Synthesis , characterization , thermodynamic and spectroscopic properties for antipyrine - azo complexes

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Abstract

This paper involved synthesis of ligand (1,5-dimethyl-2-phenyl-4-((2,3,4-trihydroxy phenyl) diazenyl)-1H-pyrazol-3(2H)-one) by coupling of diazonium salt (4-amino antipyrine) with pyrogallol in basic ethanolic media . this ligand characterized means of FTIR , ^{1}H NMR , ^{13}C-NMR and measure melting point ,then prepare three new chelating complexe for ligand with Ag^{+1} , Cu^{+2} , Au^{+4} , and determine the stability by using UV-Vis spectroscopy then their thermodynamic function of complexes formation (standard Gibbs energy ΔG^{o} , standard enthalpy ΔH^{o} and standard entropy ΔS^{o})for formation of the complexes were obtained from temperature dependence of stability constant using the (Vant Hoff) equation
using UV-Vis and FT-IR spectra techniques ,have solutions which that show red shift the compared with ligand solution ,when their FTIR spectra show many changes ,new band appears ,which were not found in ligand spectrum, while many other bands served changes in shape ,position and in tensity wich are explained by the coordination with metal ione

Key words:- Heterocyclic **,** Pyrazol , Azo , antipyrene , spectroscopy , thermodynamic

Chemistry classification : QD701-731

Introduction

Since synthesis in 1884 and was used antipyretics Antipyretic Subsequently as an analgesic. In 1930
They give off benefit of as it became the latest painkillers Larger. Later antipyretics has proved as a of big Valuable as a research tool in the pharmaceutical [1,2].
Azo days with heterocyclic diazo compound form coloured complexes with many metal ions solution[3-5] . high number of the spectrophotometric methods based on these reaction ,were developed and used in analytical chemistry [6,7] .
This dyes organic of sensitivity and selectivity [8] as well as contain more than one location for consistency [9] .
In this paper we report preparation and characterization of azo ligand (1,5-dimethyl-2-phenyl-4-((2,3,4-trihydroxy phenyl) diazenyl)-1H-pyrazol-3(2H)-one) from the reaction of 4-amino antipyrine with pyrogallol and complexes of new ligand with Cu(II) , Ag(I) , Au(IV) were prepared and characterized.
The thermodynamic study of complexes Cu(II) , Ag(I) and Au(IV) were determined from of the stability constant to the temperature according to vant hoff equation [10-12]

$$\Delta G = -RT\ln K_{st} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where K_{st} is the stability constant
ΔG is Gibbs energy or free energy chang (KJ/mol)

R is the the universal gas constant (8.314KJ/ mol.K)

T =Temperature by kelvin

The standard enthalpy chang ΔH^O (KJ/mol) from the following equation [13-15]

Ln K = constant- (ΔH/ RT) ……(2)

The standard entropy changes (ΔS^O) (KJ/mol) wrer determined by using the equation bellow [16,17].

$\Delta G^o = \Delta H^o - T\,\Delta S^O$ ……..(3)

Where the Dissociation Constants (α) Calculated from equation bellow

α =Am-As/Am ……..(4)

Constant stability Kst Calculated from equation bellow

$Kst = (1- \alpha) / \alpha^2 C$

Experimental:-

A- Meterials

All chemicals used were of reagent grad and were used without furthere purification $CuCl_2.6H_2O$,AgCl , $AuCl_4$, pyrogallol and 4-amino antipyrine were supplied by fluka .

Apparatus

(FTIR)Spectra(4000-400cm-1)in KBr disk were recorded on aSHIMADZU FTIR-8400S fourier.transform. melting point were measured using Stuart, UK.

^{1}HNMR were recorded on fourier transformation Bruker spectrometer ,operating at (400MHz) with (DMSO-ds) measurments were made at Department of chemistry ,kashan university .Iran.

Electronic spectra were recored on (shimadzu) UV-160 (A) Uletr-Visible Spectrophotometer in addition melting point were obtained using stuart melting point apparatus.

