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Study of Biological Activity of Cobalt (II), Nickel (II), Manganese (II) Complexes With 8 -Hydroxyquinoline

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Abstract: Cobalt (II), Nickel (II) and Manganese (II) complexes can be possessed biological activities, these complexes were synthesized via the reaction equimolar quantity of 8-hydroxyquinoline and saccharide such as (-) fructose and (+) glucose as a chiral secondary ligand with Cobalt (II) chloride hexahydrate {$CoCl_2.6H_2O$}, Nickel (II) chloride hexahydrate {$NiCl_2.6H_2O$} and Manganese (II) chloride tetrahydrate {$MnCl_2.4H_2O$} in ration(1:1:1) to form complexes [Co(HQ)(Glu)].$2H_2O$ (a) ,[Ni(HQ)(Fru)].$2H_2O$ (b), [Mn(HQ) (Glu)](c) respectively.

The characterization of these complexes were follow by using Fourier Transform Infrared (FT-IR) and UV-Visible spectroscopy. Also a variable temperature study of these complexes has been followed by using UV-Visible spectroscopy to follow electronic transform behaviors under temperature control also DFT study calculation was follow these complexes via the information from FT-IR and UV-Visible spectroscopy.

A coordination number of these complexes of types five and six of the geometry can be suggested. These complexes were found to shown deferent inhibition to the growth of bacterial strains of (*Staphylococcus aureus* , *Streptococcus* , *Escherichia coli* , *Klebsiella* , *Salmonella typhi* , *Sraphiaureus*) while all complexes were in deferent's concentration (0.1 , 0.01 , 0.001M) and the result as evidenced from the presence. For better understanding these

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complexes were examined by using Density functional theory (DFT) calculation.

Keywords: (8-hydroxyquinoline) (HQ), secondary legends, Cobalt (II), Nickel (II), Manganese (II) Salts, DFT.

Introduction: A great attention complexes of transition metal have received for many years. because of their biological activities, antibacterial, antiviral, antifungal and anti carcinogenic properties . In recent years, there has been renewed interest in synthesis and study of metal complexes with 8-hydroxyquinoline possessing biological activities (1).

The utility aspects of these complexes have received their share of attention as these have found applications in diverse fields . choral metal complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances, especially in asymmetric synthesis(2). Light catalyzed inversion and diastereoisomeric equilibration in choral metal complexes have been studied extensively(3,4).

The metal complex ability, weak immunogenicity and high water solubility of sacaharides are of importance in the development of choral homogeneous catalysts and as models of biologically important chelates(5,6). The biological activity of some mixed legends complexes againt pathogenic microorganisms has been reported(7). The present work comprises of synthesis and characterization of chiral mixed legends Co(II)/Ni(II)/Mn(II) complexes prepared by using 8- hydroxyquinoline as primary legends and some chiral saccharides as secondary legends.

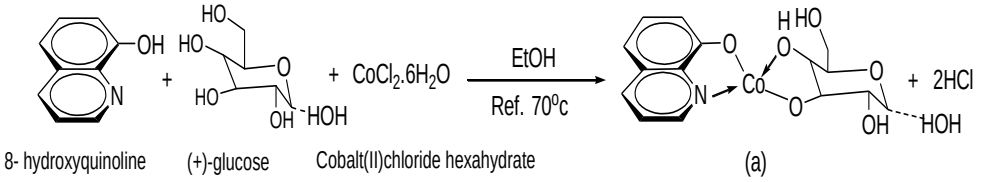
The complexes experimented with different concentrations on some types of bacteria.

Materials And Methods:

All chemical were used as received from supplied. Cobalt (II) / Nickel (II) Chloride hexahydrate and Manganese (II) Chloride tetrahydrate produced by Laboratory Reagent chemical company. Saccharides were obtained from chem King . 8-hydroxyquinoline produced by BHD chemical company. sodium hydroxide produced by Riedel-dehean chemical company . Ethanol , methanol and chloroform production company PSPARK chemical company. N,N-Dimethyl Formamide production company E.Merck chemical company .

