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# Synthesis, characterization and biological activity of bis(phenylimine) Schiff base ligands and their metal complexes

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#### Abstract

Metal complexes derived from 2,6-pyridinedicarboxaldehydebis(*p*-hydroxyphenylimine); L<sup>1</sup>, 2,6-pyridinedicarboxaldehydebis (*o*-hydroxyphenylimine); L<sup>2</sup>, are reported and characterized based on elemental analyses, IR, solid reflectance, magnetic moment, molar conductance and thermal analysis (TGA). The complexes are found to have the formulae  $[MX_2(L^1 \text{ or } L^2)] \cdot nH_2O$ , where M = Fe(II), Co(II), Ni(II), Cu(II) and Zn(II), X = CI in case of Fe(II), Co(II), Ni(II), Cu(II) complexes and Br in case of Zn(II) complexes and n = 0-2.5. The molar conductance data reveal that the chelates are non-electrolytes. IR spectra show that the Schiff bases are coordinated to the metal ions in a terdentate manner with NNN donor sites of the pyridine-*N* and two azomethine-*N*. From the magnetic and solid reflectance spectra, it is found that the geometrical structure of these complexes are trigonal bipyramidal (in case of Co(II), Ni(II), Cu(II) and Zn(II) complexes) and octahedral (in case of Fe(II) complexes). The thermal behaviour of these chelates shows that the hydrated complexes losses water molecules of hydration in the first step followed immediately by decomposition of the coordinated water, anions and ligands (L<sup>1</sup> and L<sup>2</sup>) in the subsequent steps. The activation thermodynamic parameters, such as,  $E^*$ ,  $\Delta H^*$ ,  $\Delta S^*$  and  $\Delta G^*$  are calculated from the TG curves using Coats–Redfern method. The synthesized ligands, in comparison to their metal complexes also were screened for their antibacterial activity against bacterial species, *Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus* and Fungi (*Candida*). The activity data show that the metal complexes to be more potent/antibacterial than the parent organic ligands against one or more bacterial species.

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# 1. Introduction

The preparation of a new ligand was a perhaps the most important step in the development of metal complexes which exhibit unique properties and novel reactivity. Since the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be the factor for different studies [1,2]. Schiff bases were important class of ligands, such ligands and their metal complexes had a variety of applications including biological, clinical, analytical and industrial in addition to their important roles in catalysis and organic synthesis [3–9]. A tridentate Schiff base (Structure 1, R = p-phenol) had been designed to function as molecular turn [10] by incorporating reactive *p*-phenolic groups in a bis(phenylimine) ligand.

Schiff base ligands of general structure 1 had a rich history, beginning with the preparation of the first examples, the pyridinal hydrazones, by Stoufer and Busch [11], who were motivated by the then current interest in the  $\pi$ -back-bonding by unsaturated nitrogen donors. In early work closely related to the system of interest here, Lions and Martin [12] synthesized Schiff base ligands from 2,6-pyridinedicarboxaldehyde (PDC) with aniline and benzylamine and noted that the free ligands were crystalline materials. Therefore, extensive studies ensued in which this same pair of Schiff base linkages was incorporated in many different kinds of polydentate ligands, including various macrocyclic ligands [13–15]. Pursuing the analogy to the Sauvage template, *p*-aminophenol was used

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Plate 1.

as the amine in the straightforward Schiff base condensation reaction with PDC to give the diphenolic ligand. Previous studies on ligands and metal complexes derived from the Schiff bases of o- and p-aminophenol are few. In one case, the reaction between PDC and o-, m- and p-aminophenols in the presence of cadmium ions was used to differentiate aminophenol isomers [16] and p-aminophenol had appeared in some recent publications as a Schiff base precursor. Two of these studies examined hydrogen-bonding interactions of the phenolic hydrogen [17,18] while another involved estrification of the phenolic oxygen of the free Schiff base ligand to construct potential metallomesogen components [19]. Although the preparation and X-ray crystal structure of L<sup>1</sup> and its Co(II), Fe(II), Ni(II) and Zn(II) complexes had been reported by Vance et al. [20], no studies concerning their molar conductance, thermal behaviour and antibacterial activities are not reported.

 $L^2$  is a novel ligand and no studies concerning its metal complexes had been reported. On screening literature, no thermal studies concerning complexes of bis(phenylimine) Schiff base ligands ( $L^1$  and  $L^2$ ) had been reported. Recently, the mixed ligand complexes of  $L^1$  and  $L^2$  and 2aminopyridine with some transition metals (such as Co(II), Ni(II), Cu(II) and Zn(II)) were reported by Gehad et. al. [21]. The structures of these ligands are shown in Fig. 1.

