SYNTHESIS AND CHARACTERIZATION OF TWO HYDRAZONES OF ISATINE AND THEIR SOME TRANSITION METAL COMPLEXES.

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Abstract

A series of complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) have been synthesized with two hydrazones derived from Isatin with salicylaldehyde (HL_a) and 2,4-dinitro phenyl hydrazine (L_b). The complexes have been characterized by the elemental analysis, spectral (FTIR, Mass, Electronic, ^{1}HNMR, ESR), Thermal analysis (TGA&DTA), Magnetic moments and conductance measurements. The proposed structures of the prepared complexes were octahedral (Co(II)-HL_a), tetrahedral for Ni(II), Zn(II), Cd(II)-HL_a complexes and square planar for (Cu(II)-HL_a, L_b Zn(II)-L_b complexes. The synthesized ligands (HL_a and L_b) were tested for their antibacterial activities. Only HL_a ligand displayed activity against staphylococcus aureas (g +ve)

Keywords: Isatin, salicylaldehyde hydrazones and 2,4-dinitro phenyl hydrazine

1. Introduction

Isatin and 1-alkylisatins furnish condensation products at the C-3 position when reacted with: hydrazine, alkyl and arylhydrazines [1, 2], heteroarylhydrazines derived from pyrimidine, pyrazine [3], thiazole, 1,2,4-triazine [4], quinazoline [5], benzimidazole, benzo-thiazole [6], phthalazine, triazines, as well as acylhydrazides of oxalic, benzoic, phenoxyacetic and oxanilic acids, arylsulfonylhydrazides, guanylhydra-zones, semicarbazines and thio-semicarbazides [8].

The reaction of 1-methylisatin and semicarbazone yielded methis-azone, a compound that found use in the treatment of smallpox, a viral disease that has now been eradicated [9]. Isatin-3-imines also react with hydrazine derivatives such as heteroarylhydrazines [10], thiosemicar-bazides and acylhydrazides, resulting in a substitution reaction at the C-3 position. Substitution reactions are also described to occur when O-methylisatin is treated with thiosemicarbazines, furni-shing isatin-2-thiosemicarbazones [11].

Isatin, due to its cis α-dicarbonyl moiety, is a potentially good substrate for the synthesis of metal complexes, either alone or with other ligands. Their derivatives, mostly those substituted at C-3, such as isatin-3-hydrazones and isatin- 3-imines bearing an extra heteroaromatic ring are also generally employed as ligands. In this manner, Schiff bases formed from isatin and amino silica gel are useful sorbents for divalent cations and for Fe (III) [11-14].

Due to its ability to bind ferric ions, isatin-3-thiosemicarbazone can be used to form magneto-polymer composites with poly (vinyl chloride) [15]. Here we report the synthesis and characterization of two Isatin hydrazones, also to report the structures of the metal complexes with hydrazones derived from the Isatin,

possessing donor sites oxygen of carbonyl oxygen, hydroxyl group and azomethine nitrogen.

2. Experimental.

(A) MATERIALS

Isatin (Fluka), salicylaldehyde (Fluka), Hydrazine monohydrate (Fluka), Absolute 99/100% and Methanol (Fluka), and 2,4-dinitrophenyl hydrazine (2,4DNPH) (Fluka), were used without further purification. Cobalt acetate tetrahydrate (Fluka),Copper acetate monohydrate (BDH), Nickel acetate tetrahydrate (Riedel-de Haen), zinc acetate dihydrate (Fluka), Cadmium acetate (Fluka) were reagent grade .

(B) SYNTHESIS OF THE LIGANDS :
(I) Synthesis of 3-[(2- Hydroxy– benzylidene)-hydrazono]- 1,3-dihydro- indol-2-one Ligand(HL$_a$)

Add (**2.943**g, **20** mmol) of Isatin, in **100** ml absolute ethanol drop wise with stirring to Salicylaldehyde hydrazone (**2.72**g, **20** mmol) in **100** ml absolute ethanol in **250** ml round flask. The mixture was heated to reflux for **48** hours, during which the color of the solution changed to dark red. The formed dark red solid product was left to coagulate, then filtered off and recrystallized from absolute ethanol. The yield was (2.6515g, **50.03**%)

(II) Synthesis of 3-[(2,4-dinitro-phenyl)-hydrazono]-1,3-dihydroindol-2-one Ligand (L$_b$)

Add (**1.4714** g, **10** mmol) of Isatin, in **100** ml absolute ethanol drop wise with stirring to (**1.9814** g, **10** mmol) of 2,4-dinitro phenyl hydrazine (2,4DNPH) in**100** ml absolute ethanol in **250** ml round flask. The mixture was heated to reflux for **20** hours, during which the color of the solution changed to orange reddish. The former orange reddish solid product was left to coagulate, then filtered off and recrystallized from n,n-dimethyl-formamide. The yield was (**2.6822** g, 57.37 %).

(III) Complexes of the Hydrazone HL$_a$, and L$_b$ Ligands

The HL$_a$ and L$_b$ ligands reacted with Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions to yield the corresponding metal complexes. Table 1 lists the physical and analytical data of the hydrazone, HL$_a$ and L$_b$ ligands and their transition metal complexes. The complexes were investigated by Elemental analyses, FTIR UV. Visible, mass, spectral analysis and ^{1}H-NMR for Zn(II) and Cd(II) complexes, electron spin resonance (ESR) spectra for Cu(II) complexes, molar ratio (1:1), thermal gravimetric analyses (TGA) & (DTA) for Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) Complexes, magnetic and molar conductivity measurements.

(D) Physical Measurements

(I) Melting point

All melting points reported for the compounds are uncorrected and measured on a MEL-TEMP [SMP$_3$] melting point apparatus.

