Synthesis and spectral study of Co(II) and Cu(II)complexes using the ligand 2-(2-naphthyl azo)- 4,5-diphenyl imidazole

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Abstract

In this study the ligand 2-(2- naphthyl azo) -4,5-diphenyl imidazole was prepared by the reaction between 2- naphthyl amine and 4,5-diphenyl imidazole in alkaline alcoholic solution. The ligand was examined by using element analysis, UV-Vis. and infrared spectra. Also this research involved the rapid and sensitive determination of cobalt(II) and copper(II) using this ligand at (λ_{max} =550 and 556) nm and pH (9.2 and 5.9) respectively and the mole ratio was 1:2 (metal : ligand). Beer`s law is obeyed in the range (1x10^{-4}- 5x10^{-4})M of Co(II) and (1x10^{-5}-5x10^{-5}) M of Cu(II) with molar absorpitivity (Є =2250-1550) L.mole^{-1}.cm^{-1} respectively, also these complexes were examined by using the same methods .

الخلاصة

تضمن البحث تحضير صبغة ألازو 2-(2- نفثيل أزو)-5,4- ثنائي فنيل اميدازول من خلال التفاعل الديدزة بين 2- نفثيل امين و4,5- ثنائي فنيل اميدازول في محلول كحولي قاعدي . وقد تم تشخيص الليكاند بواسطة التحليل الدقيق للعناصر ، طيف الاشعة فوق البنفسجية- المرئية وطيف الاشعة تحت الحمراء . كما تضمن البحث تقدير أيوني الكوبلت (II) والنحاس(II) بأستخدام هذا الليكاند حيث ان التفاعل بين الليكاند المذكور والايونات الفلزية يكون سريع وحساس عند الطول ألموجي للامتصاص الأعظم (550-556) نانومتر ودالة حامضية (9,2 -5,9) لمعقدي الكوبلت (II) والنحاس(II) على التوالي وبنسبة مولية 2:1 (فلز: ليكاند) وكانت التراكيز التي تطاوع قانون قانون بير مساوية الى (1x10^{-4} - 5x10^{-4}) مولاري لمعقد الكوبلت(II) وللنحاس(II) كانت (1x10^{-5} - 5x10^{-5}) مولاري وقيمة معامل الامتصاص المولاري Є = (2250 – 1550) لتر. مول$^{-1}$. سم$^{-1}$ للمعقدين على التوالي، كذلك شخصت المعقدات المحضرة بواسطة نفس الطرق المستخدمة في تشخيص الليكاند.

Introduction

Heterocyclic azo reagents are the most frequently exploited [(1,2)] as precolumn derivatizing reagents due to formation of chelates of many metal ions with high molar absorbativity , formation of chelates in multicomponent systems and high stability of formed complexes.

Heterocyclic azo ligands which containing imidazole ring are used for the spectrophotometric determination of many elements such as cobalt and copper, for example: 2-(3-bromo phenyl azo)-4,5- diphenyl imidazole used for the determination of Cu(II)(3) and 1-(2-benzimidazolylazo)-2-hydroxy-3-naphthoic acid were used for the determination of Co(II)(4), also complexes of bridged bis(imidazole) and bis (benzimidazole) ligands of various bridge types with transition metals have been examined as potential models of the structure of metal binding sites in metalloprotiens like haemerythrin, hemocyanin, tyrosinase or azurin(5-7).

In this paper the new azo ligand 2-(2-naphthyl azo) -4,5-diphenyl imidazole was prepared and use it for preparation of Co(II) and Cu(II) complexes.

Experimantal

- Apparatuses

The electronic absorption spectra were determind with Shimadzu uv-vis 1650 pc and FT-IR spectra were determind with FTIR-8400S using CsI discs in the range 400-4000cm^{-1} , Elemantal(C,H and N) analyses were carried out on a Elemantal Analyzer EURO EA 3000, pH were determind by Hanna instruments microprocessor pH meter 211, conductivity were determind by Hanna instruments EC 214 conductivity meter and melting points were determind by electrothermal Griffin apparatus .