Therefore, in continuation to our interest in Schiff base ligands and their metal chelates [21–23], this work deals with the synthesis and characterization of Schiff base ligands;  $L^1$  and  $L^2$ , and their complexes. The coordination behaviour of  $L^1$ and  $L^2$  ligands towards transition metal ions (Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)) is investigated via the IR, molar conductance, magnetic moment, solid reflectance and thermal analysis. The thermal decomposition of the complexes is also used to infer the structure and the different thermodynamic activation parameters are calculated. The biological activity of these Schiff bases and their metal chelates are reported.



Fig. 1. Structures of L<sup>1</sup> and L<sup>2</sup> ligands.

# 2. Experimental

#### 2.1. Materials and methods

All chemicals used were of the analytical reagent grade. They included FeCl<sub>2</sub>·2H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, ZnBr2 and CuCl2·2H2O (BDH). o- and p-Aminophenols (Sigma) were used as received. The elemental analyses (C, H and N) were made at the Microanalytical Center at Cairo University. IR spectra were recorded on a Perkin-Elmer FT-IR type 1650 spectrophotometer. The solid reflectance spectra were measured on a Shimadzu 3101 PC spectrophotometer. The molar magnetic susceptibilities were measured on powdered samples using the Faraday method. The molar conductance measurements were carried out using a Sybron-Barnstead conductometer. A Shimadzu TGA-50H thermal analyzer was used to record simultaneously TG and DTG curves. The experiments were carried out in dynamic nitrogen atmosphere ( $20 \text{ ml min}^{-1}$ ) with a heating rate of  $10 \degree \text{C}$  $min^{-1}$  in the temperature range 20–1000 °C using platinum crucibles. The sample sizes ranged in mass from 2.21 to 11.92 mg. Highly sintered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference.  ${}^{13}C{}^{1}H$  NMR spectra were recorded using Brucker ARX-300 spectrometer using DMSO-d<sub>6</sub> as a solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane, and all coupling constants are reported in hertz. Metal contents were determined by titration against standard EDTA after complete decomposition of the complexes with aqua regia in kjeldahl flask several times.

# 2.2. Synthesis of $L^1$ and $L^2$ ligands

2,6-Pyridinedicarboxaldehyde and 2,6-pyridinedicarboxaldehydebis(p-hydroxyphenyl-imine)( $L^1$ ) were prepared as previously reported by the modefied method of Vance et al. [20].

# 2.2.1. Synthesis of 2,6-pyridinedicarboxaldehyde $bis(o-hydroxyphenylimine), L^2$

2,6-Pyridinedicarboxaldehyde (1.00 g, 7.40 mmol) and 2aminophenol (1.62 g, 14.80 mmol) were stirred in 20 mL of absolute ethanol until a yellow precipitate appeared (within 5 min). Stirring was continued for an additional 30 min and then the yellow powder was collected by vacuum filtration and dried overnight in a vacuum desiccator. Yield 85%. Analyses: calculated: C, 71.92; H, 4.73; N, 13.25. Found: C, 72.05; H, 4.55; N, 13.00. <sup>1</sup>H NMR (DMSO $d_6$ , 25 °C):  $\delta$  8.92 (s, OH, 2H), 8.65 (s, CH, 2H), 8.30 (d, pyH, 2H), 7.98 (t, pyH, H), 7.45–6.97 ppm (m, phH, 8H). <sup>13</sup>C NMR (DMSO- $d_6$ , 25 °C):  $\delta$  163 (s, C<sub>4</sub>, azomethine (CH=N)), 156.35 (s, C<sub>1</sub>, py), 137.57 (s, C<sub>3</sub>, py), 122.99 (s, C<sub>2</sub>, py), 152.82 (s, C<sub>6</sub>, C–O), 138.40, 130.29, 120.34, 116.21 and 115.26 ppm for the <sup>13</sup>C resonance of aromatic groups.

#### 2.3. Synthesis of the complexes

The complexes of Schiff base ligands (L<sup>1</sup> and L<sup>2</sup>) were prepared by the addition of hot ethanolic solution (60 °C) of the appropriate metal chloride or bromide (1 mmol, 0.163 g FeCl<sub>2</sub>·2H<sub>2</sub>O, 0.237 g CoCl<sub>2</sub>·6H<sub>2</sub>O, 0.237 g NiCl<sub>2</sub>·6H<sub>2</sub>O, 0.1705 g CuCl<sub>2</sub>·2H<sub>2</sub>O and 0.225 g ZnBr<sub>2</sub>) to the hot ethanolic solution (60 °C) of the Schiff bases (0.317 g, 1 mmol of L<sup>1</sup> and L<sup>2</sup>). The resulting mixtures were stirred under reflux for 2 h, where upon the complexes were precipitated. They were collected by filtration, washed with 1:1 ethanol: water mixture, then diethylether and dried under vacuum over CaCl<sub>2</sub>.

