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# Transition metal complexes of isonicotinic acid (2-hydroxybenzylidene)hydrazide

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#### Abstract

A new series of transition metal complexes of Schiff base isonicotinic acid (2-hydroxybenzylidene)hydrazide, HL, have been synthesized. The Schiff base reacted with Cu(II), Ni(II), Co(II), Mn(II), Fe(III) and UO<sub>2</sub>(II) ions as monobasic tridentate ligand to yield mononuclear complexes of 1:2 (metal:ligand) except that of Cu(II) which form complex of 1:1 (metal:ligand). The ligand and its metal complexes were characterized by elemental analyses, IR, UV–vis, mass and <sup>1</sup>H NMR spectra, as well as magnetic moment, conductance measurements, and thermal analyses. All complexes have octahedral configurations except Cu(II) complex which has an extra square planar geometry distorted towards tetrahedral. While, the UO<sub>2</sub>(II) complex has its favour hepta-coordination. The ligand and its metal complexes were tested against one strain Gram +ve bacteria (*Staphylococcus aureus*), Gram –ve bacteria (*Escherichia coli*), and Fungi (*Candida albicans*). The tested compounds exhibited higher antibacterial activities.

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Keywords: Schiff base ligand; Metal complexes; Antimicrobial; IR spectra; UV-vis spectra

### 1. Introduction

Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biologically important species [1-5]. The remarkable biological activity of acid hydrazides R-CO-NH-NH<sub>2</sub>, a class of Schiff base, their corresponding aroylhydrazones, R-CO-NH-N=CH-R' and the dependence of their mode of chelation with transition metal ions present in the living system have been of significant interest [6-12]. The coordination compounds of aroylhydrazones have been reported to act as enzyme inhibitors [13] and are useful due to their pharmacological applications [14–16]. Isonicotinic acid hydrazide (INH) is a drug of proven therapeutic importance and is used as bacterial ailments, e.g., tuberculosis [17]. Hydrazones derived from condensation of isonicotinic acid hydrazide with pyridine aldehydes have been found to show better antitubercular activity than INH [18,19]. In view of the versatile importance of

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hydrazones, we herein describe the synthesis and identification of some transition metal complexes of isonicotinic acid (2-hydroxybenzylidene)hydrazide, HL (Fig. 1).

#### 2. Experimental

#### 2.1. Reagents and materials

Copper(II) chloride dihydrate, nickel(II) chloride monohydrate, cobalt(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, iron(III) chloride hexahydrate, uranyl(II) acetate dihydrate, cadmium(II) acetate monohydrate, lithium hydroxide monohydrate, salicylaldehyde and nicotinic acid hydrazide were either BDH or Merck chemicals and were used without further purification. Organic solvents were reagent grade.

# 2.2. Synthesis of the ligand

The ligand HL was synthesized as follows. Isonicotinic acid hydrazide (1.4 g, 10 mmol) was dissolved in 10 mL absolute ethanol. To this solution saclicylaldehyde (1.34 g, (1.6 mL), 11 mmol dissolved in 5 mL absolute ethanol) was added. The reaction mixture was refluxed for 2 h. After cooling, the precipitate solid was collected, filtered off and finally washed with

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Fig. 1. Structure of the ligand, Isonicotinic acid (2-hydroxybenzylidene) hydrazide.

5-10 mL cold absolute ethanol and re-crystallized from ethanol (yield 80%, m.p. 225 °C).

#### 2.3. Synthesis of the metal complexes

A solution of metal salt dissolved in ethanol was added gradually to a stirred ethanolic solution of the ligand, HL, in the molar ratio 1:2 (metal:ligand). The reaction mixture was further stirred for 2–4 h to ensure the complete precipitation of the formed complexes. The precipitated solid complexes were filtered, washed several times with 50% (v/v) ethanol–water to remove any traces of the unreacted starting materials. Finally, the complexes were washed with diethyl ether and dried in vacuum desiccators over anhydrous CaCl<sub>2</sub>. The reaction of uranyl salt was carried out in methanol as it dissolved better in this solvent. The preparations described were repeated in the presence of LiOH, as deprotonating agent, and its addition is must in order to obtain such preparation with good yield. In most cases, the same yield was obtained. Trials to prepare Cd(II) complex was unsuccessful and start materials were recovered unreacted.