(II) FT-IR Spectra

The FT-IR Spectra (400-4000 Cm^{-1}) of the compounds were measured as KBr discs using FTIR Nicolet 6700 Thermo Scientific at microanalytical Unit, Ain shams University , Cairo, Egypt; (200-400 Cm^{-1}) using FT-IR 1650 (PERKIN, Elmer cairo University, Egypt and (200-600 Cm^{-1}) using Nexus 670 spectrometer at Micro-analytical Unit, at the National Research Center Dokky, Giza, Egypt.

(III) UV-Visible

The UV-Visible spectra of the investigated compounds were obtained using 8-650UV/Vis. Spectrophotometer (UK-Tenway) with one centimeter quartz cell.

(IV) Elemental Analysis

Elemental analysis for C,H,N was performed by elemental analyzer 2400 at Ain shams university , Cairo, Egypt and the determination of the metal cations was performed using Atomic Absorption spectrophotometer, Perkin Elmer 3100(U.S.A).

(V) ^{1}H-NMR Spectra

The ^{1}H-NMR measurements were Carried out on a varian GEMINI -200 "NMR".The deuterated Dimethyl sulfoxide (DMSO-d_6) solvent is indicated in brackets and chemical shift (δ) are given down field relative to tetra methyl silane (TMS), as internal stander Egypt .

(VI) Mass Spectra

Mass Spectra were carried out On GCQ Finnigan at microaalytical Unit,Ain shams University, Cairo, Egypt.

(VII) Thermal Gravimetric (TGA) and (DTA) Analyses :

TGA and DTA Curves were obtained using Shimadzu , DTG 60 H at the Microanalytical Center, Cairo , University . Thermal analyzer equipped with a thermo balance . Samples (~ 50 mg) were heated at a programmed rate 20 ml/min in a dynmic N_2 atmospher . The sample was contained in aboat shaped platinum pan suspended in the center of furnace .

(VIII) Electronic Spin Resonance (ESR) Spectra

ESR spectra recorded on the Brucker ELXSYS 500E. X-band with auto detection for peak without needs any calibration.

(IX) Magnetic Measurements

Magnetic susceptibiliies were measured by the Gouy method at room temperature using magnetic susceptibility balance (Johnos Matthey alfa product , Model No.MKI). Diamagnetic corrctions calculated from pascals' constants.

(X) Biological activity

Antibacterial activities of the ligands were studied against two types of bacteria Escherichia coli (gram –ve) and staphylococcus aureas (gram +ve). The nutrient agar media wich used were constituent as gram/liter. The media contents from

peptone 5.0 g/L, Beef 3.0 g/L, Sodium chloride 8.0 g/L & Agar No.2 2.0g/L at pH 7.3±0.2 in DMF as solvent.

3. Results and discussion

3.1 HL$_a$ and L$_b$ ligands

Infrared spectra of the reaction products between Isatin and Salicylaldehyde hydrazone (HL$_a$) or 2,4-dinitrophenyl hydrazine (L$_b$) ligands assignments were listed in **Table 1**. The disappearance of both stretching frequency, the amino group, υ(NH$_2$) from the infrared spectra of the hydrazone (HL$_a$) and (L$_b$) ligands which were appeared as broad bands at **3286** cm^{-1} and **3105** cm^{-1} in the free salicylaldehyde hydrazone (SH) and 2,4- dinitrophenyl hydrazine (2,4DNPH); respectively, and the stretching frequency, υ(C=O) of the keto groups C=O, were appeared at **1728** cm^{-1} in the free Isatin, were shifted to low frequencies at **1720**cm^{-1} and **1636**cm^{-1} for HL$_a$ and L$_b$ respectively. The appearance of most intense band at 1620 and **1595**cm^{-1}, which was assigned to the stretching frequency, υ(-C=N), of the azomethine (-C=N) group for the HL$_a$ and L$_b$ respectively. These bands were characterized for the azomethine moiety of most the azomethine compounds [16].

Table:1. Characteristic bands of the hydrazone, HL$_a$ and L$_b$ ligands Isatin (IS), salicylaldehyde hydrazone (SH) and2,4- dinitrophenyl hydrazine (2,4 DNPH) and their assignments.

HL$_a$	Isatin	SH	Assignment
3498 w,br	3449 m,br	3480 w,br	V(OH) arom.
——	——	3286 m,br	V(— NH$_2$)
3279 s	3194 s (keto)	——	V(NH)
1569 w,sh			
1720 vs	1728 vs	——	V(C=O)
1373 w	——	1325 w	V(C-O)
1620 vs	1612vs	——	V(C=N)
1569 w,sh	——	1574 m,br	V(CH=N)
1463 m	1458 s	1486 m	δ(NH$_2$)and δ(NH)
1286 w,	1288 m	1273 s	V(C-N)
1250 w			
——	——	1314 m,sh	ρ$_t$(NH$_2$)
——	——	1196 m	ρ$_w$(NH$_2$)
1096 w 1027 sh	——	1096 m 1026 m	V(N-N)
748 s,	742 m, (Enol)	710 s	δ(N=C-C)
798 w,sh	772 s	750 vs	
875 w	880 m	——	δ(C=O)(ArC-C-C) oop

* s = strong, m = medium, w = weak, vs = very strong, sh = shoulder,
   br = broad, and oop = out of plane.

