

Synthesis and Structural Studies of Some Transition Metal Complexes Using 2-[(5'- Chloro-2'-methyl phenyl) azo]-4,5-diphenyl imidazole (CLIMPAI) as New Ligand

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Abstract

Some Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) complexes with new aryl azo-4,5-diphenyl imidazole (CLIMPAI) as ligand were synthesized and characterized spectroscopically (IR and UV-Vis) along with elemental analysis, molar conductance and magnetic susceptibility measurements.

1. Introduction

Imidazole is a ubiquitous ligand in chemical and biological systems⁽¹⁻³⁾. The molecule has two nitrogen atoms, respectively of the pyridine and pyrrole type; high reactivity with metals is expected because of the strong basicity of the pyridine-type nitrogen in compared with pyridine molecule⁽⁴⁾. In addition, various analogs can be prepared because of the coupling at 2-positions is easily achieved in compared with pyridine⁽⁵⁾. Arylazoimidazoles have been used to explore the coordination chemistry of various metal ions⁽⁶⁻¹⁰⁾. The molecules belong to unsymmetrical N,N'-chelating ligands, and the active function is the azoimine group —N=N—C=N— , which is (π - acidic) group and stabilizes low valent metal redox state^(11,12).

This paper describe the synthesis, and characterization of new arylazoimidazole ligand and some of its transition metal complexes.

2. Experimental

2.1. Materials and methods

All chemicals are of highest purity and used as supplied by the manufactures except of 4,5-diphenyl imidazole was prepared as described previously⁽¹³⁾.

Microanalysis (C,H,N) performed using on a Micro analytical unit of 1108 C.H.N Elemental analyzer. IR spectra (CsI Pellets) were recoded using a Pye-Unicom SP3-300 spectrophotometer. Electronic spectra were recorded using Shimadzu UV-Vis. 1700 spectrophotometer. Electrical conductivity was measured by (HI9321) conductivity meter with solute concentration of (10^{-3}M) in DMSO. The magnetic susceptibility were measured on powdered samples using Faraday method, Balance Magnetic (MSB-MKI) had been employed.

2.2. Synthesis of azo ligand (CIMPAl)

The azo ligand was prepared following the procedure as described for 2-(aryl azo) imidazoles⁽⁵⁾. The details are given as follows; adiazonium solution was prepared by dissolving (1.415g, 10 mmol) of 5-chloro-2-methyl aniline in 40 cm³ of ethanol-water (1:1, v/v) and 4 cm³ of concentrated hydrochloric acid. The solution cooled to 0–5°C, treated with 15 cm³ of aqueous (1.0M) sodium nitrite drop-wise with continuous stirring. The resulting solution was added drop-wise with stirring to a solution of 4,5-diphenyl imidazole (2.2g, 10 mmol) in pyridine 150 cm³. The mixture was allowed to stand overnight then acidified with dilute hydrochloric acid until (pH = 5) was reached. The precipitate was filtered off, dried, and recrystallized twice from ethanol then dried in the oven at 70°C for several hours. The structural formula of this ligand is shown in Fig.1.

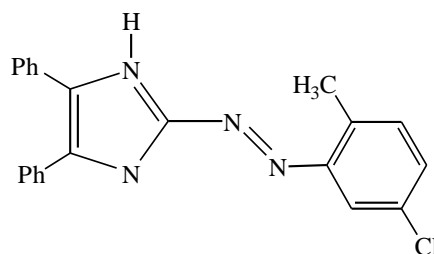


Fig.1: Structural formula of the ligand (CIMPAl)

2.3. Synthesis of complexes

The chelat complexes have been obtained by adding (0.373 g, 1 mmol) of ligand dissolved in ethanol 20 cm³ to a hot solution of metal chloride (1 mmol) dissolved in the same solvent 20 cm³. The reaction mixture was refluxed for 30 min., then concentrated until the solid compounds precipitated. They were filtered off, washed with ethanol 5 cm³ to remove the remaining un reacted substances, and dried over CaCl₂.

