexes have been characterized by elemental analysis, metal content, Chloride containing, molar conductance, FT-IR, ^{1}H and ^{13}C- NMR, UV-Vis spectra, magnetic susceptibility, thermal analysis, and mass spectra. The activation thermodynamic parameters, such as ΔE^*, ΔH^*, ΔS^* ΔG^* and K are calculated from the TGA curve using Coats-Red fern method. The all prepared complexes were assayed for antibacterial (*Escherichia coli and Staphylococcus aureus*) activities by disc diffusion method. The results indicate that all tested ligand and complexes show antibacterial activity against E. coli and S aureus, as gram negative and positive bacteria.

Keywords: Azo-Schiff base, 5-Methyltryptamine, Thermodynamic Parameters, TGA, antibacterial

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تحضير ودراسة طيفية وفعالية بيولوجية لمعقدات آزو – أسس شف – المشتقة من 5- مثيل تربتامين

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الملخص

حضرنا المرتبطة الجديدة آزو - أسس شيف

2- {1.5 – Dimethy l – 3 - [2 - (5 – methyl - 1 H – indol – 3 - yl) - ethylimino] – 2 – phenyl - 2,3 – dihydro - 1H – pyrazol – 4 - ylazo} – 5 – hydroxy - benzoic acid

من تفاعل 5.1 –ثنائي مثيل -3- [2 -(5- مثيل – 1 -اندول – 3 - ايل) اثيل ايمين] – 2 -فنيل -3،2- ثنائي هايدرو – 1 -بيرازول – 4 -ايل أمين (A) مع حمض ميتا هدروكسي حمض البنزويل. حضرنا معقدات الخارصين (II)، الكادميوم (II) والزئبق (II) مــع المرتبطــة آزو -أســس شــيف والــصيغة العامــة هي[MLCl]. إذ إن M = الخارصين (II)، الكادميوم (II) والزئبق (II). درست المرتبطة والمعقـدات الجديدة بأطياف الأشعة ما تحت الحمراء وفوق البنفسجية - مرئية وأطياف الكتلــة والطنــين النــووي المغنطيسي البروتوني والكربوني والتحلل الحراري الوزني والتحليل العنصري والتحليل المعدني وتحديـد محتوى الكلور. والعزم المغنطيسي والناقلية المولاريــة. كمــا حــددت البــارامترات الثرمودينامیكيــة *ΔG*، *ΔS*، *ΔH*، *ΔE* وK باعتماد معادلة Coats-Red fern من أطياف التحلل الحراري الــوزني للمركبات ولكل مرحلة من مراحل التحلل. كما درست الفعالية البيولوجية للمركبات ضد أنواع منتخبة من البكتريا *Escherichia coli and Staphylococcus aureus*

الكلمات المفتاحية: 5-مثيل تربتامين، آزو -أسس شف، التحلل الحــراري الــوزني، والبارامترات الثرموديناميكية الفعالية البيولوجية.

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Introduction

In recent years, there has been a considerable interest in the chemistry of 4-amino-1.5-dimethyl-2-phenyl pyrazol-3-one and its derivatives. Schiff bases are an important class of ligands in coordination chemistry and find extensive application in different fields (Abbas alhamdani *et al.,* 2011; Eichhom *et al.,* 1994; Hughes, 1984; Tarafder *et al.,* 2001). Schiff bases derived from the salicylaldehydes are well known as polydentate ligands coordinating in neutral forms (Sonmez and Sekerci, 2002; Vukadin *et al.,* 2003). The interaction of these donors ligands and metal ions give complexes of different geometries and these complexes are potentially biologically active (Harlal Singh and Varshny, 2006). Thus, in recent years metal complexes of schiff bases have attracted considerable attention due to their remarkable antifungal, antibacterial, antitumor and anticancer activity (Chakravarty *et al.,* 2002; Gao and Zheng, 2002; Hanna and Moaead, 2001; Keypour *et al.,* 2002). The aim of this paper is to synthesis, characterize and study the biological activities and Thermodynamic Parameters of the new bidentate or tridentate Schiff base-Azo ligand, 2-{1,5-Dimethyl-3-[2-(5-methyl-1H-indol-3-yl)-ethylimino]-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylazo}-5-hydroxy-benzoic acid L and its metal complexes

Experimental

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use. Elemental analyses (C, H and N) were carried out on a Heraeus instrument (Vario EL). Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as KBr discs using a Shimadzu 8300 FTIR spectrophotometer in the range (4000-400) cm^{-1}. Electronic spectra were measured in the region (200-1100) nm using 10^{-3} M solutions in DMF at 25ºC using a Shimadzu 160 spectrophotometer. NMR spectra (^{1}H-, ^{13}C-NMR) were acquired in DMSO–*d6* solution using Brucker AMX400 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ^{1}H NMR analysis. Metals were determined using a Shimadzu (A.A) 680 G atomic

absorption spectrophotometer. Chloride was determined using potentiometer titration method on a (686–Titro processor–665Dosimat–Metrohm Swiss). Conductivity measurements were made with DMF solutions using a Jenway 4071 digital conductivity meter at room temperature. Electron impact (70 eV) mass spectra were recorded on a Finnegan-MAT model 8430 GC MS-DS spectrometer. Magnetic moments were obtained using a magnetic susceptibility balance (Jonson Mattey Catalytic System Division). Thermal analysis studies of the Ligand and complexes were performed on Perkin-Elmer Pyris Diamond DTA/TG Thermal System under nitrogen atmosphere at a heating rate of 10ºC/min from 30-700ºC.