#### 2.4. Biological activity

0.5 ml spore suspension  $(10^{-6}-10^{-7} \text{ spore/ml})$  of each of the investigated organisms was added to a sterile agar medium just before solidification, then poured into stirile petri dishes (9 cm in diameter) and left to solidify. Using sterile cork borer (6 mm in diameter), three holes (wells) were made in each dish, then 0.1 ml of the tested compounds dissolved in DMF (100 µg/ml) were poured into these holes. Finally, the dishes were incubated at 37 °C for 48 h where clear or inhibition zones were detected around each hole. 0.1 ml DMF alone was used as a control under the same conditions for each organism and by subtracting the diameter of inhibition zone resulting with DMF from that obtained in each case, both antibacterial activities can be calculated as a mean of three replicates.

# 3. Results and discussion

A ligands having phenolic functional groups can be prepared by the general reaction in Fig. 2, diimine molecule, where R is a potentially reactive functional group.

The planarity of  $L^1$  and  $L^2$  ligands can be attributed to the absence of alkyl groups at the imine carbon [20]. The ligands are coordinated meridionaly to produce the desired orientation of the phenolic oxygens across and away from the center of the complex. The phenyl rings of  $L^1$  and  $L^2$  ligands in the complexes are twisted out of the plane of the pyridine rings as was observed for other similar complexes [14,24].  $L^1$  and  $L^2$  Schiff base ligands are of significant interest from the point of view that they act as a pincer ligands, often found as a merdional ligand (i.e. the three nitrogen atoms possess will be approximately coplanar in metal coordination sphere) and exhibited a great variety of coordination modes with different coordinating power and these may give rise to varied bonding and different stereochemical patterns in their coordination complexes as a result for competition between the phenolic and azomethine nitrogen groups as a coordination sites [25]. The compounds containing a pyridinium moiety attached to a heterocyclic systems are important in natural product chemistry and in organic synthesis [26]. This would us to obtain some new heterocyclic compounds with expected wide spectrum of potential applications that were extensively required for medicinal chemistry program.

The general reaction for the preparation of the complexes of  $L^1$  and  $L^2$  is given below:

$$MX_2 \cdot nH_2O + L^1 \text{ or } L^2 \rightarrow [MX_2(L^1 \text{ or } L^2)] \cdot nH_2O$$

where M = Fe(II) (X = Cl), Co(II) (X = Cl), Ni(II) (X = Cl), Cu(II) (X = Cl), Zn(II) (X = Br), n = 0-2.5).

The results of the elemental analyses of the chelates, which are recorded in Table 1, are in good agreement with those required by the proposed formulae. In all cases, 1:1 (M: L<sup>1</sup> or L<sup>2</sup>) solid complexes are isolated and found to have the general formulae  $[MX_2(L^1 \text{ or } L^2)] \cdot nH_2O$ , where M = Fe(II) (X = Cl), Co(II) (X = Cl), Ni(II) (X = Cl), Cu(II) (X = Cl) and Zn(II) (X = Br), n = 0-2.5.

## 3.1. IR spectra and mode of bonding

In the absence of a powerful technique such as X-ray crystallography, IR spectra have proven to be the most suitable technique to give enough information to elucidate the way of bonding of the ligands to the metal ions. The main stretching frequencies of the IR spectra of the ligands ( $L^1$  and  $L^2$ ) and their complexes are listed in Table 2.

The IR spectra of L<sup>1</sup> and L<sup>2</sup> and their chelates are found to be very similar to each other. Hence significant frequencies are selected by comparing the IR spectra of the ligands with those of their metal chelates. The strong bands located at  $1580 \text{ cm}^{-1}$  are assigned to the  $\nu$ (C=N) stretching vibrations of pyridyl nitrogen of the L<sup>1</sup> and L<sup>2</sup> ligands. Coordination of pyridyl nitrogen is indicted by a 20–42 cm<sup>-1</sup> shift to lower wavenumber, 9–11 cm<sup>-1</sup> shift to a higher wavenumber in all the chelates [27]. On the other hand, from the spectroscopic behaviour of a simple metallic complexes of pyridine, it is known that after complexation the vibrations in the highfrequency region are not appreciably shifted, whereas the ring deformation found at 604 and 405 cm<sup>-1</sup> in the free pyridine are shifted to higher frequencies [28]. Therefore, these



Fig. 2. Preparation of L<sup>1</sup> and L<sup>2</sup> Schiff base ligands.