Synthesis of ligand :-

The ligand was synthesis according to the gernal method[18] of shibbt and their company . this method including coupling reaction of diazonium salt solution of (1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazole-4-diazonium) with pyrogallol in alkaline alcoholic solution as seen as in fig (1)

(2.03gm , 0.01 mol) 4-amino antipyrine was dissolved in (10)ml of con. Hydrochloric acid then (30ml) of cold distilled water was added ,this solution was (0.75 gm) of sodium nitrate in(20 ml) of distilled water was added dropwise at (0-5)Co and left stirring to stand (30 min) . the resulting diazonium chloride solution was added dropwise with cooling to a solution of pyrogallol (1.26gm,0.01mol) dissolved in (100ml) alkaline ethanol .

The mixture was allowed to stand and nevralied with dilute hydrochloric acid at PH=6 . The product was filtered off and recrystallized from hot ethanol and then dried in air . The yield was 68% of purple crystals , melting point at 149-151 C^o.

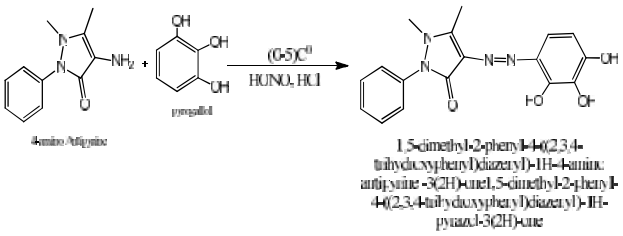


fig (1) synthesis of 1,5-dimethyl-2-phenyl-4-((2,3,4-trihydroxyphenyl)diazenyl)-1H-4-amino antipyrine -3(2H)-one.(L)

Preparation of metal complexes:-

All complexes were prepared by dissolved (0.065)gm from ligand (1,5-dimethyl-2-phenyl-4-((2,3,4-tri hydroxy phenyl) diazenyl)-1H-pyrazol-3(2H)-one) in ethanol (100)ml and added with stirring to an aqueous solution of metal ions Cu(II), Ag(I) and Au(IV) in 25ml of suitable buffer solution , This mixture was stirred and left for stilled , these complexes were filtered and precipitates were washed with distilled water and dried. , recrystallized from absolute ethanol

Standard metal solutions

The standard solution of Cu(II) , Ag(I) and Au(IV) were prepared by dissolving (2.423,1.432,3.31gm) in distilled water.

Buffer solution:

0.1 M ammonium acetate 0.771 gm. Was dissolved in 1 liter of doubly distilled deionized water (DDDW), 0.2 M acetic acid and 0.2M ammonium solution were used for PH adjustment .

Standard ligand solution

An absolute ethanolic solution (10^{-2} M) of the ligand was prepared as stock solution .This solution was stable for several months if stored in amber bottle.

Experiments thermodynamic

In this research used thermostat water bath (optima) and the temperature was kept constant during the experiment [19-22]

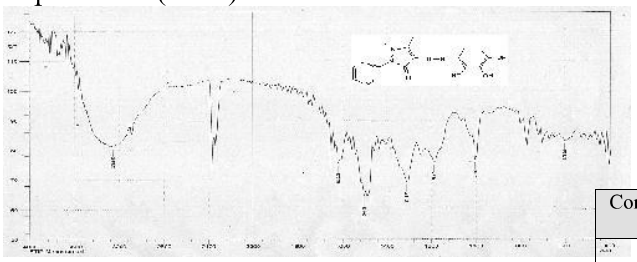
Tabl(1) :-physical properties of ligand and its complexes

No.	Compound	PH	Color	M.P ^{O}C	Yield %	Molecular formula (M.wt)
1	L	6.5	purple	149-151	68	$C_{17}H_{16}N_4O_4$ (340.333)
2	$[CuL2Cl_2].H_2O$	6	Dark red	124-126	79	$C_{34}H_{30}Cl_2CuN_8O_8$ (813.103)
3	[AgL2]Cl	7	red	76-78	72	$C_{34}H_{30}AgClN_8O_8$ (821.972)
4	$[AuL2Cl_2]Cl_2$	4	Purple reddish	133-134	73	$C_{34}H_{30}AuCl_4N_8O_8$ (1017.429)