Synthesis of [Co(HQ)(Glu)]. 2 H_2O

Co (II) complex was prepared from Cobalt (II) chloride hexahydrate {$CoCl_2.6H_2O$} , 8-hydroxyquinoline (HQ) and chiral secondary ligands such as (+) glucose and (-) fructose. In double nick flask (237mg, 1mmol) of cobalt (II) chloride hexahydrate in 10ml ethanol solution add (145mg, 1mmol) of 8- hydroxyquinoline in 10ml ethanol solution the mixture was stirred and kept in a boiling water bath for 10 minutes, during which time it turned blue in colour. To this was added an aqueous solution of the saccharides(180mg, 1mmol). This mixture (1:1:1 molar proportion) was heated in a hot water bath till the temperature reached 70 ºC. The complexes were obtained by raising the pH of the reaction mixture by adding 0.01 mole NaOH solution. The mixture was cooled and solid was filtered , washed with ice-cold water followed by 1:1 ethanol :water. The complexes thus prepared were dried under vacuum. After re crystallization we acquired the light yellow in percentage of 50% (Scheme 1).



Scheme 1: preparation of [Co(HQ)(Glu)].2H_2O (a)

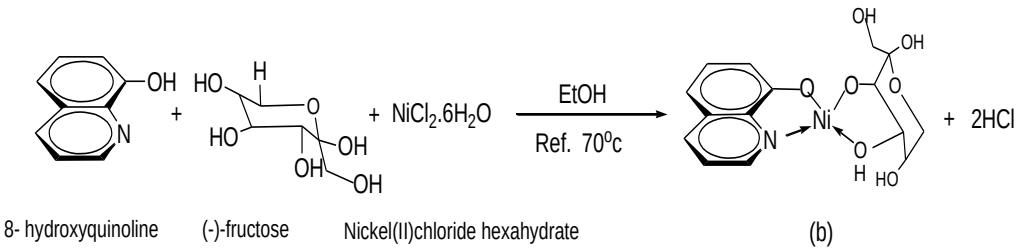
Synthesis of [Ni(HQ)(Fru)].2H_2O

Ni(II) complex was prepared from Nickl(II) chloride hexahydrate {$NiCl_2.6H_2O$} , 8-hydroxyquinoline(HQ) and chiral secondary legends such as(+)-glucose and (-)-fructose.

In double nick flask (238mg , 1mmol) of Nick(II)chloride hexahydrate in 10ml ethanol solution add (145mg , 1mmol) of 8- hydroxyquinoline in 10ml ethanol solution the mixture was stirred and kept in a boiling water bath for 10 minutes, during which time it turned green in color. To this Was added an aqueous solution of the saccharides(180mg,1mmol) .This mixture (1:1:1 molar proportion) was heated in a hot water bath till the

Temperature reached 70^0 C. The complexes were obtained by raising the pH of the reaction mixture by adding 0.01 mole NaOH solution. The mixture was cooled and solid was filtered , washed with ice-cold water followed by 1:1 ethanol:water. The complexes thus prepared were dried

under vacuum .After re crystallization we acquired the green in percentage of 50% (Scheme 2).

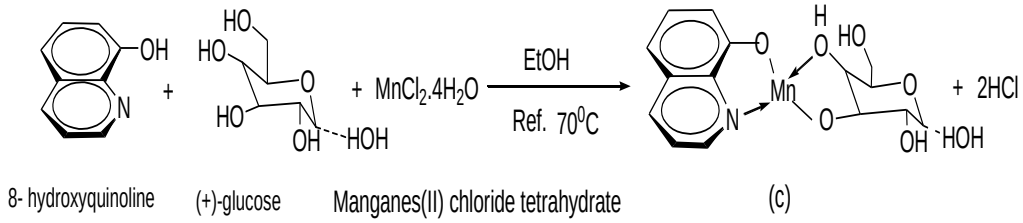


8- hydroxyquinoline (-)-fructose Nickel(II)chloride hexahydrate (b)

Scheme 2 : preparation of [Ni(HQ)(Fru)].2H_2O (b)

Synthesis of [Mn(HQ)(Glu)]

Mn (II) complexe was prepared from Manganese (II) chloride tetrahydrate {$MnCl_2.4H_2O$}, 8-hydroxyquinoline (HQ) and chiral secondary legends such as (+) glucose and (-) fructose. In double nick flask (237mg , 1mmol) of Manganese (II) chloride tetrahydrate in 10ml ethanol solution add (145mg, 1mmol) of 8- hydroxyquinoline in 10ml ethanol solution the mixture was stirred and kept in a boiling water bath for 10 minutes, during which time it turned blue in color. To this was added an aqueous solution of the saccharides (180mg,1mmol). This mixture (1:1:1 molar proportion) was heated in a hot water bath till the Temperature reached 70 ºC. The complexes were obtained by raising the PH of the reaction mixture by adding 0.01 mole NaOH solution. The mixture was cooled and solid was filtered, washed with ice-cold water followed by 1:1 ethanol:water. The complexes thus prepared were dried under vacuum. After recrystallization we acquired the light yellow in percentage of 50% (Scheme 3).