Continued:

L_b	Isatin	2,4 DNPH	Assignment
3456 w.br (Enol)	3449 m,br (Enol)	——	V(OH) arom
——	——	3090 w, 3105 w	V (CH)
3370 m	——	3325 s	V(—NH$_2$)
3254m (keto)	3194 s (keto)	——	V(NH)
1636m	1728 vs	——	V(C=O)
1595s	1612 s	——	V(C=N)
1456s	1458 s	1464 m	δ(NH$_2$) and δ(NH)
1505 m	——	——	V(N-C=O)
1281 m	1288 m (Enol)	1290 s	V(C-O)
——	——	1358 m	$ρ_t$(NH$_2$)
——	——	1225 m	$ρ_w$(NH$_2$)
1082 m	——	1075m	V(N-N)
795 m	742 m, (Enol)	——	δ(N=C-C)
854 m 974 m	772 s 880 m	——	δ(C=O)
1424m	——	1325 s	V_{sy} (NO$_2$) arom.

* s = strong, m = medium, w = weak, vs = very strong, sh = shoulder, br = broad,and vw= very weak.

^{1}H-NMR spectra of the hydrazone: The ^{1}H-NMR spectra of HL$_a$ and L$_b$ ligands in DMSO-d$_6$ and chemical shifts (ppm) of the ligands were listed in **Table 2**. The chemical shifts of proton signals of the phenolic OH of HL$_a$ ligand at **11.013** ppm and the chemical shifts of the protons N-H groups of isatin moieties for HL$_a$ and L$_b$ were assigned at **10.674** ppm and **10.294** ppm respectively.

The mass spectra of HL$_a$ and L$_b$ ligands, revealed the molecular ion peak at m/e **265** of the HL$_a$ and **327** for the L$_b$ ligands which coincident with the formula weight (265) for the HL$_a$ ligand and (327) for the L$_b$ ligand and supported the identity of the proposed structures. The base peak corresponds to the loss of the (o-ph-CN) at m/e (**118**). A peak corresponding to the loss of CO (ion a) can also be observed at m/e (**237**), whose intensity decreases to **20.61**%. Ion a usually looses HCN, leading, to a fulvene ion (ion b). An arene aziridine is also observed (ion c), which arises from a second loss of CO [17-23]. The ions **b** and **c** are also observed in the gas-phase pyrolysis of isatin [24]. In the mass fragmentation pattern of the L$_b$ ligand, a peak corresponding to the loss of CO (ion a) can also be observed at m/e (**299**),with decreased intensity (**0.94**%). Ion (a) usually looses HCN, leading to ion (b) at m/e (**272**) and ion (c) at m/e (91).

Table 2: ^{1}H-NMR chemical shifts (ppm) for the HL_a and L_b ligands and their assignments.
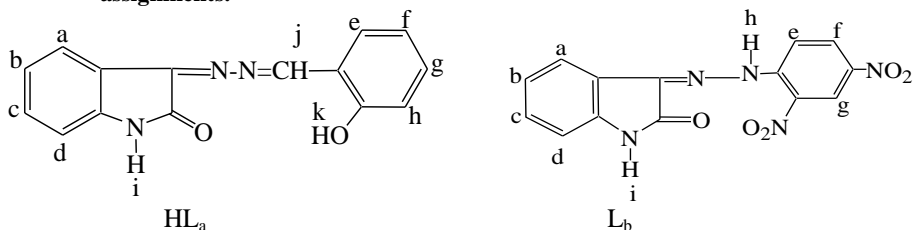
Chemical Shift δ(^{1}H) ppm		Assignment
HL_a	**L_b**	
6.895 – 7.014	5.986 – 6.681	[4H , 4CH] (a –d)
7.387 – 7.527	——	[4H , 4CH] (e – h)
——	7.290 – 7.585	[3H , 3CH](e – g)
10.674	10.294	[S ,H , NH] (i)
——	13.482	[S ,H ,NH] (h)
9.006	——	[S, H, CH] (j)
11.013	——	[S, H, OH] (k)

(1) s = singlet
(2) Chemical shift (ppm)were referenced internally at 25^0C with respect to TMS.
(3) Notations are illustrated in the above structure .
(4) Signals disappeared after the addition D_2O.

Electronic spectral analyses of the HL_a and L_b ligands and their transition metal complexes were shown in **Figures 1 and 2**; recorded in DMF solutions and listed in **Table 3**. The HL_a ligand exhibited five absorption bands at **272.5, 309, 340, 360,** and **420,** also the ligand L_b exhibited at **272.5, 309, 339, 364,** and **425**.5 nm. The first and third bands correspond to $^1L_a \rightarrow ^1A_1$ and $^1L_b \rightarrow ^1A_1$ transitions of the phenyl ring [25]. The band **309** nm for each HL_a and L_b is attributed to the $\pi \rightarrow \pi^*$ transition of the C=O group of the isatin moieties. The bands observed at **365** nm for HL_a and **364** nm for L_b ligands were corresponded to the $\pi \rightarrow \pi^*$ transition of the azomethine group (C=N), and the last band at **420**nm (HL_a) and **425** for (L_b) was corresponded to the **n** $\rightarrow \pi^*$ transition due to the lone pairs electron of the oxygen and nitrogen [26]. However, from the elemental analysis, infrared, mass spectra, ^{1}H-NMR and electronic spectra, it is expect that, the hydrazone, HL_a ligand acts as monobasic ligand with NO_2 tridentate sites, while the L_b ligand acts as monobasic ligand (Enol) with NO_2 tridentate sites.