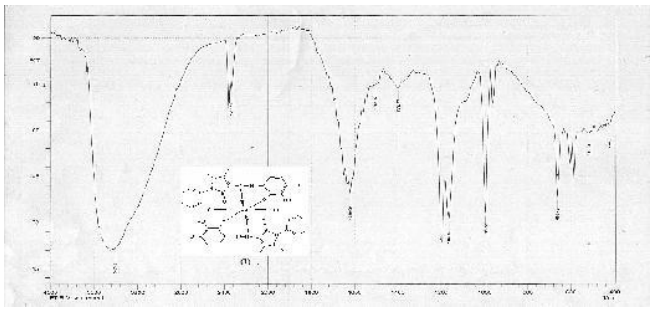
Results and discussion :-

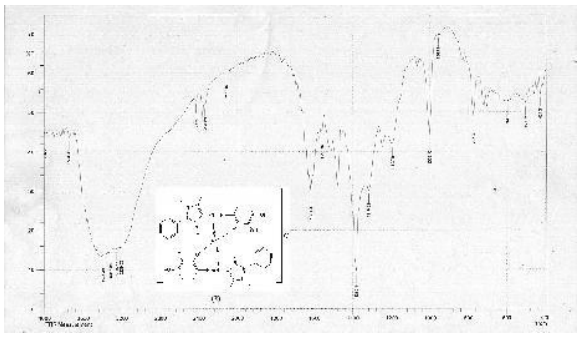
Infrared spectra

The synthesized ligand and its complexes were characterized by FT-IR show absorption at (1710) cm^{-1} for (C=O),(1504) cm^{-1} (-N=N-),(3455) cm^{-1} (OH) for phenol,and show band at (3088) for (C-H)aromatic and band for (C-H) aliphatic at (2994)cm^{-1}



New weak band in the region (516-401)cm-1 occurring in the spectrum of copper complex these bands did not spectrum of the free reagent may be attributed to υ(M-O)and υ(M-N).Show in Table (2)





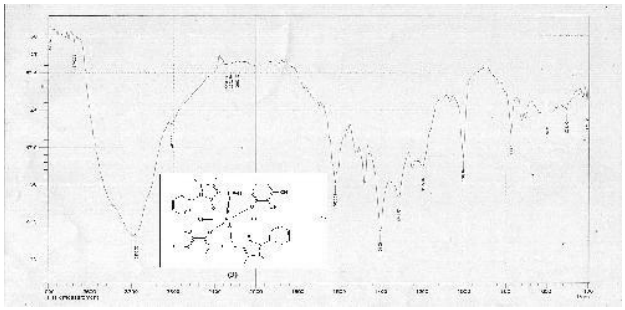


Fig (2) FT-IR spectra of (1) the ligand L , (2) $[CuL2Cl_2].H_2O$,(3) [AgL2]Cl , (4) $[AuL2Cl_2]Cl_2$

Table2: Important IR frequencies for the Ligand and its complexes (CsI disc; cm^{-1})

Compound	υ(O-H)	υ(N=N)	υ(C=O)	υ(Ar-H)	υ(M-O)	υ(M-N)
L	3380	1504	1710	3067	-	-
$[CuL2Cl_2].H_2O$	3409	1560	1709	3067	516	424
[AgL]Cl	3377	1563	1711	3088	501	401
$[AuL2Cl_2]Cl_2$	3099	1558	1707	3087	501	424

^{1}H NMR Spectra For L

The ^{1}H-NMR(DMSO) spectrum data of compound show δ:6.4-8.4(m , 7H , Ar-H),1.75 (m ,3H,C-CH_3) ,3.77 (m , 3H,N-CH_3)Ald. , 5.57 (m,3H, OH) .