#### 2.4. Physical measurements and analyses

Electronic spectra were recorded for solution of the ligand, HL in DMF, and for the metal complexes as Nujol Mull on a Jasco UV-vis spectrophotometer model V-550 UV-vis. The 1R spectra were recorded using CsI discs on FT-IR 1650 Perkin-Elmer spectrometer. <sup>1</sup>H NMR spectra were carried out in DMF- $d_6$  at room temperature using TMS as internal standard on a Brucker 250 MHz spectrophotometer. Magnetic susceptibilities of the complexes were measured by the Gouy method at room temperature using a model MK1 Johnson Matthey. Alpha products magnetic susceptibility balance. The effective magnetic moments were calculated using the relation ( $\mu_{eff} = 2.828$  $(\chi_m T)^{1/2}$  B.M.) where  $\chi_m$  is the molar susceptibility corrected using Pascal's constants for diamagnetism of all atoms in the compounds. The TG-DTA measurements were carried out on a Shimadzu thermo gravimetric analyzer in dry nitrogen atmosphere and a heating rate of  $10 \,^{\circ}\text{C}\,\text{min}^{-1}$  using the TA-50 WS1 program. Mass spectra were recorded at 70 eV and 300 °C on an MS 5988 Hewlett-Packard mass spectrometer. Conductivity measurements were measured in DMF or nitrobenzene solutions of the complexes  $(10^{-3} \text{ M})$  using a model LBR, WTWD-812 Wilhelm conductivity meter fitted with a model LTA100 cell. Analyses of the metals followed decomposition of their complexes with concentrated nitric acid. The resultant solution was diluted with distilled water, filtered to remove the precipitated ligand. The solution was then neutralized with aqueous ammonia solution and the metal ions titrated with EDTA. Analysis of the uranyl complex was carried out at the Central Laboratory for Environmental Quality Monitoring, CLQM, Kalubia, Cairo, Egypt. The complex was first dried and grind followed by digestion by nitric-HF digestion mixture using Milestone Microwave Digester Model MLS 1200 Mega. The digestible uranium metal was analyzed using Perkin-Elmer ICP OES, Model Optima-3000 coupled with an Ultra Sonic Nebulizer, USN. Microanalyses of carbon, hydrogen, nitrogen and chlorine were carried out at the Micro analytical Center, Cairo University, Giza, Egypt. Chlorine in the Fe(III) complexes was determined by ion chromatography using a (1C) Dionex 500 instrument for anions at the Central Laboratory for Environmental Quality Monitoring, El-Kanater, Cairo, Egypt.

#### 2.5. Pharmacology

The in vitro evaluation of antimicrobial activity was carried out at Saudi Pharmacutical industries and Medical Appliance Corporation. The purpose of the screening program is to provide antimicrobial activity and bacteriostatic and fungistatic efficiency of the investigated metal complexes. The prepared compounds were tested against one strain of Gram +ve bacteria (*Staphylococcus aureu*), Gram –ve bacteria (*Escherichia coli*), and Fungi (*Candida albicans*) to provide the minimum inhibitory concentration (MIC) for each complex. Bacteriostatic and fungistatic efficiency is the lowest concentration of solution to inhibit the growth of a test organism.

# 3. Results and discussion

#### 3.1. Characterization of the Ligand, HL

The reaction of Co(II), Ni(II), Mn(II), UO<sub>2</sub>(II) and iron(III) salts with the ligand, HL, results in the formation of  $[ML_2]$ ·EtOH for M = Ni(II), Co(II) and Mn(II) and  $[ML_2Cl]$ ·2EtOH for M = Fe(III) and  $[UO_2L_2(MeOH)]$ ·2MeOH. For Cu(II) salt, only, [CuLCl]·EtOH was obtained (Table 1). All complexes are quite stable and could be stored without any appreciable change. The complexes do not have sharp melting points but decompose above 260 °C. They are insoluble in common organic solvents, such as ethanol, methanol, chloroform or acetone. However, they are soluble in DMSO and DMF. The conductance measurement indicates that all complexes are essentially non-electrolytes in DMF.

Elemental analyses reflected that the ligand has the molecular formula given in Table 1. The <sup>1</sup>H NMR spectrum (Table 2) of the ligand in deuterated dimethylformamide showed two signals at  $\delta$  14.5 and 11.7 ppm for the proton of the phenolic OH and the NH groups, respectively [20,21]. A signal is also observed at  $\delta$ 