3.2 HL_a and L_b ligands complexes

IR spectra of the complexes were recorded to confirm their structures. The vibration frequencies and their empirical assignments for HL_a and L_b ligands with their transition metal complexes were listed in **Table 4** and shown in **Figures 3, 4**. The vibrational mode assignments of the metal complexes were supported by comparison with the vibrational frequencies of the free ligand and other related

complexes; such as the metal complexes of 2-hydroxy-1-naphtalideneisatinhydrazone [27]. There are main features in the infrared spectra of the investigated complexes. The first feature is the disappearance of the phenolic (OH) band of HL_a ligand and (OH) of the enolic form of isatin moiety of L_b ligand which were observed at **3498** cm^{-1} and **3456** cm^{-1} respectively, from their complexes which indicate the deprotonation of this group, and the participation of the oxygen atom in the coordination to metal. As the consequent involvement **of** the oxygen atom in the coordination to metal in all the investigated complexes of HL_a and L_b ligands the band assigned to the vibration frequency of both the phenolic and enolic (C-O) groups undergoes positive shifts, confirming that the two ligands HL_a and L_b were bonded to the metallic ions through the phenolic and enolic oxygen atoms respectively. The second feature is the shiftof the bands corresponding to υ(C=N) to lower frequencies ($\Delta\upsilon$ =3-22 cm^{-1}) in the spectra of the HL_a and L_b complexes which indicated the participation of the nitrogen atom of the (C=N) group of azomethine of
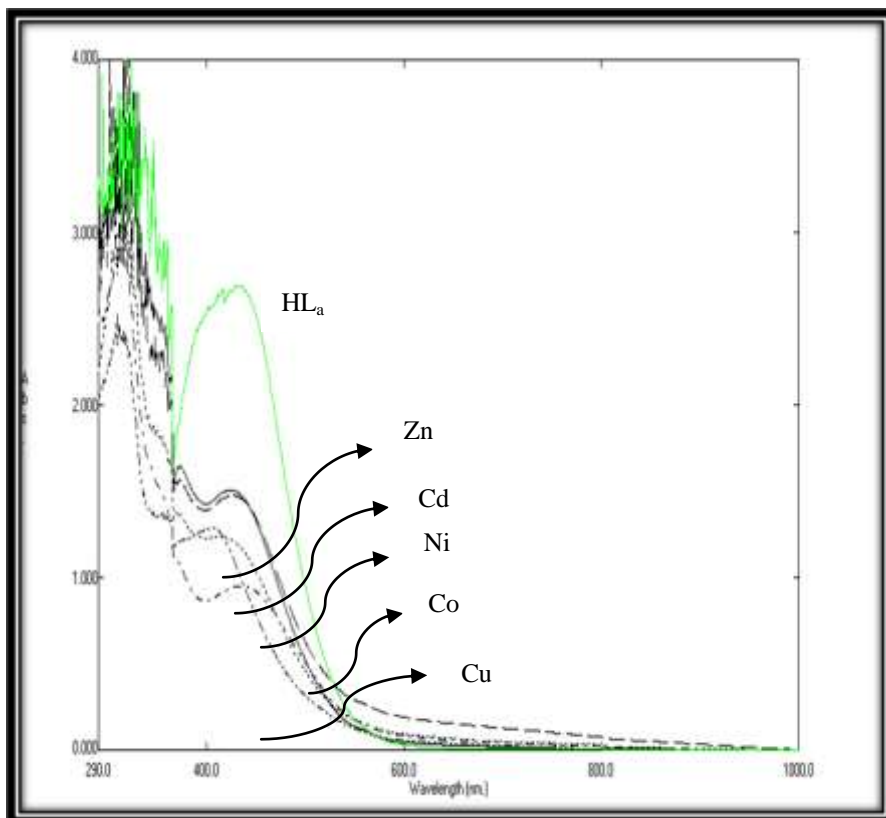

Figure 1: Electronic absorption spectra of the HL_a , ligand and its complexes with Co^{+2},Ni^{+2},Cu^{+2},Zn^{+2},andCd^{+2}ion.
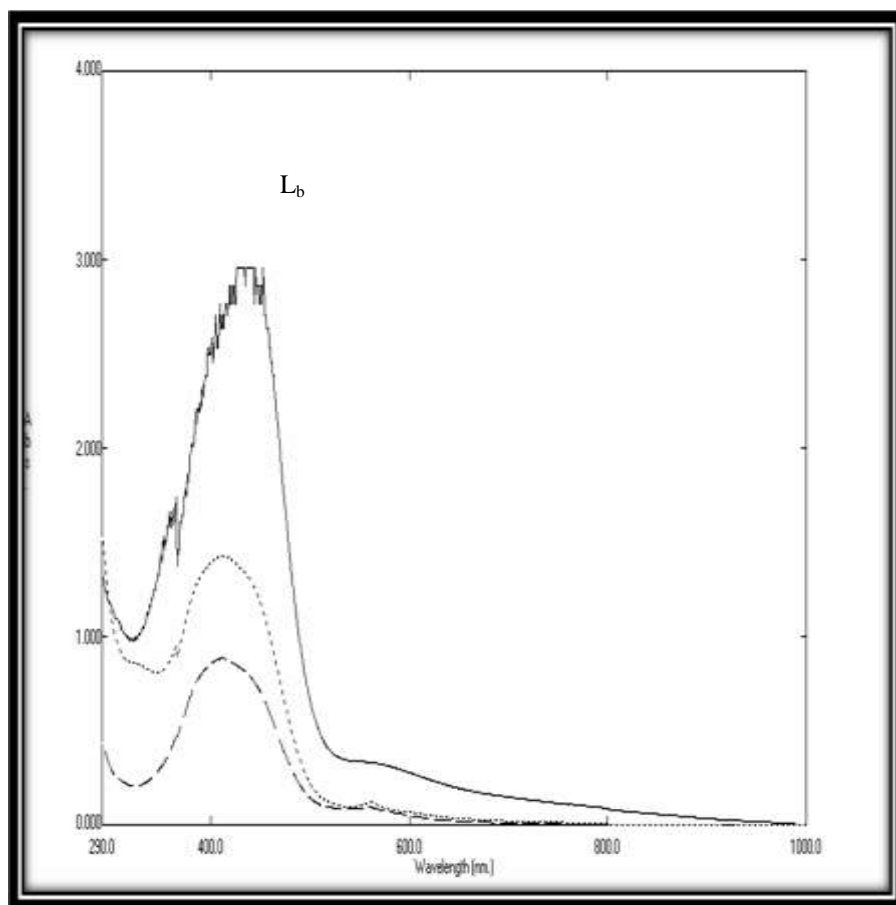
Figure 2: Electronic absorption spectra of the L_b , ligand and its complexes withCu^{+2}and Zn^{+2} ion.