-Reagents

All chemicals were used of analytical – reagent grade unless stated other wise . All solutions were prepared with de-ionized water.

Synthesis of ligand

-Synthesis of 4,5- diphenyl imidazole(8)

(100) ml of glacial acetic acid was added to amixture of (4.2 gm,0.02mol) of benzil , (0.52gm, 0.004mol) of hexamethylenetetraamine and (12gm,0.15mol) of ammonium acetate and refluxed for one hour then the solution was cooled and (400ml) of de-ionized water was added . The imidazole derivative precipitated by adding (0.88M) of ammonia solution , the white precipitate flittered , washed with de- ionized water, and recrystallized by absolute ethanol, the purity of this compound was evaluated by thin layer chromatography, its yield 80% and the melting point is(219-231°C).

- Synthesis of ligand

A diazonium solution was prepared by mixing (1.43 gm,1 mol) of 2-naphthyl amine in (2ml) of (12M) hydrochloric acid with(30ml) of de- ionized water and diazotized below 5°C with sodium nitrite (1gm,1 mol) in de- ionized water, (30ml) drop wise . The diazotized amine coupled with 4,5-diphenyl imidazole (2.2gm, 1mol) was dissolved in (20ml) of alkaline de-ionized water below 5°C , the red mixture was allowed to stand overnight, the precipitate was filtered and recrystallized from aqueous ethanol.

General procedure for determination of Co(II) and Cu(II):

An ethanolic solution (0.187gm ,0.0005 mol) of the ligand was mixed with a solution of $Co(NO_3)_2.6\ H_2O$ (0.0725gm,0.00024mol) in de- ionized water, at pH 9.2 keeping ligand –metal ratio (1:2) a direct brown precipitate was obtained , copper complex was obtained by the same method at pH 5.9 as a red precipitate . The complexes were recrystallized by absolute ethanol, filtered , washed with ed-ionized water and dried .

Results and Discussion

Absorption Curves

UV- Visible absorption spectra of the ligand and two complexes are shown in figure (3) and Table (1) shows the essential absorption values of them. For the ligand the essential absorption value at 469 nm and for Co(II) and Cu(II) complexes are 550 and 556 nm respectively which indicate abthochromic shift (red shift) for the broad peak in the ligand from 469 to 550 and 556 nm refers to the formation of the complexes, the peek of ligand refers to the electronic transition π→π* for the aromatic ring through the azo group related to the charge transfer and this transition occur mainly from the benzene ring to the heterocyclic ring(9). and in this research occur from 2-naphthyl amine to imidazole ring.

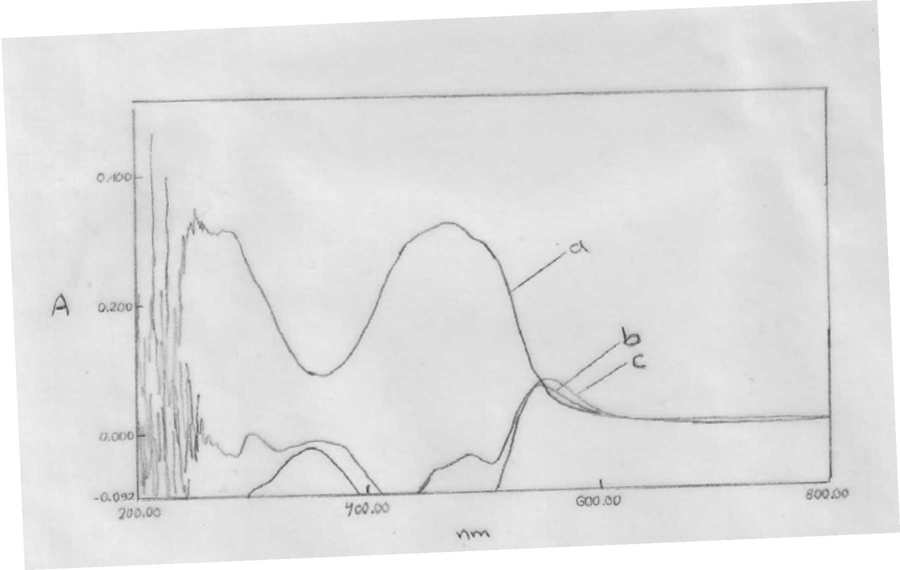

Fig.(1) Absorption Curves of (a: ligand , b: Co(II) complex, c: Cu(II) complex)

