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Preparation and Characterization, Theoretical Treatment and Antibacterial of Mixed Ligand Complexes of Indol and N-Methyl Imidazol with Some Metal Ions

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An ethanolic solution of indol (In) was added to an aqueous solution of metal salt. This is followed by adding *N*-methyl imidazol (Im) and aqueous solution to give complexes with the general formula $[M(In)(Im)Cl_2]$ where M= Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ion. The metal complexes have been prepared and characterized by different analytical and spectral methods: FT-IR and UV-VIS. Spectroscopy and atomic absorption technique. The molar conductance studies of the complexes in DMSO at 10^{-3} concentration indicate their non-electrolytic nature for all prepared complexes. Room temperature magnetic susceptibility measurements tetrahedral structure. A theoretical treatment of the formation of complexes in the gas phase was studied, this was done using the HYPERCHEM-6 program for the molecular mechanics and semi-empirical calculations. The biological evaluation of the free ligand in comparison to their metal-complexes have been determined against bacterial strains *e.g.*, *Escherichia coli* and *Staphylococcus*. Finally, it was found that compounds show different activity of inhibition on growth of the bacteria.

Key Words: Mixed ligand complexes, Indol, N-Methyl imidazol.

INTRODUCTION

For a long time it has been shown that metal ions play an important role in biological systems, as exemplified by many instances in which enzymes are known to be activated by metal ions[1]. Vitamine B6 exists in the forms pyridoxal, pyridoxine and pyridoxamine. About 70-80 % of the vitamine B6 in the body is located in muscle, bound to glycogen phosphorylas, an enzyme envolved in releasing glucose from glygogen[2]. Hence mode of coordination of pyridoxine with nickel in presence of other ligands became important. Imidazol nitrogen donor atoms of histidyl residues are the most common binding sites various metaloenzymes[3]. Therefore ligands containing imidazol rings can potentially mimic the binding sites and catalytic activities of the enzymes. The stabilities of mixed chelates are of great importance in biological systems as many metabolic and toxicological functions are dependent upon this stability. Many attempts have been made to correlate the stability of the metal-ligand complexes with their antimicrobial activity[4,5].

Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals and actinide metal ions[6,7]. Anti tumor activity of some mixed ligand complexes have also been reported[8,9]. Therefore it was through undertake the study of mixed ligand complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with indol and imidazol. The metal complexes have been characterized by metal analysis and various physic-chemical techniques such as molar conductance, magnetic susceptibility, electron spectra and FT-IR spectra.

EXPERIMENTAL

All chemicals and reagents used in this investigation were labrotary pure (BDH chemicals, Sigma-Aldrich and E. Merk) including metal chloride, DMSO, C_2H_5OH and double distilled water.

Instrumentation: A Fisher-100 infrared spectrophotometer was used to recorded the IR spectra as KBr and CsI disc, UV/VIS spectra were measured by a HITACHI U-2000 spectrophotometer, determination of all metals percentage by atomic absorption spectrophotometry on AA-680G (Shimadzu). Electrical conductance was measured on conductivity CDC304 (Jenway4070) melting points determined by an electric heated block apparatus (Gallen Kamp) and were uncorrected. Room temperature magnetic susceptibility measurements were carried out on a B.M 6 BRUKER type magnets, balance, diamagnetic correction was done using pascal constants.

Preparation of mixed ligand complexes: General procedure for the synthesis of the complexes using the appropriate amounts of the chemicals according to the molar ratio (1:1:1) (M:In:Im). An ethanolic solution of Indol was added to an aqueous solution of metal salts followed by addition of

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF THE METAL(II) COMPLEXES

No.	Complexes (m.f.)	Colour	ΔM (Ω^{-1} cm^{2}mol^{-1}) In DMSO	m.p. (?C)	Yield (%)	$?_{eff.}$ BM	Elemental analysis found (%) calcd. (%)	
							M	Cl
1	[Co(In)(Im)Cl$_2$]/ $C_{11}H_{11}$ N_3Cl_2Co/315.06	Pink	8	75	75	3.70	18.66 (18.71)	22.46 (22.51)
2	[Ni(In)(Im)Cl$_2$]/ $C_{11}H_{11}$ N_3Cl_2Ni/314.82	Green-blue	9	80	60	3.30	18.60 (18.64)	22.47 (22.52)
3	[Cu(In)(Im)Cl$_2$]/ $C_{11}H_{11}$ N_3Cl_2Cu/319.68	Gray	6	131	70	1.80	19.84 (19.88)	22.14 (22.18)
4	[Zn(In)(Im)Cl$_2$]/ $C_{11}H_{11}N_3$ Cl_2Zn/321.54	White	5	67	65	-	20.30 (20.34)	22.01 (22.05)
5	[Cd(In)(Im)Cl$_2$]/ $C_{11}H_{11}N_3$ $CdCl_2$/368.54	White	4	88	68	-	30.45 (30.50)	19.19 (19.24)

