Synthesis and Characterization of some Mixed Ligand Complexes Containing (8-hydroxyquinoline) and (2 - picoline) with some Metal Ions

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Received 2, April, 2012
Accepted 24, June, 2012

Abstract:

Complexes of some metal ions (Mn(II) , Co(II) , Ni(II) ,Cu (II) , Zn(II) , Cd (II) , and Hg(II)) with 8-hydroxyquinoline (Oxine) and 2- Picoline (2-pic) have been synthesized and characterized on the basis of their FT-IR. and Uv-visible spectroscopy ,atomic absorption molar conductivity measurements and magnetic susceptibility ,from the results obtained the following general formula has been given for prepared complexes [M $(oxine)_2$ $(2\text{-}pic)_2$]
where M = M(II) = Mn , Co , Ni , Cu , Zn , Cd , Hg
$(oxine)^-$ = ionic ligand 8-hydroxyquinolin (oxinato)
(2- pic) = 2- picoline

Key-words : Mix ligand of 8-hydroxyquinoline and 2-picoline .

Introduction :

8-hydroxyquinoline and its derivatives are widely used as analytical reagents [1-3] and anti – amoebic agents , 8-hydroxyquinoline (oxine) behaves as bidenate (N,O^-) univalent ligand to form chelates with several metal ions [4] . Markus and co work [5] synthesis and characterization of Zinc (II) complexes of amide and urea substituted of 8-hydroxyquinoline and juntaoxie and co work [6] synthesized 8-hydroxyquinolin derivative with carbazol group substituting in the 5-position of quinolone and its coordination complex with Al (III) and also shayma and co work [7] synthesis and characterization of mixed ligand complexes of 8-hydroxyquinoline and o-hydroxybenzylidene 1- phenyl -2 , 3 - dimethyl - 4 - amino – 3-pyrazolin -S - one with Fe^{+2}, Co^{+2} , Ni^{+2} and Cu^{+2} ions , and synthesized mixed ligand complexes of various metal (II) with 8-hydroxyquinoline and other different ligands [8-10] , we have investigated in this paper the preparation and properties of some metal ions with 8-hydroxyquinoline and amine adduct (2-picoline) .

Materials and Methods:

All chemicals ($MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.H_2O$, $HgCl_2$) were obtained from Fluka and used without further purification. High purity ligand (8- hydroxyl quinoline) and (2-picoline) were obtained from Merk .

Conductivity measurements were carried out using Philips pw digital meter . The FT-IR spectra in the region (4000- 400) cm^{-1} were recorded spectra photometer as (KBr) disc .The Uv-Visible spectra were recorded using (shimatzu Uv-Vis 16A) Uv-Vis. spectrophotometer

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in ethanol solution (10^{-3} M). Metal contents of the complexes were determined by Atomic absorption technique by using (shimadzu AA 680G) atomic absorption spectrophotometer . Melting point was determined by using (Stuart melting point apparatus) .The magnetic moments (μ eff B.M.) were calculated on faraday method by using (Balance magnetic susceptibility model (MSB – MKT) .

General method for synthesis of complexes

An aqueous solution of (1mmole) $MnCl_2.4H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$, $CdCl_2.H_2O$, and $HgCl_2$ (0.170 gm , 0.204 gm , 0.204 gm , 0.150 gm, 0.120 gm, 0.173 gm and 0.233 gm) respectively were added to the solution of ligand 8-hydroxyquinoline (0.25 gm) (2 mmole) was dissolved in 20 ml of pure ethanol containing (0.095gm) (2 mmole) of KOH.Mixture was stirred for an hour at room temperature. Complexes were separated by adding solution of the ligand 2- picoline (2mmole) and by treating the solution with diethyl ether until complete precipitation , the precipitation was crystallized from ethanol and dried at (50ºC).

Results and discussion:

The metal complexes obtained were solids colored .The complexes was insoluble in water and soluble in some of the common solvents such as dimethylformamide , dimethylsulphoxide and ethanol .