Table (1) the physical and spectroscopic data of the ligand and the two complexes

Compound	Color	λmax -	M : L	Melting Point C °	$K_{sta.}$	Yield %	$\Omega^{-1}cm^{2}mol^{-1}$
L	Yellow	469	----	125	----	53 %	----
$[CoL_2(NO_3)_2]$	Orange	550	1:2	144(dec.)	$0.41X10^{10}$	63%	$2.2x10^{-6}$
$[CuL_2Cl_2]$	Red	556	1:2	240 (dec.)	$0.106X10^{11}$	61%	$3.3x10^{-6}$

L : the azo ligand

Effect of pH on the ligand

Fig. (2) showes the structure of the ligand at different pH values, and it is clear the ligand converting to the azolium ion in the acidic pH values and keeping the natural form at pH (8-10) then converting to the anionic form in the basic medium .

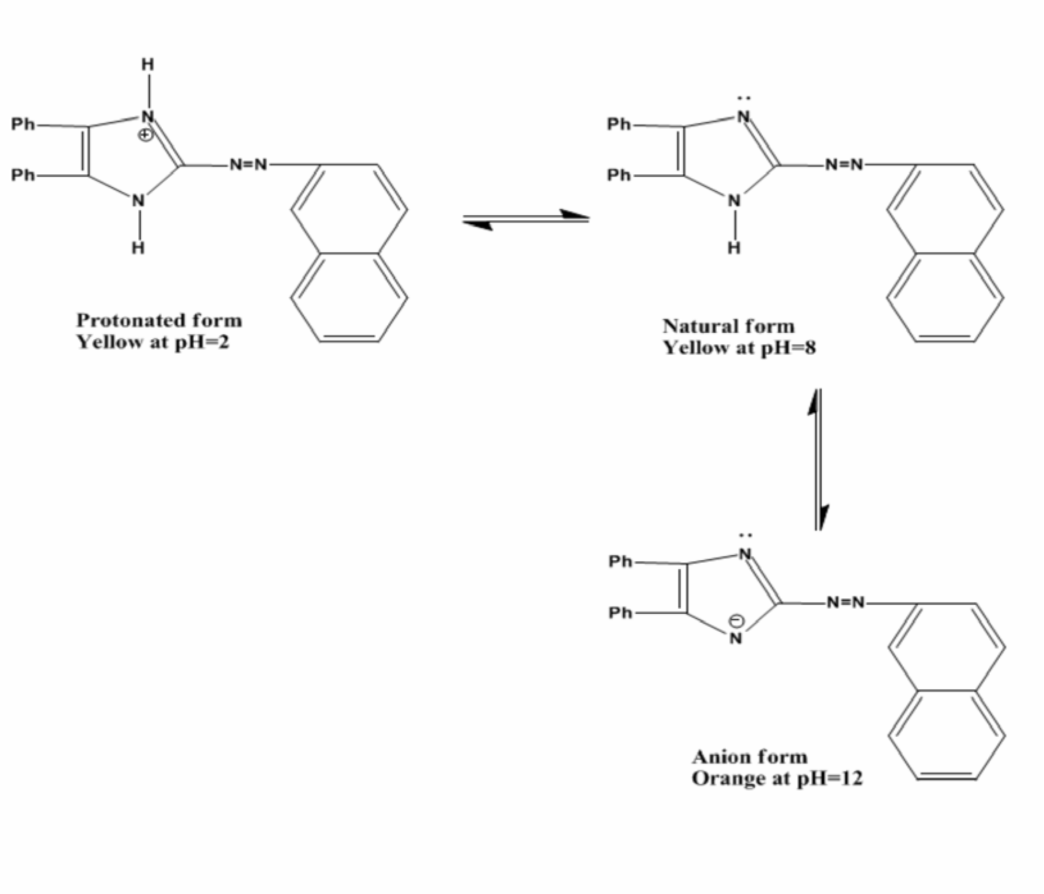

Fig. (2) Structure of the ligand at different pH values

Determination of the Optimum Amount of the Ligand

To obtain the optimum results , the order of addition of ligand should be followed as give by the procedure* .