Compund (F.wt.)	Elemental	analysis, found	Colour	Yield (%)			
	C	Н	H N		М		
HL C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> (241)	65.17 (64.73)	5.06 (4.56)	17.82 (17.43)	_	-	Pale Yellow	94
[CuL(Cl]·EtOH C <sub>15</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> ClCu (385)	46.95 (46.75)	4.50 (4.16)	10.63 (10.90)	9.56 (9.22)	15.57 (16.50)	Green	60
[NiL₂]∙EtOH C28H26N6O5Ni (585)	57.86 (57.44)	4.8.6 (4.44)	14.5.9 (14.36)	_	10.27 (10.09)	Pale Green	55
[CoL2]∙EtOH C28H26N6O5Co (585)	57.76 (57.44)	4.91 (4.44)	14.72 (14.36)	_	10.34 (10.09)	Yellowish Green	76
[MnL2]∙EtOH C28H26N6O5Mn (581)	58.13 (57.83)	4.93 (4.48)	14.92 (14.46)	_	9.97 (9.47)	Brown	60
[FeL <sub>2</sub> (Cl)]·2EtOH C <sub>30</sub> H <sub>32</sub> N <sub>6</sub> O <sub>6</sub> ClFe (663.5)	54.81 (54.26)	8.60 (8.11)	13.15 (12.66)	6.10 (5.84)	9.12 (8.44)	Deep brown	66
[UO <sub>2</sub> L <sub>2</sub> (MeOH)]·2MeOH C <sub>29</sub> H <sub>32</sub> N <sub>6</sub> O <sub>7</sub> U (814)	43.19 (42.75)	3.45 (3.93)	10.52 (10.31)	-	28.81 (29.24)	Red	72

Table 1	
Elemental analyses, colour, yield, melting points and molar conductance of HL	and its corresponding metal complexes

6.62 ppm for the HC=N– group [20,21] (Table 2). Addition of  $D_2O$  to the previous solution results in diminishing the signals due to the protons of phenolic OH and HN–N groups.

The IR spectrum of the ligand (Table 3) shows a strong band at 3530 cm<sup>-1</sup> assigned to vOH of the phenolic group. The deformation vibration,  $\delta$ , of the phenolic OH group appears at 1278 cm<sup>-1</sup>. The NH stretching [22–24] absorption appears as weak bands at 3300 and 3220 cm<sup>-1</sup>. Another important band occurs at 1585 cm<sup>-1</sup> attributed to v(C=N) (azomethine) mode [21–24]. Carbonyl–amide and NH–amide absorption bands appear at 1700 and 1655 cm<sup>-1</sup>, respectively. The strong bands observed at 1520–1575 cm<sup>-1</sup> and 1000–1080 cm<sup>-1</sup> are tentatively assigned [21–24] to asymmetric and symmetric  $\nu$ (C=C) +  $\nu$ (C=N) of pyridine ring and pyridine ring breathings and deformations.

The UV-vis spectrum (Table 4) recorded for the ethanolic solution of the ligand showed absorption bands at 48,076 and 44,642 cm<sup>-1</sup> assigned for  $\pi$ - $\pi$ \* transitions within the aromatic and pyridine rings. The band observed at 36,231 and 36,531 cm<sup>-1</sup> would be due to the n- $\pi$ \* transition of the C=N and C=O groups, respectively. The absorption bands at 26,176 and 24,752 cm<sup>-1</sup> assigned for CT transitions. The band at 24,752 cm<sup>-1</sup> encroaches on the visible region [21] and impact the ligand its colour.

The mass spectrum of the ligand (Fig. 2) showed its molecular ion at m/e 241 which coincide with formula weight. Metastable ion(s) is/are not observed. Scheme 1 represented the proposed fragmentation pattern of the ligand.

The pH-metric measurement for  $3 \times 10^{-3}$  M of 75% (v/v) ethanol–water solution of the ligand indicated that only one pro-



<sup>a</sup> s: singlet, m: multiplet.



Fig. 2. Mass spectrum of the ligand HL.

Table 3 Characteristic IR bands (cm<sup>-1</sup>) of HL and its corresponding metal complexes

Compound (F.wt.)	ν(C=N)	$\nu$ (N–H)	v(C=O)	ν(N–N)	ν(M–N)	ν(M–O)	ν(OH) phenolic	Other bands
HL C <sub>13</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> (241)	1585 s	3300 m	1700 vs	1140 s	_	_	3530	1278 (бОН)
[CuL(Cl]·EtOH C <sub>15</sub> H <sub>16</sub> N <sub>3</sub> O <sub>3</sub> ClCu (385)	1530 m	3314 w	1655 vs	1136 s	420 w	540 m	-	3385 (outer-sphere MeOH)
[NiL <sub>2</sub> ]·EtOH C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> O <sub>5</sub> Ni (585)	1525 m	3310 s	1670 vs	1137 w	425 w	520 m	-	3370 (outer-sphere MeOH)
[CoL <sub>2</sub> ]·EtOH C <sub>28</sub> H <sub>26</sub> N <sub>6</sub> O <sub>5</sub> Co (585)	1555 s	3300 w	1680 s	1125 w	410 w	515 m	-	3385 (outer-sphere MeOH)
$[MnL_2] \cdot EtOH C_{28}H_{26}N_6O_5Mn$ (581)	1535 m	3310 w	1620 s	1136 s	445 w	520 w	-	3375 (outer-sphere MeOH)
$[FeL_2(Cl)] \cdot 2EtOH$ $C_{30}H_{32}N_6O_6ClFe$ (663.5)	1530 s	3315 w	1670 vs	1137 s	465 w	520 m	-	3380 (outer-sphere MeOH)
$[UO_{2}L_{2}(MeOH)]\cdot 2MeOH \\ C_{29}H_{32}N_{6}O_{7}U (814)$	1532 s	3314 w	1662 s	1134 s	460 w	540 w	_	3380 (outer-or inner-sphere MeOH), 901 (ν <sub>3</sub> (O=U=O)

