

New metal chelate complexes of azoligand derived from 4,5-diphenylimidazole

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Abstract

Coupling reaction of (3,5-Dichlorophenyldiazonium chloride) with 4,5-diphenylimidazole in alkaline alcoholic medium yielded a new azoligand 2-[(3,5-Dichlorophenyl)azo]- 4,5-diphenylimidazole (dcpai). The structure and nature of this organic ligand and its metal complexes with Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were established on the basis of available technique such as elemental analysis, molar conductance measurements, magnetic susceptibility, IR and electronic spectral data. The spectral and analytical data revealed that this ligand coordinated through the nitrogen atom of azomethine group of heterocyclic imidazole ring and the other nitrogen atom of azo group which is the farthest of imidazole molecule. The geometry of the prepared metal complexes are discussed based on analytical and spectral data.

Keywords: *Azoligand, coupling reaction, metal complexes.*

1. Introduction

The imidazoles are common components of a large number of natural products and pharmacologically active molecules^(1,2). The biological importance of the imidazole ring system has made it a common structure in numerous synthetic compounds, such as fungicides⁽³⁾, herbicides⁽⁴⁾, plant growth regulators⁽⁵⁾, and therapeutic agents⁽⁶⁾. In recent years, substituted imidazoles have been used as components of provided ionic liquids⁽⁷⁾ that have a new approach to "Green Chemistry". Azoimidazole compounds were found to be valuable dyes⁽⁸⁾, as well as they were applied for analytical separation and microdetermination of some metal cations⁽⁹⁻¹¹⁾. This class of ligand possess active (π -acidic) azo imine ($-N=N-C=N-$), function and efficient agents to stabilize low valent metal oxidation states^(12,13), due to the presence of azo-centered π^* -molecular orbital, for this reason a number of these azo compounds were prepared and used as chelating ligands⁽¹⁴⁻¹⁶⁾. In via of this importance we report in this paper the preparation and characterization of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes with new azoimidazole ligand.

2. Experimental

2.1. Physical Measurements

All chemicals used in the syntheses were of reagent grade and used without further purification. The compound 4,5-diphenylimidazole was prepared according to the literature method⁽¹⁷⁾. All melting points were determined by the open capillary method and are reported in °C, by using a Stuart melting point SMP10. The analyses of C, H and N of the ligand and its metal complexes were carried out on a C.H.N.O.S. EA 3000 elemental analyzer. The metal contents of complexes were determined using atomic absorption technique by Shimadzu AA-6300 spectrophotometer. IR spectra were recorded in KBr disc on a Shimadzu 8400, FTIR spectrophotometer. The electronic spectra were recorded in ethanol (10^{-3} M) solution on a Shimadzu UV-Vis 1700

spectrometer. Magnetic susceptibility measurements of the complexes were done on (MSB-MKI) balance at room temperature, the diamagnetic corrections were made by Pascal's constants. Molar conductance was measured in DMSO (10^{-3} M) by using Alpha Digital conductivity meter model 800 at room temperature. IR spectra were recorded in KBr disc on a Shimadzu 8400, FTIR spectrophotometer

2.2. Preparation of the azo ligand (dcpai)

In a typical preparation, 25 mL of distilled water containing 3 mL hydrochloric acid was added to (1.62g, 0.01 mol) 3,5-dichloroaniline. The resulting mixture was stirred and cooled to 0 °C, then a solution of (0.69 g, 10 mmol) sodium nitrite in 20 mL of water was added dropwise. The so-formed diazonium chloride was consecutively coupled with an alkaline solution of (2.20 g, 10 mmol) 4,5-diphenyl-imidazole, in 150 mL of ethanol. The orange solution produced, which formed immediately, was left in the refrigerator over night. The mixture was acidified with dilute hydrochloric acid until (pH = 6). The formed precipitate was filtered off, washed several times with water and air dried. The crude product was purified by recrystallization twice from hot ethanol, then dried over anhydrous CaCl_2 . The ligand, illustrated in Fig.1.

