Synthesis and Spectral Studies of Co(II) , Ni(II), Cu(II) and Zn(II) Complexes with 2-(Sodium -4-azosalicylate) - 4,5- diphenyl imidazole Ligand

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Abstract

In this study the ligand 2-(sodium 4- azo salicylate) -4,5-diphenyl imidazole was prepared by the reaction between sodium 4- aminosalicylate 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) , nickel (II) , copper(II) and zinc(II) using this ligand at (λ_{max} =464 , 460 , 500 and 520) nm respectively , pH =8 and the mole ratio was 1:2 (metal : ligand). also these complexes were examined by using the same methods .

الخلاصة

تضمن البحث تحضير صبغة ألازو 2-(صوديوم 4- ازوساليت)-4,5- ثنائي فنيل اميدازول من خلال التفاعل الديدزة بين صوديوم 4- امينوساليت و4,5- ثنائي فنيل اميدازول في محلول كحولي قاعدي . وقد تم تشخيص الليكاند بواسطة التحليل الدقيق للعناصر و طيف الاشعة فوق البنفسجية- المرئية وطيف الاشعة تحت الحمراء . كما تضمن البحث تقدير أيوني الكوبلت (II) والنيكل (II) والنحاس(II) والخارصين (II) باستخدام هذا الليكاند حيث ان التفاعل بين الليكاند المذكور والايونات الفلزية يكون سريع وحساس عند الطول ألموجي للامتصاص الأعظم (464 ، 460 ،500 ، 520) نانومتر ودالة حامضية (8) للمعقدات على التوالي وبنسبة مولية 2:1 (فلز : ليكاند) كذلك شخصت المعقدات المحضرة بواسطة نفس الطرق المستخدمة في تشخيص الليكاند.

1- Introduction

Heterocyclic azo reagents are the most frequently exploited 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.The diazotized of heteroaromatic amines is basically analogous to that of aromatic amines(Oszwaldowski 1997;Oszwaldowski 2000; Lochma 1969) .Among the five membered systems the amino- azoles (pyrroles, diazoles, triazoles, etc----)have all been diazotized(**Zollinger** 1994). Heterocyclic azo ligands which containing imidazole ring are synthesis and used for the spectrophotometric determination of many elements such as 2- (1- hydroxy- 2-naphthylazo)-4,5- diphenylimidazole (DIAN) has been synthesized and it's potential for the the spectral photometric determination of metals as studied . It reacts with high senstivity with Zinc, Cadmium,Mercury,Cobalt,Copper and Nickel and is particulary useful for mercury determination(Al-Adely 2005), also prepared ligand 2-(3-Bromophenylazo)-4,5-diphenylimidazole(3-Br-PAI) and determination (IIIB) group's metal (Zn,Cd,Hg)(Saad 2005) . Ligand 2-[(4-carboxy methyl phenyl)azo]-4,5-diphenyl imidazole (4-CMePADI) using extractant Nickel ions Ni^{2+} from aqueous solution (Jawad 2008) ,also ligand 2-[(4-chloro-2-methoxy phenyl)azo]-4,5-diphenyl imidazole(4-VlMePADI) to extraction Cadmium ion Cd^{2+} from aqueous solution (Jawad 2008) .

2- Experimental

- 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-

$4000cm^{-1}$, pH were determind by Hanna instruments microprocessor pH meter 211, 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 deionized water.

2-1- Synthesis of ligand

2-2-Synthesis of 4,5- diphenyl imidazole (Hofmannk 1953).

(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 (1.75gm, 0.01mol) of Sodium-4-aminosalicylate in (2ml) hydrochloric acid with(30ml) of de- ionized water and diazotized below 5°C with sodium nitrite (10%) (30ml) drop wise . The diazotized amine coupled with 4,5-diphenyl imidazole (2.26gm, 0.01mol) was dissolved in (20ml) of alkaline de- ionized water below 5°C , the deep yellow mixture was allowed to stand overnight , the precipitate was filtered and recrystallized from aqueous ethanol.