3. Results and Discussion

3.1. Characterization of the (CIMPAl) ligand and its complexes

The azo ligand (CIMPAl) are orange crystals, but the prepared complexes of this ligand vary in color from red to green. The complexes are stable at room temperature and soluble in methanol, ethanol, acetone, DMF and DMSO, but insoluble in water. The elemental analyses and metal contents data, table.1, for the ligand and their complexes are in a good agreement with the suggested formula.

3.2. Metal : ligand ratios

The metal : ligand ratios of complexes were determined by the method of molar ratio at fixed wavelength of maximum absorption. The results are given in table.2. The ligand was found to form (1:1) chelates with all our metal ions mentioned above. These results are in agreement with the values reported for some aryl azo imidazoles complexes⁽¹⁴⁻¹⁶⁾.

3.3. Calculation of chelat complexes stability constants

Stability constant of our complexes are obtained spectrophotometrically by measuring the absorbance of solutions of the mixture of the ligand and metal ion at fixed wavelength. The degree of formation of the complex (β) is obtained from the relationship⁽¹⁷⁾.

$\beta = (1 - \alpha)/\alpha^2 c$ and $\alpha = (A_m - A_s)/A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complexes respectively. The calculated (β) and ($\log \beta$) values are listed in table.2.

3.4. Infrared spectra

The major IR bands of the ligand and their complexes with Co(II), Ni(II), Cu(II), Zn(II), and Pd(II) respectively are given in table.3. The major IR bands of ligand were assigned as reported in literature^(4,9,18). The complexes spectra and this of ligand have been studied as follow.

The absorption band at 3360 cm^{-1} in the spectrum of free ligand may be attributed to the $\nu(\text{N-H})$ of imidazole ring⁽¹⁹⁾. This band remains in the same region in all complexes spectra except at Cu(II) complex. Thus, the remaining of amine hydrogen group intact in solid complexes, indicating it's non involvement in coordination of the ligand to the metal ions⁽¹⁹⁾. In the spectrum of Cu(II) complex the broad band at approximately 3390 cm^{-1} belongs to the stretching mode of the (O-H) bond in water molecule like wise a weak band is observed at 830 cm^{-1} which can be assigned to the stretching vibration of the (M-OH₂)⁽²⁰⁾.

The spectrum of ligand shows absorption band at 1635 cm^{-1} due to $\nu(\text{C=N})$ of imidazole ring. This band shifts to lower frequency $1625 - 1620\text{ cm}^{-1}$ with little change in shape. These differences suggest the linkage of metal ions with N₃ imidazole nitrogen⁽²¹⁾.

The $\nu(\text{N}=\text{N})$ stretching vibration appears at 1510 cm^{-1} in the free ligand spectrum. This band appearing at $1495 - 1485\text{ cm}^{-1}$ with some decrease in intensity, of the complexes spectra. Both shift and reduced in intensity may indicate the formation of the complex ⁽²²⁾.

In the far IR spectra of all chelates, there are new bands observed in the region of $560-290\text{ cm}^{-1}$. these bands did not present in the spectrum of ligand may be attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ provide evidences concerning the bonding of nitrogen and chloride to the metal ions⁽²³⁾, therefor, the IR spectra indicate that azo ligand (CLMPAI) behaves as a bidentate N,N' - chelating agent. [N(imine) refers to N and N(azo) refers to N']. Representative example for their spectra is given in Fig. 2.

3.5. Electronic spectra, Magnetic susceptibility and Conductivity measurement

The data obtained from the measurements of electronic spectra, conductivity and magnetic susceptibility given in table.4.