Synthesis of the compound 1.5-Dimethyl-3-[2-(5-methyl-1*H*-indol-3-yl)-ethylimino]-2-phenyl pyrazol-4-ylamine (A)

An ethanolic solution (15 ml) of 5-methyltryptamine hydrochloride (1.036 g, 0.00492 mol) was added to a mixture containing an ethanolic solution (25 ml) of 4-amino-1.5-dimethyl-2-phenyl pyrazol-3-one (1g, 0.00492 mol) and. The reaction mixture was heated on water bath at (40-50 ºC for 14 h in presence of K_2CO_3 after the addition of excess of Ethanol (50 ml) The resulting mixture was refluxed under N_2. A white solid was formed, and then recrestallized from water: ethanol (1:1). The product was dried over anhydrous $CaCl_2$ in vacuum. Yield: 53.76%(0.95 g), mp 177 ºC. ^{1}H NMR (DMSO-d6, ppm): δ 1.89 (s, =CCH₃), 2.10 (s, arom-CH₃), 3.43 (s, NCH₃), 3.30 (t, NCH₂), 2.74 (t, CCH₂), 7.64-8.08 (m, arom), 12.11 (s, NH), 4.10(s, NH₂). ^{13}C-NMR (100.622 MHz, DMSO-d₆):δ 16.39(C_{20}), 18.87(C_3), 38.79(C_{13}), 45.6(C_{12}), 58(C_1), 98(C_{17}), 100($C_{7,11,14}$), 110(C_{18}), 111($C_{15,21}$), 118(C_4), 123.77(C_9), 127(C_{22}), 129(C_{19}), 130($C_{8,10}$), 140(C_6), 146(C_2), 151(C_5), (MS) m/z 360 , 164, 201.

Synthesis of Ligand (L) 2-[1.5-Dimethyl-3-[2-(5-methyl-1H-indol – 3 - yl) - ethyl imino] – 2 - phenyl pyrazol – 4 - ylazo] – 5 – hydroxy - benzoic acid(L)

A mixture solution from H_2SO_4 (18 M, 2 ml), ethanol (10 ml) and distilled water (10 ml), was charged with (A) (0.5 g, 1.39 mmol). An aqueous solution (2 ml) of $NaNO_2$ (0.0144 g, 1mmol) was added in

drops while maintaining the temperature between 0-5°C to the mixture. After that the $NaNO_2$ was added respectively with constant stirring to cold ethanolic solution of *m*-Hydroxy benzoic acid (0.192 g, 1.39 mmol), and then solution of 1 M NaOH (25 ml) was added to the dark colored mixture. The mixture was stirred for 1 h at 0 °C and acidified with 1 ml of conc. HCl. The brown product formed was suction filtered and recrystallized from ethanol-water (1:1) and dried (Scheme 1). Yield: 62.2%(0.44 g), mp>390ºC.

^{1}H NMR (DMSO-d6, ppm): 1.89 (s,C-CH$_3$), 2.10 (s,arom-CH$_3$), 3.43 (s, NCH$_3$), 3.30 (t, NCH$_2$), 2.74 (t, CCH$_2$), 4.49 (s,O-H phenol), 7 (d,C$_{25}$-H), 7.23 (s,C$_{15}$-H), 7.36 (m,C$_{7,11}$-H), 7.44 (m,C$_{9,18,21}$-H), 7.85 (d,C$_{24}$-H), 7.90 (m,C$_{8,10}$-H), 8.08 (d,C$_{17}$-H), 12.11 (d,N-H), 13 (s,O-H carboxylic).^{13}C-NMR (100.622 MHz, DMSO-d$_6$) δ 16.39 (C$_{20}$), 18.87 (C$_3$), 38.79(C$_{13}$), 45.6(C$_{12}$), 58(C$_1$), 98 (C$_{17}$), 100 (C$_{7,11,14}$), 106(C$_{25}$), 110 (C$_{18}$), 111 (C$_{23}$), 111 (C$_{15,21}$), 118 (C$_4$), 123.77(C$_9$), 127(C$_{24}$), 128 (C$_{26}$), 129 (C$_{19}$), 130 (C$_{8,10}$), 140 (C$_6$), 144 (C$_{27}$), 146 (C$_{22}$), 146 (C$_2$), 151 (C$_5$), 152 (C$_{29}$), 182 (C$_{28}$), (MS) m/z 508 (C$_{28}$H$_{28}$N$_6$O$_3$), 345 (C$_{18}$H$_{15}$N$_5$O$_3$)$^{2-}$, 159 (C$_{11}$H$_{13}$N).

General synthesis procedure of the complexes

An ethanolic solution (15 ml) of the metal salt (1 mmol) was added drop wise to an ethanolic solution (20 ml) of the Schiff base ligand L (1 mmol). The resulting mixture was refluxed under N$_2$ for 6 h, resulting in the formation of a solid mass which was crystallized in hot ethanol and dried under vacuum.
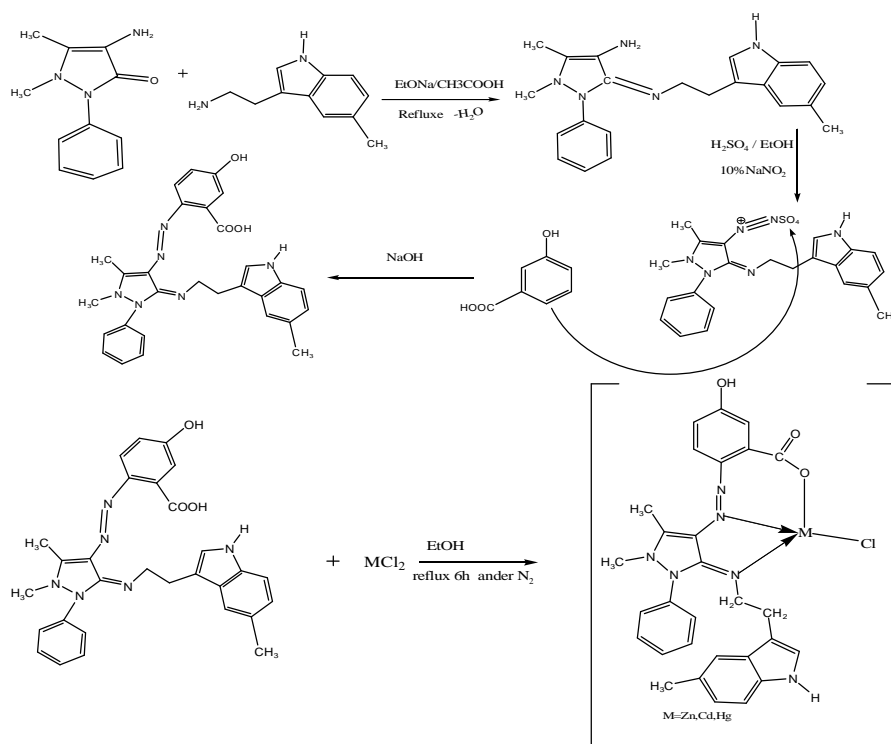
Scheme 1. Synthesis of Azo-Schiff base ligand and Complexes