s: strong, w: weak, m: medium, vs: very strong.

### Table 4

Magnetic moment, molar conductance, and electronic spectral data (cm<sup>-1</sup>) for HL and its metal complexes

$\mu_{\text{eff.}}$ (B.M.)	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$ and charge transfer transitions <sup>a</sup> (cm <sup>-1</sup> )	$d \rightarrow d \text{ transitions}^a$ (cm <sup>-1</sup> )	Molar conductance <sup>b</sup>
dia <sup>c</sup>	48,067, 44,642, 36,231, 26,176, 24,752	-	_
1.75	36,765, 28,612, 22,396	15,520, 15,850	3.7
2.85	37,037, 28,653, 22,371	1518.45, 11,957	2.6
5.13	370,307, 28,600, 22,271	15,250, 22,480	2.4
5.92	37,085, 28,500, 22,471	21,331.9, 11,733.33	5.0
5.89	37,137, 27,653, 22,571	14,331, 13,850	3.6
dia <sup>c</sup>	37,537, 27,853, 22,871	22,500, 19,040	3.7
	$\mu_{\rm eff.}$ (B.M.) dia <sup>c</sup> 1.75 2.85 5.13 5.92 5.89 dia <sup>c</sup>	$\begin{array}{lll} \mu_{\rm eff.} \mbox{ (B.M.)} & \pi \rightarrow \pi^*, n \rightarrow \pi^* \mbox{ and charge transfer transitions}^a \mbox{ (cm}^{-1}) & \\ dia^c & 48,067,44,642,36,231,26,176, \\ 24,752 & \\ 1.75 & 36,765,28,612,22,396 & \\ 2.85 & 37,037,28,653,22,371 & \\ 5.13 & 370,307,28,600,22,271 & \\ 5.92 & 37,085,28,500,22,471 & \\ 5.89 & 37,137,27,653,22,571 & \\ dia^c & 37,537,27,853,22,871 & \\ \end{array}$	$\begin{array}{c c} \mu_{\rm eff.} \ ({\rm B.M.}) & \pi \to \pi^*,  {\rm n} \to \pi^*  {\rm and}  {\rm charge} \\ {\rm transfer \ transitions^a \ (cm^{-1})} & (cm^{-1}) \\ \hline \\ {\rm dia}^c & 48,067,44,642,36,231,26,176, \\ 24,752 \\ 1.75 & 36,765,28,612,22,396 \\ 15,520,15,850 \\ 2.85 & 37,037,28,653,22,371 \\ 1518,45,11,957 \\ 5.13 & 370,307,28,600,22,271 \\ 15,250,22,480 \\ 5.92 & 37,085,28,500,22,471 \\ 21,331.9,11,733.33 \\ 5.89 & 37,137,27,653,22,571 \\ 14,331,13,850 \\ {\rm dia}^c & 37,537,27,853,22,871 \\ 22,500,19,040 \\ \hline \end{array}$

 $^a\,$  As Nujol mull.  $^b\,$  Measured for  $10^{-3}\,M$  solution in DMF,  $\Omega^{-1}\,cm^2\,mol^{-1}.$ 

<sup>c</sup> dia=diamagnetic.



Scheme 1. Mass fragmentation pattern of the ligand HL.

ton dissociates together with the value of  $pK_a$  (10.63) suggesting that the ligand behaves as a weak monobasic acid. The value of  $pK_a$  reveal that the proton dissociated from the phenolic OH group rather than from the N-proton of the hydrazino moiety which may dissociated at higher pH region.

#### 3.2. IR spectra of the metal complexes

The ligand is expected to act as tetradentate one, the possible coordination sites being pyridinic-nitrogen, azomethine nitrogen, phenolic oxygen and amide group. A study and comparison of the IR spectra of ligand and its metal complexes imply that the ligand, HL, is monobasic tridentate in nature with carbonyl–oxygen, azomethine–nitrogen and phenolic-oxygen as three, ONO, coordination sites. The IR-data are presented in Table 3.