Analytical and physical data of $L^1$ , $L^2$ and their	r complexes							
Compound	Color (% yield)	m.p. (°C)	Found (calcd.) %	-0			$\mu_{\rm eff}$ (B.M.)	$A_{ m m} \left( \Omega^2  { m mol}^{-1}  { m cm}^{-1}  ight)$
			U	Н	Z	M		
L <sup>1</sup> , C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub>	Yellow (83)	$150 \pm 2$	71.65 (71.92)	5.02 (4.73)	13.10 (13.25)	I	I	1
[Fe(L <sup>1</sup> )Cl <sub>2</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O, C <sub>19</sub> H <sub>19</sub> Cl <sub>2</sub> FeN <sub>3</sub> O <sub>4</sub>	Yellow (68)	> 300	47.44 (47.50)	4.10(3.75)	8.49 (8.75)	11.52 (11.67)	5.53	12.35
$[Co(L^1)Cl_2], C_{19}H_{15}Cl_2CoN_3O_2$	Reddish brown (73)	>300	50.81 (51.01)	3.69(3.36)	8.98 (9.40)	11.88 (12.22)	5.06	10.56
[Ni(L <sup>1</sup> )Cl <sub>2</sub> ]·2H <sub>2</sub> O, C <sub>19</sub> H <sub>19</sub> Cl <sub>2</sub> NiN <sub>3</sub> O <sub>4</sub>	Red (72)	>300	47.42 (47.20)	4.22 (3.93)	8.48 (8.70)	12.55 (12.22)	3.25	15.50
$[Cu(L^1)Cl_2] \cdot H_2O, C_{19}H_{17}Cl_2CuN_3O_3$	Reddish brown (81)	> 300	48.12 (48.56)	3.90(4.05)	8.82 (8.95)	13.62 (13.53)	2.07	17.20
$[Zn(L^1)Br_2], C_{19}H_{15}Br_2N_3O_2Zn$	Yellowish brown (78)	>300	41.88 (42.07)	3.09 (2.77)	7.57 (7.75)	11.99 (11722)	Diam.	13.45
$L^2$ , $C_{19}H_{15}N_3O_2$	Yellow (85)	$160 \pm 2$	72.05 (71.92)	4.55 (4.73)	13.00 (13.25)	I	I	I
$[Fe(L^2)Cl_2(H_2O)] \cdot H_2O, C_{19}H_{19}Cl_2FeN_3O_4$	Yellow (65)	>300	47.79 (47.50)	3.47 (3.75)	8.56 (8.75)	11.78 (11.67)	5.68	23.50
[Co(L <sup>2</sup> )Cl <sub>2</sub> ].2.5H <sub>2</sub> O, C <sub>19</sub> H <sub>20</sub> Cl <sub>2</sub> CoN <sub>3</sub> O <sub>4.5</sub>	Brown (69)	>300	46.64 (46.34)	4.19 (4.07)	8.34 (8.54)	12.15 (11.99)	4.98	14.95
$[Ni(L^2)Cl_2] \cdot H_2O, C_{19}H_{17}Cl_2NiN_3O_3$	Brown (74)	>300	49.37 (49.03)	3.85 (3.66)	8.87 (9.03)	12.32 (12.69)	3.32	15.25
$[Cu(L^2)Cl_2]\cdot 2H_2O, C_{19}H_{19}Cl_2CuN_3O_4$	Brown (73)	>300	45.22 (45.10)	3.78 (3.90)	8.30 (8.62)	13.52 (13.03)	2.16	14.20
$[Zn(L^2)Br_2], C_{19}H_{15}Br_2N_3O_2Zn$	Yellowish brown (70)	>300	41.76 (42.07)	3.15 (2.77)	7.51 (7.75)	11.63 (11.99)	Diam	19.65

two shifts may be very useful in establishing the participation of pyridine in complex formation. In the present case, the in-plane ring deformation bands are found at 638 cm<sup>-1</sup> (for L<sup>1</sup>) and 641 cm<sup>-1</sup> (for L<sup>2</sup>). After complexation, these bands are shifted to lower (11–38 cm<sup>-1</sup>) or higher (11–55 cm<sup>-1</sup>) wavenumbers, indicating coordination via the pyridine nitrogen, as previously reported for pyridine complexes [29]. Detecting the shift of the out-of-plane  $\rho(py)$  at 405 cm<sup>-1</sup> is difficult because the spectra are rich for the complexes.

The strong and sharp bands at 1618 and  $1625 \text{ cm}^{-1}$  are assigned to the  $\nu(\text{C=N})$  stretching mode of the azomethine group for L<sup>1</sup> and L<sup>2</sup>, respectively. These bands are shifted to  $1583-1652 \text{ cm}^{-1}$  in all complexes. This shift support the participation of the azomethine group of these ligands in binding to the metal ions [23,30].

The other series of weak bands between 3100 and  $2800 \text{ cm}^{-1}$  are related to (C–H) modes of vibrations. Also, some weak bands are located between 2000 and 1750 cm<sup>-1</sup> can be assigned to overtones of the aromatic rings.

The L<sup>1</sup> and L<sup>2</sup> ligands also display bands at 3061–3092 and 1344–1337 cm<sup>-1</sup> which are assigned to  $\nu$ (OH) and  $\nu$ (C–O) stretching vibrations of the phenolic-*OH*, respectively. These bands are strongly affected by chelation although the phenolic-*OH* of the Schiff bases (L<sup>1</sup> and L<sup>2</sup>) are not involved in chelate formation. The shift to higher or lower wavenumbers can be attributed to important hydrogen bonding effects [20].

