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Full Paper

Antimicrobial Activity and Spectral, Magnetic and Thermal Studies of Some Transition Metal Complexes of a Schiff Base Hydrazone Containing a Quinoline Moiety

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Abstract: A series of new copper(II), cobalt(II), nickel(II), manganese(II), iron(III), and uranyl(VI) complexes of the Schiff base hydrazone 7-chloro-4-(benzylidene-hydrazo)quinoline (**HL**) were prepared and characterized. The Schiff base behaves as a monobasic bidentate ligand. Mononuclear complexes with the general composition $[ML_2(Cl)_m(H_2O)_2(OEt)_n]\cdot xEtOH$ (M = Cu(II), Co(II), Ni(II), Mn(II), Fe(III) or UO_2(VI); m and n = 0-1; x = 1-3) were obtained in the presence of Li(OH) as a deprotonating agent. The nature of bonding and the stereochemistry of the complexes have been deduced from elemental analyses, infrared, electronic spectra, magnetic susceptibility and conductivity measurements. An octahedral geometry was suggested for all the complexes except the Cu(II) and UO_2(VI) ones. The Cu(II) complex has a square-planar geometry distorted towards tetrahedral, while the UO_2(VI) complex displays its favored heptacoordination. The Schiff base ligand, **HL**, and its complexes were tested against one strain Gram +ve bacteria (*Staphylococcus aureus*), Gram -ve bacteria (*Escherichia coli*), and Fungi (*Candida albicans*). The prepared metal complexes exhibited higher antibacterial activities than the parent ligand and their biopotency is discussed.

Keywords: Schiff base hydrazone, antimicrobial activity, IR, electronic spectra

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Introduction

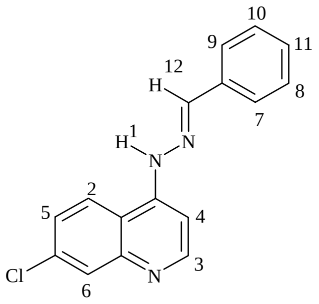
Interest in the study of Schiff base hydrazones has been growing because of their antimicrobial, anti-tuberculosis, and anti-tumour activity [1-12]. Schiff bases play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions. The development of the 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]. Coordination compounds derived from aroylhydrazones have been reported to act as enzyme inhibitors and are useful due to their pharmacological applications [6-12]. In view of the importance of such hydrazones, we describe here the synthesis and characterization of Cu(II), Ni(II), Co(II), Mn(II), Fe(III) and UO_2(VI) complexes of 7-chloro-4-(benzylidenehydrazo)quinoline (**HL**, Figure 1).

Results and Discussion

Characterization of the Ligand

The organic ligand **HL** (Figure 1) was prepared by reacting benzaldehyde with 7-chloro-4-hydrazinoquinoline in a 1:1 molar ratio. Elemental analyses indicated that the ligand has the molecular formula given in Table 1. The ^{1}H-NMR spectrum (Table 2) of the ligand in deuterated DMSO showed a signal at δ 11.52 ppm, corresponding to the HN-N group proton [13,14]. Addition of D_2O to the previous solution results in a diminution of this signal.

Figure 1. 7-Chloro-4-(benzylidinehydrazo)quinoline (**HL**).



The IR spectrum of the ligand (Table 3) shows a weak band at 3,300 cm^{-1}, assigned to νNH. The spectrum shows also vibrational bands at 1,534 and 1,578 cm^{-}1, attributed to ν(C=N) and ν(C=C), respectively [13,14].

The UV-VIS spectrum of the solid ligand (Table 4) showed two bands at 224 and 360 nm and a shoulder at 422 nm. Its ethanolic solution spectrum showed three absorption bands at 287, 353 and 394 nm. The first band would be assigned to π-π^* transitions within the aromatic and quinoline rings. The second band would be due to a n-π* transition within the C=N group. The absorption bands at 394 nm were assigned to CT transitions. This band encroaches on the visible region and impacts the ligand's color [15,16].