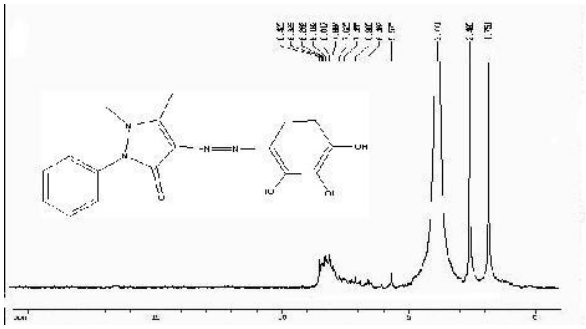


Fig (3) 1H NMR Spectra For L

^{13}C-NMR Spectra For L

The ^{13}C-NMR(DMSO) spectrum data of compound (1) show δ:198.99 (C4) , 179.77 (C2) ,169.96(C9) , 159.98(C11) , 151.90(C10) , 139.39(C12) , 138.19(C14,C16) , 128.47(C7) , 127.33(C13,C17) ,119.98 (C15), 117.77(C8) ,177.70(C5,C6) , 24.19(C3) , 12.97(C1).

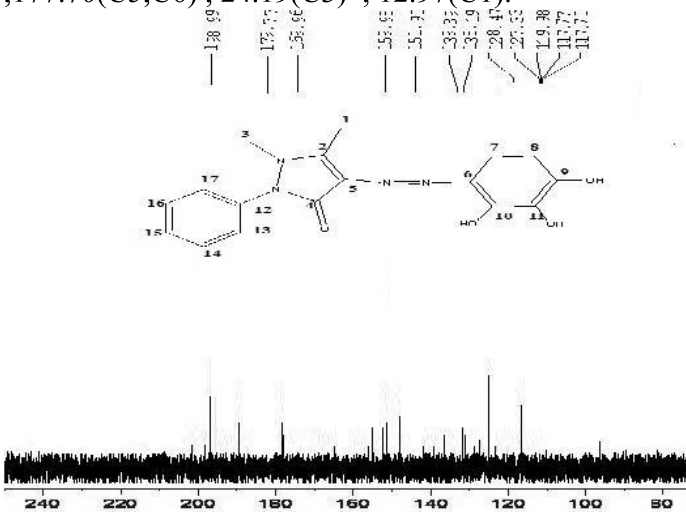


Fig (4) 13C NMR Spectra For L

Absorption spectra

The synthesized ligand and its complexes were characterized by UV-Vis spectra .The UV.Vis - spectra for Ligand shows (3) peaks (279), (236)nm and the ʎ max at (381)nm assigned to aromatic ring transition

The spectrum of Cu(II)gave absorption peak at (460)nm, and Ag(I) appeared at (410)nm and the spectrum of Au(IV)showed the peak at(435)nm. This complexes undergo shift to longer ware length refer to the coordination between the ligand and ions metel(11)

The absorption peak of Cu(II)complex show(3) peaks at(236)nm , (256)nm and third at (460)nm , the first and second due to (Π→Π*) and third due to (n→Π*) transitions with the molecule

The Ag(I)complex and Au complex appear (3)peaks (214, 381,412)nm for Ag(I)Au(IV)(212,263, 435)nm this peaks due to (Π→Π*) and (n→Π*) transitions with in the molecule , this inner ligand transitions are common que to the presence of (C=N). (N=N), and (C=C) group in the ligand structure . The UV.Vis spectra for ligand and all metal complexel shows , fig (5)

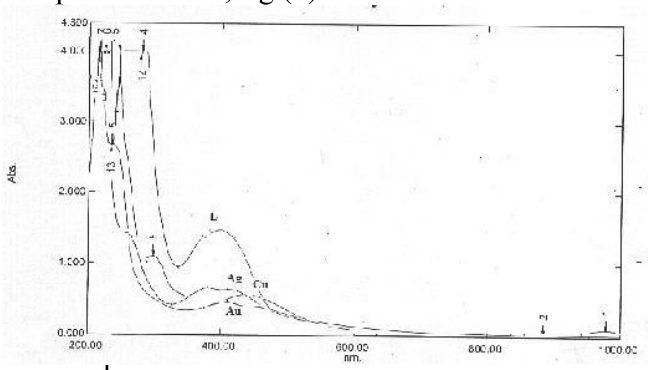


Fig (5) UV-Vis spectra of the ligand L , (Cu) $[CuL2Cl_2].H_2O$,(Ag) [AgL]Cl , (Au) $[AuL2Cl_2]Cl_2$

Effect of pH :

Suitable pH values for complex formations were found to be in the range of (3-8). For evaluation of the optimal pH values for determination of Cu(II), Ag(I), Au(IV), the effects of pH on the absorbance were studied results are shown in Figs.(6).The absorption spectra did not change over the whole range. The optimal pH and wave length (max λ)with molar absorptivity (Є)of Cu(II), Ag(I), Au(IV), complexes are shown in table (3).