Determination of Bacteriological Activity

Two pathogenic biological, *Escherichia coli and Staphylococcus aureus*, were used to test the antimicrobial activity of the ligand and its metal complexes. The nutrient agar (NA) medium was prepared and a quantity of 10 ml of the medium was poured in to the sterilized Petri plates and allowed to solidify (Atlas, Alfres, Brown and Lawrence, 1995). The plates were inoculated with spore suspensions of pathogenic bactericides. By using the sterilized cork borer, wells were dug in the center of the culture plates. The test complexes solution in DMSO was added (0.5 ml) to these wells and the plates were incubated at 25°C for 24 hour. Then the inhibition zone appeared around the wells in each plate was measured and recorded as the cytotoxic effect of the appropriate complexes

The Thermal analysis

From the TGA curves recorded for the successive steps in the decomposition process of these ligand and complexes it was possible to determine the following characteristic thermal parameters for each reaction step: Initial point temperature of decomposition (T_i): the point at which TG curve starts deviating from its base line. Final point temperature of decomposition (T_f): the point at which TG curve returns to its base line. Peak temperature, i.e. temperature of maximum rate of weight loss (T_{DTG}): the point obtained from the intersection of tangents to the peak of TG curve.

Mass loss at the decomposition step (Dm): it is the amount of mass that extends from the point T_i up to the reaction end point T_f on the TG curve, i.e. the magnitude of the ordinate of a TG curve. The material released at each step of the decomposition is identified by attributing the mass loss (Dm) at a given step to the component of similar weight calculated from the molecular formula of the investigated complexes, comparing that with literatures of relevant compounds considering their temperature. This may assist in identifying the mechanism of reaction in the decomposition steps taking place in the complexes under study. Activation energy (E) of the composition step: the integral method used is the Coats-Redfern equation (Coats and Redfern, 1964). for reaction order n≠1or n= 1, which when linearised for a correctly chosen n yields the activation energy from the slop;

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{ZR}{qE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303RT}$$ ………………..n≠1

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{\beta E}(1-\frac{2RT}{E})\right] - \frac{E}{2.303RT}$$ ………………n=1

$\Delta S^* = 2.303R[Log(Ah/K\ T_{max})]$, $\Delta H^* = E-RT_{max}$, $\Delta G^* = \Delta H^* -T_{max}\ \Delta S^*$ where: α = fraction of weight loss, T= temperature (°K), n = order of reaction, A or Z = pre-exponential factor, R= molar gas constant, E= activation energy and q = heating rate. Order of reaction (n): it is the one for which a plot of the Coats-Redfern expression gives the best straight line among various trial values of n that are examined relative to that estimated by the Horovitz-Metzger method (Horovitz and Metzger, 1963).

Result and Discussion

The synthetic procedure of Azo-Schiff base ligand and its metal complexes are presented in Scheme 1. The reactions of divalent transition metal ions *viz.,* Cd(II), Hg(II) and Zn(II). The composition of the complexes formed in solution has been established by mole ratio and job methods. In both cases the results reveal (1:1) metal to ligand ratio yielded the corresponding metal chelates. The physical and analytical data of Azo-Schiff base ligand and its metal complexes are given in table 1 .

Table 1. The characterization data of the prepared compounds

Compound Formula	M wt=g Yield%	Color	MP °C	Elemental Analysis Calculated (Found) %				
				Cl	M	N	H	C
A $C_{22}H_{25}N_5$	0.95 53.76	White	177			19.48 (21.23)	7.01 (6.87)	73.51 (75.55)
(L) $C_{28}H_{28}N_6O_3$	0.44 62.2	Brown Yellow	>390	-	-	(16.52) 16.56	(5.55) 5.83	(68.49) 67.76
[ZnLCl] $C_{28}H_{27}N_6O_3ClZn$	0.608 75	Light red Brown	260d	(5.83) 4.98	(10.75) 11.08	(13.81) 14.23	(4.47) 5.01	(57.25) 56.77
[CdLCl] $C_{28}H_{27}N_6O_3ClCd$	0.655 58	Light red Brown	235d	(5.41) 4.88	(17.15) 16.74	(12.82) 13.11	(4.15) 5.02	(53.14) 54.05
[HgLCl] $C_{28}H_{27}N_6O_3ClHg$	0.743 79	red Violet	305d	(4.77) 3.89	(26.98) 26.33	(11.30) 10.64	(3.66) 4.12	(46.84) 47.52

