

## SYNTHESIS, SPECTRAL AND BIOLOGICAL STUDIES ON SOME MIXED LIGAND Ni(II) COMPLEXES

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**Abstract:** Mixed ligand Ni(II) complexes of the type  $[M(Q)(L)_2 \cdot 2H_2O]$  have been synthesized by using 8-hydroxyquinoline (HQ) as a primary ligand and N- and/or O- donor amino acids (HL) such as L-serine, L-isoleucine, L-proline, 4-hydroxy-L-proline and L-threonine as secondary ligands. The metal complexes have been characterized on the basis of elemental analysis, electrical conductance, room temperature magnetic susceptibility measurements, spectral and thermal studies. The electrical conductance studies of the complexes in methanol at  $10^{-3}$  M concentration indicate their non-electrolytic nature. Room temperature magnetic susceptibility measurements revealed paramagnetic nature of the complexes. Electronic absorption spectra of the complexes show intra-ligand, charge transfer and d-d transitions, respectively. The thermal analysis data of the complexes indicate the presence of coordinated water molecules. Tube dilution method has been used to study the antibacterial activity of the complexes against the pathogenic bacteria *C. diphtheriae*, *S. aureus* and *C. albicans*. The results have been compared with those of control tetracycline, which was screened simultaneously and indicated mild antibacterial activity of the complexes.

**Keywords:** mixed ligand nickel complexes; biological study

The role of mixed ligand complexes in biological process has been well recognized (1, 2). The stabilities of mixed chelates are of great importance in biological systems as many metabolic and toxicological functions are dependent upon this stability. Many attempts have been made to correlate the stability of the metal-ligand complexes with their antimicrobial activity (3-7).

It is well established that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances (8). Ogunniran et al. have proved that physical properties and antimicrobial activities are enhanced upon complexation (9). It has been found that a majority of the metal complexes with 8-hydroxyquinoline possess biological activity (10-12). Amino acids are well known for their tendency to form complexes with metals having biological significance and metabolic enzymatic activities (13). Many researchers have studied characterization, antimicrobial and toxicological activity of mixed ligand complexes of transition metals and actinide metal

ions (14-19). Antitumor activity of some mixed ligand complexes have also been reported (20, 21). Therefore it was thought to undertake the study of mixed ligand complexes of nickel, with 8-hydroxyquinoline (HQ) as a primary ligand and different amino acids (HL) such as: L-serine, L-isoleucine, L-proline, 4-hydroxy-L-proline and L-threonine, as secondary ligands. The metal complexes have been characterized by elemental analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic spectra, IR spectra and thermal studies.

### EXPERIMENTAL

#### Materials

Analytical grade nickel(II) chloride hexahydrate was used as such without further purification. Amino acids, L-isoleucine, L-proline and L-threonine were obtained from S. D. Fine Chemicals, Mumbai, while 8-hydroxyquinoline, 4-hydroxy-L-proline and L-serine were obtained from E. Merck. Solvents ethanol,

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methanol, chloroform and dimethylformamide whenever used were distilled and purified according to standard procedures (22-24).

#### Preparation of mixed ligand complexes

Mixed ligand Ni(II) complexes were prepared from nickel(II) chloride hexahydrate, 8-hydroxyquinoline (HQ) and different amino acids (HL) such as L-serine, L-isoleucine, L-proline, 4-hydroxy-L-proline and L-threonine as secondary ligands.

To an aqueous solution (10 mL) of nickel(II) chloride hexahydrate (237 mg, 1 mmol), ethanolic solution (10 mL) of 8-hydroxyquinoline (145 mg, 1 mmol) was added. The mixture was stirred and kept in a boiling water bath for 10 min. To this hot solution, an aqueous solution (10 mL) of amino acid (1 mmol) was added with constant stirring. The mixture was again heated in the water bath. The complexes were obtained by raising pH of the reaction mixture by adding diluted ammonia solution. The mixture was cooled and solid complex obtained was filtered, washed with water followed by ethanol. The complexes thus prepared were dried under vacuum.