2-3- Synthesis of complexes

All the complexes were prepared by adding an ethanolic solution (0.0005mol) (0.203 gm) of the ligand was mixed with a solution of $Co(NO_3)_2.6H_2O$ (0.00025mol , 0.0497 gm) in de- ionized water keeping ligand –metal ratio (1:2),for cobalt complex a orange precipitate was obtaind . The complexes were recrystallized from ethanol, filtared , washed with de-ionized water and dried , us same method we prepaed result complexes . Table (1) The physical and spectroscopic data of the ligand and its metal complexes.

3- Results and discussion

3-1- Electronic absorption spectra

Table(1) shows the essential absorption values of the ligand at 422nm and for complexes are Co(II) 464 nm , Ni(II) 460 nm , Cu(II) 500 nm and Zn(II) 520 nm complexes .UV-Vis spectra indicated abthochromic shift(red shift) for the broad peak in the ligand about complexes , the peek of ligand refers to the electronic transition $\pi \rightarrow \pi^*$ 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(Mohamoud 1964) .

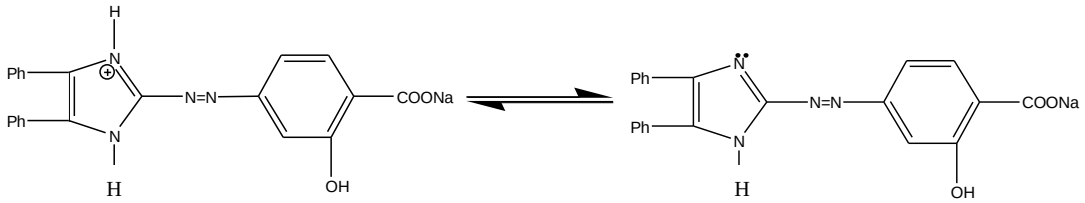
Table(1) The physical and spectroscopic data of the ligand and its metal complexes

Compound	Color (complex solution)	λ max	M : L	Yield %	Melting Point
L	Pale yellow	420	----	67	181-182
$[CoL_2(NO_3)_2]$	Orange	464	1: 2	69	196-198
$[NiL_2Cl_2]$	Orange	460	1: 2	71	228-230
$[CuL_2Cl_2]$	Grayish-rad	500	1: 2	70	198-199
$[ZnL_2Cl_2]$	Deep orange	520	1: 2	68	202-204

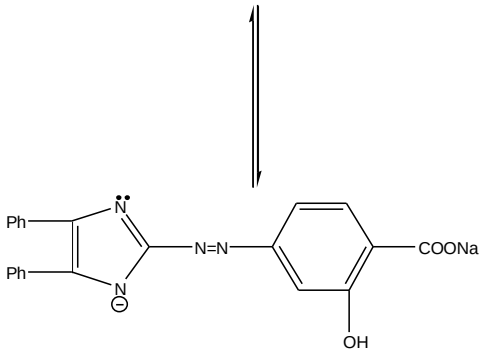
L : azo ligand

3-2 Effect of pH on the ligand

Fig. (1) 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) then converting to the anionic form in the basic medium .



Protonated form at PH=2 Protonated form at PH=8



Anion form at PH=12

Fig .(1) structure of the ligand at different PH values

3-3 Nature of Complexes

The empirical formula of two complexes was determined by the spectrophotometric method (Job method) at pH (8) for Co(II) , Ni(II), Cu(II) and Zn(II) respectively. The curve indicated the formation a (1:2) metal : ligand at (λ_{max}= 464 ,460 , 500 and 520) for complexes was obtained as shown in fig.(2)- (5).