Results of the molar conductivity indicated that the complexes have no electrolyte behavior . Table (1) includes the physical properties of the ligands and its complexes .

Spectral studies:

Infrared spectra

The characteristic vibration and assignments of ligand (oxine) and (2-pic) and their complexes are described in table (2) .The spectrum of (oxine) (fig. 1) exhibited the strong band of 1280 cm^{-1} this could be υ (C- O) while another strong absorption bands at (1095) cm^{-1} and (3178) cm^{-1} this could be attributed to υ (C-N) and υ (O-H) respectively [11-14]. The spectra of free 2- picoline showed band absorbed at (1627) cm^{-1} was assigned to υ (C=N) [15] .

The spectra of complexes:

The spectra exhibited amerked difference the absorption band (Fig. 2) belonging to the stretching vibration of υ(C-O) of the carbonyl group have been found in the range between (1272 -1234) cm^{-1} shifted to lower frequencies, expect in the case of Hg(II) complex this band was found at higher range (1288)cm^{-1}. Suggesting the possibility of the coordination of the ligand (Oxine) through the oxygen atom in the carbonyl group [16-18] .

Absorption assigned for υ(C-N) was noticed at the range (1103-1175) cm^{-1} shifted to the higher frequencies which indicate the coordination of nitrogen atom of the υ (C- N) group to the central metal ion [16] .

The stretching vibration band υ (C=N) has been found in the range (1465 -1442) cm^{-1} shifted to lower frequency which means the nitrogen atom of 2- picoline was involved in the coordination [15] . Metal – nitrogen and metal – oxygen bonds were further confirmed by the presence of the stretching vibration of υ (M-N) and υ(M-O) around (401- 578)cm^{-1} and (648- 486)cm^{-1} respectively [16].

Electronic spectra

The absorption and assignments related to the ligands and their complexes listed in table (3) .The

ligand oxine (fig.3) exhibited an absorption band number 314 nm (31847cm^{-1}) which may be attributed to (n→π) . Free 2- picoline (fig. 4) showed absorption band in (uv) region at 301 nm (33222cm^{-1}) which expressed at the (n→π) [19] .

The spectra of complexes

[Mn (oxine)$_2$ (2- pic)$_2$]d^5

The brown complex spectrum showed absorption at 391 nm (25575cm^{-1}) attributed to $^6A_{1g}\rightarrow{}^4A_{1g}$ [20-21].

[Co (oxine)$_2$ (2-pic)$_2$] d^7

The brown complex spectrum gave one band at 390 nm (25641cm^{-1}) caused by $^4T_{1g\ (F)}\rightarrow{}^4T_{1g\ (P)}$ transition [22] .

[Ni (oxine)$_2$(2-pic)$_2$] d^8

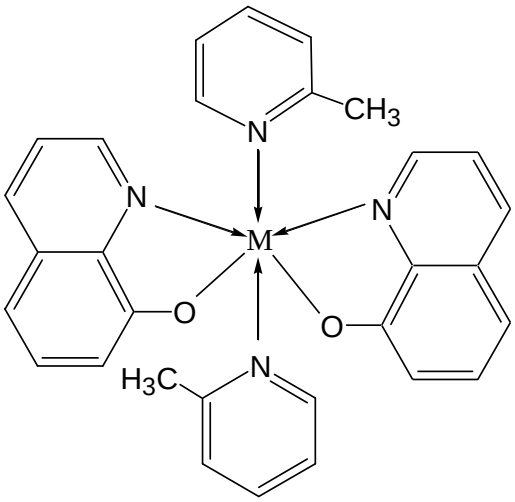
The spectrum of green complexes gave band at 371 nm (26954 cm^{-1}) caused by $^3A_{2g}\rightarrow{}^3T_{1g}(p)$ transition [23] .

[Cu (oxine)$_2$ (2- pic)$_2$] d^9

The spectrum (fig.5) of green complex gave band at 389nm (26041cm^{-1}) caused by $^2E_g\rightarrow{}^2T_{2g}$ transition [24-26] .

