

Preparation and Characterization of Co(II), Ni(II) and Cu(II) New Schiff base complexes derived from acetoacetanilide

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Abstract

Solid metal complexes of Co(II), Ni(II), and Cu(II) have been prepared and characterized using a new Schiff base (ANPHA) derived from a new azo dye β -[(*p*-Nitrophenyl)azo] diketone and 4-aminoantipyrine characterized by several techniques, including elemental analysis (C.H.N), molar conductance, magnetic measurements, electronic spectral and IR spectral studies. The data show that these complexes have a composition of $[ML_2]$ type. The electronic spectral, and magnetic susceptibility data of the complexes suggest octahedral geometry for all complexes, and the ligand (ANPHA) behaves in a mono basic tridentate manner, by coordination through the azomethine nitrogen atom and oxygen atoms.

Key words: Tridentate, Transition metal complexes, spectral studies.

1. Introduction

Tridentate Schiff bases are well known for their coordination with various metal ions, forming stable compounds⁽¹⁾. Schiff base metal complexes have played a major role in the development of bioinorganic chemistry because of many of these complexes provide biological models in understanding the structure of bimolecular and biological processes⁽²⁻⁶⁾. Schiff base complexes derived from acetoacetanilide are extensively studied due to synthetic flexibility, selectivity and sensitivity towards a variety of metal ions^(7,8). A large number of reports are available on the biochemistry and the microbial activities of transition metal complexes containing O,N^(9,10) donor atoms. In this paper, we report the preparation of a new type of tridentate ligand formed by the condensation of β -[(*p*-Nitrophenyl)azo]diketone with 4-aminoantipyrine. This ligand system has both nitrogen and oxygen donor sites.

2. Experimental

2.1. Materials and measurements

All chemicals used in this work of highest purity and used as supplied by the manufacturers. The melting point of ligand and its metal complexes were determined by Electro thermal melting point apparatus. Elemental analysis was measured by Eurovetro EA3000, Italy-biochemical laboratory-kufa university. FTIR spectra were recorded using (KBr pellets) 4000-400 cm^{-1} on FTIR tests can Shimadzu 8000 series. Electronic spectra were recorded in ethanol using Shimadzu Uv-Vis 1700 spectrophotometer. Electrical conductivity was measured by Digital conductivity meter Alpha-800 with solute concentration (10^{-3}) in DMSO. The magnetic Susceptibility were measured on powder samples using Faraday method for this

purpose, Balance magnetic (MSB-MKI) had been employed. The diamagnetic corrections were made by Pascal's constant⁽¹¹⁾.

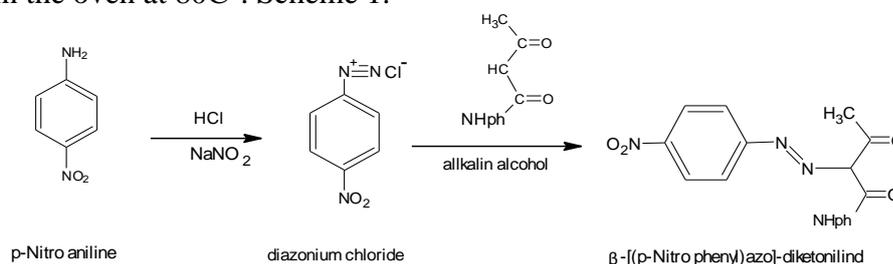
2.2. Preparation of Schiff base ligand (ANPHA)

The method of preparation was as follows:

a) Preparation of the diazo dye.

The diazo dye was prepared using the following⁽¹²⁾:

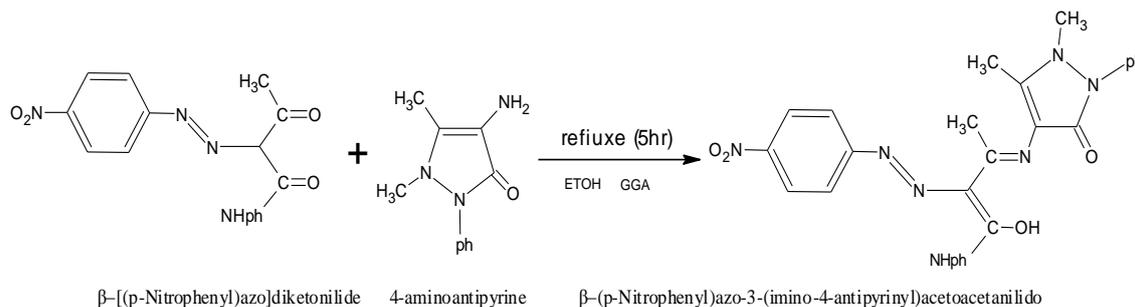
diazonium chloride solution was prepared by dissolving (1.38 g, 0.01 mol) of P-Nitro aniline in 50 ml of water and 4 ml of concentrated HCl. The solution was treated with 5 ml of aqueous (1 M) sodium nitrite drop wise and stirred for 30 min at 0C, acetoacetinilide (1.77 g, 0.01 mol) was dissolved in 200 ml of ethanol, and 80 ml of 10% sodium hydroxide was added the diazonium chloride solution prepared above was then added drop wise for coupling. After the mixture had been stirred for (3h) at 0-5C°, the product was filtered, air dried and recrystallized twice from hot ethanol and then dried in the oven at 80C°. Scheme 1.



Scheme.1:Preparation of the azo dye

b) Preparation of the a new Schiff base ligand

The new Schiff base ligand was prepared by condensation of azodye and 4-aminoantipyrine in equimolar (1:1) ratio, in absolute alcohol. Few drops of glacial acetic acid were added to the reaction mixture and refluxed for (5h) while refluxing the orange solution mixture charges into red in colored the product was recrystallized from ethanol, and dried over anhydrous CaCl₂ in a desiccator. The reaction mixture gave single product. m.p (113-115 C°) Scheme 2.



Scheme.2: Preparation of the ligand (ANPHA)

2.3. Preparation Schiff base metal complexes

The complexes were prepared by adding the appropriate amount of the metal salt (1mmol), namely ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) dissolved in the least amount of absolute ethanol to (0.511, 1mmol) of ligand (ANPHA) dissolved in (50ml) of ethanol. The reaction mixture was refluxed for (30 min) with constant stirring. The precipitated solid complexes were filtered, washed with (10ml) of hot ethanol to remove any traces of the unreacted starting materials. Finally, the complexes were dried under vacuum.

3. Results and discussion

The ligand is red crystal which is soluble in common organic solvents. The reaction of the ligand with metal ions mentioned above gives vary in color depending of metal ion. All complexes are quiet air-stable, insoluble in water, but its soluble in solvents (DMF, DMSO, methanol, ethanol and acetone) some physical and chemical properties for ligand and its complexes are listed in table 1. The elemental analysis and metal contents data are show in table (1). In all cases (1:2) (metal: ligand) solid complexes are isolated, that is agreement with the stoichimetric ratio found using molar ratio methods. The conductivity values of the chelates complexes support no electrolytic nature of the metal complexes attempts suggest the structure of the isolated complexes come from full investigation using the following studied.

3.1. Infrared spectra

In order to study the binding mode of the Schiff base to the metal ion of the complexes. The IR spectrum of the free ligand was compared with the spectra of the complexes in table(2).

The IR spectrum of the ligand shows band in the region (3406 cm^{-1}) indicate the existence of strong intramolecular hydrogen bonding in these compound. Thus, the IR spectra strongly support the existence of the compound in the intermolecular hydrogen-bonded azo-enol tautomeric form⁽¹³⁾. Absence of this band in complexes indicates the deprotonation of the intramolecular hydrogen bonded azo and enolic groups. Both the ligand and the complexes shows an intense peak at (3338 cm^{-1}), which is a characteristic feature of the (-NH) stretching frequency, indicating the existence of a free (NH) group⁽¹⁴⁾. The band observed at (1665 cm^{-1}) is characteristic of the keto group in apyrazolone ring. In the complexes, this band is shifted to lower frequency $1650\text{-}1614 \text{ cm}^{-1}$, indicating the coordination of carbonyl oxygen to the metal ions⁽¹⁵⁾. The ligand shows its characteristic (-C=N-) band at (1597 cm^{-1}), which are also shifted to lower frequencies in the spectra of the complexes ($1566\text{-}1560 \text{ cm}^{-1}$). The $\nu(\text{N}=\text{N})$ stretching vibration appears at (1492 cm^{-1}) in the free ligand spectra⁽¹⁶⁾, this band remains in the same region in free ligand in complexation. The spectra of chelate complexes showed new weak bands in the region ($580\text{-}455 \text{ cm}^{-1}$), these bands did not present in the spectrum of ligand may be attributed to vibration $\nu(\text{M-O})$ and (M-N) provide evidences concerning the bonding of oxygen and nitrogen the metal ions^(17,18). Representative example for their spectra is given in Fig.1.