Scheme 3: preparation of [Mn(HQ)(Glu)]

Instrumentation:

The complexes were analyzed for the electronic absorption spectra in the ultraviolet range in methanol at 10^{-4}M concentration were measured on a shimadzu UV-160A and spectronic-20spectrophotometer. Reflectance spectra of the solid complexes in the visible region were recorder against $BaSO_4$ on a shimadzun UV-2100 spectrophotometer. FT-IR spectra were recorded as KBr discs on a model 160 perkin-Elmer spectrophotometer. Thermal studies of the complexes were made on a Mettler TC 10A TA processor by re cording the change in weight of the complexes on increasing the temperature up to 70 ºC at a heating rate of 10 ºC/min.

Antimicrobial screening

The antibacterial activities of the complexes were assayed against some of the bacteria . The paper technique disks method (11) was used to assay antibacterial activity against *Streptococcus, Staphylococcus-aureus, Escherichia coli, Klebsiella, Salmonella typhi* and *Sraphiaureus*.The solvent used was dimethyl formamide (DMF),and the samples concentration were (0.1 , 0.01 , 0.001M).

Paper technique disks method

Used the nomination papers to prepare tablets after puncture and distributed these tablets on petri dishes then sterilized by sterilizer "oven" at a temperature of 170 ºC added to these sterile disks complexes prepared concentrations (0.1 , 0.01 , 0.001M) and then left to dry. Prepare agricultural center Muller-Hinton agar then planted bacterial strains developing on the agricultural center "Blood agar" certain intensity and planted disks containing concentrations complexes prepared on the agricultural center containing the microbial growth and by eight tablets per dish .These dishes were placed in the incubator for 24 hours at a temperature of 37 ºC . After 24 hours read results and select the range of inhibition around each disk using the ruler.

RESULTS AND DISCUSSION

Characterization of metal complexes :

All of the complexes are non-hygroscopic stable solids. They are colored and thermally stable(Table 1),indicating a strong metel-ligand bond (12, 13). The all complexes were characterized using, melting point determination, Fourier Transform Infrared (FT-IR) and UV-Visible spectrometer studies. The melting points of the complexes were carried out on a Bamslead Electro thermal melting point apparatus. The IR spectrum was recorded in the range 4000 – 400 cm^{-1} on a Fourier Transform Infrared (FT-IR) spectrometer Bruker tensor 37 Gemany (ATR). The electronic spectra in ethanol solution were recorded in the range 200 – 900 nm on a Schimadzu UV – VIS 9200 spectrophotometer Japan. The antibacterial studies were conducted with bacterial stains of *staphylococcus aureus*, *streptococcus*, *Escherichia*, *Klebsiella Salmonella typhi* and *Sraphiaureus* in cultural medium of nutrient Agar. This Agar medium was prepared in distilled water and inoculation was

done in petri dishes using platinum wire .The compounds were dissolved in mixture of water and ethanol (10:1ml) and 3mm diameter blotting paper disc are dipped in this solution and then dried in an incubator. This was applied on the bacteria and plates were kept in incubator at for 37 ºC for 24 hours. The zone of inhibition was measured in mm and its percentage is calculated.

Spectrometers Studies:

UV-Vis. Spectral study:

Co[(HQ)(Glu)].2H_2O

Was examined in spectrally by using a ultraviolet and visible radiation UV-Vis . has given peaks absorption of initial at 257nm,203nm and 201nm in frequency (1.298cm^{-1}, 3.471cm^{-1} and 3.321 cm^{-1}) respectively which's demonstrates the transmission of the types $\prod \rightarrow \prod^*$, $n \rightarrow \prod^*$ and C - T (Chage Transfer) transition respectively and these identical with those reported in some literature.

Ni[(HQ)(Fru)].2H_2O

Was examined in spectrally by using a ultraviolet and visible radiation UV-Vis . has given peaks absorption of initial at 260nm,208nm and 206nm in frequency (1.965cm^{-1} , 3.097cm^{-1} and 3.097 cm^{-1}) respectively which's demonstrates the transmission of the types $\prod \rightarrow \prod^*$, $n \rightarrow \prod^*$ and C - T (Chage Transfer) transition respectively and these identical with those reported in some literature .