TABLE-2
IR AND ELECTRONIC SPECTRAL DATA OF THE METAL(II) COMPLEXES

No.	Complexes	UV/ VIS λ_{max} (cm^{-1})	IR spectra (cm^{-1})		
			ν(C=N)	ν(N=H)	ν(M-N)
1	[Co(In) (Im) Cl$_2$]	37755, 23510, 18835, 12398, 10185	1610 m	3271 m	460 w
2	[Ni(In) (Im) Cl$_2$]	37215, 24710, 10135	1605 m	3265 m	465 w
3	[Cu(In) (Im) Cl$_2$]	12790, 18676	1615 m	3270 m	455 w
4	[Zn(In) (Im) Cl$_2$]	36198	1630 m	3260 m	460 w
5	[Cd(In) (Im) Cl$_2$]	36995, 29211	1625 m	3275 m	450 w

imidazol. Successively, the mixture was continuously stirred at 35 ºC and immediate precipitates were obtained. The products were filtered off, washed with ethanol, recrystallization from ethanol and dried at 60 ºC.

Antibacterial studies: The synthesized complexes, in comparison to the uncomplexed Schiff-base ligands were screened for their antibacterial activity against pathogenic bacterial species, which included *Escherichia coli*, as gram negative (-Ve) and *Staphylococcus aureus* as gram positive (+Ve). The paper disc diffusion method[9] was adopted for the determination of antibacterial activity.

RESULTS AND DISCUSSION

All the complexes prepared in this work were insoluble in common organic solvents such as water, methanol, ethanol, acetone, *etc*. but fairly soluble in dimethyl formamide and dimethyl sulfoxide. All the complexes were decomposed above 240 ºC.

The magnetic moments of the metal complexes were calculated from the measured magnetic susceptibility after employing diameter corrections. The observed μ_{eff} values presented in Table-1 suggest the tetrahedral geometry for all prepared complexes. The magnetic moments of the compounds investigated support the conclusion. The magnetic moments μ_{eff} of the metal complex of Cu(II) (d^9) was found to be 1.80 BM within the expected value for one electron. The μ_{eff} value for the following high spin tetrahedral complex was found to be as follows, for Co(II) (d^7) complex was 3.70 BM within the expected spin-only values[10]. The higher value of μ_{eff} for Ni(II) (d^8) complex was 3.30 BM, which may be due to orbital contribution[11]. The complexes of Zn(II) and Cd(II) were diamagnetic as expected from their electron configuration.

The molar conductivity of the mixed ligands complexes with the mentioned metal ion was measured using 10^{-3} DMSO solvent (Table-1) the obtained value suggest the presence of non-electrolyte nature[12].

Electronic spectra of free ligand: The electronic absorption spectra data in DMSO shows strong absorption band of indol, which is attributed to π→π*, another band is assigned to n→π*. The *N*-methyl imedazol spectra shows absorption bands due to π→π* and the other bands are due to n→π*.

[Co(In)(Im)Cl₂]: The electronic spectrum of the pink complex showed an absorption 37755 cm^{-1}, which is attributed to shift of ligand band to higher wave charge transfer, another absorption appeared at 23510, 18835 cm^{-1} was attributed to $^{4}A_{2(F)} \rightarrow {}^{4}T_{1(F)}$ transition. A third absorption appeared at 12398, 10185 cm^{-1} was assigned to $^{4}A_{2(F)} \rightarrow {}^{4}T_{2(F)}$ electronic transition. These value are accepted for cobalt(II) tetrahedral complex[13] (Table-2).

[Ni(In)(Im)Cl₂]: The spectrum of the green-blue complex of Ni(II) shows an absorption at 37215 cm^{-1} and it indicates a charge-transfer. Another absorptions appeared at 24710 and 10135 cm^{-1} were attributed to the electronic transitions: $^{3}T_{1(F)} \rightarrow {}^{3}A_{2(F)}$, $^{3}T_{1(F)} \rightarrow {}^{3}T_{1(P)}$ and $^{3}T_{1(F)} \rightarrow {}^{3}T_{2(F)}$, respectively. These transitions characteristic for tetrahedral complexes of Ni(II)[13] (Table-2).