3.2. Magnetic measurement and electronic spectra

The electronic absorption spectra of Schiff base and its complexes were recorded in absolute ethanol Table(3). The Schiff base shows to absorption, 385nm(25974cm^{-1}), and 245nm(40816cm^{-1}), intra ligand charge transfer transitions. The UV spectrum of the Co(II) complex display in the 650 nm (15384cm^{-1}), 609nm(16420cm^{-1}) and 404nm (24752cm^{-1}) region, which is assigned as a ${}^4\text{T}_{1g}\rightarrow{}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}\rightarrow{}^4\text{A}_{2g}(\text{F})$, and ${}^4\text{T}_{1g}\rightarrow{}^4\text{T}_{1g}(\text{P})$, transitions, attributable to an octahedral geometry around the central metal ion⁽¹⁹⁾. The magnetic moment value of the Co (II) complex (3.43 B.M) which may suggesting octahedral structure⁽²⁰⁾. The magnetic moment for the complex of Ni(II) (d^8) was found to be (3.32 B.M), which is with the range of octahedral Ni(II) complexes⁽²¹⁾.

The electronic spectrum of this complex show bands at 761nm(13140cm^{-1}), and 689nm(14513cm^{-1}) which can be assigned to ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g}\rightarrow{}^3\text{T}_{1g}(\text{P})$, respectively⁽²²⁾. The electronic spectrum of Cu(II) complex show bands at 635nm(15748cm^{-1}) which can be assignment to ${}^2\text{E}_g\rightarrow{}^2\text{T}_{2g}$ transition and an octahedral geometry was proposed for this complex⁽²³⁾. The magnetic moment value of the Cu(II) (d^9) complex (1.73 B.M), this value indicate within the expected for one electron. According to these results the following structure formal of these chelate complexes may be proposed in Fig (2).

3.3. Conductivity measurement

All chelate complexes prepared in this work showed conductivity values ranged between (5.56-7.64) S. $\text{mol}^{-1}\cdot\text{cm}^2$ in DMSO at room temperature these values indicating that non conductivity of the complexes⁽²⁴⁾. According to these results the structural formula of the metal complexes may be proposed as in Fig 3.

4. Conclusion

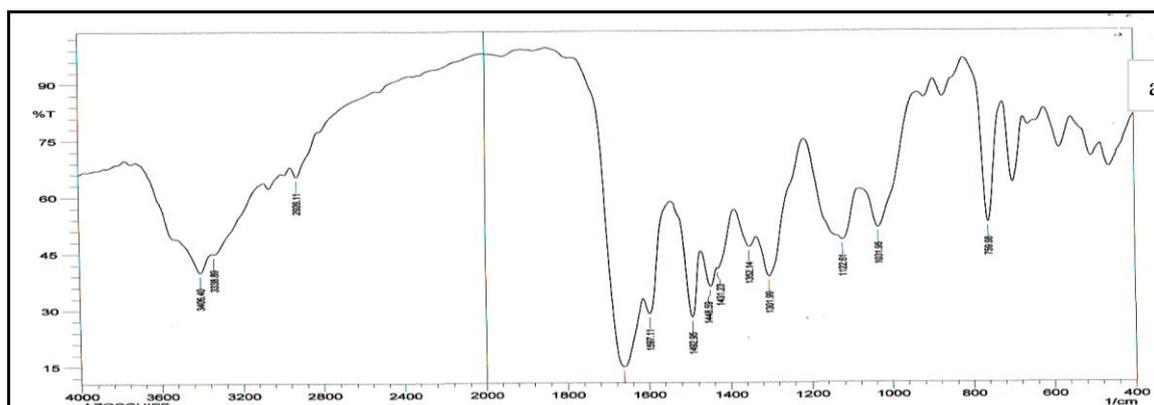
This paper report including flowing:

- 1- the ligand (ANPHA) behaves mono basic tridentate manner, by coordination with Co(II), Ni(II), and Cu(II) metal ions.
- 2- All the complexes are stable and non ionic.
- 3- All the proposed Geometry of the complexes are octahedral. According to these results the structural formulas of these complexes may be proposed in Fig.(3).