d: degree of the decomposition

^{1}H NMR spectra

The newly synthesized (A) and ligand gave a satisfactory spectral data and the molecular structure was assigned on the basis of ^{1}HNMR and ^{13}CNMR chemical shift. NMR spectra were determined in DMSO with TMS as an internal reference. The identification was based on using simple splitting patterns that were produced by the coupling of protons and carbons which have very different chemical shifts. According to the results obtained from the spectra. ^{1}H NMR spectrum of starting material (A) in DMSO gives the following signals: phenyl as multiple at 7.64-8.08 ppm, $=C-CH_3$ at 1.89 ppm, $-C-CH_3$ at 2.10
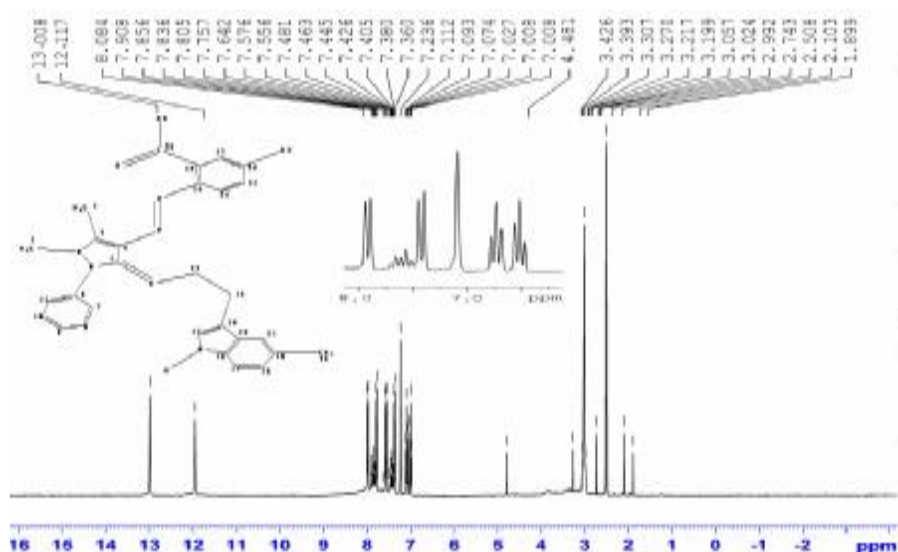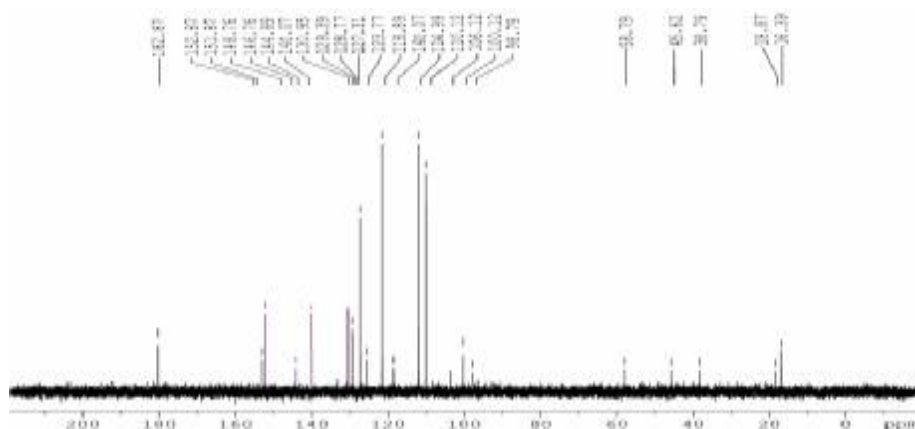
ppm, -C -CH$_3$ at 2.74 ppm, -N –CH$_2$ at 2.31 ppm, -N –CH$_3$ at 3.44 ppm, peak at 12.1 ppm is attributable to the primary amine –NH group, peak at 4.1 ppm is attributable to the amine –NH$_2$ group present in the 4-aminoantipyrine of the starting material (A) (Sonmez and Sekerci, 2002; Vukadin *et al.,* 2003), (Figs. 1-2).

Fig. 1-a. ^{1}HNMR spectra of A

Fig. 1-b. ^{13}CNMR spectra of A

29

Fig. 2-a. ¹HNMR spectra of L

Fig. 2-b. ¹³CNMR spectra of L

^{1}H NMR spectrum of ligand (L) in DMSOgives the following signals: phenyl as multiple at 7.00-8.2 ppm, =C-CH$_3$ at 1.89 ppm, -C - CH$_3$ at 2.10 ppm, -C -CH$_3$ at 2.74 ppm, -N –CH$_2$ at 3.01 ppm, -N – CH$_3$ at 3.44 ppm, peak at 12.11 ppm is attributable to the primary amine –NH group present in the free Ligand (L)., peak at 4.49, 13.0 ppm is attributable to the phenolic -OH group and carboxylic-OH

group respectively of the free ligand. The presence of this peak at 4.5-4.8 ppm for the zinc, cadmium and mercury complexes confirms the phenolic -OH group proton free from complexation and showed a signal at 12.11 ppm attributable to the primary amine NH group present in the free ligand, (Abbas et at., 2011; Eichhom et al., 1994) (Fig 3).
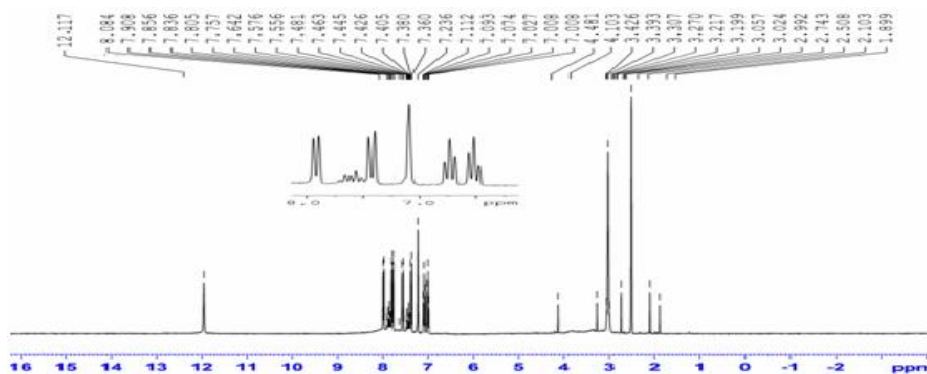
Fig. 3. ^{1}HNMR spectra of [ZnLCl]

Mass spectrum

The electron impact mass spectrum of the starting material (A) and Schiff base-Azo (L) confirm the probable formula by showing a peak at 360 m/z, corresponding to the starting material (A) and 508 m/z, corresponding to the Schiff base-Azo (L). The electron impact mass spectrum of the complexes confirm the probable formula by showing peaks at 608, 655 and 743 m/z, corresponding to [ZnLCl], [CdLCl] and [HgLCl] respectively. The series of peaks in the table 2 may be assigned to various fragments (Figs. 4-5).