[Cu(In)(Im)Cl₂]: The gray complex of Cu(II) exhibited absorption band in the visible region at 12790 and 18676 cm^{-1}, which belong to electronic transition $^{3}T_{1(D)} \rightarrow {}^{2}E_{(D)}$ (Table-2).

[Zn(In)(Im)Cl₂] and [Cd(In)(Im)Cl₂]: The electronic configuration of Zn(II) and Cd(II) complexes were (d^0), which confirms the absence of any (d-d) transitions. The absorption bands in their spectra were suffered blue shift with hypo or hyper chromic effect[13]. All the data and remarks are included in Table-2.

The infrared spectrum of indol shows weak band at 3298 cm^{-1}, which belong to ν(N=H). Weak and sharp band at 3111 cm^{-1}, which belongs to ν(C-H) aromatic[14]. Another weak band belong to ν(C-H) aliphatic was found at 2952 cm_{-1}[15]. The strong broad band at 1658 cm^{-1} was attributed to ν(-N=C)[16]. The ν(C=C) was noticed at 1546 cm^{-1} with shoulder at 1600 cm^{-1}.

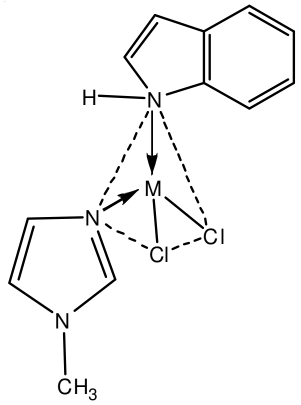
In the spectrum of *N*-methyl imidazol two bands were noticed at 3050 cm^{-1} and 2950 cm^{-1}, which are attributed to ν(C-H) aromatic and aliphatic respectively. The band at 1645 cm^{-1} was assigned as ν(N=C) whereas the ν(C-C) was found at 1550 cm^{-1}.

The FT-IR spectra of the metal complexes were obtained in KBr discs over range 4000-400 cm^{-1} (Table-2) exhibited ν(C-H) aromatic in the region of 3030-3050 cm^{-1}. The bands in the range of 1610-1630 cm^{-1} belong to the ν(-N=C). It shows a shift to lower frequencies by 40-25 cm^{-1} compared with Indol and by 30-15 cm^{-1} compared with imidazol spectra which indicates the coordination of the ligands with the metal ions through the nitrogen atoms in their structures.

The coordination of the ligands to the metal ions was further confirmed by the weak bands between 540-510 cm^{-1} indicating the ν(M-N) bond[17], which are absent in the spectra obtained for the ligands.

Conclusion

In this paper, new Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) coordination with indol and *N*-methyl imidazol were synthesized. The molar conductivity of complexes in DMSO solution were non-electrolyte. The configuration was performed to coordinate the indol and *N*-methyl imidazol through the nitrogen atom. Thus, from the results presented the metal complexes have tetrahedral configuration (Fig. 1).



M= Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

Fig. 1. Proposed structure of metal(II) complexes

Theoretical study: The ball and cylinders and some of selected structural parameters (bond length and angles) of the optimized geometries are shown in Fig. 2 (Table-3). As shown in this figure, there is no obvious trend for the variation of these parameters. The values of the bond length and angles of the optimized geometries are quite similar to the experimental results of the corresponding compounds.

Antibacterial properties: The Schiff-base ligands and their transition metal complexes were evaluated for their antibacterial activity against bacterial species *Escherichia coli* and *Staphylococcus aureus* of bacteria[18,19]. The compounds were tested at a concentration of 10^{-3} M in DMSO solution using the paper disc diffusion method. The susceptibility zones were measured in diameter (mm) and the results are reproduced in (Fig. 3). The susceptibility zones measured were the clear zones around the discs killing the bacteria.