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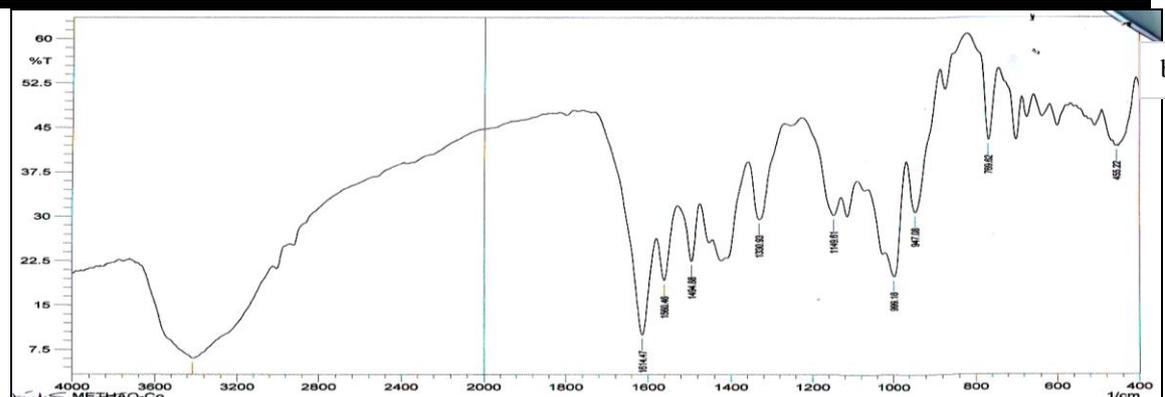


Fig.(1): IR spectra of : (a) the ligand (ANPHA) & (b) [CoL₂]

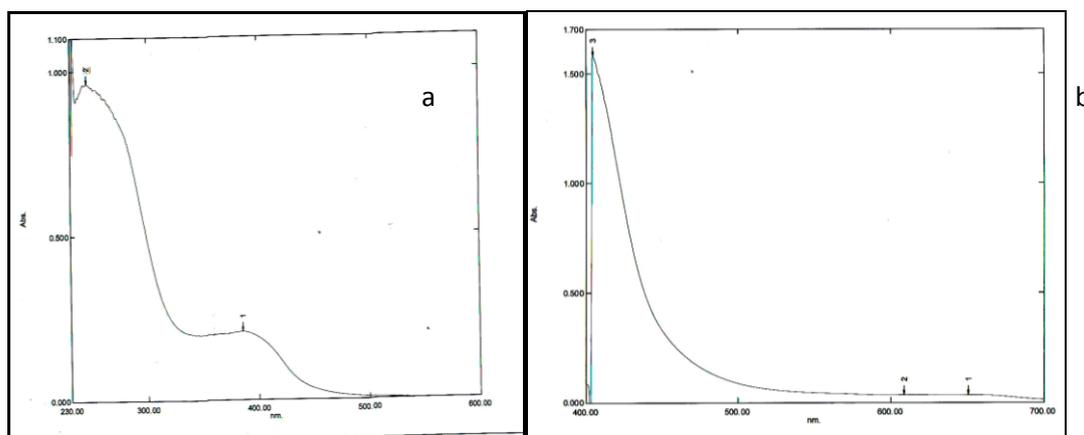


Fig.(2). Electronic spectrum of : (a) the ligand (ANPHA)&(b) [CoL₂]

Table.1: Physical data and analysis of ligand and its complexes.

No	Compound	Color	M.P °C	Yield %	Formula	Found,(calc.)%			
						C	H	N	M
1	L=(ANPHA)	Red	113 - 115	73	[C ₂₇ H ₂₅ N ₇ O ₄]	63.0 (63.4)	4.6 (4.8)	19.2 (19.1)	----
2	[CoL ₂]	Pale Green	175 - 177	68	[(C ₂₇ H ₂₄ N ₇ O ₄) ₂ Co]	60.9 (60.0)	4.9 (4.4)	18.8 (18.1)	5.2 (5.4)
3	[NiL ₂]	Pale Green	162 - 165	69	[(C ₂₇ H ₂₄ N ₇ O ₄) ₂ Ni]	60.2 (60.0)	4.2 (4.4)	18.3 (18.1)	5.9 (5.4)
4	[CuL ₂]	Dark green	175 - 176	75	[(C ₂₇ H ₂₄ N ₇ O ₄) ₂ Cu]	59.1 (59.8)	4.0 (4.4)	18.9 (18.0)	5.7 (5.8)

Table.2: Some IR frequencies in (cm⁻¹) of the ligand and its metal complexes

Ligand/complexes	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
L= C ₂₇ H ₂₅ N ₇ O ₄	1665	1597	1492	---	---
[CoL ₂]	1614	1560	1494	580	455
[NiL ₂]	1643	1566	1493	536	451
[CuL ₂]	1650	1662	1495	516	452