Most of the band shifts observed at the wave number region  $1150-994 \text{ cm}^{-1}$  are in agreement with the structural changes observed in the molecular carbon skeleton after complexation, which cause some important changes in (C–C) bond lengths. The bands appeared in the wave number range 419-484 and  $500-522 \text{ cm}^{-1}$  [23,29] can be attributed to  $\nu$ (M-N) of the pyridine and azomethine nitrogen atoms, respectively [31].

# 3.2. Molar conductivity

The molar conductivity  $(\Lambda_m)$  of  $10^{-3}$  M solutions of the complexes in DMF at 25 °C is listed in Table 1. The complexes are found to be non electrolyte in DMF solution, implying the coordination of halide anions. Elemental analyses identified the complexes as  $[MX_2(L^1 \text{ or } L^2)] \cdot nH_2O$ .

#### 3.3. Magnetic susceptibility and electronic spectra

As the result of failer to obtain a single crystal for X-ray analyses to confirm the octahedral and trigonal bipyramidal structures for these complexes, solid reflectance spectra and magnetic moment measurements are used for this purpose.

The diffuse reflectance spectra of the Fe(II) complexes give two bands at 12,685–12,820 cm<sup>-1</sup> and 17,543–17,605 cm<sup>-1</sup> which are assigned to  ${}^{5}T_{2g} \rightarrow {}^{5}E_{g}$  transition, suggesting an octahedral geometry around Fe(II) ion [32]. The band at 22,321–24,096 cm<sup>-1</sup> refers to the charge transfer band (L  $\rightarrow$  MCT). The observed magnetic moments

Table 2	
Characteristic IR bands $(4000-400 \text{ cm}^{-1})$ of L <sup>1</sup> and L <sup>2</sup> and their c	omplexes

Compound	$\nu$ (CH=N)	ν(C=N)	$\rho(py)$	ν(OH)	v(C-O)	ν( <b>M</b> - <b>N</b> )	ν( <b>M</b> — <b>N</b> )
L1	1618sh	1580sh	638s	3061br	1344s	_	_
$[Fe(L^1)Cl_2(H_2O)]\cdot H_2O$	1583sh	1538sh	617m	3055br	1366m	522m	479s
$[Co(L^1)Cl_2]$	1592sh	1544sh	600m	3068br	1365m	500m	424m
$[Ni(L^1)Cl_2]\cdot 2H_2O$	1585sh	1542sh	600sh	2992brs	1359m	500m	419m
$[Cu(L^1)Cl_2]\cdot H_2O$	1591sh	1542sh	620m	3073br	1367m	501m	436m
$[Zn(L^1)Br_2]$	1592sh	1548sh	649m	3050br	1370m	500m	422s
L <sup>2</sup>	1625sh	1580sh	641s	3092br	1337s	_	_
$[Fe(L^2)Cl_2(H_2O)]\cdot H_2O$	1652s	1591sh	664m	3166br	1349m	505m	440m
$[Co(L^2)Cl_2]\cdot 2.5H_2O$	1613m	1589sh	652m	3026br	1383m	506m	470s
$[Ni(L^2)Cl_2] \cdot H_2O$	1642s	1593sh	596m	3140br	1375s	520m	484s
$[Cu(L^2)Cl_2]\cdot 2H_2O$	1596sh	1560sh	660m	3249br	1349m	505s	440m
$[Zn(L^2)Br_2]$	1590m	1556m	630m	3220br	1383m	505s	450s

Sh: sharp, s: small, w: weak and br: broad.

Table 3 Thermoanalytical results (TGA) of  $L^1$  and  $L^2$ -metal complexes

Complex	TG range (°C)	DTG (°C)	Number of steps	Mass loss	Total mass loss found (calcd. %)	Assignment	Metallic residue
$\overline{[Fe(L^1)Cl_2(H_2O)]} \cdot H_2O$	30–110 110–800	64 450	1 1	81.23 (80.83)	3.95 (3.75) 85.18 (84.58)	Loss of $H_2O$ Loss of $H_2O$ , 2HCl and $L^1$	FeO
$[Ni(L^1)Cl_2]{\cdot}2H_2O$	40–140 140–800	78 230	1 1	65.79 (65.63)	7.15 (7.45) 73.24 (73.08)	Loss of $2H_2O$ Loss of $L^1$	NiCl <sub>2</sub>
$[Zn(L^1)Br_2]$	350-650	420, 550	2		85.78 (85.06)	Loss of 2HBr and L <sup>1</sup>	ZnO
$[Co(L^2)Cl_2]\cdot 2.5H_2O$	30–150 150–350 350–700	60, 110 270 420, 570	2 1 2	60.85 (60.77)	9.17 (9.15) 14.76 (14.84) 84.78 (84.76)	Loss of 2.5H <sub>2</sub> O Loss of 2HCl Loss of L <sup>2</sup>	CoO
$[Cu(L^2)Cl_2]{\cdot}2H_2O$	30–130 130–500 500–900	60 120, 240 520, 620	1 2 2	62.08 (61.40)	7.56 (7.39) 14.79 (14.99) 84.43 (83.78)	Loss of 2H <sub>2</sub> O Loss of 2HCl Loss of L <sup>2</sup>	CuO
$[Zn(L^2)Br_2]$	220–450 450–800	315 615	1 1	55.27 (55.17)	30.19 (29.89) 85.46 (85.06)	Loss of 2HBr Loss of L <sup>2</sup>	ZnO