The mass spectrum of the ligand consists of a base peak at m/e = 178 amu, due to the $[C_9H_7N_2Cl]^+$ fragment. The molecular ion (M^+) appears at m/e 281 amu with 5.7% intensity. Other fragments observed at m/e = 266, 151 and 77 amu were assigned to $[C_{15}H_9N_3Cl]^+$, $[C_6H_6NCl]^+$ and $[C_6H_5N]^+$ ions, respectively. Metastable ion(s) is/are not observed [13,14].

Table 1. Elemental analyses, color, yields and melting points of the ligand and its metal complexes.

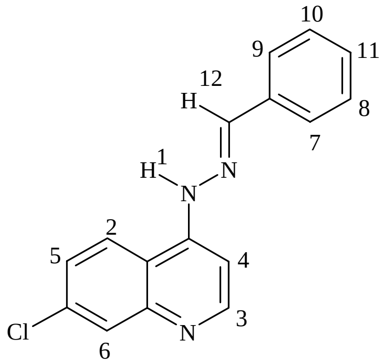
Compound / (F.wt.)	Color	Yield (%)	M.p. (°C)	Elemental analysis, Found / (Calcd) %					Solubility
				C	H	N	Cl	M	
$C_{16}H_{12}N_3Cl$ (**HL**) (281)	Deep yellow	66	225	68.64 (68.21)	4.62 (4.26)	15.12 (14.92)	13.20 (12.61)	---	Soluble in most common organic solvents
$[Cu((L)_2]\cdot EtOH$ (**1**) $C_{34}H_{28}N_6OCl_2Cu$ (670)	Green	33	287	61.23 (60.85)	4.60 (4.18)	12.92 (12.53)	11.00 (10.59)	10.00 (9.47)	Soluble in DMF, DMSO, acetone and insoluble in methanol and ethanol
$[Ni(L)_2(OH_2)_2]\cdot 2EtOH$ (**2**) $C_{36}H_{38}N_6O_4Cl_2Ni$ (747)	Pale Green	25	220	58.23 (57.79)	5.56 (5.08)	11.44 (11.24)	9.87 (9.50)	8.23 (7.83)	Soluble in DMF, DMSO, and insoluble in methanol and ethanol
$[Co(L)_2(OH_2)_2]$ (**3**) $C_{32}H_{26}N_6O_2Cl_2Co$ (656)	Brown	34	260*	(58.54)	(3.96)	(12.80)	(10.82)	(8.99)	Soluble in DMF, DMSO, acetone and insoluble in methanol and ethanol
$[Mn(L)_2(OH_2)_2]$ (**4**) $C_{32}H_{26}N_6O_2Cl_2Mn$ (652)	Deep brown	48	255	59.23 (58.90)	4.30 (3.99)	13.41 (12.88)	11.21 (10.89)	9.84 (8.44)	Soluble in DMF, DMSO, acetone and insoluble in methanol and ethanol
$[Fe(L)_2(Cl)(OH_2)_2]$ $\cdot 3EtOH$ (**5**) $C_{38}H_{44}N_6O_5Cl_3Fe$ (826)	Reddish brown	55	250*	55.65 (55.17)	5.72 (5.32)	10.23 (10.16)	13.11 (12.89)	6.87 (6.78)	Soluble in DMF, DMSO, acetone and insoluble in methanol and ethanol
$[UO_2(L)_2(OEt)]\cdot EtOH$ (**6**) $C_{36}H_{33}N_6O_4Cl_2U$ (922)	Red	75	225*	46.95 (46.85)	4.78 (3.58)	9.32 (9.11)	7.90 (7.70)	26.11 (25.81)	Soluble in DMF, DMSO, acetone and insoluble in methanol and ethanol