#### Instrumentation

The complexes were analyzed for C, H, and N contents in Thermo Finnigan Elemental Analyzer, Model No. FLASH EA 1112 Series at the Department of Chemistry, I.I.T., Mumbai. Metal content was estimated complexometrically by standard procedure (25, 26).

The molar conductance values were measured in methanol ( $10^{-3}$  M) on an Equiptronics Autoranging Conductivity Meter Model No.-EQ-667 with a dip type conductivity cell fitted with platinum electrodes (cell constant =  $1.0 \text{ cm}^{-1}$ ).

The room temperature magnetic susceptibility measurements of the complexes reported in the present study were made by the Guoy's method using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant at the Department of Chemistry, I.I.T., Mumbai.

The electronic spectra of all the complexes in chloroform solution ( $10^{-3}$  M) in the visible region were recorded on Spectronic-20 spectrophotometer. The electronic spectra of all the complexes in methanol ( $10^{-3}$  M) in the ultraviolet region were recorded on Shimadzu UV/VIS-160 spectrophotometer using a quartz cell of 1 cm optical path. Calibration of the instrument was checked with 0.0098%  $\text{KMnO}_4$  solution (27).

Infrared spectra of all the ligands and their metal complexes were recorded in KBr disc on a Perkin-Elmer FT-IR spectrophotometer Model 1600 in the region  $4000\text{-}400 \text{ cm}^{-1}$ . The pellets were pre-

pared taking necessary precautions to avoid moisture. The instrument calibration with respect to wave number and percent transmission was confirmed by recording the spectrum of standard polystyrene film. From the spectra, the characteristic groups were assigned the respected frequencies (28).

Thermal Analysis (TG and DTA) were carried out in controlled nitrogen atmosphere on a Perkin-Elmer Diamond TG-DTA instrument at the Department of Chemistry, I.I.T., Mumbai, by recording the change in weight of the complexes on increasing temperature up to  $900^\circ\text{C}$  at the heating rate of  $10^\circ\text{C}/\text{min}$ .

#### Antibacterial screening

##### Agar cup method

In the agar cup method, a single compound can be tested against number of organisms or a given organism against different concentrations of the same compound. The method was found suitable for semisolid or liquid samples and was used in the present work. In the agar cup method, a plate of sterile nutrient agar with the desired test strain was poured to a height of about 5 mm, allowed to solidify and a single cup of about 8 mm diameter was cut from the center of the plate with a sterile cork borer. Thereafter, the cup was filled with the sample solution of known concentration and the plate was incubated at  $37^\circ\text{C}$  for 24 h. The extent of growth inhibition from the edge of the cup was considered a measure of the activity of the given compound. By using several plates simultaneously, the activities of several samples were quantitatively studied.

##### Tube dilution method

The method was used to study the antifungal activity of the complexes against some of the pathogenic fungi. Fungus inoculum was prepared by inoculating the selected fungus into sterilized Sabouraud's broth to which  $0.1 \text{ mg}/\text{cm}^3$  of streptomycin was added to prevent bacterial contamination. After sporulation, the spores were harvested in the same media by gentle stirring using a magnetic stirrer and the spore suspension was poured into another sterile flask.

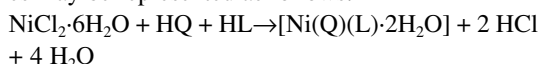
To a  $5 \text{ cm}^3$  of Sabouraud's broth contained in  $15 \text{ cm}^3$  corning test tube,  $0.1 \text{ cm}^3$  of the test solution of the complex in DMF was added. It was autoclaved at 15 lb pressure for 15 min. The tubes were cooled and inoculated with  $0.1 \text{ cm}^3$  of spore suspension. The tubes were then kept on a rotary shaker and incubated at room temperature for 24 h. The percentage growth of the fungus was calculated after determining the optical density (OD) of the solution on a spectrophotometer at 530 nm with inoculated

Sabouraud's broth as a blank. The growth of the fungus in the tube, which contained none of the anti-fungal agent, was assumed as 100%. The results were compared with those of the control (amphotericin), which was screened simultaneously.