- a. **Co(II) complex:** the electronic spectrum of Co(II) complex show one absorption band at 13200 cm^{-1} characteristic of tetrahedral geometry⁽²⁴⁾. This band assigned to the transition $^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{p})$ (ν_3). The magnetic moment value of the complex (4.51 B.M.) which is well within the range of tetrahedral complex⁽²⁵⁾. The conductivity value of ($5.3\text{ S.mol}^{-1}\text{ cm}^2$) refers to nonionic structure ⁽²⁶⁾.
- b. **Ni(II) complex:** the electronic spectrum of this complex exhibit one band at 15820 cm^{-1} may be due to $^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{p})$ (ν_3) transition, and another band at 28900 cm^{-1} which assigned to charge transfer band. The complex has magnetic moment value of (3.8 B.M.) which is within the range for tetrahedral complex⁽²⁷⁾. Electrical conductivity ($4.5\text{ S.mol}^{-1}\text{ cm}^2$) shows nonionic structure.
- c. **Cu(II) complex:** the electronic spectrum of this complex shows a band centered at 16393 cm^{-1} which may assigned to $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ transition in an approximately octahedral geometry⁽²⁸⁾. The magnetic moment value of this complex is (1.7 B.M.), which may suggest an octahedral structure. The conductivity value ($6.2\text{ S.mol}^{-1}\text{ cm}^2$), is indicating noconductive species.
- d. **Pd(II) complex:** the electronic spectrum of this complex showed absorption band at the position 23310 cm^{-1} which is refers to the transition $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$. the appearance of this band confirmed the square planar geometry ⁽²⁹⁾. Moreover, the magnetic moment has a value

of (0.3 B.M.) which supports this suggestion⁽³⁰⁾. Electrical conductivity of ($6.1 \text{ S.mol}^{-1} \text{ cm}^2$) shows nonionic structure.

- e. Zn(II) complex:* this complex does not show any d–d transition bands, its diamagnetic moment. Finally the conductivity value of this complex ($5.95 \text{ S.mol}^{-1} \text{ cm}^2$) indicates nonionic structure.

According to these results the structural formulas of these complexes may be proposed in Figs. 3, 4 and 5.

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Table.1: Analytical and physical data of the ligand and its complexes

No.	Compound	Color	M.P °C	Yield%	Formula	Found, (calc.)%			
						C	H	N	M
1	L = (CLMPAI)	Orange	112	73	C ₂₂ H ₁₇ N ₄ Cl	70.68 (70.87)	4.42 (4.56)	15.17 (15.03)	----
2	[CoLCl ₂]	Pale- brown	139	62	C ₂₂ H ₁₇ N ₄ Cl ₃ Co	52.37 (52.54)	3.22 (3.38)	11.25 (11.14)	11.38 (11.73)
3	[NiLCl ₂]	Pale- brown	166	65	C ₂₂ H ₁₇ N ₄ Cl ₃ Ni	52.29 (52.57)	3.19 (3.38)	11.02 (11.15)	11.25 (11.68)
4	[CuLCl ₂ (H ₂ O) ₂]	Green	195	59	C ₂₂ H ₂₁ N ₄ O ₂ Cl ₃ Cu	48.44 (48.61)	3.62 (3.87)	10.17 (10.31)	11.92 (11.70)
5	[PdLCl ₂]	Brown	182	70	C ₂₂ H ₁₇ N ₄ Cl ₃ Pd	51.67 (51.87)	3.22 (3.34)	11.16 (11.00)	-----
6	[ZnLCl ₂]	Red	173	67	C ₂₂ H ₁₇ N ₄ Cl ₄ Zn	47.88 (48.00)	3.00 (3.09)	10.29 (10.18)	12.54 (12.85)

Table.2: Metal : Ligand ratios determination by the method of mole ratio and stability constant values

Ligand	Metal ion	pH	λ_{\max} (nm)	Metal : ligand	β	Log β
CIMPAl	Co(II)	6.5	430	1 : 1	1.031×10^5	5.013
	Ni(II)	6.5	620	1 : 1	2.158×10^5	5.334
	Cu(II)	5.5	610	1 : 1	4.927×10^7	7.692
	Zn(II)	6.0	486	1 : 1	8.527×10^4	4.930
	Pd(II)	6.5	429	1 : 1	1.316×10^6	6.119