Table 2. Mass spectrum data for (A), L and its complexes

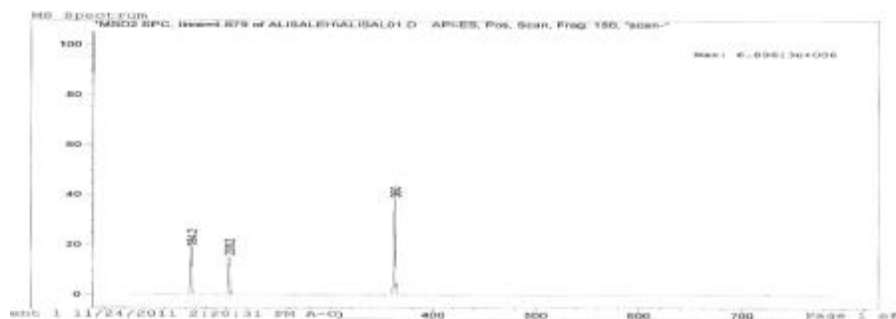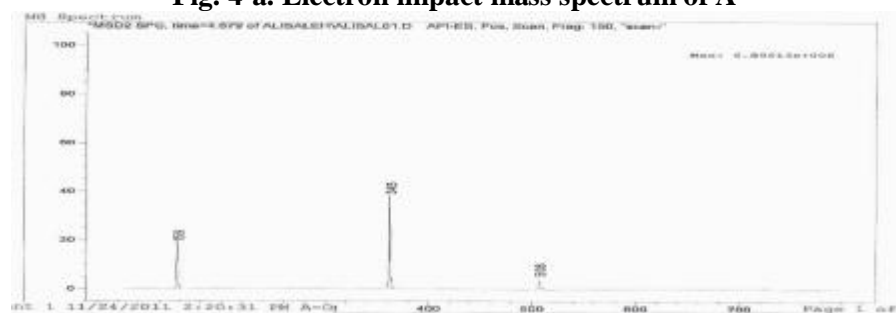| compounds	peaks m/z
A	360, 164 ,201
L	508, 345, 159
[ZnL$_1$Cl]	(608, 592, 576, 564, 546, 527, 236, 160, 129, 117, 108, 71, 55
[CdL$_1$Cl]	655, 647, 369, 354, 229, 128
[HgLCl]	743, 730, 703, 666, 562, 486, 474, 402, 217, 159, 147, 92, 58

Fig. 4-a. Electron impact mass spectrum of A
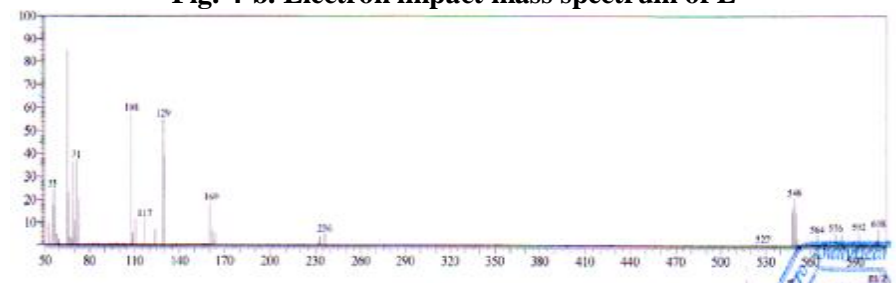

Fig. 4-b. Electron impact mass spectrum of L

Fig. 5. Electron impact mass spectrum of [ZnLCl]

IR spectra

The IR spectrum of the compound (A), L and complexes (Figs.6-8) show characterization bands at 3485, 3305, 3271 and 1641 cm^{-1} due to the as$\nu(NH_2)$, s$\nu(NH_2)$, $\nu(NH)$, and $\nu(C=N)$ functional groups, respectively. The ligand show characterization bands at 3699, 3429, 1288, 1728, 1692, 1444, 1601, 1342 and 3234 cm^{-1}due to the $\nu(OH)$ phenolic, $\nu(OH)$ carboxyl,$\nu(CO)$ phenolic, $\nu(C=O)$, $\nu(C=N)$, $\nu(N=N)$,

as ν(COO), sν(COO) and ν(NH) functional groups, respectively (Abbas., 2005; Silverstein et al.,1981; Ravichandran and Thangaraja, 2004) .The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complexes formation table 3. (Abbas *et at.,* 2011; Eichhom *et al.,* 1994).
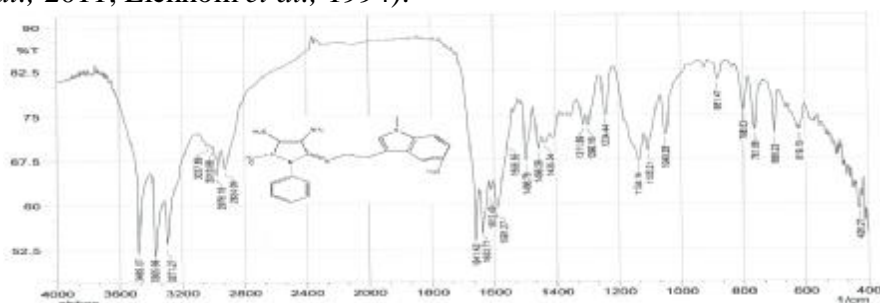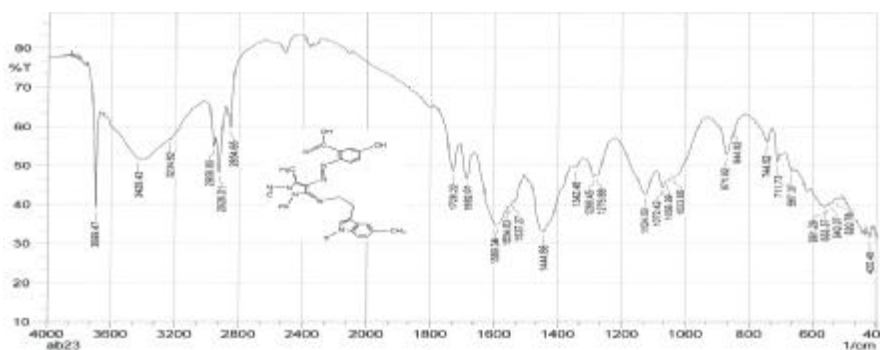