* Decomposition point

Metal Complexes

The Schiff base hydrazone ligand **HL** behaves as monobasic bidentate ligand containing an NN coordination site. The ligand reacts with Cu(II), Ni(II), Co(II), Mn(II), Fe(III) and UO_2(VI) ions in the presence of Li(OH) as a deprotonating agent to yield mononuclear complexes with the general composition $[ML_2(Cl)_m(H_2O)_2(OEt)_n]\cdot xEtOH$ (M = Cu(II), Co(II), Ni(II), Mn(II), Fe(III) or UO_2(VI); m and n = 0-1; x = 1-3) (Table 1). Table 3 shows the characteristic IR bands of the ligand and its metal complexes. Table 4 shows the magnetic moments, conductance and UV-VIS bands of the complexes. The chemical analyses, UV-VIS and IR bands of the parent ligand are also included for comparison purposes.

Table 2. ^{1}H-NMR data of the ligand HL in DMSO-d_6**.**



7-Chloro-4-(benzylidinehydrazo)quinoline, **HL**

Chemical shift, δ_{TMS} (ppm)	Assignment^a
11.5	[s, 1H] (1)
8.2	[s, 1H] (2)
7.24-7.32	[m, 6H] (3,4,5,6,7 and 11)
7.16	[m, 1H] (8)
9.0	[m, 1H] (9)
7.8	[m, 1H] (10)
8.6	[m, 1H] (12)

^{a}s = singlet, m = multiplet

Table 3. Characteristic IR bands (cm^{-1}) of the ligand **HL** and its metal complexes.

Compound	ν(C=N)	ν(N-H)	ν(N-N)	ν(M-N)	ν(C=C)	Other bands
$C_{16}H_{12}N_3Cl$ (**HL**)	1534 s	3300 m	1140 s	---	1578 s	---
[Cu((L)$_2$]·EtOH (**1**) $C_{34}H_{28}N_6OCl_2Cu$	1520 s	---	1136 s	420 w	1580 s	3426 m, br (νOH-alcohol)
[Ni(L)$_2$(OH$_2$)$_2$]·2EtOH (**2**) $C_{36}H_{38}N_6O_4Cl_2Ni$	1510 m	---	1137 w	425 w	1577 s	3440 m, br (νOH-coordinated water, overlapped with νOH-alcohol)
[Co(L)$_2$(OH$_2$)$_2$] (**3**) $C_{32}H_{26}N_6O_2Cl_2Co$	1514 sh	---	1125 w	410 w	1577 s	3436 m, br (νOH-coordinated water)
[Mn(L)$_2$(OH$_2$)$_2$] (**4**) $C_{32}H_{26}N_6O_2Cl_2Mn$	1527 sh	---	1136 s	445 w	1582 s	3438 m, br (νOH-coordinated water)
[Fe(L)$_2$(Cl)(OH$_2$)$_2$]·3EtOH (**5**) $C_{38}H_{44}N_6O_5Cl_3Fe$	1507 m	---	1137 s	465 w	1577 s	3440 m, br (νOH-coordinated water, overlapped with νOH-alcohol). 395 m (νFe-Cl)
[UO$_2$(L)$_2$(OEt)]·EtOH (**6**) $C_{36}H_{33}N_6O_4Cl_2U$	1505	---	1134 s	460 w	540 w	3435 m, br (νOH-coordinated alcohol) 901 s ν_3(O=U=O)

s: strong, w : weak, m : medium, br. : broad, sh : shoulder

IR Spectra of the Metal Complexes

The IR spectra of the mononuclear complexes (Table 3) showed that the band due to NH group that appeared in the spectrum of the ligand at 3,300 cm^{-1} had disappeared in the spectra of these complexes. This may be due to the displacement of its proton by the metal ion. Moreover, the spectra showed that the C=N group vibrations were shifted to a lower frequency, due to the coordination of the azomethine group nitrogen atom. As a result, the Schiff base hydrazone behaves as monobasic bidentate ligand with NN coordination sites via the nitrogen atom of the azomethine C=N and the nitrogen atom of the NH group [17]. For the uranyl complex, the ν_3(O=U=O) appeared as a strong band at 901 cm^{-1}. In all spectra, new bands appeared at 410-465 cm^{-1} that would be assigned to ν(M-N).The spectrum of Fe(III) complex showed an extra moderate band at 395 cm^{-1} which could be assigned for ν(Fe-Cl)

*Magnetic Moments and Electronic Spectral Data of the Metal Complexe*s

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 π-π* and n-π* transitions that observed in the spectrum of the free ligand higher than 422 nm have shifted to lower frequencies due to the coordination of the ligand with metal ions.