Table 4

Thermodynamic data of the thermal decomposition of  $L^1 \mbox{ and } L^2 \mbox{ complexes }$ 

Complex	Decomposition range (°C)	$E^*$ (kJ mol <sup>-1</sup> )	$A(S^{-1})$	$\Delta S^*  (\mathrm{kJ}^{-1}  \mathrm{mol}^{-1})$	$\Delta H^* (\mathrm{kJ}\mathrm{mol}^{-1})$	$\Delta G^* (\mathrm{kJ}\mathrm{mol}^{-1})$
$[Fe(L^1)Cl_2(H_2O)] \cdot H_2O$	30–110	65.85	$3.08 \times 10^7$	-45.63	65.22	56.86
	110-800	176.8	$6.40 \times 10^9$	-75.47	97.78	135.6
$[Ni(L^1)Cl_2]\cdot 2H_2O$	40-140	68.73	$6.04  imes 10^{11}$	-43.06	60.23	94.71
	140-800	166.3	$4.83\times10^{14}$	-78.98	185.3	180.3
$[Zn(L^1)Br_2]$	350-430	53.20	$4.66 \times 10^{8}$	-63.34	76.53	36.77
	430-600	153.9	$2.05\times10^{11}$	-96.56	169.5	185.9
$[Co(L^2)Cl_2]\cdot 2.5H_2O$	30-150	40.23	$1.77 \times 10^5$	-28.33	98.28	66.95
	150-350	49.30	$5.08 \times 10^{9}$	-83.17	206.5	217.0
	350-700	187.3	$3.97 \times 10^7$	-108.2	246.3	237.4
$[Cu(L^2)Cl_2]\cdot 2H_2O$	30-90	54.23	$3.50 \times 10^8$	-45.52	87.55	96.53
	90–160	87.57	$6.09 \times 10^{7}$	-35.93	101.2	63.03
	200-300	157.9	$2.39 \times 10^{12}$	-55.33	142.9	195.2
	400-550	166.4	$6.89  imes 10^{14}$	-65.43	187.9	202.6
	550-700	212.6	$4.37\times10^{19}$	-85.69	201.5	254.9
$[Zn(L^2)Br_2]$	220-450	98.79	$4.92 \times 10^{9}$	-48.99	76.42	76.06
	450-800	197.7	$5.92\times10^{11}$	-96.69	122.4	189.32

of the Fe(II) complexes lie in the range 5.22–5.43 B.M. which are an indicative of octahedral geometry.

The electronic spectra of the Co(II) complexes resembles those of other five coordinate Co(II) complexes [33], where three bands are observed at 12,820–12,987, 15,673–15,772 and 17,391–17,452 cm<sup>-1</sup>. The fourth band at 21,786–23,255 cm<sup>-1</sup> refers to the charge transfer band. The low magnetic moment values ( $\mu_{\text{eff}} = 4.95-5.06$  B.M.) range compared with those observed for octahedral or tetrahedral complexes, may support the five coordinate geometry [33].

The reflectance spectra of the Ni(II) complexes show recognizable spectral bands at 13,570-13,789, 17,561-17,905 and  $21,091-21,756 \text{ cm}^{-1}$ . The positions of these spectral bands are quite consistent with those predicted for five coordinate Ni(II) complex whose structure had been established by X-ray crystallographic measurements [24]. The bands can be assigned respectively [24] to  ${}^{3}B_{1} \rightarrow {}^{3}E, {}^{3}B_{1} \rightarrow {}^{3}A_{2}$  and  ${}^{3}B_{1} \rightarrow {}^{3}E$  transitions assuming the effective symmetry to be C<sub>4V</sub>. The bands at 27,569–28,450 cm<sup>-1</sup> may assign to  $L \rightarrow M CT$  band. The Cu(II) complexes exhibit a broad bands at 12,658-12,903, 15,600-15,649 and 19,193-19,569 cm<sup>-1</sup>. These bands are generally consistent with a five coordinate geometry for Cu(II) complexes [32,34a,36]. The spectra also show a band at  $30,078-30,576 \text{ cm}^{-1}$  which may assign to  $L \rightarrow Cu CT$  band. The magnetic moment values of 2.07-2.16 B.M. are indicative of trigonal bipyramidal structure [23,32a,34]. In analogy with those described for Zn(II) complexes containing N–O donor Schiff bases [35] and according to the empirical formulae of these complexes, we proposed trigonal bipyramidal geometry for the Zn(II) complexes.