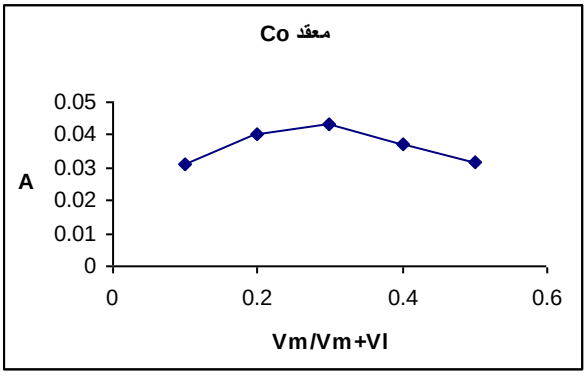


Fig.(2) Job method (variation method) for Cobalt complex

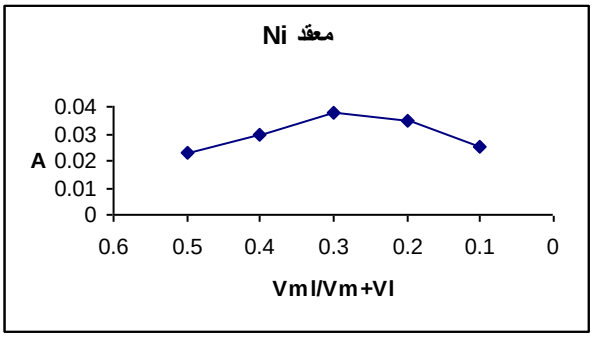


Fig.(3) Job method (variation method) for Nickel complex

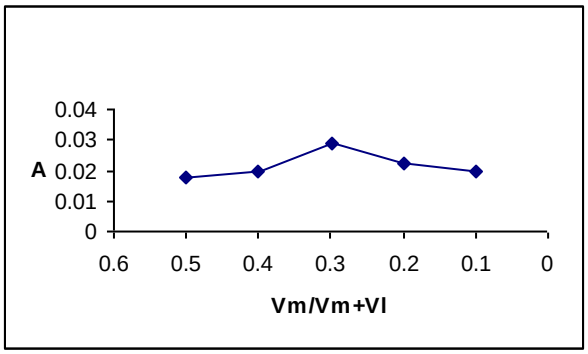


Fig.(4) Job method (variation method) for Copper complex

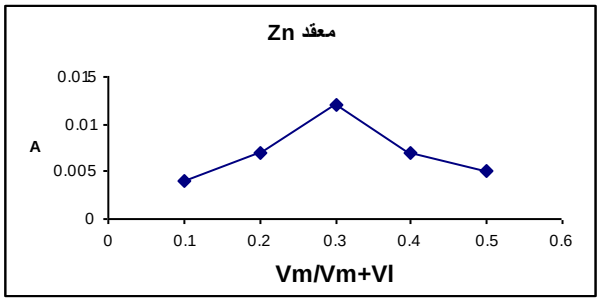


Fig.(5) Job method (variation method) for Zinccomplex

3-4 FT-IR Spectra

The FTIR spectra of ligand and two complexes showed in fig.(6 - 10) respectively. In fig.6 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 (Tein 1990)(Dash 1975).

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 (Byabartta 2002) (Ghally 2003).

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 (Ueno 1957) (Rao 1979).

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(Ueno 1957).

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 (Saad 2005) (Wolodkiewicz 2002)(Refat 2006).

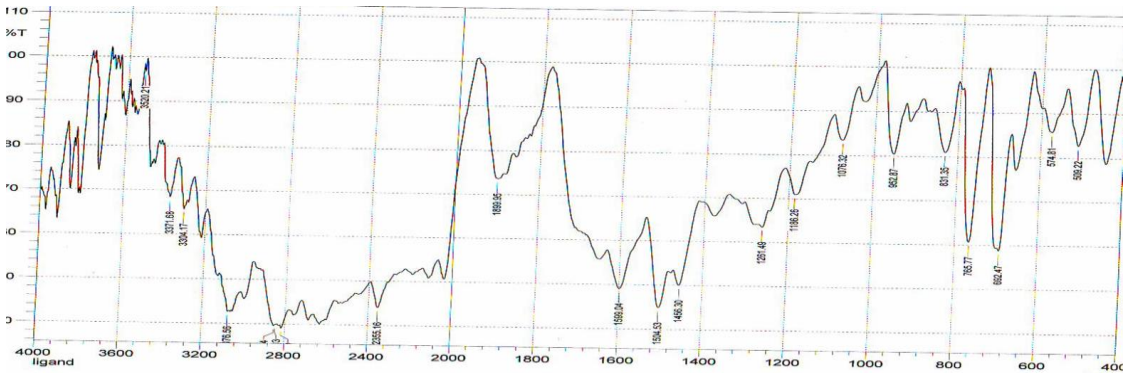


Fig.(6) FTIR spectra of the ligand 2-(Sodium -4-azosalicylate) - 4,5- diphenyl imidazole