In all the reflectance spectra of the complexes, four absorption bands appeared at >240, >311, >325 and >348 nm due to the ligand absorptions which are shifted from those of the parent ligand due to complex formation. The spectrum of Cu(II)-complex (**1**) showed absorption band at 665 nm which could be attributed to the $^2A_{1g}(F) \rightarrow {}^2B_{1g}(P)$ transitions characterized Cu(II) ion in a square-planar geometry [18]. The shift of the absorption band to lower energy than that expected for square-planar geometry, exemplified by the 550 nm band seen for the square-planar complex N,N'-ethylenebis-(salicylideneimine)copper(II), Cu(acacen) [19], may be due to the distortion of the square-planar geometry towards tetrahedral [18,19]. 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 acting as a monobasic bidentate ligand, to the copper(II) ion [18].

The reflectance spectrum of the mononuclear Ni(II) complex **2** (Table 4) showed a broad and main absorption band at 768 nm and a shoulder at 670 nm. The main band may be due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ electronic transition of Ni(II) in an octahedral geometry. The $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transition may be overlapped by the ligand absorption bands which appeared at 355 nm [18]. The third transition due to $^3A_{2g}(F) \rightarrow {}^3T_{2g}$ is out of the range of the spectrophotometer used. This indicates that the Ni(II) ion coordinated to $(N_2)_2$ sites in an octahedral geometry [18]. The Ni(II) ion completes its hexa-coordination sphere with two water molecules. The third transition due to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ would be outside the scale of the spectrophotometer used. The magnetic moment of the complex is 3.19 B.M. which agrees well with the known values for Ni(II) complexes in octahedral geometry [18].

Octahedral, tetrahedral and square-planar cobalt (II) complexes show magnetic moment between 4.7-5.2, 4.2-4.8 and 2.2-2.9 B.M., respectively [18]. The $\mu_{eff.}$ value measured for the Co(II)-complex **3** (Table 4) is 5.32 B.M, indicating octahedral geometry of the Co(II) ion in the complex. The reflectance spectrum of the complex showed a band at 656 nm and a shoulder at 477 nm, besides the ligand absorptions. The former band would be due to a $^4T_{1g} \rightarrow {}^4A_{2g}$ electronic transition [19,20], indicating an octahedral configuration around Co(II) ions.[18,20].

The reflectance spectrum of the Mn(II)-complex **4** showed a series of weak bands in the range 469-853 nm. These bands are both Laporte and spin-forbidden. However, due to instantaneous distortion of the octahedral structures around the metal cation, weak bands sometimes do appear [18,20]. The magnetic moment of the complex is 5.39 B. M. and indicates antiferromagnetic interaction between the adjacent metal cations.

The reflectance spectrum of Fe(III)-complex **5** showed broad bands at 552 and 392 nm. The former may be due to the spin forbidden transition $^6A_{1g} \rightarrow {}^4T_{2g}(G)$, 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 $^6A_1 \rightarrow {}^4T_1(G)$ transitions [18]. The magnetic moment of complex is 4.91 B.M. This value is quite low compared to the calculated magnetic moment value for mononuclear iron complexes [18,20].

On the other hand, the reflectance spectrum of the diamagnetic uranyl complex **6** showed two bands, in addition to the ligand bands The first band observed at >600 nm corresponding to charge transfer from equatorial donor atoms of the ligand to the uranyl ion which imparing the complex its red clour. The second band observed at 525 nm due to electronic transitions from apical oxygen atom to the f-orbitals of the uranyl atom characteristic of the uranyl moiety [18].