Table.3 : Electronic spectra, conductivity and magnetic moment of complexes

Complexes	Abs. nm (cm ⁻¹)	Transition	Conductivity S.mol ⁻¹ . cm ²	$\mu_{\text{eff}}(\text{B.M})$
L= Ligand	385 (25974) 245 (40816)	n→ π^* π → π^*	---	---
[CoL ₂]	650 (15384) 609 (16420) 404 (24752)	⁴ T _{1g} → ⁴ T _{1g} (F) ⁴ T _{1g} → ⁴ A _{2g} (F) ⁴ T _{1g} → ⁴ T _{1g} (P)	7.64	3.43
[NiL ₂]	761 (13140) 689 (14513)	³ A _{2g} → ³ T _{1g} (F) ³ A _{2g} → ³ T _{1g} (P)	5.56	3.32
[CuL ₂]	623 (16051)	² E _g → ² T _{2g}	6.32	1.73

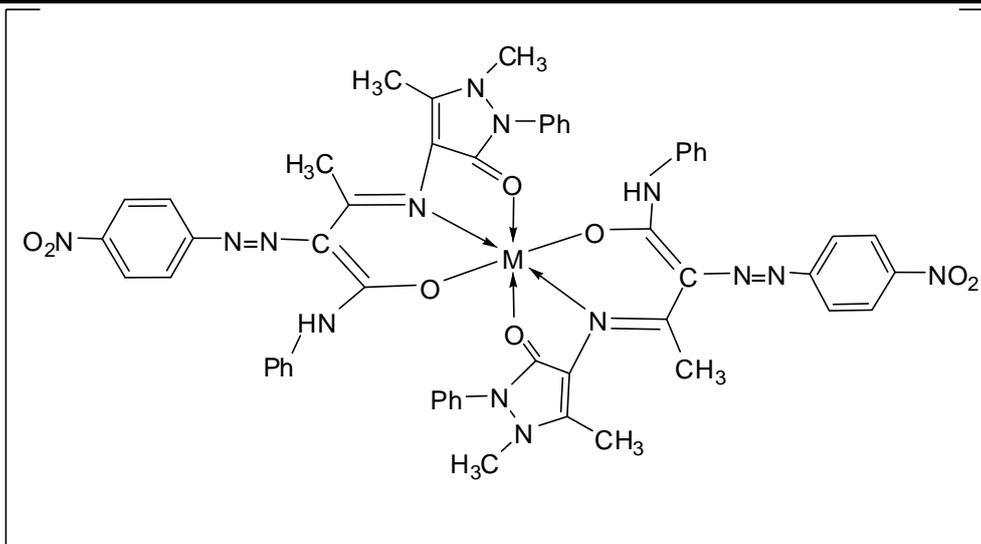


Fig.3: The proposed structural formula of prepared chelate complexes.

M= Co(II), Ni(II),and Cu(II)

تحضير وتشخيص معقدات قاعدة شف جديدة لايونات الكوبلت (II)، النيكل (II) والنحاس (II) مشتقة من اسيتواستلايد

تاريخ القبول : 2013\1\20

تاريخ الاستلام : 2012\11\5

منى عباس هادي ،ميثاق سعيد محمد ، نادية صادق مجيد
قسم الكيمياء / كلية التربية للبنات / جامعة الكوفة

الخلاصة

تضمن البحث تحضير وتشخيص بعض معقدات الايونات الصلبة Co(II), Ni(II),and Cu(II) مع ليكاند قاعدة شف المشتق من صبغة الازو β-[p-(Nitrophenyl)azo]diketonilide وقد شخّصت المعقدات من قياسات التحليل الدقيق للعناصر والعزوم المغناطيسية والتوصيلية المولارية واطياف الاشعة فوق البنفسجية واطياف الأشعة تحت الحمراء. كما بينت الدراسة أن الصيغ التركيبية للمعقدات هي من نوع [ML₂] من نتائج طيف الأشعة فوق البنفسجية والحساسية المغناطيسية اقترح الشكل الثماني السطوح لجميع المعقدات الصلبة. كما تبين أن الليكاند يسلك كليكاند احادي الشحنة السالبة ثلاثية المخلب يرتبط مع الايونات الفلزية من خلال ذرتي النيتروجين وللأوكسجين وذرتي الأوكسجين.