

# *Synthesis and Characterization of Some transition metal complexes with mannich bases Derived from 8- Hydroxyquinoline*

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## **Abstract**

New bidentate mannich base having nitrogen and oxygen atom was prepared by condensation of the formaldehyde with piperidine and 8-hydroxyquinoline in ethanol. An ethanolic solution of the prepared ligand was reacted with an ethanolic solution of metal ions Cr(III), Fe(III), Co(II), Ni(II) and Cu(II) to give new complexes. All the prepared compounds were isolated and characterized by their melting points, FTIR and UV-Vis., spectroscopy. Elemental analyses have been performed using C, H, N and atomic absorption technique, and the magnetic susceptibility have also been measured.

Keywords: Mannich Reaction of 8-hydroxyquinolion, metal complexes.

## **Introduction**

Active hydrogen compounds react by simple condensation with formaldehyde and a primary or secondary amine to yield compounds called "Mannich Bases". Mannich bases compounds with the general formula ( $R-CH_2NR_2$ ) are an important class of ligands in coordination chemistry and have been studied intensively, mainly because of their application in organic synthesis, pharmaceutical, industrial and polymer chemistry [1-2]. Recently, great attention has been given to the synthesis and biological evaluation of mannich bases compounds containing heterocyclic ring. Heterocyclic bases (8-hydroxyquinoline) have a great importance in biological (against microbes, viruses, and cancer cell) and industrial field [3-4]. Recently, another applications of quinoline complex as, the quinoline ligands effectively sensitize neodymium ion emission following photo-excitation of the polymer host [5], and also used as the electron transport light emitting layer in such organic light emitting diodes (OLED) [6].

## **Experimental**

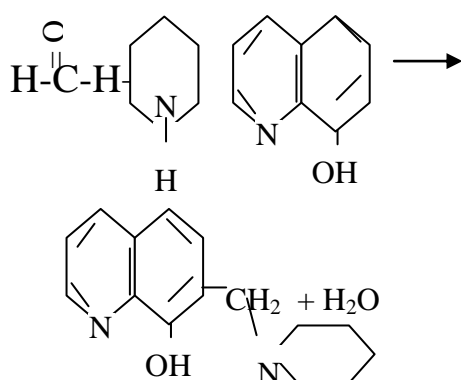
### **Chemicals:**

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All chemicals and reagents were of reagent-grade quality. The purity of the ligand and its complexes were checked by TLC using silica gel as adsorbent.

### Synthesis of the Mannich base:

The mannich base ligand was prepared by the condensation of formaldehyde (0.1 mole) with piperidine (0.1 mole) and 8-hydroxyquinoline (0.1 mole) in ethanol (15 ml). The resulting mixture was then refluxed for 24 hours. The white precipitate formed was filtered and crystallized from ethanol to give the final product. The steps of synthesis of mannich base ligand are shown below:



### General method for preparation of the complexes:

Ethanol solution of the suitable metal salts (CrCl<sub>3</sub>.6H<sub>2</sub>O, FeCl<sub>3</sub>.9H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuSO<sub>4</sub>.5H<sub>2</sub>O) was added to an ethanolic solution of the ligand in 1:2 (metal:ligand) molar ratios and refluxed for 3 hours, crystalline colored precipitates was formed at room temperature. The resulting solids were filtered off, washed with ethanol and dried at 50 °C for 1 hour. Table (1) shows the melting points of the prepared complexes.

### Instrumentation :

Melting points were recorded by using Gallen Kamp 600.01 of melting point apparatus. FTIR specter were recorded as CsI discs using FTIR 8300 Shimadzu in the range 4000-200 cm<sup>-1</sup>. UV-Visible spectra were measured using Shimadzu UV-Vis 160A Ultra-violet spectrophotometer in the range (200-1100 nm).The metal percent in the prepared complexes were determined using Shimadzu 680 cc-flame, Elemental analysis C,H,N were performed using Carlo Erba 1106 elemental analyzer. Magnetic susceptibility for the prepared complexes were obtained at room temperature using magnetic susceptibility balance Jhonson Mattey catalytic system division

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**Table (1)** Physical data for preparation ligand and the complexes