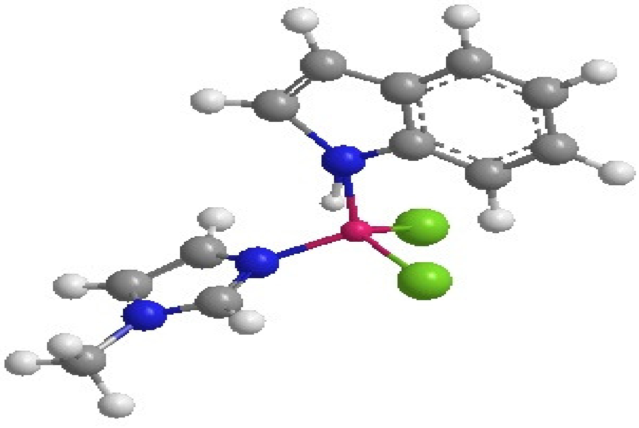


Fig. 2. Optimized structural geometry of Co(II) complexes

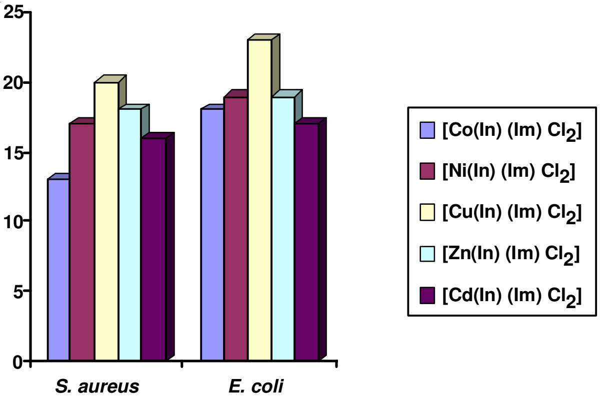


Fig. 3. Effect of the transition metal complexes toward bacteria

All the Schiff-bases and their transition complexes individually varying degrees of inhibitory effects on the growth of the tested bacterial species. The antibacterial results evidently show that the activity of the Schiff-base compounds became more pronounced when coordinated to the metal ions.

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TABLE-3
STRUCTURAL PARAMETERS, BOND LENGTH (Å) AND ANGLES (°) OF THE [Co(In)(Im)Cl_2] COMPLEXES