Table 4. Magnetic moment, spectral data (nm) and conductance measurements of **HL** and its metal complexes.

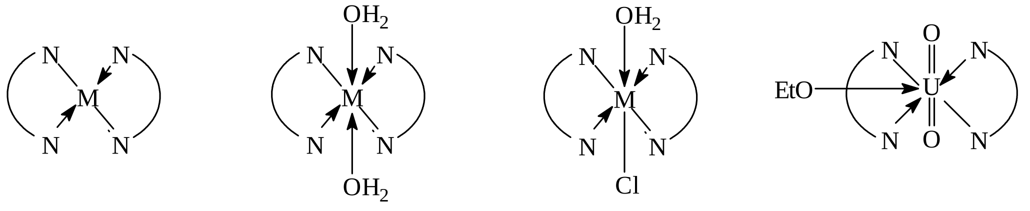
Compound	**$\mu_{eff.}$ B.M.**	$\pi \rightarrow \pi^*, n \rightarrow \pi^*$ and charge transfer transitions	$d \rightarrow d$ transitions	**EC[a]**
$C_{16}H_{12}N_3Cl$ (**HL**)	---	244, 325, 360, 422 (sh)	---	---
[Cu((L)$_2$]·EtOH (**1**) $C_{34}H_{28}N_6OCl_2Cu$	1.75	240, 321, 325, 348	665	2.4
[Ni(L)$_2$(OH$_2$)$_2$]·2EtOH (**2**) $C_{36}H_{38}N_6O_4Cl_2Ni$	3.19	235, 330, 355, 440	670 (sh), 768	2.0
[Co(L)$_2$(OH$_2$)$_2$] (**3**) $C_{32}H_{26}N_6O_2Cl_2Co$	5.32	235, 320, 355, 348	656, 477 (sh)	2.6
[Mn(L)$_2$(OH$_2$)$_2$] (**4**) $C_{32}H_{26}N_6O_2Cl_2Mn$	5.39	245, 315, 385, 349	469-853	2.4
[Fe(L)$_2$(Cl)(OH$_2$)$_2$]·3EtOH (**5**) $C_{38}H_{44}N_6O_5Cl_3Fe$	4.91	225, 315, 385, 340	552, 392	3.6
[UO$_2$(L)$_2$(OEt)]·EtOH (**6**) $C_{36}H_{33}N_6O_4Cl_2U$	---	245, 320, 355, 342	600, 525	1.5

[a] EC = Electrical Conductance, 10^{-3} M solution in DMF, Ohm^{-1} cm^{2}mol^{-1}.

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 are non-conducting indicating their neutrality and that the divalent cation have replaced the imine protons of two ligand molecules. Based on the above results the structures in Figure 2 are suggested for the metal complexes.

Figure 2. Suggested structures of the metal complexes of the **HL** ligand.



M = Cu(II) (**1**)

M = Ni(II) (**2**), Co(II)(**3**) or Mn(II) (**4**)

M = Fe(III) (5)

UO_2(VI) complex (**6**)

Thermal Analyses

The TG-DTA results of the solid complexes **1-6** are listed in Table 5. The results show good agreement with the formulae suggested from the analytical data (Table 1). A general decomposition pattern was concluded, whereby the complexes decomposed in three stages. Besides these three decomposition stages, those complexes which have coordinated water and/or alcohol exhibited additional decomposition steps.

Table 5. Thermal analyses data for some metal complexes of **HL**.