Compound	color	Melting Point, °C	Found (Calc)%				Suggested formula
			C	H	N	M	
L	white	140-142	74.00 (74.38)	7.42 (7.44)	11.50 (11.57)		C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O
CrL	Dark green	150	49.60 (49.65)	4.40 (4.41)	7.68 (7.72)	7.00 (7.17)	[Cr(L) <sub>2</sub> ClH <sub>2</sub> O].3C <sub>2</sub> H <sub>5</sub> OH
FeL	Greenish blue	250	55.40 (55.81)	4.80 (4.96)	10.10 (10.25)	8.01 (8.66)	[Fe(L) <sub>2</sub> H <sub>2</sub> OCl].3H <sub>2</sub> O
CoL	Light green	200	62.00 (62.40)	5.20 (5.55)	9.20 (9.70)	10.15 (10.21)	[Co(L) <sub>2</sub> ].2H <sub>2</sub> O
NiL	Yellowish green	255	63.22 (63.49)	4.99 (5.55)	9.60 (9.72)	10.03 (10.08)	[Ni(L) <sub>2</sub> ].2H <sub>2</sub> O
CuL	Yellowish green	268	63.00 (63.86)	5.6 (5.67)	9.40 (9.93)	11.12 (11.29)	[Cu(L) <sub>2</sub> ].H <sub>2</sub> O

## Infrared spectra studies

### Infrared spectra of free ligand:

The characteristic vibrations assignments of ligand (L) and their complexes are described in Table (2). Ligand spectra showed that some changes appeared on comparison with that of 8-hydroxyquinoline. The appearance of a band at 2854 cm<sup>-1</sup> and 2925 cm<sup>-1</sup>, due to  $\nu$  (C-N) and  $\nu$  (C-H) aliphatic respectively, these bands are attributed to the formation of the mannich product, mannich base as a potential ligand which may acts as bidentate ligand [2,7].

### Infrared spectra of complexes:

A broad band present in the region 3600-3200 cm<sup>-1</sup> which may possibly be due to asymmetric and symmetric O-H stretching vibrations. Another band present at ~1605 cm<sup>-1</sup> is due to H-O-H bending vibrations, representing the presence of a coordinating water molecule [8] which was further confirmed by C,H,N analysis.

An important feature of infrared spectra of metal complexes with ligand is the absence of the band at 3440 cm<sup>-1</sup> due to the O-H stretching vibration of the OH group of the ligand. This observation specifies that complexes are formed by deprotonation of the hydroxyl group of the ligand [8,9]. The ligand behave as a bidentate coordinating with metal through oxygen of hydroxyl group and nitrogen of methylene group, therefore the bands due to  $\nu$  (C-O) and  $\nu$  (C-N) were shifted to a lower frequency respectively, these observation were further indicate by the appearance of some new bands of weak intensity observed in the region 520-440 cm<sup>-1</sup> may be ascribed to  $\nu$  (M-N),  $\nu$  (M-O) and  $\nu$  (M-Cl) vibrations, respectively [9-10].

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**Table(2)**The characteristic bands of infrared spectra of the ligand and their complexes

Compound	$\nu$ (O-H)	$\nu$ (C-H) aromatic	$\nu$ (C=C)	$\nu$ (C=N)	$\nu$ (C-N)	$\nu$ (C-O)	$\nu$ (M-O)	$\nu$ (M-N)
L	3440	3050	1502	1575	2854	1265	—	—
CrL	—	3050	1502	1571	2810	1126	455	502
FeL	—	3050	1505	1575	2818	1120	464	500
CoL	—	3050	1502	1573	2800	1118	451	505
NiL	—	3050	1502	1571	2815	1101	460	509
CuL	—	3050	1505	1575	2825	1125	450	501

### Ultraviolet –Visible Spectroscopy:

The ultraviolet visible electronic spectrum of the prepared ligand (L) in DMF solvent and their complexes were recorded and shown in Table(3). A band at(328 nm) may be attributed to  $\pi \rightarrow \pi^*$  electronic transition and the other band appearing at (380 nm) could be assigned to  $n \rightarrow \pi^*$  electronic transition. The electronic spectra of the prepared complexes showed, as expected, different absorption from that of the free ligand, these bands were shifted to different wavelength than the corresponding bands in the ligand. The spectrum of the dark green complex of CrL gave two bands due to three allowed transitions which indicates an octahedral geometry [11]. The electronic spectrum of FeL complex in DMF solvent showed three bands at (678, 433, 309 nm) respectively, so the octahedral geometry was suggested [12]. The electronic spectrum of CoL complex showed two bands at (627 and 343 nm) which assigned to  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$  and  $L \rightarrow Co$ (charge transfer ) transitions, respectively in tetrahedral geometry[13].