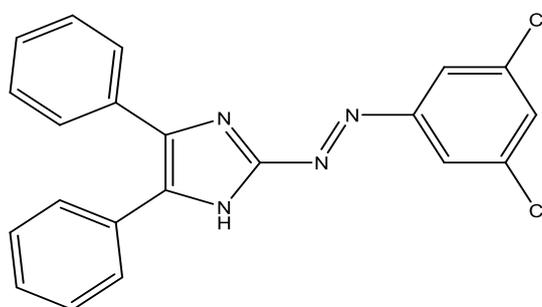


Fig.1 : Structural formula of azoligand (dcpai)

2.3. Preparation of chelate complexes

The complexes were prepared by adding the appropriate amount of the metal salt (1mmol), namely $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, ZnCl_2 and CdCl_2 dissolved in the least amount of distilled water to (0.786 g, 2 mmol) of ligand (dcpai) dissolved in 50 cm^3 of ethanol. The reaction mixture was refluxed for 30 min with constant stirring. The precipitated solid complexes were filtered, washed with 3 mL hot 1:1 ethanol-water to remove any traces of the unreacted starting materials. Finally, the complexes were washed with 2 mL diethyl ether and dried over anhydrous CaCl_2 .

3. Results and discussion

3.1. Characterization of ligand and its metal complexes

The ligand was orange powder, but the obtained complexes were found to be amorphous deep coloured compounds and stable at room temperature. The ligand and its chelate complexes were insoluble in water but soluble in most organic solvents. The elemental analysis are in agreement with the formulae of the ligand and its complexes given in Table.1.

3.2. The effect of pH

The pH of metal complex solutions was adjusted using dilute solutions (0.1M) sodium acetate, acetic acid and ammonia, and the effect on absorbance was studied. A maximum absorbance was obtained in the pH range given in Table.2.

3.3. Composition of the complexes

The composition of the complexes was studied by molar ratio method at fixed pH and concentration at wavelengths of maximum absorption. A break at a 1:2 (M:L) mole ratio suggested the formation of $M(dcpai)_2$ where $M = Co(II), Ni(II), Cu(II), Zn(II)$ and $Cd(II)$ under the given conditions. The results are given in Table.2, these results are in agreement with the values reported for some aryl azo 4,5-diphenyl-imidazole complexes^(18,19).

3.4. Calculation of the metal complexes stability constant

Stability constants are obtained spectrophotometrically by measuring the absorbance of solutions mixture of ligand and metal ion at fixed wavelength λ_{max} and optimum pH values. The degree of formation of the complexes is calculated according to the relationship⁽²⁰⁾, $\beta = (1 - \alpha) / (4\alpha^3 c^2)$, and $\alpha = (A_m - A_s) / A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The calculated β and $\log \beta$ values for the prepared complexes are listed in Table.2, the stability follows the sequence; $Co(II) < Ni(II) < Cu(II) > Zn(II) < Cd(II)$, the sequence of metal ions of the first row transition metal agree with Irving-Williams series of stability constant⁽²¹⁾.

3.5. IR spectra

Selected IR absorption of the ligand and its complexes are given in Table.3. In order to study the binding mode of the azo ligand to the metal ion of the complexes, the IR spectrum of the free ligand was compared with the spectra of the chelate complexes. The IR spectrum of the ligand shows a weak broad band at 3380-3320 cm^{-1} assignable to the $\nu(N-H)$ of imidazole ring⁽²²⁾. This band remains in the same region in the free ligand and in solid complexes spectra. Thus, the remaining of the hydrogen of (N-H) group indicates non involvement in coordination of the ligand to the metal ions⁽²³⁾. The ligand shows its characteristic $\nu(=C=N-)$ band of the N3 imidazole nitrogen at 1600 cm^{-1} , which shows little change in shape and shifted to lower frequencies 1590-1580 cm^{-1} in the spectra of the complexes. These differences suggest the chelation of metal ion with nitrogen of azomethine group⁽²⁴⁾. Upon comparison, it was found that the $\nu(N=N)$ stretching vibration in free ligand was at 1450 cm^{-1} which shifted to 1435-1420 cm^{-1} in complexes, indicating the participation of azo nitrogen in coordination^(25,26). New bands found in the spectra of complexes in the region 535-520 cm^{-1} have been assigned to $\nu(M-N)$ mode⁽²⁷⁾. Hence, it is concluded that the coordination to the metal ion occurs through the nitrogen atom of azo group nearest to a phenyl ring, and N3 atom of the imidazole ring, to give five-membered chelate ring.