### 3.4. Thermogravimetric analysis (TGA)

Thermal data of the complexes are given in Table 3, and the activation thermodynamic data associated with the loss of water of crystallization (dehydration process) and ligand molecules are listed in Table 4. The thermal analysis of the chelates under study evinces the following weight losses:

- 3.95–9.17% loss of water molecules of hydration over the range 30–150 °C interval (calculated 3.75–9.15%) for the Fe(II) and Ni(II)-L<sup>1</sup> and Co(II)- and Cu(II)-L<sup>2</sup> complexes.
- 14.76–30.19% elimination of 2HX gases (X = Cl or Br) over the 130–500 °C interval (calculated 14.84–29.89%) for Co(II)-, Cu(II)- and Zn(II)-L<sup>2</sup> complexes.
- 55.27–62.08% elimination of L<sup>2</sup> ligand over the temperature range 350–900 °C (calculated 55.17–61.40%) for Co(II)-, Cu(II)- and Zn(II)-L<sup>2</sup> complexes.
- 81.23% elimination of H<sub>2</sub>O, 2HCl and L<sup>1</sup> ligand for Fe(II)-L<sup>1</sup> complex over the temperature range 350–650 °C (calculated 80.83%).
- 65.79% elimination of L<sup>1</sup> ligand for Ni(II)-L<sup>1</sup> complex over the temperature range 140–800 °C (calculated 65.63%).

85.72% elemination of 2HBr and L<sup>1</sup> ligand for Zn(II)-L<sup>1</sup> complex within the temperature range 350–650 °C (calculated 85.06%).

#### 3.5. Kinetic studies

The kinetic parameters such as activation energy  $(\Delta E^*)$ , enthalpy  $(\Delta H^*)$ , entropy  $(\Delta S^*)$  and free energy change of the decomposition  $(\Delta G^*)$  were evaluated graphically by employing the Coats–Redfern relation [36]:

$$\log\left[\frac{\log\{W_{\rm f}/(W_{\rm f}-W)\}}{T^2}\right]$$
$$= \log\left[\frac{AR}{\theta E^*}\left(1-\frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.303RT} \tag{1}$$

where  $W_f$  is the mass loss at the completion of the reaction, W is the mass loss up to temperature T; R is the gas constant, E is the activation energy in kJ mol<sup>-1</sup>,  $\theta$  is the heating rate and  $(1 - (2RT/E^*)) \cong 1$ . A plot of the left-hand side of Eq. (1) against 1/T gives a slope from which  $E^*$  was calculated and A (Arrhenius constant) was determined from the intercept. The entropy of activation ( $\Delta S^*$ ), enthalpy of activation ( $\Delta H^*$ ) and the free energy change of activation (( $\Delta G^*$ ) were calculated (Table 4).

According to the kinetic data obtained from DTG curves, all the complexes have negative entropy, which indicates that activated complexes have more ordered systems than reactants.

#### 3.6. Structural interpretation

From all of the above observations, the structure of these complexes may be interpreted in accordance with complexes of ligands with a similar distribution of like coordination sites [12,14,15,20]. Vance et al. [20] and Curry [37] (based on X-ray structural data) and Gehad et al. [21], reported that L<sup>1</sup> and 2,6-diacetylpyridinebis(*p*-methoxyphenylimine) were coordinated to Fe(II), Co(II), Ni(II) and Zn(II) through the pyridine-N and azomethine-N. Thus their coordinating behaviour described in the crystal structure of their complex is relevant for the interpretation of L<sup>1</sup> and L<sup>2</sup> coordinating capacity. The structural information from these complexes



M = Co(II), Ni(II), Cu(II), Zn(II).

 $L^2: R = o-OH.$   $L^1: R = p-OH$ 

Fig. 3. Structure of  $L^1$  and  $L^2$  complexes.

Table 5	
Antibacterial activity of Schiff base ligands (L <sup>1</sup> and L <sup>2</sup> ) and their complexe	s