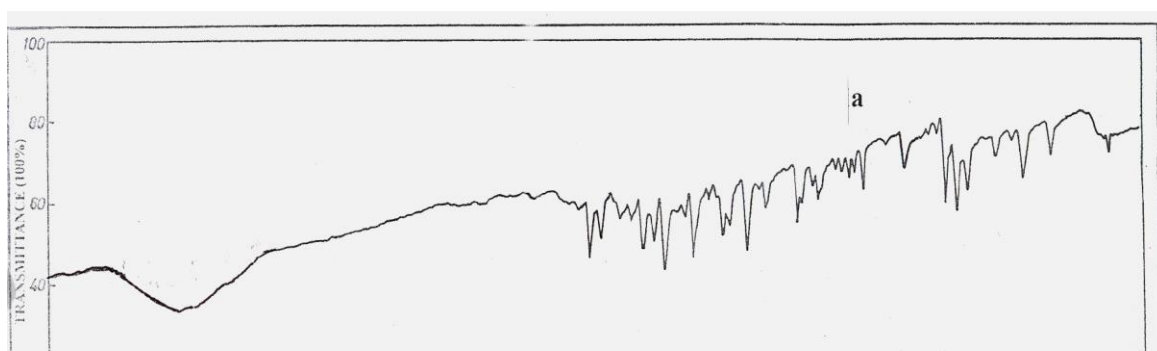
Table.3: IR spectra frequencies for the ligand and its metal complexes in cm^{-1} units

Compound	$\nu(\text{O—H})$	$\nu(\text{N—H})$	$\nu(\text{C=N})$	$\text{N}(\text{N=N})$	$\nu(\text{M—OH}_2)$	$\nu(\text{M—N})$	$\nu(\text{M—Cl})$
L = (CIMPAl)	----	3360 w	1635 s	1510 m	-----	-----	-----
[CoLCl ₂]	----	3360 w	1625 m	1495 m	-----	560 w	300 w
[NiLCl ₂]	----	3360 w	1620 s	1490 w	-----	555 w	295 w
[CuLCl ₂ (H ₂ O) ₂]	3390 w.br	----	1620 m	1490 w	830 w	540 w	290 w
[PdLCl ₂]	----	3360 w	1625 m	1485 m	-----	540 w	290 w
[ZnLCl ₂]	----	3360 w	1620 m	1490 m	----	545 w	290 w

L = ligand, w = weak, s = strong, m = medium, br = broad

Table.4: Electronic spectra, Conductivity, and Magnetic moment of complexes

Compound	Absorption bands (cm^{-1})	Transition	Conductivity $\text{S.mol}^{-1} \text{cm}^2$	μ_{eff} (B.M)
[CoLCl ₂]	13200	$^4\text{A}_2(\text{F}) \rightarrow ^4\text{T}_1(\text{p}) \nu_3$	5.3	4.51
[NiLCl ₂]	15820 28900	$^3\text{T}_1(\text{F}) \rightarrow ^3\text{T}_1(\text{p}) \nu_3$ C.T	4.5	3.8
[CuLCl ₂ (H ₂ O) ₂]	16393	$^2\text{E}_g \rightarrow ^2\text{T}_{2g}$	6.2	1.7
[PdLCl ₂]	23310	$^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$	6.1	0.3
[ZnLCl ₂]	----	----	5.9	dia.



