

Preparation and Spectral Study of Some Metal(II)-Azo Complexes With Bidentate Azo Ligand

Sba.A. Aty

Dep. of Chemistry, College of Pharmacy, University of Kufa

Abid Allah. M. Ali

Dep. of Chemistry, College of Education for Women, University of Kufa

ABSTRACT

Five coordination compounds, with general formula $[M(HL)_2Cl_2] \cdot xH_2O$, $[M=Co(II), Ni(II), Cu(II), Zn(II) \text{ and } Cd(II), x=1 \text{ or } 2]$ were prepared by reacting chloride salts of these metal with new azo-oxime ligand (E)-1-(4-((E)-(4,5-dimethyl-1-H-imidazole-2-yl) diazenyl) phenyl) ethanone oxime (HL), which was prepared by coupling of diazonium salt of 4-Aminoacetophenoneoxime with 4,5-diphenylimidazole. The heterocyclic azo-oxime ligand and its chelate complexes were identified by available techniques and the results showed that all chelate complexes have octahedral geometry.

Keywords: *Azo -oxime, chelate complexes, preparation, identification.*

INTRODUCTION

Imidazole is a class of heterocyclic organic compound with the formula $C_3H_4N_2$. This aromatic molecule is a "1, 3-diazole" and is classified as an alkaloid⁽¹⁾. Aryl azoimidazoles play an important role as chelating agents for a large number of metal ions⁽²⁻⁹⁾. Different oximes and their metal complexes have shown notable bioactivity as chelating therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides^(10,11). Azo-oxime compounds possessing both azo and hydroxyimino groups, and the area for preparation of this class of organic compounds has not been developed so far. To our knowledge the literature survey showed that no work has been reported about preparation of metal-azo complexes derived from 2-arylaazo-4,5-diphenyl imidazole-oxime. In this study, the preparation and identification of new azo-oxime ligand and some of its metal(II) chelate complexes is described.

This work is a part of M. Sc Thesis

EXPERIMENTAL

Materials and method

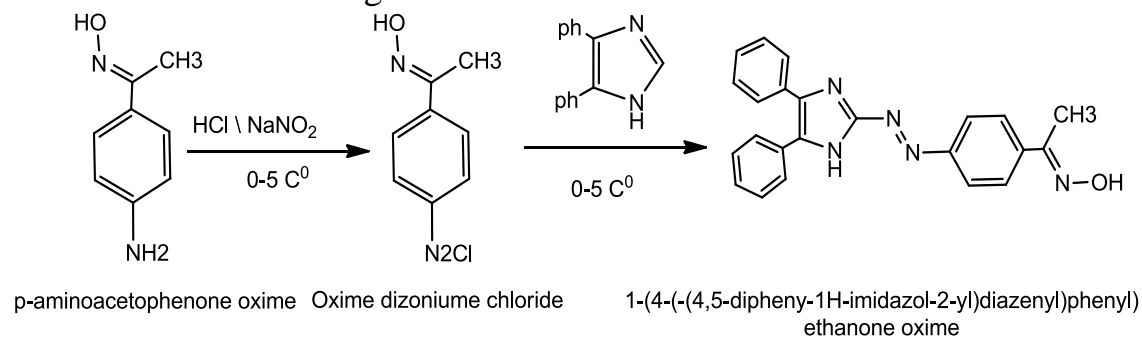
All chemicals used were of analytical reagent grade and employed directly without further purification, except of 4,5-diphenyl imidazole was

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prepared and characterized as reported procedure⁽¹²⁾. All melting points were determined on an Stuart melting point SMP10 apparatus and are uncorrected. Elemental analyses (C, H, and N) were performed using a C.H.N.O EA- 034mc elemental analyzer. The content of metal ions was measured using atomic absorption technique by Shimadzu AA-6300. Molar conductance measurements of ligand complexes with (1.0×10^{-3} mol L⁻¹) in ethanol were carried out using Digital conductivity series. Lab. 720. Magnetic measurements were determined by faraday method at room temperature using Balance Magnetic (MSB-MKI) apparatus, and diamagnetic corrections for the ligand were calculated using Pascal's constant⁽¹³⁾. The UV-Vis spectra were recorded in ethanol (1.0×10^{-3} mol L⁻¹) for the ligands and their metal chelate complexes with a Shimadzu 1700 UV Spectrophotometer using 1 cm quartz cell from (1100-200) nm range. Infrared (IR) spectra ($4000-400$ cm⁻¹) were recorded as KBr pellets on a Shimadzu FT-IR 8400 Spectrophotometer.