3.6. Magnetic Properties and Electronic Spectra

As further structural tools, magnetic and electronic spectra studies have been used to confirm the geometry of the complexes. The spectral data and magnetic moments are listed in Table.4.

1- Cobalt (II) Complex

The magnetic moment of this complex was measured at room temperature and found to be (4.42 B.M) which correspond to three unpaired electrons⁽²⁸⁾. The 10^{-3} ethanolic solution spectrum of above complex exhibited two absorption bands at 16260 and 20790 cm^{-1} , respectively. The spectrum resemble those reported for octahedral complexes⁽²⁹⁾. Thus, the various bands can be assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$, respectively.

2- Nickel (II) Complex

The value of magnetic moment for Ni(II) complex was found to be (3.12 B.M), which can be a normal value for octahedral Ni(II) complexes⁽³⁰⁾. The electronic spectrum of this complex show bands at 16639 cm⁻¹ and 21930 cm⁻¹, which suggests the existence of ³A_{2g} → ³T_{1g}(F), and ³A_{2g} → ³T_{1g}(P) transitions with an octahedral spatial configuration⁽³¹⁾.

3- Copper(II) Complex

The magnetic moment value of the Cu(II) complex is (1.76 B.M), which may suggest an octahedral structure. It's electronic spectrum shows a band centered at 15748 cm⁻¹ which may assigned to ²E_g → ²T_{2g} transition in an approximately octahedral environment⁽³²⁾.

4- Zinc(II) and Cadmium(II) Complexes

The magnetic susceptibility show that these complexes have diamagnetic moment, and do not show any d→d transition band.

3.5. Conductivity Measurements

All metal complexes showed the conductivity measurement values ranging between (6.82 - 8.35) S. mol⁻¹. cm², Table.4, in DMSO at room temperature, these values indicating that no conductive species exist⁽³³⁾.

According to there results the structural formula of chelate complexes may be proposed as shown in Fig.2.

4. Conclusions

In this paper, coordination chemistry of arylazo ligand(dcpai), obtained from the coupling reaction of 3,5-dichlorophenyl diazonium chloride salt with 4,5-diphenyl-imidazole, is described, Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes have been prepared using the above azoligand and characterized by spectral and analytical data. Based on these data, the octahedral geometry has been suggested to all chelete complexes.

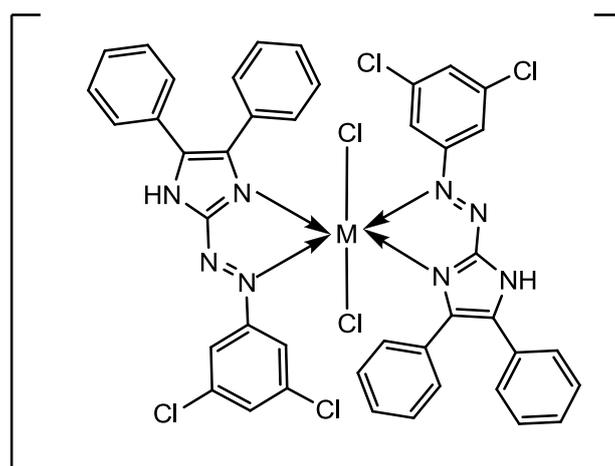


Fig.2: The suggested geometry of chelete complexes
M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)

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

Compound	Color	M.P. °C	Yield %	Formula	Found (Caled) %			
					C	H	N	M
L=(dcpai)	Orange	265-266	77	C ₂₁ H ₁₄ N ₄ Cl ₂	63.89 (64.12)	3.50 (3.56)	14.32 (14.25)	-----
[Co(L) ₂ Cl ₂]	Brown	208-210	69	CoC ₄₄ H ₂₈ N ₈ Cl ₆	55.12 (55.02)	2.98 (3.05)	12.31 (12.22)	6.27 (6.44)
[Ni(L) ₂ Cl ₂]	Brown	177-178	75	NiC ₄₄ H ₂₈ N ₈ Cl ₆	54.87 (55.05)	3,00 (3.05)	12,14 (12.23)	6.22 (6.41)
[Cu(L) ₂ Cl ₂]	Deep Black	169-171	81	CuC ₄₄ H ₂₈ N ₈ Cl ₆	54.65 (54.75)	2.91 (3.04)	12.02 (12.16)	6.68 (6.89)
[Zn(L) ₂ Cl ₂]	Red	185-186	72	ZnC ₄₄ H ₂₈ N ₈ Cl ₆	54.70 (54.64)	2.96 (3.03)	12.23 (12.14)	6.89 (7.08)
[Cd(L) ₂ Cl ₂]	Red	230-231	62	CdC ₄₄ H ₂₈ N ₈ Cl ₆	51.73 (51.99)	2.83 (2.88)	11.68 (11.55)	-----