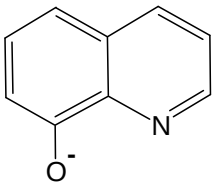
The complexes [Zn (oxine)$_2$ (2- pic)$_2$] , [Cd (oxine)$_2$ (2- pic)$_2$] and [Hg (oxine)$_2$ (2- pic)$_2$] where the electronic configuration of the metal d^{10} confine absorption of any (d→ d) transition .

According to spectral data as well as those obtained from elemental analysis the chemical structure of the complexes may be suggested to be octahedral for [M (oxine) (2-pic)$_2$]



where M = M(II) = Mn , Co , Ni , Cu ,Zn , Cd , Hg

(Oxine)$^-$ = ionic ligand 8- hydroxyquinoline (oxinato)



2- pic = 2- picoline

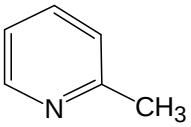


Table (1) Physical properties of the ligand 8- hydroxyquinoline (oxine) , 2-picoline and its complexes [M(oxine)$_2$ (2- pic)$_2$] .

Compound	M.wt.	Color	m.p. ^oC or dec.	M% Calculate (Found)	Molar conductivity $\mu s.cm^{-1}$ in ethanol	µeff (B.M.)
Oxine	145.16	Pale yellow	72.5	-----	-----	-----
2-picoline	93	Pale yellow (liquid)	------	-----	-----	-----
[Mn(oxine)$_2$ (2-pic)$_2$]	529.5	Brown	300dec.	10.37 (10.12)	12	5.62
[Co(oxine)$_2$ (2-pic)$_2$]	533.25	Brown	320dec.	11.05 (10.2)	10.5	4.56
[Ni(oxine)$_2$ (2-pic)$_2$]	533.27	Green	300dec.	11.00 (10.73)	21	3.11
[Cu(oxine)$_2$ (2-pic)$_2$]	538.1	Green	290dec.	11.80 (12.6)	15,6	1.76
[Zn(oxine)$_2$ (2-pic)$_2$]	539.94	Yellow	285dec.	12.10 (15.2)	3.3	0
[Cd(oxine)$_2$ (2-pic)$_2$]	586.26	Yellow	300dec.	19.14 (18.7)	11.8	0
[Hg(oxine)$_2$ (2-pic)$_2$]	675.16	Orange	293dec.	------	10	0

dec. = decompose

Table (2) : The characteristic infrared band for the ligand 8-hydroxyquinoline(oxine) , 2-picoline and its complexes.

Compound	υ (O-H)	υ(C=N)	υ(C-O)	υ (C-N)	υ(M-N)	υ(M-O)
Oxine	3178	-----	1280	1095	-----	-----
2-picoline	-----	1627	-----	-----	-----	-----
[Mn(oxine)$_2$ (2-pic)$_2$]	-----	1465	1272	1103	493	540
[Co(oxine)$_2$ (2-pic)$_2$]	-----	1465	1240	1175	410	520
[Ni(oxine)$_2$ (2-pic)$_2$]	-----	1465	1242	1110	440	580
[Cu(oxine)$_2$ (2-pic)$_2$]	-----	1465	1234	1110	401	516
[Zn(oxine)$_2$ (2-pic)$_2$]	-----	1465	1272	1110	501	601
[Cd(oxine)$_2$ (2-pic)$_2$]	-----	1458	1234	1110	578	648
[Hg(oxine)$_2$ (2-pic)$_2$]	-----	1442	1288	1126	401	486

Table (3) : UV - visible absorption for the free ligand 8- hydroxtquinoline (oxine) , 2-picolin and its complexes.