Table 3: *Electronic absorption band (nm) of the HL_a and L_b ligands and their transition metal complexes and their assignment.*

	$^1L_a \rightarrow {}^1A$ phenyl ring	$\pi \rightarrow \pi^*$ C=O	$^1L_b \rightarrow {}^1A$ Phenyl ring	$\pi \rightarrow \pi^*$ C=N	$n \rightarrow \pi^*$	d-d transition	Assignments	Magnetic Moments(nm) μ_{eff}	$^b\Lambda$
HL_a	280.5 (3.2)	309 (3.5)	340 (0.82)	360 (2.9)	420 (2.7)	—	—	—	1.78
L_b	272.5 (1.95)	309 (1.04)	339 (1.17)	364 (1.7)	425.5 (2.96)	—	—	—	2.40
(1)[Co(L_a)(Ac)(C_2H_5OH)(H_2O)]	272 (2.7)	312 (3.1)	336.5 (2.1)	370 (1.4)	412 (1.24)	635.5 (0.07)	$^4T_{2g}(F)\leftarrow{}^4T_{1g}(F)$	1.82	0.99
(2) [Ni(L_a)(Ac)].H_2O	272 (2.6)	307.5 (2.5)	355 (1.4)	362.5 (1.7)	404.5 (1.3)	682.5 (0.03)	$^4A_2 \rightarrow {}^4T_1(p)$	4.45	0.4
(3) [Cu(L_a)(Ac)].CH_3OH	262 (3.9)	307 (3.11)	341.5 (1.7)	465 (1.2)	434.5 (0.95)	646 (0.06)	$^2B_{1g}\rightarrow{}^2A_{1g}$	2.02	15.6
(4) [Zn(L_a)(Ac)].CH_3OH, H_2O	276 (2.8)	302 (3.33)	357.5 (2.4)	373.5 (1.7)	424 (1.5)	—	—	0.00	4.33
(5) [Cd(L_b)(Ac)]	276 (3.2)	307.5 (3.1)	349.5 (2.3)371	371 (1.6)	423 (1.5)	—	—	0.00	4.01
(6) [Cu(L_b)(Ac)]	273 (0.6)	281.5 (0.6)	352 (0.3)	362.5 (0.5)	410 (0.9)	560 (0.09)	$^2B_{1g}\rightarrow{}^2A_{1g}$	1.87	2.73
(7) [Zn(L_b)(Ac)]	276 (1.8)	284 (1.74)	336.5 (0.8)	368 (0.9)	425 (1.4)	—	—	0.00	—

Ligand/complexes	V(OH)	V(C=O)	V(C=N)/V(CH=N)	V(C-O)	V(NH)/δ(NH)	acetate V_as(V_s)	V(M-O)	V(M-N)
HL_a	3498 w,br	1720 vs	1620 vs / 1569 w,sh	1373 w	3279 s / 1461 s	—	—	—
L_b	3456 w,br	1636 s	1595 s	1281 s	3254 w / 1456 s	—	—	—
(1) [Co(L_a)(Ac)(C_2H_5OH)(H_2O)]	—	1725 vs	1616 s / 1533 w,sh	1383 w	3281 m / 1463 m	1548 (1430)	482 w	388 w
(2) [Ni(L_a)(Ac)].H_2O	—	1723 s	1612 vs / 1575 vw	1388 vw	3240 s,br / 1465 s	1538 (1432)	492 w	383 w
(3) [Cu(L_a)(Ac)].CH_3OH	—	1725 s	1609 vs / 1568 w,sh	1373 w,sh	3283 w / 1460 s	1534 (1426)	499 w	384 w
(4) [Zn(L_a)(Ac)].CH_3OH.H_2O	—	1725 vs	1615 s / 1535 w,sh	1376 w,sh	3281 s,br / 1462 m	1549 (1428)	486 w	392 w
(5) [Cd(L_a)(Ac)]	—	1724 s	1619 vs / 1544 w	1373 w,sh	3280 m / 1465 m	1544 (1433)	480 m	391 w
(6) [Cu(L_b)(Ac)]	—	—	1573 s	1337 vs	—	1573 (1417)	493 w	398 w
(7) Zn(L_b)(Ac)]	—	—	1594 s	1337 vs	—	1576 (1428)	491 w	388 w