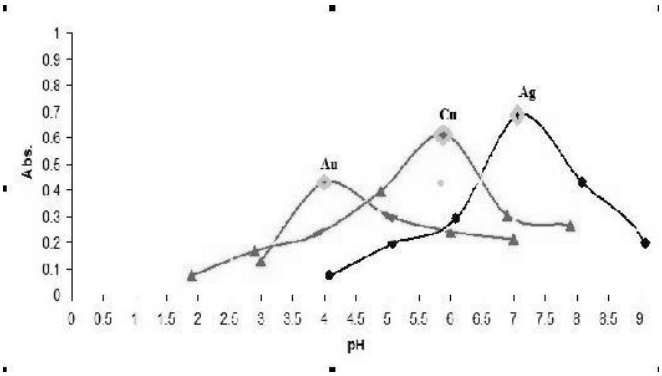
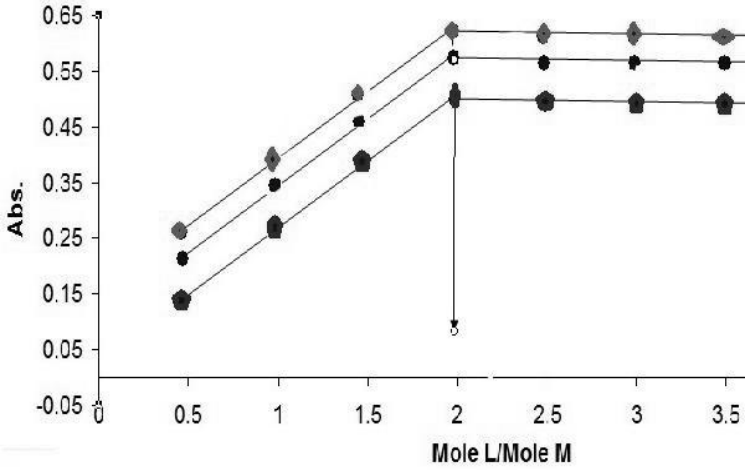


Fig6: The effect of PH on the absorbance L-metal chelats. Ligand conc. =2×10^{-3} M,metal ions conc. = 2 ×10^{-3}M, υs. ligand blank ^{1}-cm cells .



Fig(7):- The Mole ratio (M:L) of L-metal chelats

According to these results the structural formula of prepared complexes in this work may be proposed in fig.(8) .

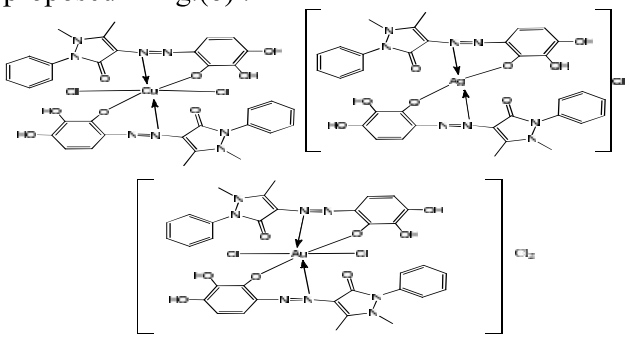


Fig: (8) :- The proposed structural formula of complexes.M=Cu(II), Ag(I), Au(IV)

Table(3): The optimal pH values and wave length (max λ)with molar absorptivity (Є)of metal ions in aqueous 50%(v/v) ethanol solution.