Preparation of the ligand

The azo-oxime ligand (HL) was prepared using the known coupling procedure⁽¹⁴⁾. A mixture of 4-aminoacetophenone oxime (1.50 g, 10 mmol), ethanol (50 mL), and concentrated hydrochloric acid (2.5 mL) was stirred until a clear solution was obtained. This solution was cooled to 0°C and a solution of sodium nitrite (0.70 g, 11 mmol) in water (10 mL) was added drop wise while the temperature was maintained below 5°C. The resulting diazonium chloride solution was added slowly to the solution of 4,5-diphenyl imidazole (2.20 g, 10 mmol) dissolved in (150 mL) alkaline ethanol cooled below 5°C. In the course of dropping, the temperature and pH of the mixture were maintained at 0-5°C and 9-10, respectively. The reaction mixture was stirred for 1 h at 5 °C, allowed to warm slowly to room temperature and then acidified with (2 mol L⁻¹) hydrochloric acid. The product was collected by filtration and washed with (500 mL) cooled water and air dried. The obtained deep orange solid was dried under vacuum at 80 °C overnight.



Scheme.1: Preparation of heterocyclic azo-oxime (HL) ligand

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Preparation of chelate complexes

Metal chelate complexes were prepared by mixing (50 mL) hot ethanolic solution containing (0.381g, 1mmol) of (HL) ligand with (0.5mmol) from [Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)] chlorides respectively, dissolved in (4 mL) of distilled water. The resultant mixtures were stirred for 30 min, solid complexes precipitated, were collected by filtration, washed several times with (1:1) ethanol: water mixture and dried over anhydrous CaCl₂.

RESULTS AND DISCUSSION

The prepared ligand and its metal complexes were stable in atmosphere and were found to be solids, insoluble in water but soluble in most common organic solvents such as methanol, ethanol, acetone, chloroform, DMF, DMSO and pyridine. The experimental results of the elemental analyses of the ligand and its chelate complexes are in good agreement with theoretical expectations. The elemental analyses of the complexes indicate that the (metal : ligand) ratios were 1:2 in the [M(HL)₂Cl₂]. xH₂O [M = Co(II), Ni(II), Cu(II), Zn(II), or Cd(II)] metal complexes. Table.1 gives some physical properties and analytical data of the ligand and its mononuclear complexes.

Infrared Spectra

The main infrared bands and their assignments are listed in Table 2. The IR spectra of the complexes were compared carefully with that of ligand in order to determine the involvement of coordination sites in chelation. Weak and broad band around (3200 cm⁻¹) which can be attributed to (-N-H-)⁽¹⁵⁾.stretching vibration of the imidazole moiety, we were unable to locate this band in the spectra of complexes in order to receive the band characteristic of hydrated water molecules which were associated with chelate complexes⁽¹⁶⁾. The band, appearing at (1651 cm⁻¹) due to (-C=N-) group of oximate moiety⁽¹⁷⁾, remains unaffected in the spectra of complexes which clearly indicates its non-participation in the process of complexation^(18,19). The spectrum of the ligand shows absorption band at(1600 cm⁻¹) due to (-C=N-) of the N3 imidazole nitrogen, its observed with a little change in shape and shifted to lower frequencies (1575-1616 cm⁻¹) in the complexes spectra these differences suggest the linkage of metal ion with nitrogen imidazole ring⁽²⁰⁻²¹⁾. A band, observed at (1445 cm⁻¹) in the ligand spectrum, due to (-N=N-) group appearing in the region (1440-1467 cm⁻¹) with different in shape and reduced in intensity in the spectra of prepared complexes, confirming involvement of azo-nitrogen in bonding with metal ions⁽²²⁾. This was also supported by appearance of a new band at (418–430 cm⁻¹) due to $\nu(M-N)$ ⁽²³⁾. These results indicate that

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the ligand is coordinated to metal ions through the azomethine nitrogen of heterocyclic imidazole molecule and nitrogen atom of azo group to form five member chelating ring. Figures. 1 and 2, shows the infrared spectra of (HL) and [Cu(HL)₂Cl₂]. H₂O complex.