NiL complex assigned to the transition  ${}^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$  at 427 nm [14]. The electronic spectrum of green CuL complex showed a shoulder at 605 nm and a broad band at 416 nm which may be assigned to  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  $\rightarrow {}^2B_{1g} \rightarrow {}^2A_{1g}$  transitions, respectively.

Cu (II) ion in the present complex showed square planar geometry. The band at 331 nm may be due to charge transfer [14].

**Table (3)** Electronic spectra, magnetic moment for metal complexes

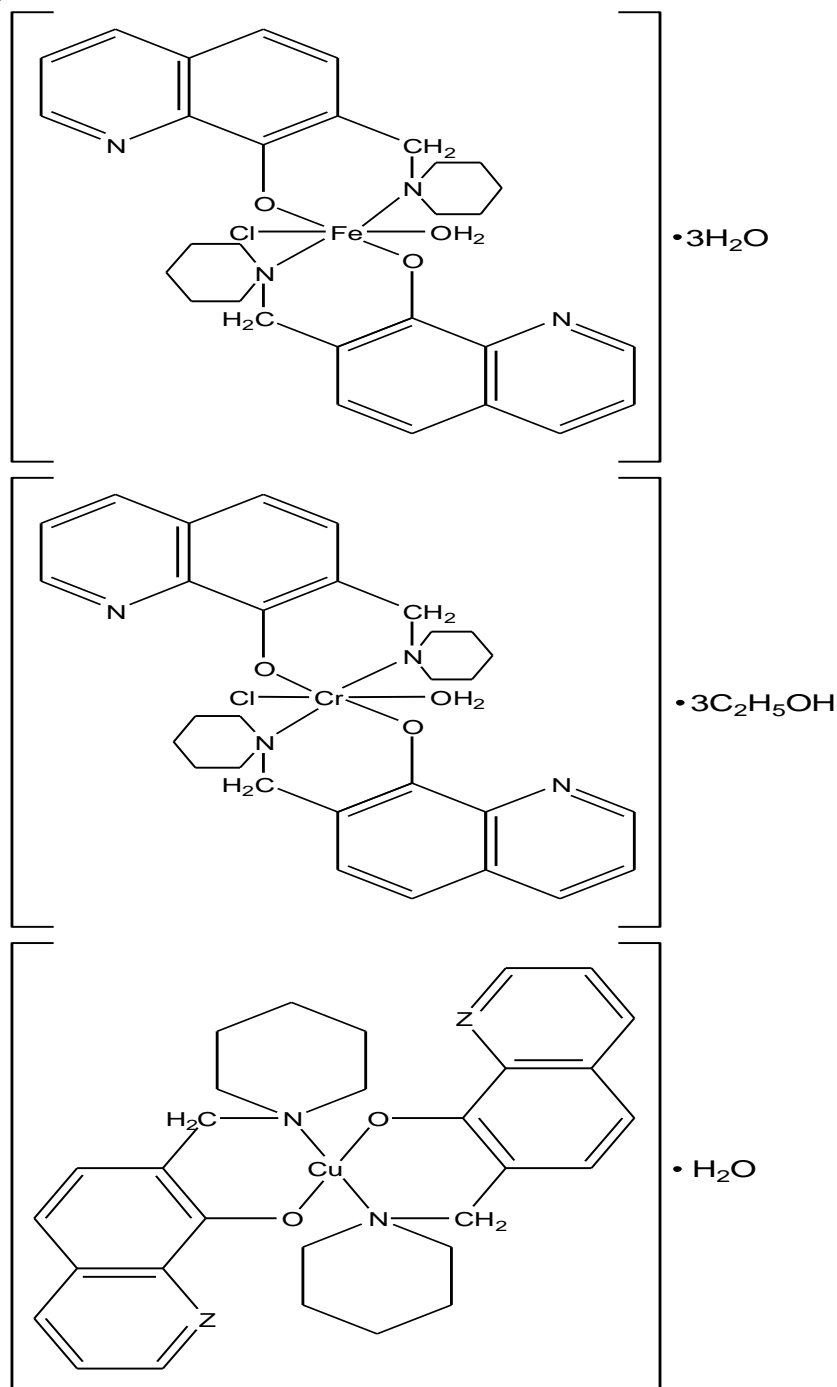
compound	Band nm	Assignment	$\mu_{\text{eff}}$ B.M.	Suggested Structure
CrL	560 352 —	${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	3.9	Octahedral
FeL	678 433 309	${}^6A_{1g} \rightarrow {}^4T_{1g}$ ${}^6A_{1g} \rightarrow {}^4T_{2g}$ $L \rightarrow Fe$ (C.T)	5.9	Octahedral
CoL	— 343 627	$L \rightarrow Co$ (C.T) ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$	4.5	Tetrahedral