Conformity to Beer̀ s Law

Linear calibration graph was obtained and showed that the two complexes obeyed Beer ̀s low over the range ($1x10^{-4}$- $5x10^{-4}$) M of Co(II) and ($1x10^{-5}$-$5x10^{-4}$)M of Cu(II). The molar absorpitivity (Є) was found to be(2250 and 1550) $L.mol^{-1}.cm^{-1}$ for the two complexes respectively.

Nature of Complexes

The empirical formula of two complexes was determined by the spectrophotometric method (Job method) at pH 9.2 and 5.9 for Co(II) and Cu(II) respectively. The curve indicated the formation a (1:2) metal : ligand at (λ_{max}= 550 and 556) for two complexes was obtained as shown in fig.(3)and fig.(4).

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* Result of five determination

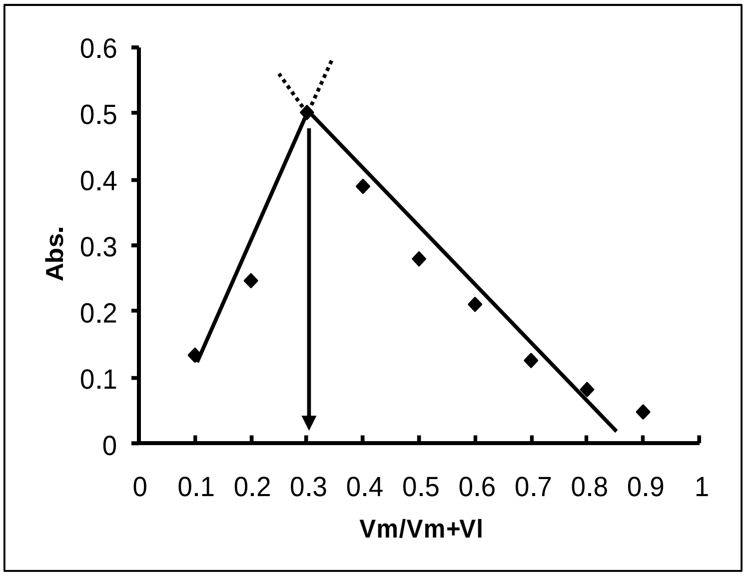


Fig.(3) Job method(variation method) for Cobalt complex

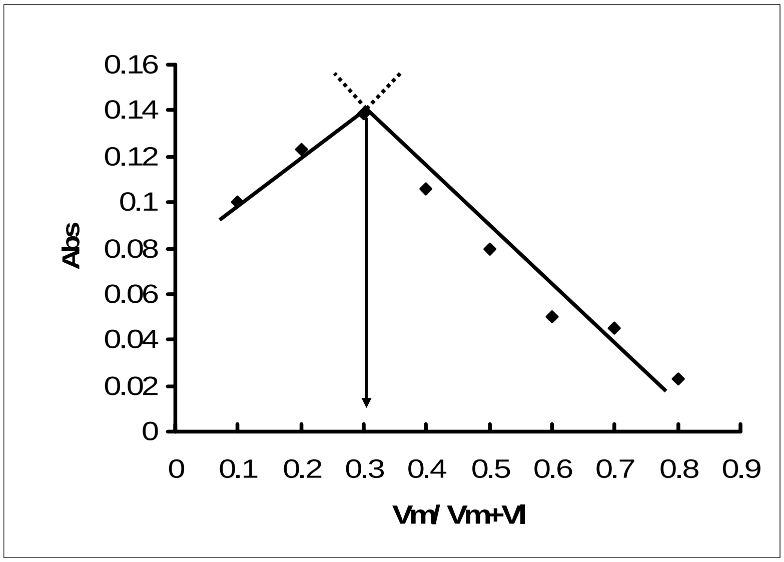


Fig.(4) Job method (variation method) for Copper complex

The stability constant

Table(1) shows the stability constant of the two complexes. When the ratio of components that formed the complex are known , equal concentrations of the metal ion solution and the ligand solution are taken and the absorbance of the two complexes at λ_{max} are measured twice according to the known procedure(10). And it is clear that Cu(II) complex is more stable than Co(II) complex according to Irving-Williams series and the ionic potential(11, 12) .