Compound (F. W.)	Dissociation Stages	Temp range in TG °C	Weight loss Found (Calcd.) %	Decomposition assignment
$[Cu((L)_2]\cdot EtOH$ (**1**) $C_{34}H_{28}N_6OCl_2Cu$ (670.5)	Stage I	75-110	7.40 (7.00)	Outer sphere EtOH
	Stage II	250-450 started	58.20 (57.60)	$C_{16}H_{11}N_3Cl$, N_2, C_6H_6
	Stage III	deligation	12.00 (11.53)	C_4H_2, HCN
	Stage IV	processes	13.30 (13.03)	C_2H_2, C_2HCl
$[Ni(L)_2(OH_2)_2]\cdot 2EtOH$ (**2**) $C_{36}H_{38}N_6O_4Cl_2Ni$ (747.5)	Stage I	75-110	12.63 12.31)	Outer sphere EtOH
	Stage II	250-450 started	5.21 (4.82)	Coordinated water molecules
	Stage III	deligation	52.00 (51.64)	$C_{16}H_{11}N_3Cl$, N_2, C_6H_6
	Stage IV	processes	11.10 (10.30)	C_4H_2, HCN
	Stage V		12.12 (11.60)	C_2H_2, C_2HCl
$[Co(L)_2(OH_2)_2]$ (**3**) $C_{32}H_{26}N_6O_2Cl_2Co$ (656)	Stage I	75-110	6.11 (5.50)	Coordinated water molecules
	Stage II	250-450 started	59.20 (58.84)	$C_{16}H_{11}N_3Cl$, N_2, C_6H_6
	Stage III	deligation	12.20 (11.74)	C_4H_2, HCN
	Stage IV	processes	13.81 (13.20)	C_2H_2, C_2HCl
$[Mn(L)_2(OH_2)_2]$ (**4**) $C_{32}H_{26}N_6O_2Cl_2Mn$ (652)	Stage I	75-110	5.56 (5.52)	Coordinated water molecules
	Stage II	250-450 started	59.64 (59.21)	$C_{16}H_{11}N_3Cl$, N_2, C_6H_6
	Stage III	deligation	12.51 (11.81)	C_4H_2, HCN
	Stage IV	processes	13.91 (13.30)	C_2H_2, C_2HCl
$[Fe(L)_2(Cl)(OH_2)_2]\cdot 3EtOH$ (**5**) $C_{38}H_{44}N_6O_5Cl_3Fe$ (826.5)	Stage I	75-110	17.30 (16.70)	Outer sphere EtOH
	Stage II	250-450 started	5.10 (4.40)	Coordinated water molecules
	Stage III	deligation	50.54 (50.88)	$C_{16}H_{11}N_3Cl$, N_2, C_6H_5Cl
	Stage IV	processes	9.00 (9.32)	C_4H_2, HCN
	Stage V		11.10 (10.50)	C_2H_2, C_2HCl

The first decomposition stage for complexes **1**, **2**, and **5** is the loss of the outer sphere ethanol molecules at 75-110 °C, followed in a second decomposition stage by the loss of the coordinated water molecules at 130-220 °C. After that, the deligation process started at a temperature range of 250-450 °C. Finally, at ~ 516 °C, metal-oxide formation takes place [21].

^{1}H-NMR Spectrum of the Uranyl Complex

The uranyl complex **6** was selected as it is diamagnetic. Its ^{1}H-NMR spectrum in DMSO-d_6 and after deuteration were examined. The spectrum of the complex differs from that of the free ligand in the following aspects:

1- The disappearance of the signal due to the imine group NH, is attributed to its involvement in coordinating the uranyl ion.
2- The signals due to the aromatic and quinoline rings appeared at δ = 7.26-8.67 ppm and showed fine structure.
3- The HC=N signal was unchanged, as observed in the parent ligand.

Antimicrobial Activitiy

The Schiff base and its metal complexes were evaluated for antimicrobial activity against one strain Gram +ve bacteria (*Staphylococcus aureus*), Gram -ve bacteria (*Escherichia coli*) and a fungus (*Candida albicans*) (Table 6).

Table 6. Antimicrobial activity of the Schiff base ligand and its metal complexes.