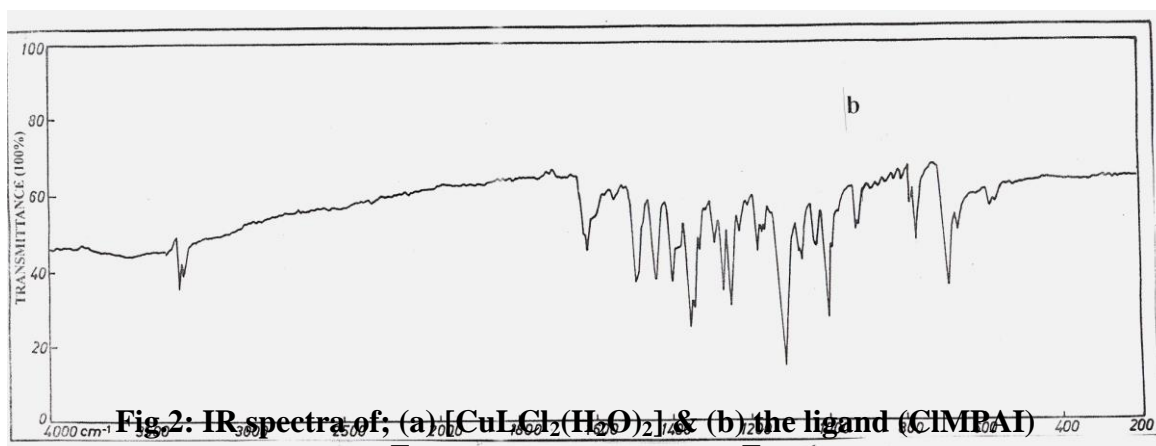
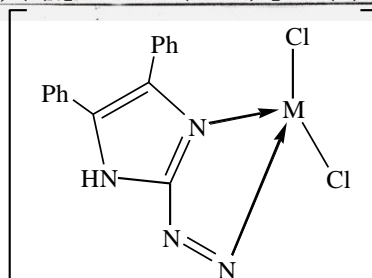


Fig.2: IR spectra of; (a) $[CuLCl(H_2O)]$ & (b) the ligand (ClMPAI)



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

Fig.3: The proposed structural formula of Co(II), Ni(II), Zn(II) complexes

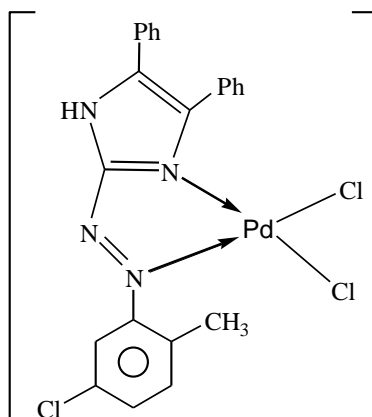


Fig.4: The proposed structural formula of Pd(II) complex

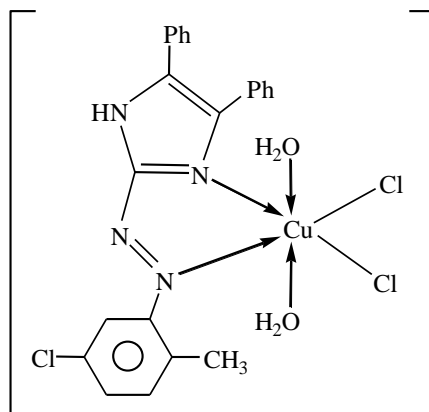


Fig.5: The proposed structural formula of Cu(II) complex

تحضير ودراسة تراكيب بعض معقدات العناصر الانتقالية باستخدام 2-[5'-كلورو-2'-مethyl فنيل] آزو-5,4-ثنائي فنيل
اميدازول [CIMPAL] كليكاند جديدة

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الخلاصة

تضمن البحث تحضير معقدات جديدة لأيونات الكوبلت (II) والنيكل (II) والنحاس (II) والخاصين (II) والبلاد يوم (II) مع مركب أريل آزو-5,4-ثنائي فنيل إمدازول (CIMPAL) كليكاند جديدة شخضت المعقدات الصلبة طيفياً باستخدام الأشعة تحت الحمراء وفوق البنفسجية المرئية بالإضافة إلى التحليل الدقيق للعناصر والتوصيلية المولارية والحساسية المغناطيسية كما تم اقتراح الهندسة الجزيئية لكل منها.