The IR spectra of the metal complexes showed that the band due to phenolic OH group that appeared in the spectrum of the ligand at 3530 cm<sup>-1</sup> have disappeared in the spectra of the complexes, may be due to the displacement of its proton by the metal ion in accordance with the pH-metric and dissociation constant of the ligand. The  $\delta$ (COH)ip mode which appeared at 1355 cm<sup>-1</sup> in the spectrum of the ligand, was not observed in the spectra of the complexes and thus supported the suggestion that the ligand coordinate to the metal through its deprotonated form. Moreover, the band observed at 1585 cm<sup>-1</sup> in the spectrum of the ligand which attributed to  $\nu$ (C=N) (azomethine) mode [21–24] is shifted, in spectra of all the complexes to lower wave number and appears at 1525–1555 cm<sup>-1</sup> region indicating the involvement of N-atom of the azomethine group in coordination [25–28].

In addition, in the spectra of the complexes, a considerable negative shift in  $\nu$ (C=O) is observed indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the carbonyl–oxygen atom of the free ligand. The NH stretching absorption in free ligand occurs [28] at 3300 and 3220 cm<sup>-1</sup> which remains unaffected after complexation. This precludes the possibility of coordination through imine nitrogen atom.

The strong bands observed at  $1520-1575 \text{ cm}^{-1}$  and  $1000-1080 \text{ cm}^{-1}$  are tentatively assigned [21–24] to asymmetric and symmetric  $\nu(C=C) + \nu(C=N)$  of pyridine ring and pyridine ring breathings and deformations remain practically unchanged in frequency and band intensities revealing non involvement of pyridinic-nitrogen and metal bond.

The IR spectrum of the mononuclear  $UO_2(II)$  complex showed a broad band at  $3459 \text{ cm}^{-1}$  assigned to  $\nu(OH)$  of the coordinated methanol group and  $\nu(NH)$  of the uncoordinated NH groups appeared as a shoulder at  $3314 \text{ cm}^{-1}$ , exactly at the same frequency as for the parent ligand. However, no splitting of this band was observed, which may be due to the larger separation of the two ligand molecules, due to the larger volume of the  $UO_2(II)$  cation in the complex molecules. A well-characterized band appeared at  $1532 \text{ cm}^{-1}$  assigned to the coordinated C=N group. The band recurs at a lower frequency compared to that of the parent ligand indicating its involvement in coordinating the  $UO_2(II)$  cation, in addition to the phenolic-oxygen atoms after replacing its hydrogen ions by the uranyl(II) cation. The  $\nu_3$ (O=U=O) appeared as a strong band at 901 cm<sup>-1</sup> overlapping with another band already present in the spectrum of the parent ligand and thus gaining higher density [20,21].

The overall IR spectral evidence suggests that the HL acts as monobasic tridentate ligand and coordinate through amide–oxygen, azomethine–nitrogen and phenolic-oxygen atoms forming a six-membered chelate ring. In all spectra, new bands appeared, for all types of the complexes, at 515–540 cm<sup>-1</sup> and 410–465 cm<sup>-1</sup> that would be assigned to  $\nu$ M–O and  $\nu$ M–N, respectively [25].

# 3.3. Magnetic moments and electronic spectral data of the metal complexes

The electronic spectra and magnetic moments of the metal complexes are listed in Table 4. Generally, in all spectra of metal complexes, the absorption bands due to  $\pi - \pi^*$  and  $n - \pi^*$  transitions that observed in the spectrum of the free ligand higher than 22,300 cm<sup>-1</sup> have shifted to lower frequencies due to the coordination of the ligand with metal ions.

The spectra of the Cu(II) complex (Table 4) showed absorption bands at  $15,520-15,850 \text{ cm}^{-1}$  which could be attributed to the  ${}^{2}A_{1g} \rightarrow {}^{2}B_{1g}$  transitions characterized Cu(II) ion in a square-planar geometry [29]. The square-planar geometry of Cu(II) ion in the complex is confirmed by the measured magnetic moments values, 1.75 B.M. The square-planar geometry is achieved by the coordination of two molecules of HL each as monobasic tridentate ligand, to the copper(II) ion [29–31]. The Cu(II) completed its four coordination by the attachment of one chlorine ion. The shift of the absorption band to lower energy than that expected for square-planar geometry, at 18,191.8 cm<sup>-1</sup> for square-planar *N,N'*-ethylenebis-(salicylideneimine)copper(II), Cu(acacen) [21] may be due to the distortion of the square-planar geometry towards tetrahedral [21,29].