Compound	Gram positive						Gram negative					
	Staph	Staphylococcus aureus			us subti	llis	Pseud	Pseudomonas aereuguinosa		Escherichia coli		
	5 <sup>a</sup>	2.5	1	5	2.5	1	5	2.5	1	5	2.5	1
L1	++	++	nd	++	++	+	+	+	nd	++	+	+
$[[Fe(L^1)Cl_2(H_2O)] \cdot H_2O$	+++	++	+	++	+	+	+++	++	+	++	++	+
$[Co(L^1)Cl_2]$	+++	++	+	++	+	nd	+++	++	+	++	++	+
$[Ni(L^1)Cl_2] \cdot 2H_2O$	++	+	+	+++	++	+	++	+	nd	++	nd	nd
$[Cu(L^1)Cl_2]\cdot H_2O$	+++	++	+	++	++	+	+++	++	+	+++	++	+
$[Zn(L^1)Br_2]$	++	+	nd	++	+	nd	++	+	nd	+++	++	+
$L^2$	++	+	+	+	+	nd	+	+	+	++	+	nd
$[Fe(L^1)Cl_2(H_2O)] \cdot H_2O$	+++	++	+	+++	++	+	++	+	nd	++	++	+
$[Co(L^2)Cl_2] \cdot 2.5H_2O$	+++	++	+	++	+	nd	+++	++	+	++	+	+
$[Ni(L^2)Cl_2] \cdot H_2O$	++	+	nd	++	+	nd	+++	++	nd	++	+	nd
$[Cu(L^2)Cl_2]\cdot 2H_2O$	++	+	+	+++	++	+	++	++	+	+++	++	+
$[Zn(L^2)Br_2]$	++	++	+	+++	++	+	++	++	+	+++	++	+
Chloroamphinicol (standard)	++	++	++	+++	+++	++	+++	+++	++	++	++	++

Inhibition values = 0.1-0.5 cm beyond control = + (less active); inhibition values = 0.6-1.0 cm beyond control = ++ (moderate active); inhibition values = 1.1-1.5 cm beyond control = +++ (highly active).

<sup>a</sup> Concentration in mg/ml. nd: non detected.

is in agreement with the data reported in this paper based on the IR, molar conductivity, solid reflectance and magnetic moment measurements. Consequently, the structures proposed are based on trigonal bipyramidal (Co(II), Ni(II), Cu(II) and Zn(II)) complexs. L<sup>1</sup> and L<sup>2</sup> ligands always coordinate via the pyridine-N and two azomethine-N forming a three binding chelating sites. The trigonal bipyramidal complexs, the two extra positions are provided by the two-halide ions. While in octahedral Fe(II) complexes, the extra position is provided by the coordinated water molecule. According to the above data and similar to those proposed previously, the structures of the complexes are shown in Fig. 3.

#### 3.7. Antibacterial activity

The biological activity of the two Schiff base ligands ( $L^1$  and  $L^2$ ), their complexes and chloroamphenicol (as a standard compound) were tested against bacteria because bacteria can achieve resistance to antibiotics through biochemical and morphological modifications [38]. The organisms used in the present investigations included *Staphylococcus aureus* and *Bacillus subtillis* (as gram positive bacteria) and *Pseudomonas aereuguinosa* and *Escherichia coli* (as gram negative bacteria). The diffusion agar technique was used to evaluate the antibacterial activity of the synthesized mixed ligand complexes [39].

The results of the bactericidal screening of the synthesized compounds are recorded in Table 5. The data obtained reflect that the two Schiff base ligands;  $L^1$  and  $L^2$ , have moderate activity in comparison with *Staphylococcus aureus*, *Escherichia coli* and less active in comparison with *Pseudomonas aeruginosa*.  $L^1$  ligand shows a moderate activity towards *Bacillus subtillis* while  $L^2$  ligand is less active. The remarkable activity of the two Schiff base ligands may be arise from the pyridyl-N and the hydroxyl groups, which may play an important role in the antibacterial activity [40], as well as the presence of two imine groups which imports in elucidating the mechanism of transformation reaction in biological systems [38].

Antibacterial activity of all complexes at low concentrations towards gram positive and negative bacteria are not detected or low. The activity of the two schiff base ligands and their complexes increases as the concentration increases because it is a well known fact that concentration plays a vital role in increasing the degree of inhibition [41]. Against all the organisms, ligands L1 and L2 did not exhibit any remarkable activity compared with standard chloroamphinicol, whereas all the complexes showed moderate to high activities. It is suggested that the complexes having antimicrobial activity may act either by killing the microbe or by inhibiting multiplication of the microbe by blocking their active sites [42]

# 4. Conclusion

The design and synthesis of the first member of a new family of tridentate Schiff base ligands for use in trigonal bipyramidal complexes have been successfully demonstartaed. As anticipated, the ligand coordinates merdionaly to six coordinate transition metal ions to give trigonal bipyramidal oriented molecular turns around the metal ion anchor. The vacant position is occupied by the water molecules to give octahedral oriented molecular turns around Fe(II) ion anchor. The syntheses of the ligands and their complexes proved to be as straightforward as expected, giving high yields of either the free ligands or their complexes in simple, one-pot reactions. Upon chelation, the phenolic groups are directed across and beyond the metal ion center, and, unlike earlier ligands of this general type which lacked reactive moieties, substitution reactions may be carried out at the free phenolic groups of octahedral complex. These reactions must yet be optimized in order to achieve the long-term goal of proving their value as precursors for supramolecular species. This optimization, along with the preparation and study of complexes with different functional groups, represents the focus of ongoing studies.

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