Table 4: *Vibrational frequencies of HL_a and L_b ligands and their transition metal complexes and their assignments.*
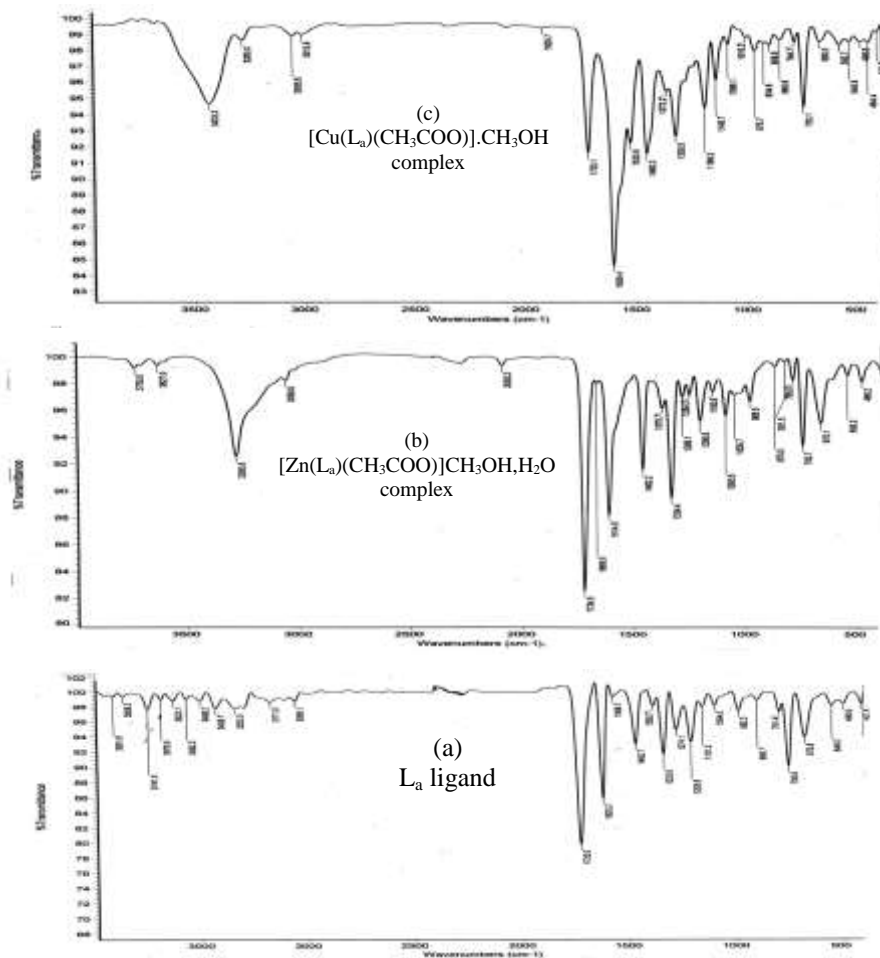
Figure 3. Infrared spectra of the: (a) HL$_a$ ligand,

(b) [Zn(L$_a$)(CH$_3$COO)]CH$_3$OH,
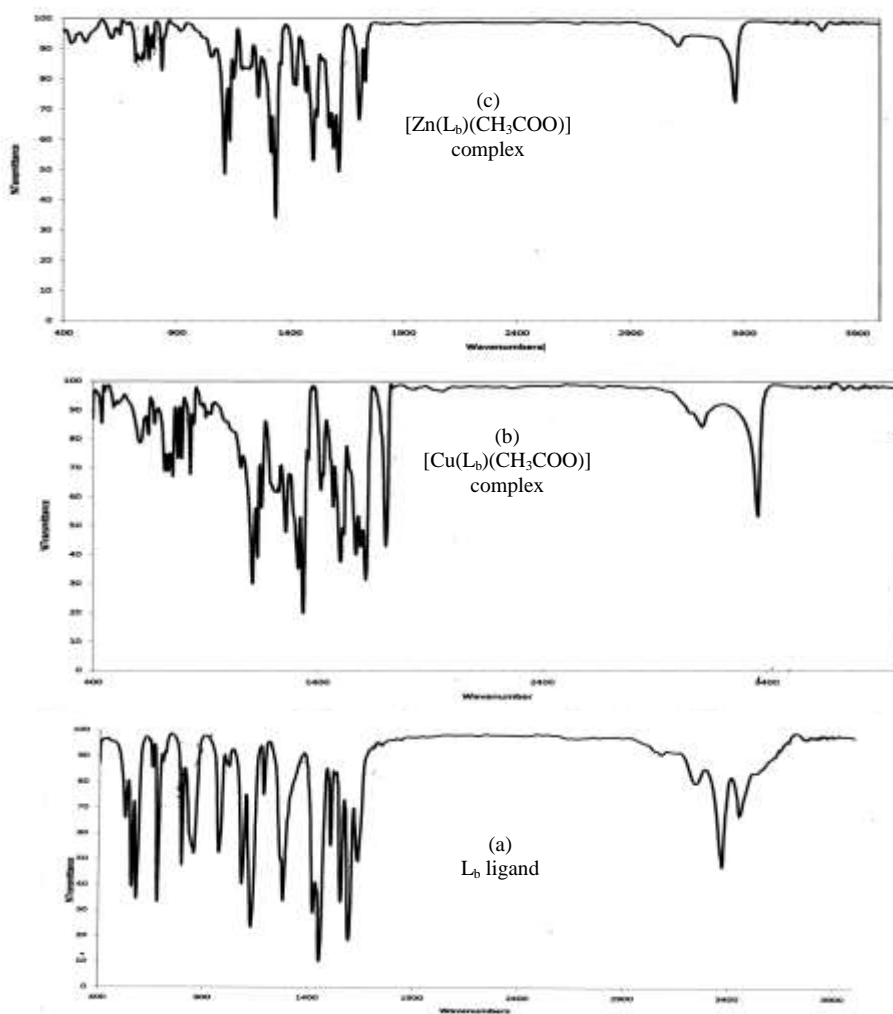
(c) [Cu(La)(CH$_3$COO)].CH$_3$OH complexes.