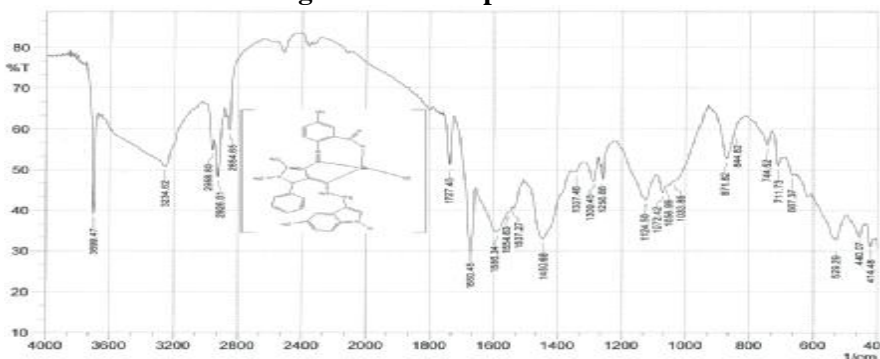**Fig. 6. Infrared spectra of A**

Fig. 7. Infrared spectra of L

Fig. 8. Infrared spectra of [ZnL$_1$Cl]

Moreover, the ν(C=N), ν(N=N), bands of the ligand was observed at 1692, 1444 cm^{-1} and this band was shifted to the lower frequencies by (12-10 cm^{-1}), and the ν(N=N), bands of the ligand was observed at 1444 cm^{-1} and this band was shifted to the lower or high frequencies by (6-7 cm^{-1}), in the spectra of the complexes. This indicates that the ligand was coordinated with the metal ions through the N atom. So, it is noticed that both of the ν(COO) asymmetric and symmetric band of the ligand exhibited at 1601 and 1342 cm^{-1}. On Zn(II), Cd(II) and Hg(II) complexes these two bands were shifted to the lower frequencies by 17-5 cm^{-1}. This indicates that the ligand was mono dentate ligand which coordinated with the metal ions through the O atom and terminal carboxyl oxygen atom (Shayma, 2010).The reduction in bond order, upon compexation, can be attributed to delocalization of metal electron density (t$_2$g) to the π-system of the ligand. These shifts confirm the coordination of the ligand via the nitrogen of azomethine and the azo groups to metal ions and the ν(OH) carboxylic 3429 cm^{-1} in the free ligand not founds in the complexes for (Zn, Cd and Hg) because of the coordination of the ligand via the oxygen of carboxyl group to (Zn, Cd and Hg) metals. The ν(NH) band at 3234 cm^{-1} in the free ligand was not shifting for the complexes. At lower frequency the complexes exhibited bands around 540-529 cm^{-1} assigned to the ν(M-N) and exhibited bands around 440-454 cm^{-1} assigned to the ν(M-O) for (Zn, Cd and Hg) complexes (Nakamoto, 1997).

Table 3. Infrared data of Ligand and its metal complexes (cm^{-1})

Com	ν(OH) carboxy	ν(OH)ph ν(CO)ph	ν(NH)	ν(C=O) ν(C=N)	ν(N=N) ν(C-N=N-C)	ν(M-N) ν(M-O)	asv(COO) sv(COO)	Additional Bands
A			3271	- 1641				asv(NH)=3485 sv(NH)=3305
L	3429	3699 1288	3234	1728 1692	1444 1124	-	1601 1342	
[ZnLCl]	-	3699 1300	3234	1727 1680	1450 1124	529 440	1586 1337	ν(Zn-Cl)=414
[CdLCl]	-	3699 1289	3234	1727 1680	1437 1124	540 454	1584 1334	ν(Cd-Cl)=410
[HgLCl]	-	3693 1290	3234	1727 1682	1450 1124	529 452	1586 1333	ν(Hg-Cl)=414

Electronic spectra studies

The electronic spectra of the free ligand L shows electronic transitions $\pi \to \pi^*$ and $n \to \pi^*$ at 275 and 300 nm respectively.

Finally, the diamagnetic of Zn(II), Cd(II) and Hg(II) complexes exhibited absorption bands at 296, 297 and 280 nm due to $n \to \pi^*$. Appearance of these band are due to $n \to \pi^*$ transition associated with azomethine linkage and $M \to L$ (C.T) charge transfer transition. Moreover, the spectrum of the complexes also shows bands at 322, 380 and 325 nm due to the charge transfer as the electronic configuration of these complexes Zn(II), Cd(II) and Hg(II) respectively, confirming the absence of any d-d transition (Lever, 1968; Shayma, 2010). All the data of the magnetic susceptibility and electronic spectra of the free ligand and its complexes are listed in table 4. The molar conductance values in table 4 of 23-43 ohm^{-1}cm^2 mol^{-1} in DMSO medium indicate that the metal complexes are non electrolytes (Abbas *et at.,* 2011).

Table4. The electronic spectra data and magnetic moments of the compounds.