Electronic Spectra

The electronic spectra of the azo-oxime ligand and all metal complexes were recorded in ethanol at room temperature. The UV-Vis spectral data of the ligand and its complexes are given in Table.3. The aromatic peaks of (HL) at (23474 and 37593 cm⁻¹), which may be ascribed to, ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$), intra-ligand charge transfer transitions respectively^(24,25). Solution electronic spectra of Co(II), Ni(II) and Cu(II) chelate complexes showed intense transition peaks at (22935, 21097 and 20080 cm⁻¹) which are assigned to ligand centered transitions, along with another intense peaks at longer wavelength, (35211, 36496 and 35971 cm⁻¹), may be referred to the combination of MLCT [$d\pi(M^{2+}) \rightarrow \pi^*(L)$] transitions where $\pi^*(L)$ is believed to be primarily dominated by the LUMO of the azoimine chromophore^(26,27). Zn(II) and Cd(II) metal complexes have (d^{10}) configuration and the electronic spectra of these coordination compounds exhibit high intense charge transfer transition in the visible region (20080 and 37593 cm⁻¹) which are assigned to (MLCT)⁽²⁸⁾.

Magnetic measurements

The magnetic moment value for the Co(II) complex at (4.83 B.M.) it consistent with stated in letriture⁽²⁹⁾. regarding the value of the magnetic moment of the cobalt(II) high-spin octahedral complexes, when the effective magnetic moment lies between (5.20 - 3.87 B.M) at room temperature there is consistently a considerable orbital contribution. The magnetic moment for the complex of Ni(II) (d^8) was found to be (3.26 B. M) which is with the range of octahedral Ni(II) complexes. While Cu(II) (d^9) complex has magnetic moment value at (1.82 B.M., this value indicate to magnetic properties for single electron of copper(II), octahedral geometry. Zn(II), and Cd(II) metal complexes are diamagnetic consistent with the (d^{10}) configuration⁽³⁰⁾. The magnetic moment data of prepared complexes are listed in Table.3.

Molar Conductance

The conductance of solutions of the complexes in ethanol (10^{-3} M) at room temperature are shown in Table.3. The low molar conductance values lying in the range (9.88 – 12.29) S. cm². mol⁻¹ confirmed the nonionic behavior of all the complexes⁽³¹⁾.

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Conclusions

The spectral, molar conductance and magnetic studies of the azo-oxime ligand and complexes derivatives from 4,5-diphenylimidazole reveals that Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) metal complexes are having octahedral geometry. According to the above data the structural formula of metal complexes may be proposed in Figure.3.

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

Compound	Formula (F.W. g/mol)	m.p. °C	Yield %	Color	Calculated (Found) (%)			
					C M	H	N	
C ₂₃ H ₁₉ N ₅ O =HL	HL = C ₂₃ H ₁₉ N ₅ O 381.43	-128 125	81.9	Deep orange	72.44 (72.19)	4.98 (4.89)	18.37 (18.18)	---
[Co(HL) ₂ Cl ₂]. H ₂ O	[C ₄₆ H ₄₀ N ₁₀ O ₃ Cl ₂ Co] 908.90	167- 169	78.7	Redish brown	60.73 (60.55)	4.40 (4.28)	15.40 (15.19)	4.48 (4.21)
[Ni(HL) ₂ Cl ₂]. H ₂ O	[C ₄₆ H ₄₀ N ₁₀ O ₃ Cl ₂ Ni] 908.70	162- 164	74.3	Brown	60.74 (60.49)	4.40 (4.26)	15.40 (15.26)	6.45 (6.23)
[Cu(HL) ₂ Cl ₂]. H ₂ O	[C ₄₆ H ₄₀ N ₁₀ O ₃ Cl ₂ Cu] 913.50	d >375	76.8	Red	60.42 (60.21)	4.37 (4.26)	15.32 (15.16)	6.95 (6.80)
[Zn(HL) ₂ Cl ₂]. H ₂ O	[C ₄₆ H ₄₀ N ₁₀ O ₃ Cl ₂ Zn] 915.40	171- 173	70.9	Deep brown	60.30 (60.19)	4.36 (4.22)	15.29 (15.11)	7.14 (7.29)
[Cd(HL) ₂ Cl ₂]. 2H ₂ O	[C ₄₆ H ₄₂ N ₁₀ O ₄ Cl ₂ Cd] 980.40	141- 143	74.5	Brown	56.30 (56.12)	4.28 (4.16)	14.54 (14.38)	11.46 (.....)