Compound	nmλ	Abs.	Wave number cm^{-1}	Emax (L. mol^{-1}. cm^{-1})	Remarks
Oxine	314	2.230	31847	2230	$n\rightarrow\pi^*$
2- picoline	301	0.966	33222	966	$n\rightarrow\pi^*$
$[Mn(oxine)_2 (2\text{-}pic)_2]$	391	2.477	25575	2477	$^6A_{1g} \rightarrow {}^4A_{1g}$
$[Co(oxine)_2 (2\text{-}pic)_2]$	390	2.497	25641	2497	$^4T_{1g} \rightarrow {}^4T_{1g(p)}$
$[Ni(oxine)_2 (2\text{-}pic)_2]$	371	0.122	26954	122	$^3A_{2g} \rightarrow {}^3T_{1g(p)}$
$[Cu(oxine)_2 (2\text{-}pic)_2]$	389	0.422	26041	422	$^2E_g \rightarrow {}^2T_{2g}$
$[Zn(oxine)_2 (2\text{-}pic)_2]$	370	0.188	27027	188	C.T.
$[Cd(oxine)_2 (2\text{-}pic)_2]$	369	0.052	27100	52	C.T.
$[Hg(oxine)_2 (2\text{-}pic)_2]$	319	1.294	31347	1294	C.T.

C.T.= Charge transfer .