Ligand	Metal ions	Optimal PH	Molar absorptivity Ex10^{2}L.mol^{-1}.Cm^{-1}	Wave length Λmax nm
L λmax=381 ε=2.7x10^{2} L.mol^{-1}.Cm^{-1}	Cu(II)	6	3.02X10^{2}	460
	Ag(I)	7	3.14X10^{2}	410
	Au(IV)	4	2.14X10^{2}	435

Nature of complexes

These complexes are stable in air and insoluble in water but soluble in most organic solvents.

The composition of these complexes were determined by mole ratio method .

This method showed that the molar ratio of all complexes are(1:2) , the structural formula of prepared complexes can be suggested and showed in fig(7) .

Thermodynamic calculated

From the dependence of stability (Kst) on temperature (T) the thermodynamic function (ΔG^{o}, ΔH^{o} ,ΔS^{O}) . The values of standurd Gibbs energy chang is obtanied from equation (1,2,3) .

From the negative values of ΔG^{o} that obtained the reaction of complexex formation ($[CuL2Cl_2].H_2O$, $[AgL2]Cl$ and $[AuL2Cl_2]Cl_2$) were spontenous respectivety .

The values of standerd enthalpy chang ΔH^{o} that obtained all of complexes have experienced an exothermic complexation reaction .

That mean decreasing in temperature due to increasing in stability of complexes . while the positive values of ΔS^{O} for complexese

([$CuL2Cl_2$].H_2O , [AgL2]Cl and [$AuL2Cl_2$]Cl_2) that indicates the complexes were forming .
The results show that the complexes are both enthalpy and entropy stabilized .show in table (4)

Table(4): The Thermodynamic values for complex

Compound	α	Kst	ΔG^o J/mol.K	ΔH^o J/mol.K	ΔS^O J/mol.K
[$CuL2Cl_2$].H_2O	0.3	3888.888	-20479.309	-0.2306	+68.7222
[AgL2]Cl	0.26	5473.372	-21326.073	-0.2401	+71.5645
[$AuL2Cl_2$]Cl_2	0.17	14359.861	-23715.79	-0.26705	+79.584

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تحضير,تشخيص ,ترموداينمك ودراسة طيفيه لمعقدات ازو-انتي بايرين

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الخلاصة :-

1,5-dimethyl-2-phenyl-4-((2,3,4-trihydroxyphenyl) diazenyl)-1H-pyrazol-3(2H)-one تضمن البحث تحضير الليكاند من خلال ازدواج ملح الديازونيوم للمركب (4-امينو انتي بايرين) مع البايراكول في محيط كحولي قاعدي وقد تم تشخصيه بطيف الاشعه .13C-NMRو للكاربون 1H-NMRوطيف الرنين النووي المغناطيسي للبروتون FT-IRتحت الحمراء وتم تعيين صيغتها باستخدام طريقه النسب الموليه ,تم Au^{+4} , Cu^{+2} , Ag^{+1}حضرت ثلاث معقدات كيليتيه جديده لليكاند مع الايونات حساب ثوابت الاستقرار لهذه المعقدات باستخدام مطيافيه الاشعه فوق البنفسجيه –المرئيه بعد دراسه الضروف المثلى لكل معقد. تم حساب بعض الدوال الثرموديناميكيه لتكوين هذه المعقدات (طاقة كبس القياسيه , وطاقه الانثالبي القياسيه وطاقه الانتروبي القياسيه) باستعمال ثابت الاستقراروmعادلة اعتماديه درجه الحراره لفانت هوف. تم تشخيص ودراسه المعقدات الصلبه بعد عزلها باستخدام الاشعه فوق البنفسجيه –المرئيه فظهرت محاليلها في الايثانول ازاحه حمراء مقارنه بمحلول الليكاند في حين اظهرت طيف الاشعه تحت الحمراء تغيرات عديده اذ ظهرت حزم جديده لم تكن موجوده بينما عانت حزم اخرى من تغيرات بالشكل والشده والموقع وذلك بسبب حصول عمليه تناسق مع الايونات الفلزيه .

كلمات مفتاحية :- مركبات حلقيه غير متجانسة , بايرازول , ازو , انتي بايرين , الطيف , ثرموداينمك