The molar conductivity

The conductivity measurements for the two complexes in non aqueous solution have been used in the structural studies, they provide a method of testing the degree of ionization of the complexes , the molar ions that a complex librate in solution, the higher will be its molar conductivity and vice versa. The non-ionized complexes have negligible value of molar conductance. The molar conductivities of the solid chelates are measured in ethanolic solution (10^{-3} M) were in the range($2x10^{-6}$- $3x10^{-6}$) $\Omega^{-1}cm^{2}\ mol^{-1}$, it is clear from the conductivity data that the complexes present behave as week electrolytes and they indicate that the anions may be present inside the coordination sphere or absent. This result was confirmed from the chemical analysis where Cl^{-} and NO_3^{-} ions are not precipitated colored by the addition of Ag NO_3 solution or the brown ring test(13).

FT-IR Spectra

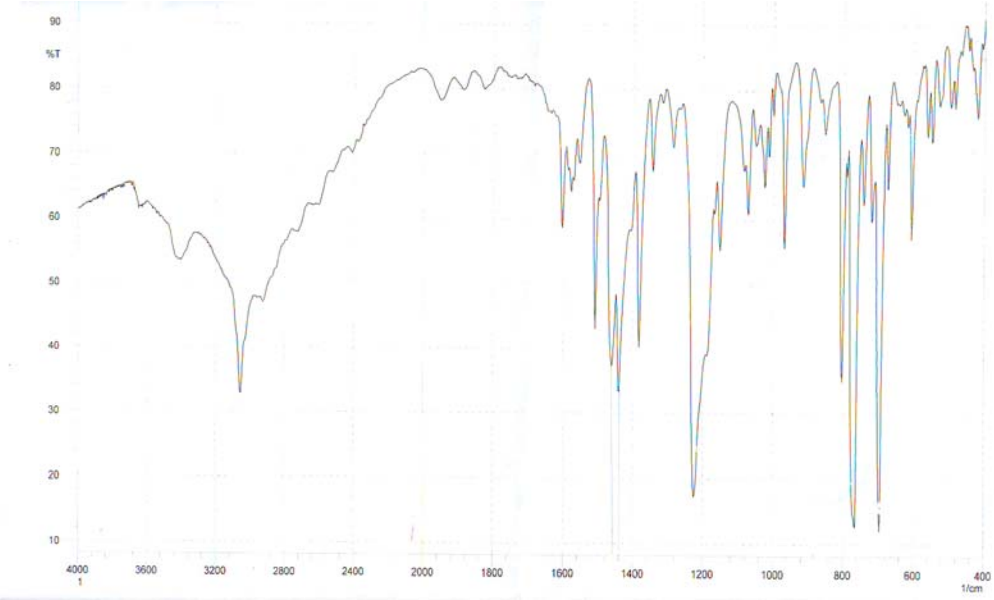
The FTIR spectra of ligand and two complexes showed in fig.(3- 5) respectively. In fig.3 the absorption bands appeared (3400-3500) cm^{-1} represent the N-H stretching band and it doesn't change during the compelaxation which explained that the compelaxation doesn't occur with the N-H group of the imidazole ring (14,15), also the band at 2900 cm^{-1} represent the stretching vibration of N-H group(7).

The peak in the range (1500-1600) cm^{-1} of the ligand spectra which represent the stretching vibration of C=N group of the imidazole ring and during the compelaxation there is a change in its intensity and shape refers to the sharing in the compelaxation through the non bonding ion pair on the nitrogen atom(16,17) .

The bands in the range (1400-1560)cm^{-1}represent the stretching vibration of C=C and N=N groups which changed in its intensity(to a lower wave number) and the shape refers to the compelaxation of the azo group with the metal ion(18,19).