The electronic spectrum of the Ni(II) complex, Table 4, showed broad absorption band at 16,220 cm<sup>-1</sup> which may be assigned to  ${}^{3}A_{1g}(F) \rightarrow {}^{3}T_{2g}(F)$ , while the absorption due to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  is overlapped with the ligand absorption bands. This indicates that the Ni(II) ion coordinated to NNO sites in an octahedral geometry [29–33]. The third transition due to  ${}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P)$  would be out of the scale of the used spectrophotometer. The magnetic moment of the complex is 2.85 B.M. which agrees with the presence of Ni(II) ion in octahedral geometry [21,29].

The measured magnetic moment of cobalt(II) complex is given in Table 4. The theory of magnetic susceptibility of cobalt(II) ion was given originally by Schlapp and Penney [30] and the best summary of results on the magnetic behaviour of cobalt compound is that of Figgis and Nyholm [31]. The observed values of magnetic moments for cobalt(II) complexes are generally diagnostic of the coordination geometry about the metal ion. The low-spin square-planar cobalt(II) complexes may be 2.9 B.M., arising from one unpaired electron plus an apparently large orbital contribution [31]. Both tetrahedral and high-spin octahedral cobalt(II) complexes possess three

unpaired electrons but may be distinguished by the magnitude of the deviation of  $\mu_{eff}$  from the spin-only value. The magnetic moment of tetrahedral cobalt(II) complexes with an orbitally non-generate ground term is increased above the spinonly value via contribution from higher orbitally degenerate terms and occurs in the range [31,33] 4.2-4.7 B.M. octahedral cobalt(II) complexes, however, maintain a large contribution due to  ${}^{4}T_{g}$  ground term and exhibit  $\mu_{eff}$  in the range [31,33] 4.8–5.6 B.M. The magnetic measurement on the complex reported herein is 5.1 B.M showing that it has three unpaired electrons indicating a high-spin octahedral configuration. The electronic spectrum of the complex showed two d-d transitions in the range  $15,250-15,390 \text{ cm}^{-1}$  and  $18,410-18,480 \text{ cm}^{-1}$  due to the transitions  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$  and  ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(P)$ , respectively, [31] indicating an octahedral configuration around Co(II) ion. The  ${}^{4}T_{2g}(F) \rightarrow {}^{4}T_{1g}(F)$  transition (9510 cm<sup>-1</sup>) would be observed in near IR region [31]. This region is out of the scale of our spectrophotometer [31,33].

The spectrum of the Mn(II) complex showed a series of weak bands in the range  $21,331.96-11,733.33 \text{ cm}^{-1}$ . Mn(II) ion is d<sup>5</sup> system and its d–d transitions are both Laporte and spin-forbidden. However, due to instantaneous distortion of the octahedral structures around the metal cation, weak bands sometimes do appear [31,33] The magnetic moment of the complex is 5.94 B.M. and indicates antiferromagnetic interaction between the adjacent metal cations.

The electronic spectra of the diamagnetic uranyl complex showed two bands, in addition to the ligand bands. The first band observed at  $22,500 \text{ cm}^{-1}$  corresponding to charge transfer

from equatorial donor atoms of the ligand to the uranyl ion. The second band observed at  $19,040 \text{ cm}^{-1}$  due to electronic transitions from apical oxygen atom to the f-orbitals of the uranyl atom characteristic of the uranyl moiety [34].

On the other hand, the electronic spectra of Fe(II) complex showed broad bands 14,331 and 13,850 cm<sup>-1</sup>. The former band may be due to the spin forbidden transition  ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$ , which may gain intensity as a result of the vibronic mechanism in the octahedral field around ferric ion. The second bands may be attributed to  ${}^{6}A_{1} \rightarrow {}^{4}T_{1}(G)$  transitions. In addition, a third absorption band with high intensity observed at 25,252 cm<sup>-1</sup> assigned for charge transfer transition. The magnetic moment of complex is 5.89 B.M. [31,33].

# 3.4. Molar conductance of the metal complexes

The conductance measurements, recorded for  $10^{-3}$  M solutions of the metal complexes in DMF, are listed in Table 4. All complexes, except two, are non-conducting and the measured molar conductance ranged from ~2.0 to 3.6 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating their neutrality.