**Figure 4. Infrared spectra of the :(a) L_b ligand, (b)[Cu(L_b)(CH_3COO)]
(c)[Zn(L_b)(CH_3COO)]complexes.**

the Isatin moiety in the coordination. Unfortunately the participation of the oxygen of keto form of HL_a ligand in the coordination with metal ions did not identify because of the appearance of $\upsilon(C=O)$ of the coordinated acetate group at the same region. The participation of the acetate groups in coordination with metal ions in all the complexes of HL_a and L_b ligands, as a monodentate acetate group, show two bands at (**1534–1549** cm^{-1}) and (**1426 – 1433** cm^{-1}) ranges for HL_a complexes and (**1573, 1576** cm^{-1}) and (**1417, 1428** cm^{-1}) for Cu(II) and Zn(II) complexes of L_b which were assigned to υ_{as} acetate and υ_s acetate vibrations respectively [28].

The electronic spectrum of the Cu(II) complexes (HL$_a$, L$_b$) exhibited two broad bands for each at **19350** and **13760** cm^{-1} for copper complex of HL$_a$ and **22321** and **13860** cm^{-1} for L$_b$ copper complex. They were assigned to $^2\mathbf{B_{1g}} \rightarrow {}^2\mathbf{A_{1g}}$ and $^2\mathbf{B_{1g}} \rightarrow {}^2\mathbf{E_g}$, respectively [29]. These transitions, as well as the measured magnetic moments (μ_{eff}) **2.02** and **1.87** BM for HL$_a$ and L$_b$ copper complexes respectively, suggest a square–planar geometrical structure for (3) and (6) complexes. The molar conductance of Cu(II) complexes (3) and (6) were **15.6** and **2.73** ohm^{-1}cm^{2}mol^{-1} respectively, which indicate the neutral nature of the complexes.

X-Band ESR spectra of Cu(II) complexes(3) and (6), were recorded in the solid state at 25^{0}C and shown in **Figures 5 and 6**. The spectra showed two bands with g = **2.0523** and g = 2.207 for complex (3) and g = **1.998** and g = **2.159** for complex (6), which attributed to large component of low symmetry in the ligand field. The shape of the spectra was consistent with the square planar geometrical structure around the Cu(II) environment in the complexes [30].
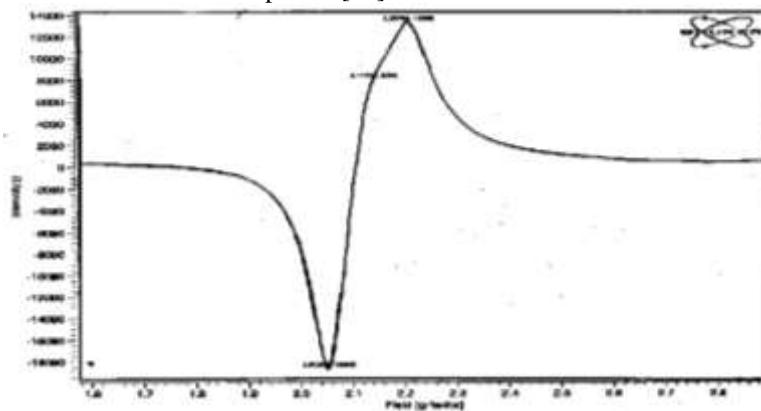

Figure 5: ESR spectrum of the: [Cu(L$_a$)(CH$_3$COO)].CH$_3$OH complex
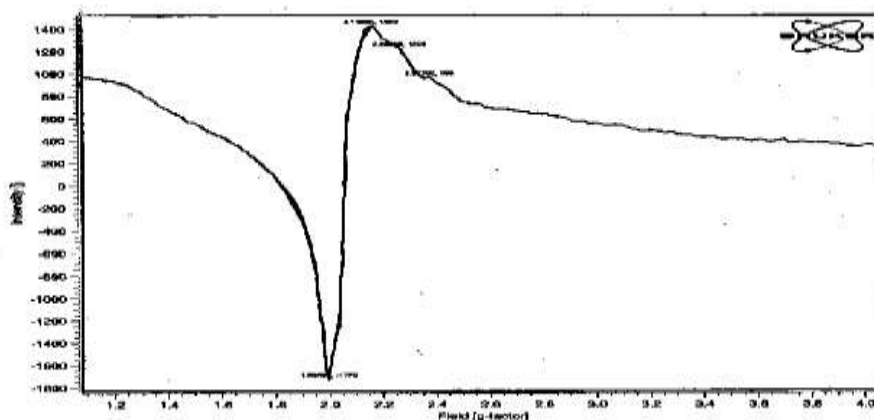
Figure 6: ESR spectrum of the: [Cu(L$_b$) (CH$_3$COO)] complex

The mass spectrum of [Cu(La)(CH$_3$COO)].CH$_3$OH complex (3), revealed the molecular ion peak at m/e 418.32 which coincident with the formula weigh [418.54] and support the identity of the structure.

Thermal gravimetric analysis for [Cu(La)(CH$_3$COO)].CH$_3$OH complex (3), was obtained to give information concerning the thermal stability of the complex to decide whether the Methanol molecule was in the inner or outer coordination sphere of the central metal ion. From TGA data methanol molecule was lost within the temperature range 25-100 ^{0}C (weight loss, Found /calc., 7.65/7.64) which indicate that methanol molecule was uncoordinated. The thermal gravimetric analysis of the [Cu(La)(CH$_3$COO)].

The electronic spectrum of the Zn(II) complexes and Cd(II) complex exhibited shift to lower and higher frequencies, for the n→π* and π→π* transitions, compared to those of the ligands as shown in Table 3.4, indicating the coordination of the ligands HLa and Lb to the Zn(II) and Cd(II) ions. The Zn(II) and Cd(II) complexes (4), (7), and (5) are diamagnetic and there is no either electronic d-d transition or significant magnetic moment. The absorption bands observed at 29481cm^{-1}, 29412cm^{-1}, and 29550cm^{-1} for Zn(II) and Cd(II) complexes (4), (7) and (5) respectively were assigned as charge transfer transitions [31, 32]. On the base of the spectra and the magnetic moments measurements of the complexes (4), (7) and (5), a tetrahedral geometrical structure could be suggested for the investigated complexes of Zn(II) and Cd(II) ions with HLa and Lb ligands.