Mn[(HQ)(Fru)].2H_2O

Was examined in spectrally by using a ultraviolet and visible radiation UV-Vis . has given peaks absorption of initial at 597nm and 240nm in frequency (0.201cm^{-1} , 0.949cm^{-1}) respectively which's demonstrates the transmission of the types $\prod \rightarrow \prod^*$, $n \rightarrow \prod^*$ and C - T (Chage Transfer)

transition respectively and these identical with those reported in some literature .

$Mn[(HQ)(Glu)].2H_2O$

Was examined in spectrally by using a ultraviolet and visible radiation UV-Vis . has given peaks absorption of initial at 261nm in frequency 0.930cm^{-1} respectively which's demonstrates the transmission of the types $\prod\rightarrow\prod^*$, $n\rightarrow\prod^*$ and C - T (Change Transfer) transition respectively and these identical with those reported in some literature.

Infra-red spectral study:

The FT-IR spectra of the CML metal complexes were recorded as KBr discs over the range 4000-400 cm^{-1} .

On the basis of reported infra-red spectra of glucose, fructose, 8-hydroxyquinoline and their metal complexes(14-16)some of the important bands have been assigned :

1-A broad band observed in the region between 3180-3174cm^{-1} due to asymmetric and symmetric O-H stretching modes and a strong peak in the range 1578cm^{-1} due to H-O-H bending showing the presence of water of crystallization(13).

2- It has been reported(17) that for several metal complexes with HQ , the position of this band undergoes variation depending on the metal complex under study. A strong v(C-O) band is observed at about 1106cm^{-1} indicating the presence of oxine moiety in the complexes coordinating though its nitrogen and oxygen atoms as uninegative bidentate ligand. The v(C=N) mode in oxine occurs at 1499cm^{-1} in the spectra of metal complexes. This band is observed in the spectrum of the ligand in the higher region (1578cm^{1}). A negative shift in this vibration mode on complexation indicates

the coordination through the tertiary nitrogen donor of HQ. The in plane and out of plane ring deformation modes are observed at ~ 505 and ~ 791cm^{-1} respectively, confirming coordination through the nitrogen atom of HQ with metal.

3- The merging and broadening of bands was found to be a common feature of transition metal-saccharide complexes(18). The spectra of all the complexes with saccharides showed broad bands in the O-H and C-H regions , indicating a merging of individual bands.

The spectral characteristics is similar to those observed with other 1st row transition metal complexes (19). The structural vibrations of the intermolecular hydrogen bonded O-H groups of the free saccharides were affected ionization and exhibited a broad but nearly symmetrical band at ~3400cm^{-1}. The strongly coupled ring vibration frequencies for bending modes COH, CH_2 and CCH of the free saccharides (1460-1340cm^{-1})showed merging at 1427cm^{-1} upon complex formation. Similarly, the C-O and C-C stretching vibrations in the region 1140-990cm^{-1} were also merged at ~ 1037cm^{-1} upon complex formation, in contrast to the sharp bands observed for the free saccharides and other metal - saccharide adducts. The anomeric region (950-500cm^{-1}) showed very weak marker bands of mostly α-anomer. It was clear from the spectra that the saccharides were involved in coordination through some deprotonated -OH groups as observed from the broad bands in v(O-H) region, 3500-3200cm^{-1} . On the basis of coordinating abilities of the various saccharides reported (20-22), a 3,4-trans-diol arrangement has been proposed for CML complexes with glucose and fructose.

4- the C-O and C-C stretching vibrations in the region 1140-990cm^{-1} were also merged at ~ 1037cm^{-1} upon complex formation, in contrast to the sharp bands observed for the free saccharides and other metal- saccharide adducts. The new bands of weak intensity, observed in the regions about 625-591cm^{-1} and 435-420cm^{-1} ,may be ascribed to M-N and M-O vibrations,respectively.