Table.2: The optimum pH, λ_{max} and the calculated stability constant values

Ligand	Metal ion	pH	λ_{max} nm	β	log β
(dcpai)	Co(II)	8.0	615	2.015×10^7	7.312
	Ni(II)	7.5	601	2.228×10^8	8.348
	Cu(II)	6.5	635	2.951×10^9	9.470
	Zn(II)	7.5	581	2.588×10^6	6.413
	Cd(II)	8.0	595	6.668×10^6	6.824

Table.3: Some IR frequencies (in cm⁻¹) of the azo imidazole ligand and its metal complexes

Compound	$\nu(N-H)$	$\nu(C=N)$	$\nu(N=N)$	$\nu(C-Cl)$	$\nu(M-N)$
(dcpai)	3380-3320 wbr	1600 m	1450 wsh 1430 m	710 m	-----

[Co(L) ₂ Cl ₂]	3370-3330 wbr	1590 m	1420 wsh 1400 m	705 m	520 w
[Ni(L) ₂ Cl ₂]	3370-3335 wbr	1585m	1415 wsh 1400 m	715m	535w
[Cu(L) ₂ Cl ₂]	3385-3340 wbr	1590 w	1420 s 1400 w	705 m	525 w
[Zn(L) ₂ Cl ₂]	3380-3335 wbr	1580 s	1425w 1410 m	710 m	530 w
[Cd(L) ₂ Cl ₂]	3385-3350 wbr	1590 s	1435 msh -----	710 m	530w

s = strong, w = weak, m = medium, br = broad, sh = shoulder

Table.4: Electronic spectra, conductivity and magnetic moment of complexes

Complex	Absorption bands (cm ⁻¹)	Transition	Conductivity S. mol ⁻¹ . cm ²	μ _{eff} (B.M)
[Co(L) ₂ Cl ₂]	16260 20790	⁴ T _{1g} → ⁴ A _{2g} (F) ⁴ T _{1g} → ⁴ T _{1g} (P)	8.35	4.42
[Ni(L) ₂ Cl ₂]	16639 21930	³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (p)	6.82	3.12
[Cu(L) ₂ Cl ₂]	15748	² E _g → ² T _{2g}	8.37	1.76
[Zn(L) ₂ Cl ₂]	-----	-----	7.41	dia
[Cd(L) ₂ Cl ₂]	-----	-----	6.94	dia

معقدات فلزية كلابية جديدة لليكاند آزو مشتق من 4,5- ثنائي فنيل إמידازول

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الخلاصة

تضمن البحث تفاعل إزواج كلوريد (3,5- ثنائي كلورو كلورو فنيل الديدازونيوم) مع 4,5- ثنائي فنيل إמידازول في محيط قاعدي كحولي لتحضير ليكاند الأزو الجديد 2- [(3,5- ثنائي كلورو فنيل) أزو]-4,5- ثنائي فنيل إמידازول (dcpai). تم معرفة تركيب الليكاند وطبيعته بالإضافة إلى معقداته الكلابية مع أيونات كل من الكوبلت (II) و النيكل (II) والنحاس (II) والخاصين (II) والكادميوم (II) من خلال معطيات تحاليل التقنيات المتاحة مثل التحليل الدقيق للعناصر و التوصيل الكهربائي المولاري و قياسات الحساسية المغناطيسية و أطيف الأشعة تحت الحمراء و الأطيف الإلكتروني. لقد بينت نتائج هذه التحاليل أن الليكاند تتناسق عن طريق ذرة نيتروجين مجموعة الأزوميثين لحقة الاميدازول غير المتجانسة من جهة ذرة نيتروجين مجموعة الأزو البعيدة عن جزيئة الاميدازول. كما تم اقتراح الأشكال الفراغية للمعقدات المحضرة بالاستناد إلى نتائج التحاليل المذكورة.

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