# 3.5. <sup>1</sup>H NMR spectrum of the uranyl complex

The uranyl complex was selected as it is diamagnetic. Its <sup>1</sup>H NMR spectrum in DMF and after deuteration are discussed. The spectrum of the complex differs from that of the free ligand in the following aspects:

Table 5

Thermal analyses data for some metal complexes of HL

Compound (F.wt.)	Dissociation stages	Temperature range in TG °C	Weight loss found (calcd.) %	Decomposition assignment
[CuL(Cl]·EtOH C15H16N3O3ClCu	Stage I	130–150	8.16 (7.79)	Loss of one mol outer-sphere EtOH
(385)	Stage II	223-383	72.00 (71.56)	Loss of one mol of the ligand-Cl
	Stage III	385–545	63.15 (62.60)	Formation of CuO
[NiL2]·EtOH C28H26N6O5Ni (585)	Stage I	120–135	5.73 (5.13)	Loss of one mol outer-sphere EtOH
	Stage II	234-373	42.00 (41.03)	Loss of one mol of the ligand
	Stage III	375-438	41.70 (41.03)	Loss of one mol of the ligand
	Stage VI	439–510	13.20 (12.82)	Formation of NiO
[CoL2]·EtOH C28H26N6O5Co (585)	Stage I	130–145	5.61 (5.16)	Loss of one mol outer-sphere EtOH
	Stage II	240-378	42.00 (41.31)	Loss of one mol of the ligand
	Stage III	380-448	42.20 (41.31)	Loss of one mol of the ligand
	Stage VI	460-550	13.60 (12.82)	Formation of CoO
[MnL2]·EtOH C28H26N6O5Mn (581)	Stage I	125–155	4.45 (4.52)	Loss of one mol outer-sphere EtOH
	Stage II	234-375	37.20 (36.17)	Loss of one mol of the ligand
	Stage III	380-438	36.73 (36.17)	Loss of one mol of the ligand
	Stage VI	459–510	13.00 (12.22)	Formation of MnO
[FeL2(Cl)]·2EtOH C30H32N6O6ClFe	Stage I	130–145	4.43 (4.52)	Loss of 2 mol outer-sphere EtOH
(663.5)	Stage II	240-378	41.10 (41.522)	Loss of one mol of the ligand-Cl
	Stage III	380-448	37.21 (36.32)	Loss of one mol of the ligand
	Stage IV	459–550	23.90 (24.12)	Formation of Fe <sub>2</sub> O <sub>3</sub>
[UO <sub>2</sub> L <sub>2</sub> (MeOH)]·2MeOH	Stage I	80-110	7.21 (7.37)	Loss of the 2 mol outer-sphere MeOH
C <sub>29</sub> H <sub>32</sub> N <sub>6</sub> O <sub>7</sub> U (814)	Stage II	130-145	4.10 (3.68)	Loss of one mol coordinated MeOH
	Stage III	240-378	30.10 (29.48)	Loss of one mol of the ligand
	Stage IV	380-448	29.30 (29.48)	Loss of one mol of the ligand
	Stage V	459–550	32.23 (33.17)	Formation of UO <sub>2</sub>



Fig. 3. Suggested structures of  $[ML_2]$ ·EtOH (M = Co(II), Ni(II) or Mn(II); (b)  $[ML_2CI]$ ·2EtOH (M = Fe(III); (c)  $[UO_2L_2(MeOH)]$ ·2MeOH and (d) [CuL(CI)]·EtOH.

- 1. The disappearance of the signal due to the phenolic OH group is attributed to its involvement in coordinating the uranyl cation, while the signal due to the NH group was broad and appeared at  $\delta = 12.4$  ppm compared to that of the ligand which appeared at,  $\delta = 11.7$  ppm, i.e. shifted to low-field. This signal disappeared on deuteration.
- 2. The signals due to the aromatic and pyridine rings showed fine structure and appear as four separate signals.
- 3. New signals for CH<sub>3</sub> group of the coordinated and the outer-sphere methyl alcohol molecule appeared at  $\delta = 3.6$  and 3.5 ppm, respectively, while the OH group of the alcohol did not appear as it would be masked by other signals.

 Table 6

 Results of anti-microbial activity of some tested complexes

Compound	Concentration (%)	Staphylococcus aureus ATCC <sup>a</sup> 6538 MIC <sup>b</sup> 25%	<i>Escherichia coli</i> ATCC 8739 MIC 25%	<i>Candida albicans</i> ATCC 10,231 MIC 25%
HL	1 <sup>c</sup>			
	25	+ve	-ve	-ve
	50	-ve	-ve	+ve
	100	-ve	+ve	+ve
[CuL(Cl)]·EtOH	1	+ve	+ve	+ve
	25	+ve	+ve	+ve
	50	+ve	+ve	-ve
	100	-ve	-ve	-ve
[NiL <sub>2</sub> ]·EtOH	1 <sup>c</sup>			
	25	-ve	+ve	-ve
	50	-ve	-ve	-ve
	100	-ve	-ve	-ve
[CoL <sub>2</sub> ]·EtOH	1 <sup>c</sup>			
	25	-ve	-ve	-ve
	50	-ve	-ve	-ve
	100	-ve	-ve	-ve
[MnL <sub>2</sub> ]·EtOH	1	+ve	+ve	+ve
	25	-ve	+ve	-ve
	50	-ve	-ve	-ve
	100	-ve	-ve	-ve
[FeL2(Cl)]·2EtOH	1	+ve	+ve	+ve
	25	-ve	-ve	+ve
	50	+ve	-ve	-ve
	100	-ve	-ve	-ve
UL2(MeOH)]·2MeOH	1	+ve	+ve	+ve
	25	-ve	+ve	-ve
	50	-ve	+ve	-ve
	100	-ve	-ve	-ve

Key to symbols: Active and inhibit the growth of the strain: -ve; Inactive: +ve.