Compound	**Micro-organism**		
	Staphylococcus aureus **ATCC* 6538**	***Escherichia. coli*** **ATCC* 8739**	***Candida albicans*** **ATCC* 10231**
$C_{16}H_{12}N_3Cl$ (**HL**)	++	+	++
$[Cu((L)_2]\cdot EtOH$ (**1**) $C_{34}H_{28}N_6OCl_2Cu$	+++	+++	++
$[Ni(L)_2(OH_2)_2]\cdot 2EtOH$ (**2**) $C_{36}H_{38}N_6O_4Cl_2Ni$	++++	+++	++
$[Co(L)_2(OH_2)_2]$ (**3**) $C_{32}H_{26}N_6O_2Cl_2Co$	+++	++	+++
$[Mn(L)_2(OH_2)_2]$ (**4**) $C_{32}H_{26}N_6O_2Cl_2Mn$	++++	+++	+++
$[Fe(L)_2(Cl)(OH_2)_2]\cdot 3EtOH$ (**5**) $C_{38}H_{44}N_6O_5Cl_3Fe$	+++	+++	++++
$[UO_2(L)_2(OEt)]\cdot EtOH$ (**6**) $C_{36}H_{33}N_6O_4Cl_2U$	+++	+++	++
Streptomycin	++++	+++	+++

* number of strain in the ATCC collection
(a) *S. aureus*, (b) *E. coli*, (c) = *C. Albicans*. Inhibition zone diameter in nm (% inhabitation): +, 8-10 (36-45%); ++, 10-16 (45-73%); +++, 16-19 (73-86); ++++, 19-22 (86-100%). Percent inhibition values are relative to the zone (22 mm) with 100% inhabition.

The Schiff base ligand was found to be biologically active. It is known that chelation tends to make ligands act as more powerful and potent bactericidal agent and this was confirmed by the fact that the metal complexes showed enhanced antimicrobial activity against one or more strains, with complexes **4** and **5** remarkably showing 100% inhibition against *S. aureus* and *C. albicans*, respectively. It may be suggested that the chelated complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms. It has also been proposed that the ultimate action of the toxicant is the denaturation of one or more proteins of the cell, which as a result, impairs normal cellular process [1-12, 22].

Conclusions

The results of this investigation support the suggested structures of the metal complexes. Only mononuclear complexes were obtained for Cu(II), Ni(II) Co(II), Mn(II), Fe(III) and UO_2(II) cations in presence of LiOH. An octahedral geometry was suggested for all the complexes, except the Cu(II) and UO_2(VI) ones. The Cu(II) complex has a square-planar geometry distorted towards tetrahedral, while the U_2O(VI) one shows its favored heptacoordination. The Schiff base ligand was found to be biologically active and its metal complexes displayed enhanced antimicrobial activity against one or more strains. Chelation tends to make the ligand acts as more powerful and potent bactericidal agent

Experimental

General

Copper(II) acetate monohydrate, nickel(II) acetate tetrahydrate, uranyl(VI) acetate dihydrate, iron(III) chloride hexahydrate, cobalt(II) acetate tetrahydrate, manganese(II) acetate tetrahydrate, and lithium hydroxide monohydrate were obtained from BDH. 4,7-Dichloroquinoline, benzaldehyde, and hydrazine hydrate (100 %), were either BDH or Merck products and were used without further purification. Organic solvents used were reagent grade. Reflectance spectra of the ligand and its metal complexes were recorded as $BaSO_4$ discs using a model 1601 Shimadzu UV-Visible spectrophotometer in the 190-1100 nm range. The solution spectrum of the ligand in ethanol was recorded on a JASCO V-550 UV-Visible spectrophotometer in the 200-900 nm range. IR spectra were recorded using KBr discs on a FT-IR 1650 Perkin Elmer spectrometer. ^{1}H-NMR spectra were recorded in DMSO-d_6 at room temperature using TMS as internal standard on a Bruker 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 ($\mu_{eff} = 2.828 (\chi_m T)^{½}$ B.M. where χ_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 thermogravimetric analyzer in dry nitrogen atmosphere and a heating rate of 10 ^{o}C/min using the TA-50 WS1 program. Mass spectra were recorded at 70 eV and 300 ^{o}C on an MS 5988 Hewlett-Packard mass spectrometer. Conductance measurements of 10-3 M solutions of the complexes in DMF were carried out on a Corning 441 instrument. Melting points of the compounds were determined using a Gallenkamp (U.K.) electric melting point apparatus in the range of 0-400 ^{o}C. 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.