d = decomposed

Table.2: FT.IR frequencies (in cm⁻¹) of the azo-oxime ligand and its chelate complexes

Compounds	(N-H)	(NO-H)	(C-H)Ar	(C=N) _{Schi}	ν (N=N)	ν (C=N)	(N=O)	(M-N)
(H L)	3200	3050	3061 w	1651	1454	1600	----
[Co(HL) ₂ Cl ₂]. H ₂ O	32200	3097	2902	1681	1456	1599	1525 (1348)	418
[Ni(HL) ₂ Cl ₂]. H ₂ O	3200	3059	2890	1680	1467	1597	1525 (1350)	430
[Cu(HL) ₂ Cl ₂]. H ₂ O	3180	3090	2933	1681	1460	1620	1525 (1346)	425
[Zn(HL) ₂ Cl ₂]. H ₂ O	3200	3080	2900	1681	1456	1575	1525 (1350)	426
[Cd(HL) ₂ Cl ₂].2H ₂ O	3200	3057	2900	1683	1440	1616	1525 (1350)	428

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Table.3: Electronic spectra, magnetic measurements, and molar conductance of metal complexes

Compounds	$(\pi \rightarrow \pi^*)(\text{cm}^{-1})$	$(n \rightarrow \pi^*)(\text{cm}^{-1})$	μ_{eff} (B.M)	Λ_M (S.cm ² .mol ⁻¹)
[Co(HL) ₂ Cl ₂].H ₂ O	22935	35211	4.83	11.22
[Ni(HL) ₂ Cl ₂].H ₂ O	21097	36496	3.26	10.75
[Cu(HL) ₂ Cl ₂].H ₂ O	20080	35971	1.82	9.88
[Zn(HL) ₂ Cl ₂].H ₂ O	20080	36231	Dia	12.29
[Cd(HL) ₂ Cl ₂]. 2H ₂ O	22321	37593	Dia	11.52