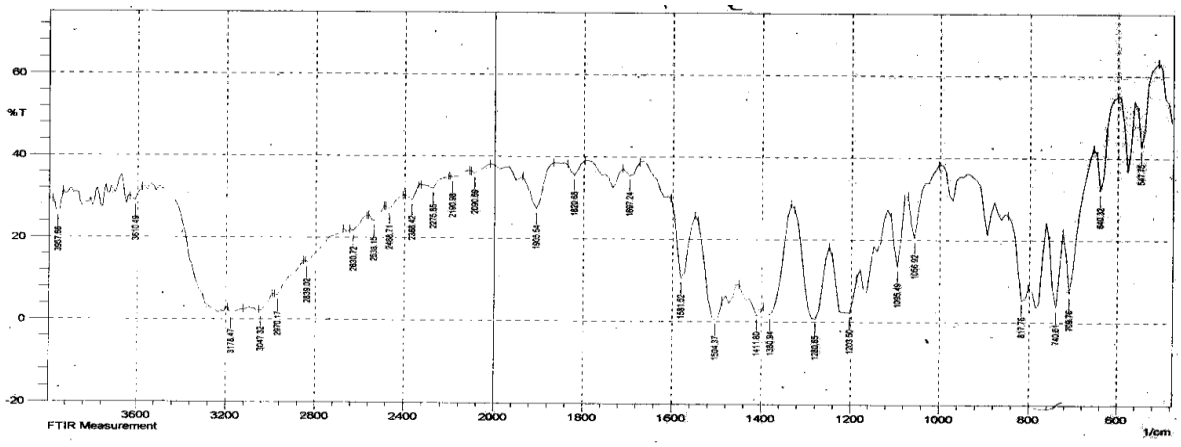


Fig. (1) : Infrared spectrum of 8 –hydroxyquinoline

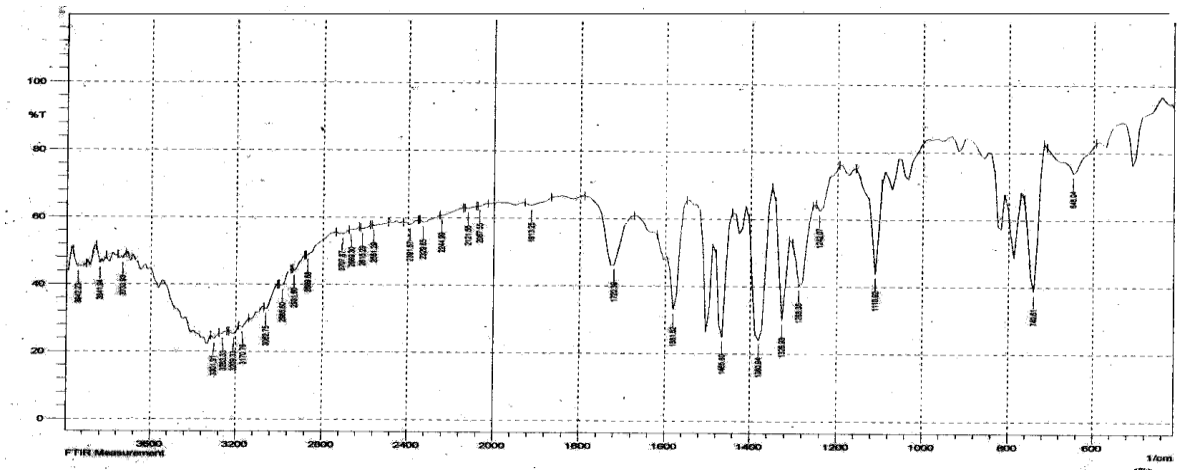


Fig. (2) : Infrared spectrum of the complex [$Ni(oxine)_2(2\text{-}pic)_2$] .

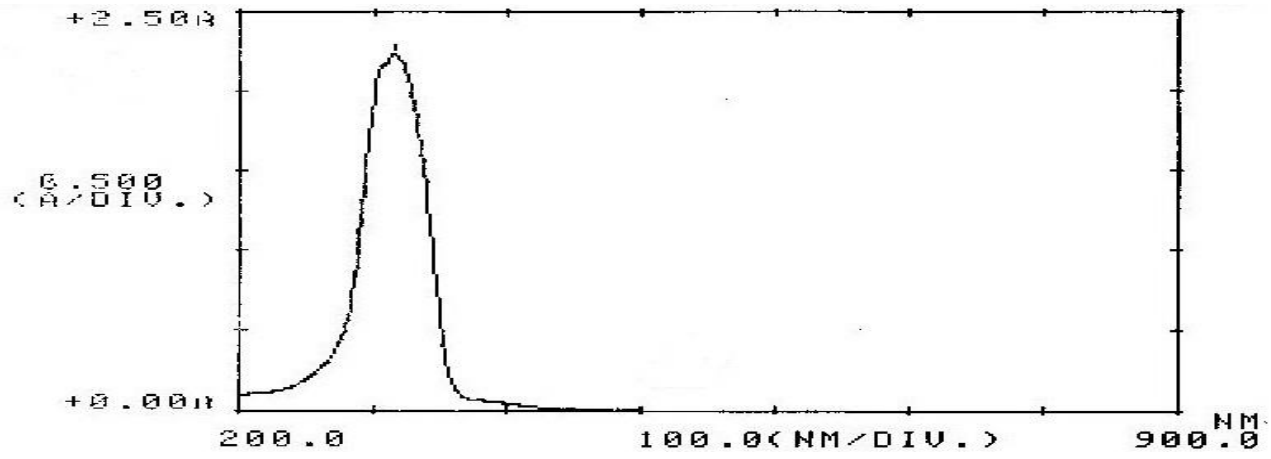


Fig. (3) : UV - visible spectrum of the ligand 8-hydroxyquinoline .