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NiL	— 427	${}^3T_1 g(F) \rightarrow {}^3T_2 g(F)$ ${}^3T_1 g(F) \rightarrow {}^3A_2 g(F)$ ${}^3T_1 g(F) \rightarrow {}^3T_1 g(P)$	2.5	Tetrahedral
CuL	605 416 331	${}^2B_1 g \rightarrow {}^2B_2 g$ ${}^2B_1 g \rightarrow {}^2A_1 g$ L $\rightarrow$ Cu(C.T)	1.67	Squar planar

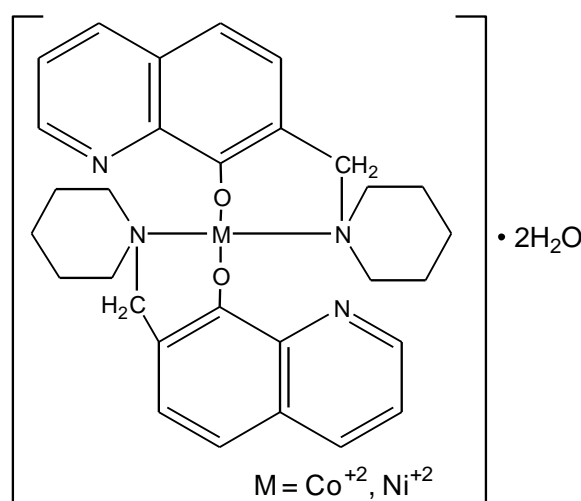
## Magnetic susceptibility of complexes:

The experimental magnetic moment for each metal complexes is listed in Table (3). Magnetic measurement are widely used in studing transition metal complexes. The magnetic properties are due to the presence of unpaired electrons in the



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Partially filled d-orbital in the outer shell of these elements. These magnetic measurements give an idea about the electronic state of the metal ion in the complex. The magnetic moment of  $\text{Cr}^{+3}(\text{d}^3)$  was found to be 3.9 B.M. which gave a good agreement for octahedral structure [13]. The magnetic moment for the complexes of  $\text{Fe}^{+3}(\text{d}^5)$  and  $\text{Co}^{+2}(\text{d}^7)$  were found to be 5.9 B.M. and 4.5 B.M., respectively [15]. The  $\mu_{\text{eff}}$  value for  $\text{Ni}^{+2}(\text{d}^8)$  2.5 B.M. This value refers to a high spin tetrahedral structure, while the value of  $\text{Cu}^{+2}(\text{d}^9)$  approximately 1.67 B.M. led to suggest the square planar structure which can become in a good agreement with the data of electronic transition [11, 14].



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### الخلاصة

الفعالية حيائية لمشتقات ٨- هيدروكسي كوينولين ضد انواع مختلفة من البكتريا والفطريات لذلك جرى تحضير الليكاند الجديد من تكاثف كل من الفورمالديهايد والبيريدين مع ٨- هيدروكسي كوينولين في محلول الايثانول واستعمل الليكاند المحضر (قاعدة مانخ) لتحضير عدد من المعقدات الجديدة مع ايونات بعض العناصر الانتقالية المنتخبة  $Cr(III)$  و  $Fe(III)$  و  $Co(II)$  و  $Ni(II)$  و  $Cu(II)$ . فضلا عن التعرف على السلوك التناسقي لليكاند الجديد تجاه هذه العناصر الانتقالية حيث أظهرت معقدات (III)  $Cr$  و  $Fe(III)$  تركيب ثماني السطوح،  $Co(II)$  و  $Ni(II)$  تركيب رباعي السطوح وظهر معقد  $Cu(II)$  تركيب المربع المستوي. تم عزل وتشخيص الليكاند المحضر ومعقداته الجديده بالطرائق الفيزيائية المناسبة (طيف الاشعه تحت الحمراء، الامتصاصات الالكترونية وتحليل العناصر والحساسية المغناطيسية ودرجة انصهار المركبات)، حيث تم اقتراح هندسة الوحدة الاساسية للمعقدات.