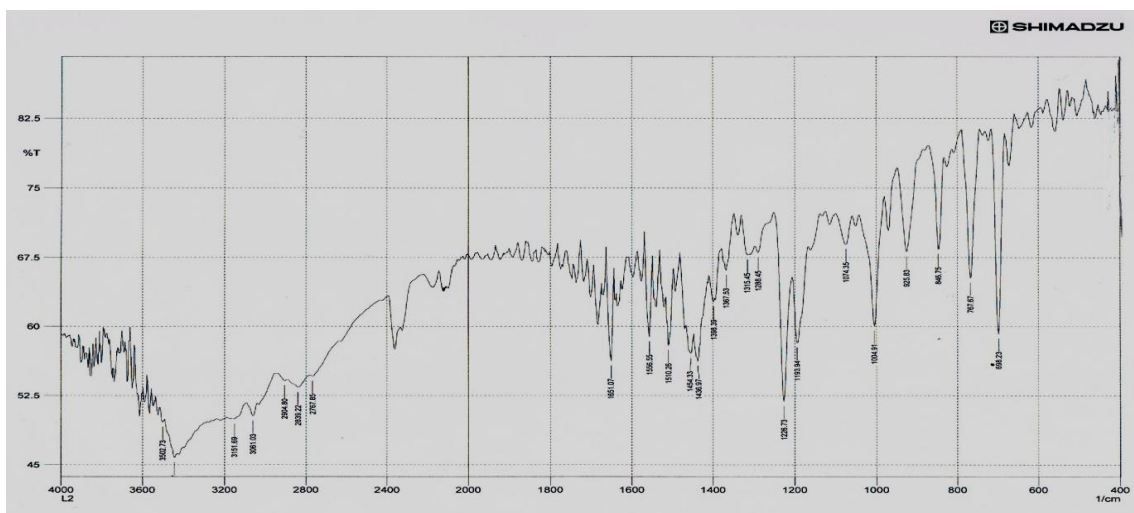


Fig (1): FT-IR spectrum of (HL) ligand

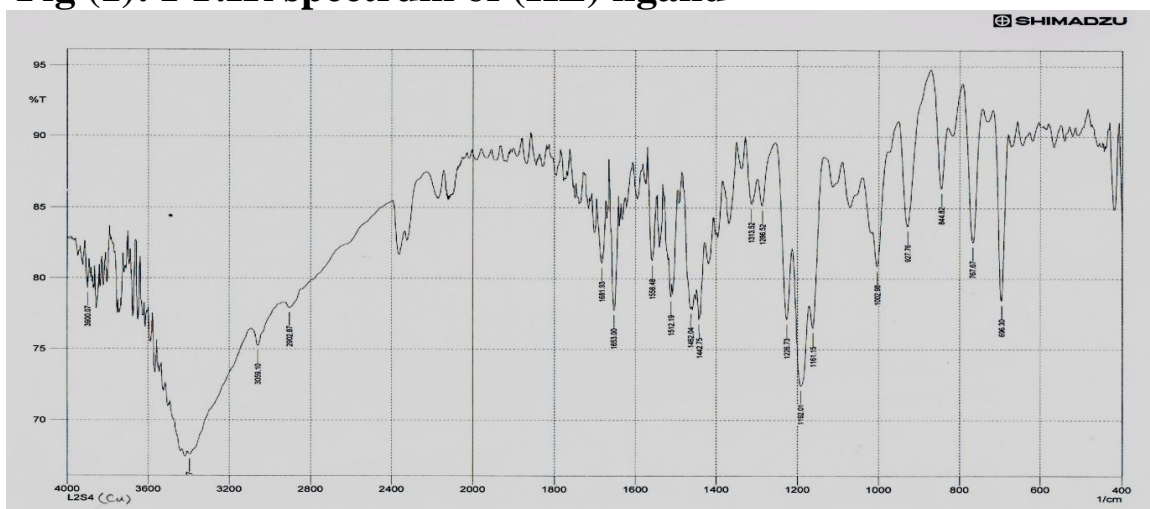


Fig (2): FT-IR spectrum of [Cu(HL)₂Cl₂]. H₂O complex

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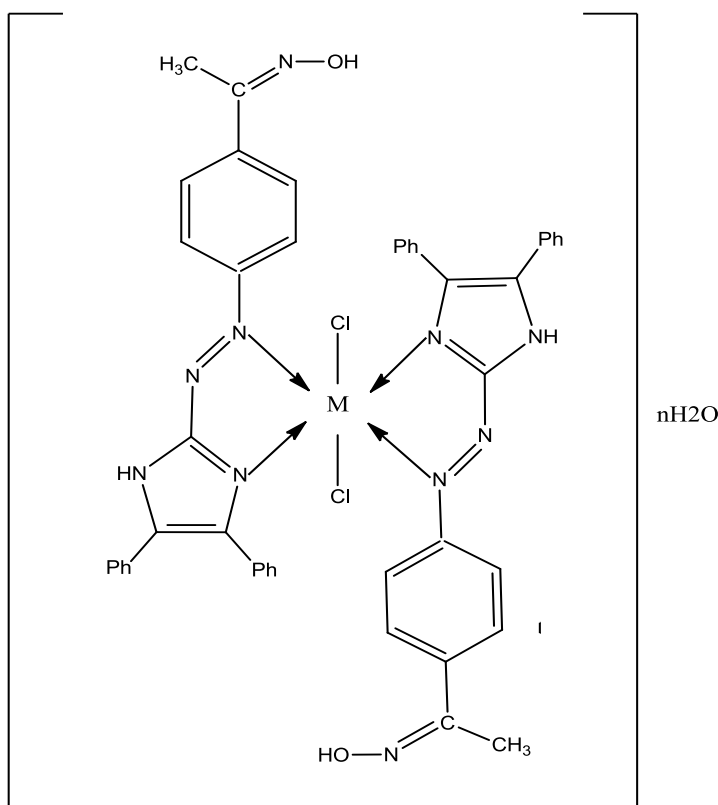


Figure.3: The structural formula of metal complexes n=2 to the Cd

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