Complex	A_m cm^2 Ω^{-1}mol^{-1}	μ_{eff} B.M	λ_{max} (nm)	λ_{max} (cm^{-1})	ε_{max} L mol^{-1}cm^{-1}	Assignments
A			280	35714	35000	$\pi \to \pi^*$
			300	33333	36900	$n \to \pi^*$
L			275	36363	30000	$\pi \to \pi^*$
			300	33333	34500	$n \to \pi^*$
[ZnLCl]	39	dia	296	33783	34500	$n \to \pi^*$
			322	31055	35000	ML$\to$CT
[CdLCl]	43	dia	297	33670	28600	$n \to \pi^*$
			380	26315	34100	ML$\to$CT
[HgLCl]	36	dia	280	35714	35300	$n \to \pi^*$
			325	30769	40000	ML$\to$CT

Thermal analysis

To understand thermal decomposition process, Azo-Schiff base ligand and its metal complexes were examined by thermo gravimetric analysis in the temperature range of 35–700 ºC. The obtained thermo analytical results from TGA curves for all these compounds are given

in table 5. The decomposition was complete at 693 ºC for all the complexes. The data from the thermo gravimetric analyses indicated that the decomposition of the complexes and the ligand proceeds in (two – four) steps. The comparison of ligand and the complexes shows that the complexes were more thermally stable at about 10– 35 ºC higher than that of the Azo-Schiff base. The final decomposition products were metal oxide mixture formed above 598 ºC for the Cd(II), and zinc(II) complexes (Sarika et al.,2009) .(Figs. 9-10). The thermal data have been analyze for thermodynamic parameters by using Coats-Redfern (Sahoo *et al.,* 2003) table 6. From the half decomposition temperature, the relative thermal stability of the compounds is to be : HgL > CdL > ZnL > L

$(L_1) = C_{29}H_{28}N_6O_3$ [101.131% Found (99.999% Cal) (158-348ºC) $\rightarrow$ $C_{23}H_{23}N_5O_3$ [82.648 % Found (82.085 % Cal)] (348-598 ºC)$\rightarrow$ $C_6H_5N^-$[18.483% Found (17.914%Cal)

1-$C_{29}H_{27}N_6O_3ClCd$ (655.43) (45-145ºC) $\rightarrow$ CH_2O [4.931% Found (4.623%Cal)]

2-$C_{28}H_{25}N_6O_2ClCd$ (625.43) (145-445ºC) $\rightarrow$ C_6H_8OClN [22.003% Found (22.214%Cal)]

3-$C_{22}H_{17}N_5OClCd$ (479.93) (445-598ºC) $\rightarrow$ $C_{22}H_{17}N_5$ [53.537% Found (53.536%Cal)]

4-CdO [19.529% Found (19.6%Cal)]

Total wt. loos= 80.471% Found (80.363% Cal) and final residue :19.529% Found (19.6% Cal)

1-$C_{29}H_{27}N_6O_3ClZn$ (608.41) (45-170ºC) $\rightarrow$ C_7H_6O [16.823% Found (17.442%Cal)]

2-$C_{22}H_{21}N_6O_2ClZn$ (502.29) (170-355ºC) $\rightarrow$ C_8H_7N [20.175% Found (19.230%Cal)]

3-$C_{14}H_{14}N_5O_2ClZn$ (385.29) (355-698ºC) $\rightarrow$ $C_{14}H_{14}N_5ClO$ [52.903% Found (49.884%Cal)]

4-ZnO [10.099% Found (13.377%Cal)]

Total wt. loos= 89.901% Found (86.556% Cal) and final residue: 10.099% Found (13.444% Cal).

1-$C_{29}H_{27}N_6O_3ClHg$(743.61) (45-180ºC) $\rightarrow$ C_6H_6O[13.593%Found (12.655%Cal)]

2-$C_{23}H_{21}N_6O_2ClHg$(649.5) (180-294ºC) $\rightarrow$ C_9H_9N [18.581% Found (17.639%Cal)]

3-$C_{14}H_{12}N_5O_2ClHg$(518.33)(294-480ºC) $\rightarrow$ $C_{11}H_6N_3$ [25.043% Found (24.241%Cal)]

4-$C_3H_6N_2O_2ClHg$(338.07) (480-695ºC) $\rightarrow$ $C_3H_6N_2OCl$ [16.771% Found (16.355%Cal)]

4-HgO [29.261% Found (29.126%Cal)]

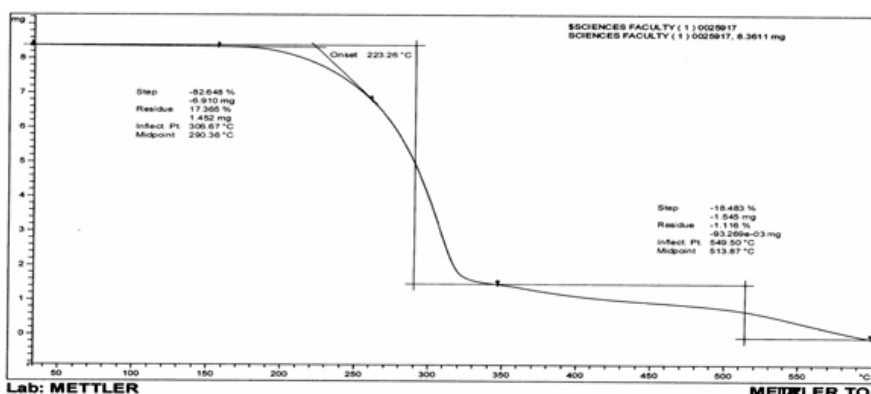Total wt. loos= 73.988% Found (70.89% Cal) and final residue: 29.261% Found (29.11% Cal)
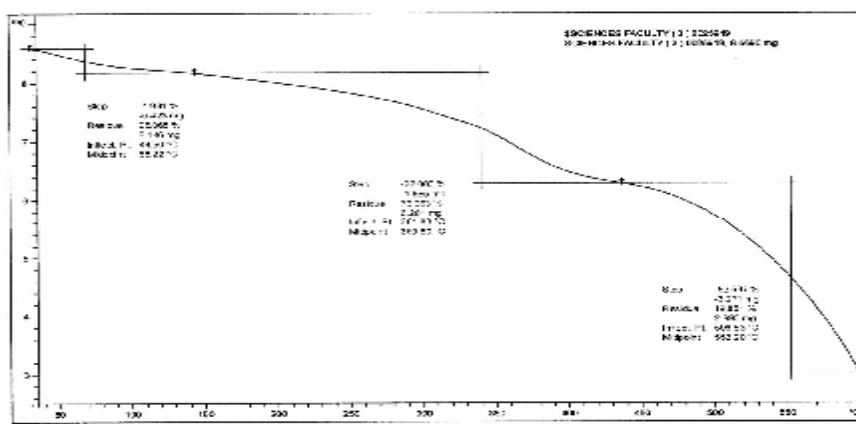