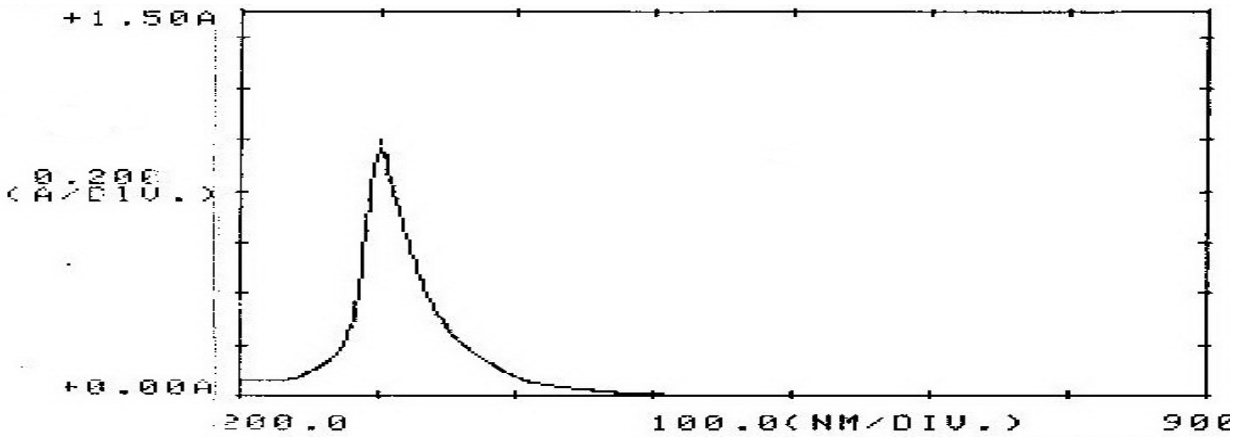


Fig. (4) : UV - visible spectrum of the ligand 2-picolne .

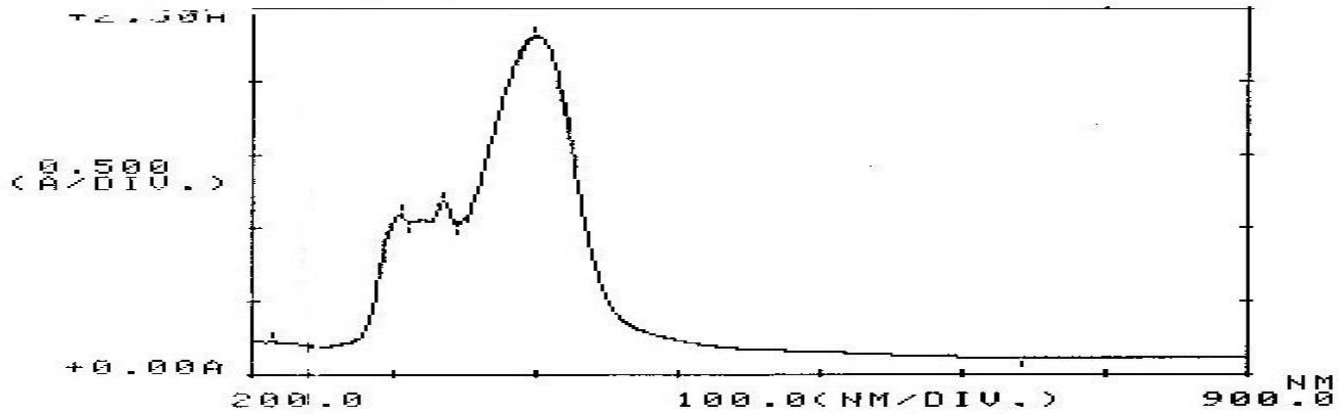


Fig. (5) : UV - visible spectrum of the complex [$Cu(oxine)_2$ $(2-pic)_2$] .

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تحضير وتشخيص بعض معقدات الليكاندات المختلطة من (8- هيدروكسى كوينولين) و(2- بيكولين) مع بعض ايونات الفلزات

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الخلاصة:

يتضمن البحث تحضير وتشخيص بعض معقدات الايونات الفلزية Co(II) ,Mn(II), Cu(II), Ni(II) ، Hg(II) , Cd(II), Zn(II) مع ليكاندات مختلطة 8- هيدروكسي كوينولين (اوكسين) و 2- بيكولين . وتمت دراسة هذه المعقدات بالطرائق الطيفية مثل (الاشعة تحت الحمراء و الاشعة المرئية - فوق البنفسجية) وتعيين نسبة الفلز فى المعقدات باستخدام تقنية الامتصاص الذرى وقياس التوصيلية المولارية والحساسية المغناطيسية . ومن نتائج هذه الدراسات التشخيصية امكن اعطاء الصيغة العامة لهذه المعقدات وكالاتى :-

$[M(oxine)_2(2\text{-}pic)_2]$

حيث M = M(II) = Mn ,Co , Ni , Cu , Zn , Cd , Hg

$(oxine)^-$= الليكاند الايونى 8- هيدروكسى كوينولبن (اوكسيناتو)

2-pic = 2-بيكولين