Synthesis of the Organic Ligand

The ligand was synthesized in two steps according to the reported method [23]. The first step is the synthesis of 7-chloro-4-hydrazinoquinoline, followed by the synthesis of the actual 7-chloro-4-(benzylidenehydrazo)quinoline ligand (**HL**) in the second step.

Synthesis of 7-Chloro-4-hydrazinoquinoline

Hydrazine hydrate (100 %, 25 mL, 50 mmol) in absolute ethanol (30 mL) was added to 4,7-dichloroquinoline (10 g, 5 mmol) dissolved in absolute ethanol (20 mL). The mixture was refluxed for 2h. After ½ h, a golden yellow precipitate started to precipitate. After the reflux time was reached, the mixture was allowed to cool for 6 h. The golden yellow precipitate was filtered and washed with absolute ethanol (5 mL) and recrystallized from ethanol to give the title compound (80 % yield, m.p. 223-225 ^{o}C).

Synthesis of 7-Chloro-4-(benzylidenehydrazo)quinoline (**HL**)

7-Chloro-4-hydrazinoquinoline (2 g, 1 mmol) was dissolved in absolute ethanol (10 mL). To this solution benzaldehyde (11.7 mL, 1.1 mmol) was added. The reaction mixture was refluxed for 2 h. After cooling, the formed yellow precipitate was collected, filtered and finally washed with absolute ethanol (5-10 mL) and purified by recrystallization from ethanol (85 %, m.p. 242 ^{o}C) [23].

Synthesis of the Metal Complexes **1-6**

First the reaction of a solution of the metal salt with the ligand solution was tried. If no or an extremely low yield of product was obtained, the same reaction was tried again after prior deprotonation of the ligand with LiOH. In practice deprotonation was a must in all reactions in order to obtain a good yield of product. The complexes were prepared using of 2:2:1 molar ratios of Li(OH)-ligand-metal salt. LiOH (0.42 g, 10 mmol) was dissolved in methanol (10 mL) and added dropwise to a stirred solution of the ligand (2.82 g. 10 mmol dissolved in 10 mL methanol). A solution of metal salt (5 mmol) dissolved in methanol (10 mL) was added gradually to the stirred solution of the lithium salt of the ligand. The reaction mixture was further stirred for 8-12 h to ensure the complete precipitation of the formed complexes. The precipitated solid complexes were filtered, washed several times with 50 % (v/v) methanol-water to remove any excess of the unreacted starting materials. Finally, the complexes were washed with diethyl ether and dried in vacuum desiccators over anhydrous $CaCl_2$.

Antibacterial and Antifungal Studies

The *in vitro* evaluation of antimicrobial activity was carried out at the Central Laboratory for Environmental Quality Monitoring, CLQM, El-Kanater, Kalubia, Cairo, Egypt. The tests were performed according to the diffusion technique [11,12, 22].

Microbial Cultures and Growth Conditions

Bacteria, including *Staphylococcus aureus* and *Escherichia coli* were grown in nutrient broth at 37 °C for 24 h. *Candida albicans* was grown in malt broth at 28 °C for 48h.

Activity Screening

The ligand and complexes were tested on solid media using the diffusion technique. Sterile diameter sensitivity discs (5 mm) were impregnated with different concentrations of the ligand or complexes in DMF. Discs of each tested compound were laid onto nutrient agar for bacteria or potato dextrose agar for fungi. Plates were surface spread with logarithmic phase bacteria or fungi cultures (0.2 mL). A spore suspension (10^8 spores/mL) for bacteria or filamentous fungi (0.5 mL) was also spread onto potato dextrose agar plates. The plates were then incubated for 24 h at 37 °C for bacteria and 28 °C for 48 h for fungi. Antibiotic discs for Streptomycin were additionally tested as positive control.

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Sample Availability: Samples are available from the author.