Molar conductance values of Zn(II) and Cd(II) complexes in DMF solution were 4.33, 19.79 and 4.01 ohm^{-1}.cm^2.mol^{-1}, for the complexes (4),(5) and (7) respectively, which indicated the non electrolytic nature of the complexes .

Thermal gravimetric analysis for the [Zn(La)(CH$_3$COO)]. CH$_3$OH, H$_2$O complex (4) was obtained to give information concerning the thermal gravimetric stability of the complex and to decide whether the methanol and water molecules were in the inner or outer coordination sphere of the central ion. From the TGA data methanol and water molecules were lost at the temperature range 25-170^{0}C (weigh loss; Found /Calc; 12.44/11.48) which indicate that methanol and water molecules were uncoordinated.

The electronic spectrum of Ni(II) complex (2) of HLa ligand showed several bands. Generally, three spin allowed transition are expected, because of the splitting of the free ion, ground ^{3}F term and the presence of the ^{3}p term. Tanab-sugano diagram can be used to interpret the spectra, usually, the spectra of tetrahedral Ni(II) complexes consist of bands which are accordingly assigned as charge transfer like that observed at 30902 cm^{-1}, 18315 cm^{-1} (^{4}A$_2$ → ^{4}T$_1$(p)) transition, 40650 cm^{-1} and 34482 cm^{-1} which were found in the spectrum of the HLa ligand of the ππ* transitions but they were shifted to lower and higher frequencies, confirming the coordination of the ligand to the metallic ion.

The measured value of the magnetic moment μ$_{eff}$, was 4.45 BM, which indicate the tetrahedral geometrical structure of the complex (2). The molar conductance of Ni(II) complex (2) was measured in DMF solvent and the measured value was

0.4 $ohm^{-1}cm^2mol^{-1}$ which indicate the non electrolytic nature of the complex (2). Thermal gravimetric diagram for the $[Ni(La)(CH_3COO)].H_2O$ complex (2) was measured to obtaine information concerning the thermal gravimetric stability of the complex and decide whether the water molecule was in the inner or outer coordination sphere of the central ion. From the TGA data water molecule was lost with the temperature rang $25-100^0C$ (weigh loss; Found/calc.; 4.3/4.5 which indicated that water molecule was uncoordinated.

The electronic spectrum of the Co(II) complex of HLa ligand (1) is expected for the octahedral structure. According to Tanade – sugano diagram [33] the possible transitions of the Co(II) octahedral complex can be interpreted. Three bands are usually associated with the spectrum of the Co(II) octahedral complex. The first band, which is assigned to $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ transition, which occurs in the near infrared region, was not observed because it is out of the range of the used instrument. The second band was not observed which is due to $^4A_{2g}(F) \leftarrow {}^4T^{1g}(F)$ transition. The third band observed at 635 nm is due to $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ transition. This transition may be overlapped by the ligand n→π* transition which was observed at 420 nm for HLa ligand.

The magnetic moment measured, 1.82 B.M. indicated the octahedral geometrical structure for the complex (1) [34]. The molar conductance of Co(II) complex (1) was measured in DMF solvent and the measured value was 0.99 $ohm^{-1}cm^2mol^{-1}$ which indicate the non electrolytic nature of the complex (1).

Thermal analysis diagrams of the [Co(La)(Ac)] complex (1) was measured to obtain information concerning the thermal gravimetric stability of the complex and to decide whether the ethanol and water molecules were in the inner or outer coordination sphere of the central ion. From TGA and DTA one endothermic with loss in weight, due to the elimination of water molecule with the temperature range over 190 ^0C to 210 ^0C (weight loss; Found/calc.; 4.01/4.03 which indicated that water molecule was coordinated to the central metal ion Co(II). Also, the ethanol molecule was lost after awhile to at 255 ^0C (weight loss; Found/calc.; 14.45/14.35 %).

From the results and Discussion given above, one can expect the metal chelates of the ligands HLa and Lb would acquire structures.

The Biological activity

The effect of the HLa ligand on germination of the types of bacteria was studied against two types of bacteria: Escherichia Coli (g –ve) and staphylococcus aureas (g +ve). The effect of the ligand on the growth of E.coli (g -ve) there was no inhibition zone formed in the petridish which was contained the media with bacteria but the effect on staphylococcus aureas (gram +ve) there was presence of inhibition zone surrounded the ligand HLa. The resulted were presented here indicated that, generally the ligand HLa inhabited and killed the cells of bacteria (staphylococcus aureas, g +ve) may be by a decline in the mitotic division and destroy all bacteria, and stopped the growth, finally killed all the bacteria (staphylococcus aureas, g +ve) with used HLa ligand.

Conclusion

The hydrazone, HLa and Lb, ligands and their corresponding transition metal complexes were prepared by the condensation of isatin with salicylaldehyde hydrazone or 2,4-dinitrophenyl hydrazine, respectively, in the molar ratio 1:1. These compounds were characterized by elemental analyses, IR, 1H-NMR, Electronic and Mass spectra. From the obtained data, the physical, analytical data and the structures were proposed, which are were octahedral (Co(II)-HLa), tetrahedral for Ni(II), Zn(II), Cd(II)-HLa complexes and square planar for (Cu(II)-HLa, Lb Zn(II)-Lb complexes. We can used the ligand HLa as antibacterial for type of bacteria (staphylococcus aureas, g +ve).

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