While the bands in the range (1200-1400) cm^{-1} represent the stretching vibration of (C-N=N-C) and(C=N-N=C) which changed during the compelaxation which occur between the metal ion and the nitrogen atom that far off the hetero cycle (20,21), also the bands in the range (1100-1200) $cm^{-1}$and (800-1000) cm^{-1} represent the vibration of (C-N=N-C) and (C-N) which changed in the intensity and the shape during the compelaxation(18).

While the band in the range (400-800)cm^{-1} refers to the compelaxation between the metal ion and the nitrogen atom of the azo group(7,22,23).

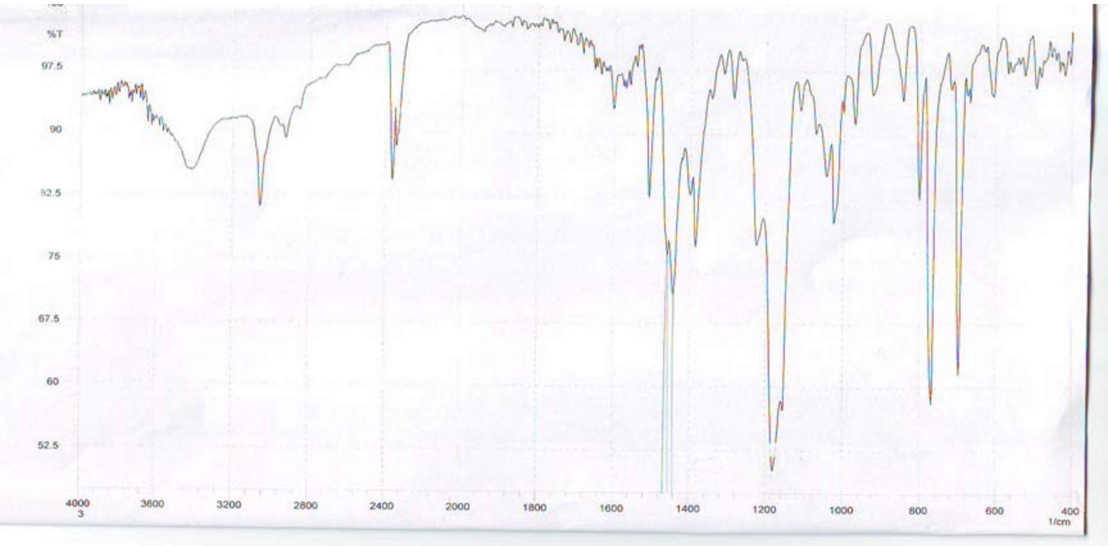


cm^{-1}

Fig.(5) FTIR spectra of the ligand 2-(2- naphthyl azo) -4,5-diphenyl imidazole

cm^{-1}

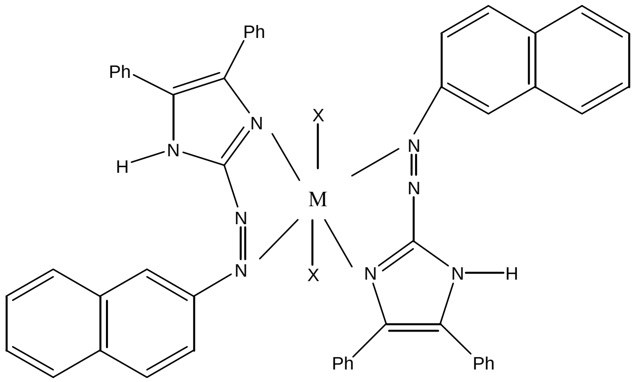
Fig.(6) FT-IR spectra of cobalt(II) complex



cm^{-1}

Fig.(7) FT-IR spectra of copper(II) complex

n the bases of IR data, electronic spectra , C.H.N data and conductivity measurements the proposed structure of complexes shown in fig. (8).



M(Co(II) and Cu(II)) , X (Cl^{-1}, NO_3^{-1})

Fig.(8) Trans or cis structure of two complexes

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