<sup>a</sup> Number of strain in the American collection.

<sup>b</sup> MIC is the lowest concentration of the product material solution to inhibit the growth of the microorganism.

<sup>c</sup> Not tested in this concentration.

#### 3.6. Thermal analyses

The TG-DTA results of the solid Ni(II), Co(II) and Mn(II) complexes are listed in Table 5. The results show that all complexes have similar decomposition pattern which is in good agreement with the formulae suggested from the analytical data, Table 1. A general decomposition patterns was concluded in which the complexes decomposed in four stages except Cu(II) complex which decomposed in three stages. Beside the four stages, uranyl complex, which has coordinated MeOH molecule, exhibited additional stage to be decomposed in five stages (Table 5) and lost its outer-sphere MeOH molecule at relatively low temperature, after that, the decomposition process will started which is similar to the decomposition process of the other complexes. All complexes lost one mol of the ligand at 230-370 °C. The second mol of the ligand was lost at 380-4550 °C accompanied with the formation of the metal oxides. Based on the above results, the structures in Fig. 3 are suggested for the metal complexes.

# 3.7. Antimicrobial activity and minimum inhibitory concentration, MIC

The test was performed according to the method reported previously [35]. A 0.02 g of each complex was dissolved in 100 ml dimethylsulfoxide, DMSO, to produce 0.02% solutions. To a series of culture tubes, in which each tube containing sterile 5 ml double strength solution of Soyabean Casein Digest Medium (Tryptic Soy Broth), 5 ml of the 0.02% DMS solution was added to each tube and mixed. To determine the bacteriostatic efficiency of the S. aureu and E. coli organism, 1 ml of a 1:10 diluted solution of Tryptic Soy Broth (TSB) was added to each culture tube. A 1:10 diluted solution of Tryptic Soy Broth (TSB) was prepared by pipetting 1 ml of bacterial cultures incubated at 37 °C for 24 h into 9 ml of sterile Tryptic Soy Broth. For the test of the fungistatical efficiency, 0.1 ml of undiluted sample incubated for 72 h at 37 °C TSB cultivation of C. albicans was used. All inoculated culture tubes were incubated at 30-35 °C for 18-24 h. After that, the "MIC" level was assessed visually. MIC was recorded as the first clear tubes after turbidity, starting with the blank broth. In other words, the highest dilution of the antiseptic/disinfectant preventing growth is taken as the "MIC" of the test organism [35].

The tests were carried for concentrations of 1, 25, 50, 100% DMSO solutions of the compounds. The inhibition zones caused by the various compounds on the microorganisms were examined. The results of the preliminary screening test are listed in Table 6. Remarkable result is that the metal complexes, [NiL<sub>2</sub>]·EtOH, [CoL<sub>2</sub>]·EtOH, [MnL<sub>2</sub>]·EtOH and [FeL<sub>2</sub>(Cl)]·2EtOH were found to have highly activity against all strains in all of their concentrations expect their 1% concentration. While the free exhibited its activity at its 100% concentration for only *E. coli* and does not affect the other tested strain organisms in all of its concentration. The [UO<sub>2</sub>L<sub>2</sub>(MeOH)]·2MeOH complex was found to have higher activity against strains *S. aureus* and *C. albicans* in its 25, 50, and 100% concentrations, while for *E. coli*, its activity was

exhibited for 25, and 50% concentrations. However, Cu(II) complex [CuL(Cl)]·EtOH exhibited its activity only at its 100 and 50% concentration. The tested compounds showed an inhibitory activity of 25%.

## 4. Conclusion

The present study revealed octahedral geometry around Ni(II), Co(II), Mn(II) and Fe(III) complexes. However, square-planar geometry is suggested for copper ion in the Cu(II)-complex, In all cases, the ligand HL acts as monobasic tridentate coordinating through ONO coordination sites and thus forming stable six- and four-membered chelates. The results of antimicrobial activity show that the metal complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to the parent ligand. It has also been proposed that concentration plays a vital role in increasing the degree of inhabitation.

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