Parameters		Parameters		Parameters	
Bond lengths	Å	Dihedral angles	Å	Bond angles	Å
CC(13)-H(26)	1.1000	C(2)-N(1)-Co(15)-Cl(17)	-133.8916	N(1)-Co(15)-N(14)	180.0000
C(12)-H(25)	1.1000	C(2)-N(1)-Co(15)-Cl(16)	46.1084	N(1)-Co(15)-Cl(16)	90.0000
C(10)-H(24)	1.1000	C(2)-N(1)-Co(15)-N(14)	-89.9997	N(1)-Co(15)-Cl(17)	90.0000
C(8)-H(23)	1.1000	C(9)-N(1)-Co(15)-Cl(17)	46.1084	N(14)-Co(15)-Cl(16)	90.0000
C(7)-H(22)	1.1000	C(9)-N(1)-Co(15)-Cl(16)	-133.8916	N(14)-Co(15)-Cl(17)	90.0000
C(6)-H(21)	1.1000	C(9)-N(1)-Co(15)-N(14)	90.0003	Cl(16)-Co(15)-Cl(17)	180.0000
C(5)-H(20)	1.1000	C(13)-N(14)-Co(15)-Cl(17)	133.8912	Co(15)-N(14)-C(10)	124.5000
C(3)-H(19)	1.1000	C(13)-N(14)-Co(15)-Cl(16)	-46.1088	Co(15)-N(14)-C(13)	124.5000
C(2)-H(18)	1.1000	C(13)-N(14)-Co(15)-N(1)	89.9993	C(10)-N(14)-C(13)	111.0000
N(1)-Co(15)	1.8360	C(10)-N(14)-Co(15)-Cl(17)	-46.1088	H(26)-C(13)-N(14)	129.4041
N(14)-Co(15)	1.8360	C(10)-N(14)-Co(15)-Cl(16)	133.8912	H(26)-C(13)-C(12)	129.4041
Co(15)-Cl(16)	2.1500	C(10)-N(14)-Co(15)-N(1)	-90.0007	N(14)-C(13)-C(12)	101.1918
Co(15)-Cl(17)	2.1500	N(11)-C(10)-N(14)-C(13)	0.0010	H(25)-C(12)-C(13)	123.5959
C(10)-N(14)	1.2660	N(11)-C(10)-N(14)-Co(15)	-179.9990	H(25)-C(12)-N(11)	123.5959
C(13)-N(14)	1.2660	H(24)-C(10)-N(14)-C(13)	-179.9990	C(13)-C(12)-N(11)	112.8082
C(12)-C(13)	1.3460	H(24)-C(10)-N(14)-Co(15)	0.0010	C(12)-N(11)-C(10)	104.0000
N(11)-C(12)	1.2600	C(12)-C(13)-N(14)-C(10)	-0.0014	H(24)-C(10)-N(14)	124.5000
C(10)-N(11)	1.2600	C(12)-C(13)-N(14)-Co(15)	179.9986	H(24)-C(10)-N(11)	124.5000
C(4)-C(9)	1.3370	H(26)-C(13)-N(14)-C(10)	179.9986	N(14)-C(10)-N(11)	111.0000
N(1)-C(9)	1.2660	H(26)-C(13)-N(14)-Co(15)	-0.0014	C(4)-C(9)-N(1)	111.0000
C(8)-C(9)	1.3370	N(11)-C(12)-C(13)-N(14)	0.0014	C(4)-C(9)-C(8)	119.9986
C(7)-C(8)	1.3370	N(11)-C(12)-C(13)-H(26)	-179.9986	N(1)-C(9)-C(8)	128.9980
C(6)-C(7)	1.3372	H(25)-C(12)-C(13)-N(14)	-179.9986	H(23)-C(8)-C(9)	120.0000
C(5)-C(6)	1.3370	H(25)-C(12)-C(13)-H(26)	0.0014	H(23)-C(8)-C(7)	120.0000
C(4)-C(5)	1.3370	C(10)-N(11)-C(12)-C(13)	-0.0009	C(9)-C(8)-C(7)	120.0000
C(3)-C(4)	1.3370	C(10)-N(11)-C(12)-H(25)	179.9991	H(22)-C(7)-C(8)	120.0023
C(2)-C(3)	1.3370	N(14)-C(10)-N(11)-C(12)	0.0000	H(22)-C(7)-C(6)	120.0023
N(1)-C(2)	1.5975	H(24)-C(10)-N(11)-C(12)	180.0000	C(8)-C(7)-C(6)	119.9955
		C(3)-C(4)-C(9)-C(8)	179.3824	H(21)-C(6)-C(7)	120.0023
		C(3)-C(4)-C(9)-N(1)	0.0000	H(21)-C(6)-C(5)	120.0023
		C(5)-C(4)-C(9)-C(8)	-1.2353	C(7)-C(6)-C(5)	119.9955
		C(5)-C(4)-C(9)-N(1)	179.3824	H(20)-C(5)-C(6)	120.0000
		C(2)-N(1)-C(9)-C(8)	-179.3123	H(20)-C(5)-C(4)	120.0000
		C(2)-N(1)-C(9)-C(4)	-0.0005	C(6)-C(5)-C(4)	120.0000
		Co(15)-N(1)-C(9)-C(8)	0.6877	C(9)-C(4)-C(5)	119.9986
		Co(15)-N(1)-C(9)-C(4)	179.9995	C(9)-C(4)-C(3)	111.0000
		C(7)-C(8)-C(9)-N(1)	-179.9993	C(5)-C(4)-C(3)	128.9980
		C(7)-C(8)-C(9)-C(4)	0.7426	H(19)-C(3)-C(4)	124.5000
		H(23)-C(8)-C(9)-N(1)	0.0007	H(19)-C(3)-C(2)	124.5000
		H(23)-C(8)-C(9)-C(4)	-179.2574	C(4)-C(3)-C(2)	111.0000
		C(6)-C(7)-C(8)-C(9)	0.2426	H(18)-C(2)-C(3)	129.4884
		C(6)-C(7)-C(8)-H(23)	-179.7574	H(18)-C(2)-N(1)	129.4884
		H(22)-C(7)-C(8)-C(9)	-179.7574	C(3)-C(2)-N(1)	101.0232
		H(22)-C(7)-C(8)-H(23)	0.2426	Co(15)-N(1)-C(9)	127.0116
		C(5)-C(6)-C(7)-C(8)	-0.7352	Co(15)-N(1)-C(2)	127.0116
		C(5)-C(6)-C(7)-H(22)	179.2648	C(9)-N(1)-C(2)	105.9768
		H(21)-C(6)-C(7)-C(8)	179.2648		
		H(21)-C(6)-C(7)-H(22)	-0.7352		
		C(4)-C(5)-C(6)-C(7)	0.2426		
		C(4)-C(5)-C(6)-H(21)	-179.7574		
		H(20)-C(5)-C(6)-C(7)	-179.7574		
		H(20)-C(5)-C(6)-H(21)	0.2426		
		C(3)-C(4)-C(5)-C(6)	-179.9993		
		C(3)-C(4)-C(5)-H(20)	0.0007		
		C(9)-C(4)-C(5)-C(6)	0.7426		
		C(9)-C(4)-C(5)-H(20)	-179.2574		

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