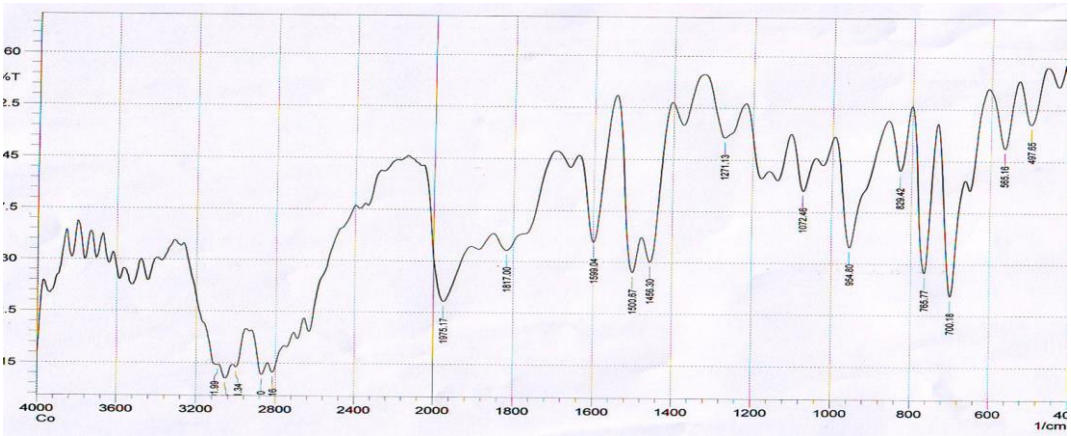


Fig.(7) FT-IR spectra of cobalt(II) complex

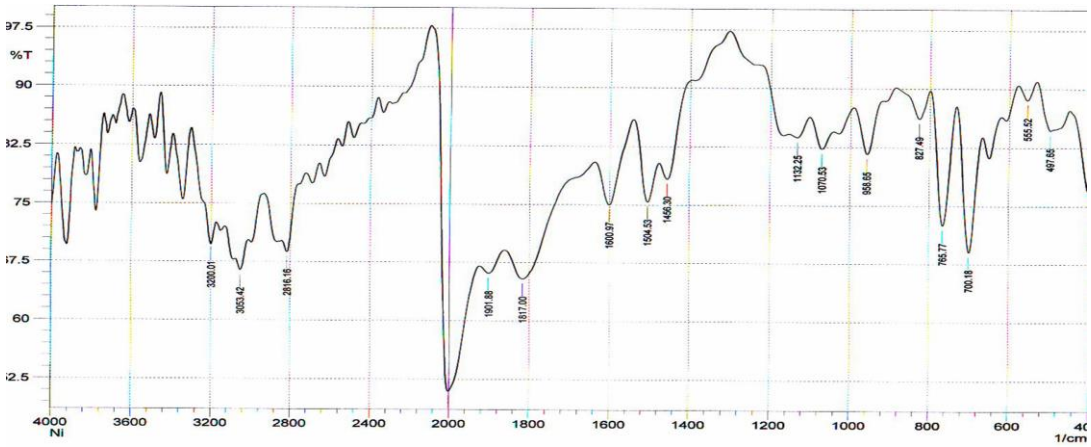


Fig.(8) FT-IR spectra of nickel (II)complex

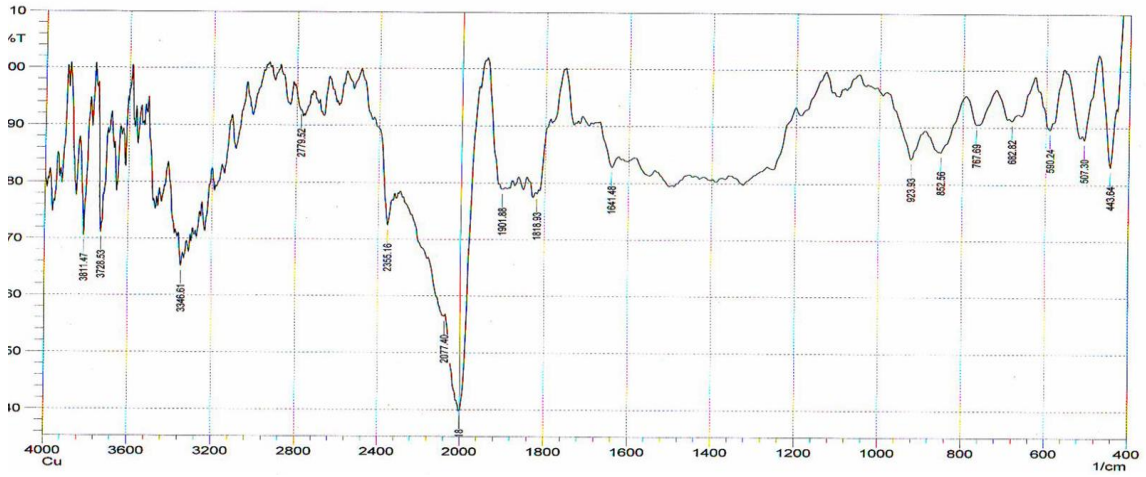


Fig.(9) FT-IR spectra of copper(II) complex

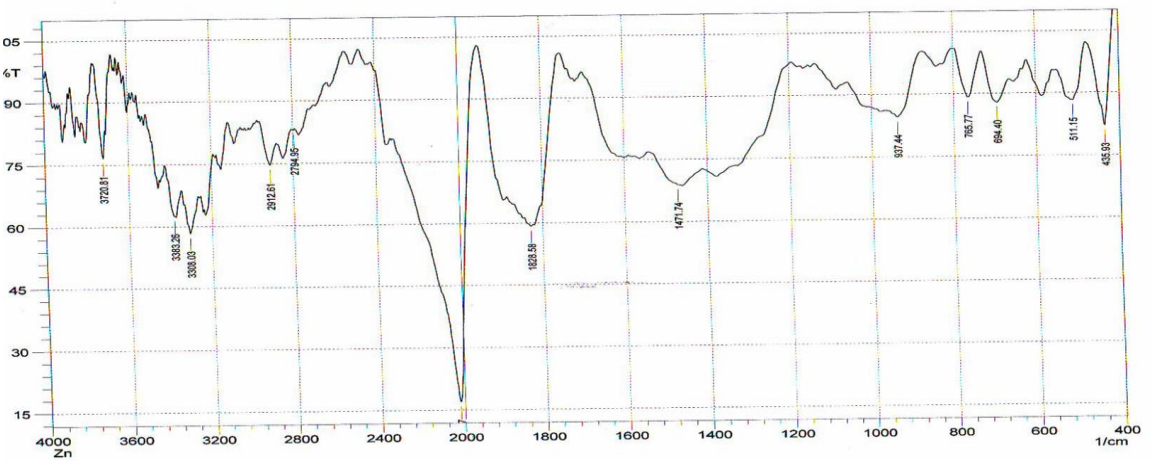
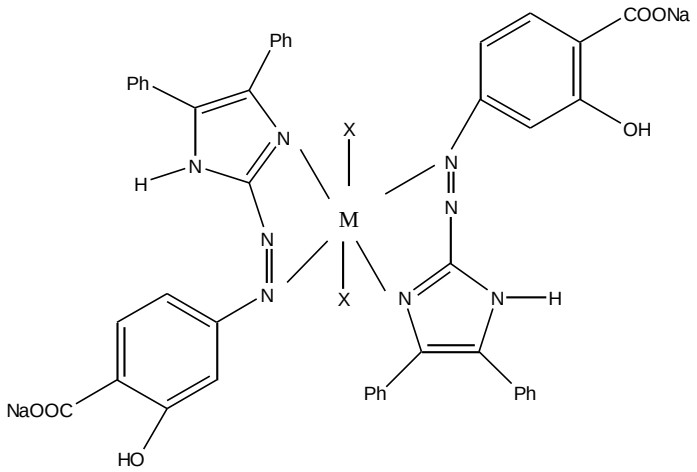


Fig.(10) FT-IR spectra of zinc(II) complex

On the bases of IR data, electronic spectra and C.H.N data and the proposed structure of complexes shown in fig. (11).



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

Fig.(11) trans or cis structure of four complexes

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