Fig. 9. TGA curves of Ligand

Fig. 10. TGA curves of [CdLCL]

37

Table 5. Thermal analysis data of some metal complexes of L

Com	TG range (°C)	DTG max (°C)	%Estimated (calculated)		Assignment
			Mass Loss	Total mass Loss	
L	158-348 348-598	290.36 513.87	82.648 (82.085) 18.483 (17.914)	101.131 (99.999)	$C_{23}H_{23}N_5O_3$ $C_6H_5N^-$
[ZnLCl]	45-170 170-355 355-698	77.35 266.96 475.38	16.823 (17.442) 20.175 (19.23) 49.884 (52.903) 10.099 (13.377)	89.901 (86.556)	C_7H_6O C_8H_7N $C_{14}H_{14}ClN_5O$ ZnO
[CdLCl]	45-145 145-445 445-598	68.22 359.6 552.2	4.931 (4.623) 22.003 (22.214) 53.537 (53.536) 19.529 (19.6)	80.471 (80.363)	CH_2O C_6H_8OClN $C_{22}H_{17}N_5$ CdO
[HgLCl]	45-180 180-294 294-480 480-695	141.42 232.9 381.01 576.04	13.593 (12.655) 18.581 (17.639) 25.043 (24.241) 16.771 (16.355) 29.261 (29.126)	73.988 (70.89)	C_6H_6O C_9H_9N $C_{11}H_6N_3$ $C_{11}H_6N_2OCl$ HgO

Table 6. Thermodynamic parameters of the ligand and metal complexes

Sam (step)	Trange °C	n	R^2	T_{max} °K	Ea K.J mol⁻¹	ΔH^* KJ mol⁻¹	ASec⁻¹ x10⁵	ΔS^* J mol⁻¹K⁻¹	ΔG^* KJ mol⁻¹	K x 10⁻⁶
$L_1(1)$	158-348	1	0.99	563.51	7.6669	2.982	425.5	-104.171	61.983	1.7958
$L_1(2)$	348-598	1	0.99	786.85	12.2404	5.6986	830.9	-101.378	85.467	2.1189
$CdL_{1=1}$	45-145	0.9	0.99	341.37	5.792853	2.9547	146.04	-108.895	40.12847	0.72377
$CdL_{1=2}$	145-445	0.9	0.99	632.75	12.11535	6.85467	477.78	-104.171	72.76927	0.98303
$CdL_{1=3}$	445-598	0.9	0.99	825.35	12.36905	5.050709	977.70	-100.426	8.839419	2.544185
$ZnL_1=1$	45-170	0.9	0.99	348.5	6.79244	3.8784	970.1152	-93.3712	36.605	3.50428
$ZnL_1=2$	170-355	0.9	0.99	537.11	8.6145	4.124	361.2055	-105.181	60.9324	1.27922
$ZnL_1=3$	355-698	0.9	0.99	750.53	12.19515	6.80327	706.2673	-101.126	72.3868	1.4775
$HgL_1=1$	45-180	0.9	0.99	414.57	6.289215	2.84248	203.6714	-107.745	47.51068	1.03174
$HgL_1=2$	180-294	0.9	0.99	506.05	7.706092	3.4988	314.8201	-105.782	57.03	1.29757
$HgL_1=3$	294-480	0.9	0.99	654.16	10.67851	5.239813	534.2383	-103.519	72.95827	1.49305
$HgL_1=4$	480-695	0.9	0.99	849.19	13.42782	6.36765	926.9402	-101.106	722.6238	2.14988

Anti bacterial Activates

The data of antimicrobial activates of the prepared ligand and its complexes are given in table 7, the result showed that the complexes have more toxicity against the bacterial species than the free ligand. This can be attributed to the tweeds chelation theory (Morad., Elajaily.and Ben Gweirif, 2007), according to which the chelation

reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with donor group and possible electro delocalization over the whole ring. This increases the lipophilic character of the lipid layers of the cell membranes. Furthermore, the mode of action of compounds may involve the (C=N), (CH$_3$), (OH), (NH) and (N=N) groups with active centers of the cell constituents resulting in the interference with normal cell process.

Table 7. Antibacterial activities for the Schiff base and its complexes

Compounds	*Staphylococcus aureus*(+)		*Escherichia coli (-)*	
	5mM	10mM	5mM	10mM
L	++	+	+	++
[ZnLCl]	+++	++++	++++	+++
[CdLCl]	+++	++++	++++	+++++
[HgLCl]	++++	++	++	++++

(+) = (2-5) mm = active,(++) = (5-8) mm = highly active

Conclusions

In this paper we have explored the synthesis and coordination chemistry of some monomeric complexes obtained from the reaction of the ligand L with some metal ions. The mode of bonding and overall structure of the complexes were determined through physico-chemical and spectroscopic methods. Complex formation study via molar ratio has been investigated and results were consistent with those found in the solid complexes with a ratio of (M:L) as (1:1). The thermodynamic parameters, such as ΔE^*, ΔH^*, ΔS^* ΔG^* and K are calculated from the TGA curve using Coats-Red fern method. Biological activity studies of the ligand and its metal complexes against several organisms, *Escherichia coli and Staphylococcus aureus* are reported, Compounds exhibited the high effect of activity.

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