Biological activity

The antibacterial studies were tested on the six species of the bacteria such *(Staphylococcus-aureus, Streptococcus, Escherichia coli, Klebsiella, Salmonella typhi* and *Sraphiaureus*) while all complexes were in deferent's concentration (0.1 , 0.01 , 0.001M) and the result is given in (Table 2,3,4). In concentration of 0.1M complexes [Co(HQ)(Glu)].2H_2O and [Ni(HQ)(Fru)] .2H_2O showed a positively influence on five types of bacterial *(Staphylococcus-aureus, Streptococcus, Escherichia coli, Salmonella typhi* and *Sraphiaureus*),whiling the other complex [Mn(HQ)(Glu)] showed mildly influential on the four species of the bacteria *(Staphylococcus-aureus, Escherichia coli ,Salmonella typhi* and *Sraphiaureus),*the result is given in (Table 2). In concentration of 0.01M complexes [Co(HQ)(Glu)].2H_2O and [Ni(HQ) (Fru)] .2 H_2O showed a positively influence on four types of bacterial *(Staphylococcus-aureus, Escherichia coli, Salmonell* typhi and *Sraphiaureus*), whiling the other complex [Mn(HQ) (Glu)] showed low influential on the six species of the bacteria mentioned above,the result is given in(Table 3) . In concentration of 0.001M Most complexes gave a negative result on the six species of the bacteria mentioned above, the result is given in (Table 4).

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Table 1. colour,decomposition temperature of the metal complexes

Compound	Empirical Formula	Colour	Decomp.temp.(^{0} C)
[Co(HQ)(Glu)].2H_2O	$CoC_{15}H_{21}O_9N$	Light yellow	270
[Ni(HQ)(Fru)].2H_2O	$NiC_{15}H_{21}O_9N$	Green	230
[Mn(HQ)(Glu)]	$MnC_{15}H_{17}O_7N$	Light yellow	270

Table 2. Antibacterial Activities in concentration 0.1M

Complex	*S.aureus*		*Streptococcus*		*E.coli*		*Klebcella*		S. typhi		*Sraphiaureus*	
	Act.	%	Act.	%	Act.	%	Act.	%	Act.	%	Act	%
[Co(HQ)(Glu)].2H_2O	+++	75%	+	25%	+++	75%	_	15%	+++	75%	++	% 60
[Ni(HQ)(Fru)].2H_2O	++	70%	+	25%	++	60%	_	10%	++	60%	++	% 60
[Mn(HQ)(Glu)]	++	50%	_	10%	++	50%	_	10%	++	50%	++	% 50

Percentage of Inhibition: Below 5mm=(-) low active, 5mm-10mm=(+)Active,10mm-15mm=(++) Mildly active & 15mm-20mm=(+++)moderately active,(20mm,up)=(++++)highly active

Table 3. Antibacterial Activities in concentration 0.01M

Complex	*S.aureus*		*Streptococcus*		*E.coli*		*Klebcella*		S. typhi		*Sraphiaureus*	
	Act	%	Act.	%	Act.	%	Act.	%	Act.	%	Act.	%
[Co(HQ)(Glu)].2H_2O	++	60%	_	10%	++	60%	_	10%	++	60%	++	50%
[Ni(HQ)(Fru)].2H_2O	++	50%	_	10%	++	50%	_	5%	++	50%	++	50%
[Mn(HQ)(Glu)]	+	30%	_	5%	+	30%	_	5%	+	35%	+	30%

Percentage of Inhibition: Below 5mm=(-) low active, 5mm-10mm=(+)Active,10mm-15mm=(++)
Mildly active & 15mm-20mm=(+++)moderately active,(20mm,up)=(++++)highly active

Table 4. Antibacterial Activities in concentration 0.001M

Complex	*S.aureus*		*Streptococcus*		*E.coli*		*Klebcella*		S. typhi		*Sraphiaureus*	
	Act.	%	Act.	%	Act.	%	Act.	%	Act.	%	Act.	%
[Co(HQ)(Glu)].2H_2O	+	%25	_	5%	+	30%	_	5%	+	30%	+	25%
[Ni(HQ)(Fru)].2H_2O	+	%25	_	5%	+	25%	_	5%	+	25%	_	10%
[Mn(HQ)(Glu)]	_	%20	_	5%	_	10%	_	5%	_	10%	_	5%

Percentage of Inhibition: Below 5mm=(-) low active, 5mm-10mm=(+)Active,10mm-15mm=(++)
Mildly active & 15mm-20mm=(+++)moderately active,(20mm,up)=(++++)highly active

Conclusions:

Based on the above discussion and information available in the literature, the following conclusions may be drawn. Higher decomposition temperature show the presence of strong metal-ligand bonding of the complexes. therefore the complexes were followed by the UV-Vis study and showed the transition that of the these complexes .IR spectra show bonding of the metal ion through N/O and O of the two ligands and presence of water of crystallization, confirmed by thermal analysis. The studies on antimicrobial

activity indicate that behavior comes affects in increased antibacterial activity under deferent concentration.

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