## RESULTS AND DISCUSSION

### Characterization of metal complexes

The synthesis of mixed ligand Ni(II) complexes may be represented as follows:



where HQ is 8-hydroxyquinoline and HL is an amino acid.

All the complexes are colored, non-hygroscopic and thermally stable solids (Table 1), indicating a strong metal-ligand bond. The complexes are insoluble in common organic solvents such as ethanol, acetone, etc. but are fairly soluble in methanol, chloroform, DMF and DMSO. The elemental analysis data (Table 2) of metal complexes is consistent with their general formulation as 1:1:1, mixed ligand complexes of the type  $[\text{Ni}(\text{Q})(\text{L}) \cdot 2\text{H}_2\text{O}]$ . The molar conductance values of the complexes in DMF at  $10^{-3}$  M concentration are very low ( $< 1$ ) indicating their non-electrolytic nature (29).

### Magnetic studies

The magnetic moments of the metal complexes were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections. The observed  $\mu_{\text{eff}}$  values presented in Table 2 suggest the octahedral geometry for nickel complexes. The magnetic moments of the compounds investigated support the conclusions.

### Electronic absorption spectra

The electronic spectra of the metal complexes in methanol recorded in the UV region exhibit intra ligand and charge transfer transitions. The spectra

show three transitions in the range 203-261 nm, 336 nm and 385-386 nm which can be assigned to  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$  and the charge transfer transitions (LMCT) from ligands to the metal, respectively. The spectra of metal complexes in chloroform recorded in the visible region show transitions in the range 400-410 nm, ascribed to charge transfer transition. Two transitions around 560-600 nm and 820-840 nm may be ascribed to d-d transitions which are characteristic feature of transition metal complexes. (30-33).

### Infra-red spectra

The FTIR spectra of the metal complexes were complicated due to the presence of numerous bands with varying intensities, making the interpretation difficult. However, an attempt has been made to assign some of the important bands on the basis of reported infrared spectra of several N and/or O donor ligands, 8-hydroxyquinoline and their metal complexes (34-37).

An important feature of these infrared spectra is the absence of band at  $\sim 3440 \text{ cm}^{-1}$  due to the O-H stretching vibration of the free O-H group of HQ. This observation leads to the conclusion that complex formation takes place by deprotonation of the hydroxyl group of HQ moiety. A strong  $\nu(\text{CO})$  band observed in the range  $1111-1107 \text{ cm}^{-1}$  in the spectra of the complexes, indicates the presence of the 8-hydroxyquinoline moiety in the complexes coordinating through its nitrogen and oxygen atoms as uninegative bidentate ligand. The  $\nu(\text{C}=\text{N})$  mode observed at  $1580 \text{ cm}^{-1}$  in the spectrum of free HQ ligand is found to be shifted to lower wave number, i.e.  $1469-1467 \text{ cm}^{-1}$  in the spectra of the complexes, suggesting coordination through the tertiary nitrogen donor of HQ. The in-plane and out-of-plane deformation modes observed at  $\sim 500 \text{ cm}^{-1}$  and  $\sim 780 \text{ cm}^{-1}$ , respectively, in the spectrum of HQ are shifted to higher wave numbers  $\sim 505 \text{ cm}^{-1}$  and in the range  $790-784 \text{ cm}^{-1}$ , respectively, confirming coordination through the nitrogen atom of HQ with the metal ion (10, 11, 34).

Table 1. Color, molecular weight, decomposition temperature and pH of the nickel complexes

No.	Complex <sup>a</sup>	Empirical Formula	Molecular Weight	Color	Decomposition temperature (°C)	pH
1	$[\text{Ni}(\text{Q})(\text{Ser}) \cdot 2\text{H}_2\text{O}]$	$\text{NiC}_{12}\text{H}_{16}\text{O}_6\text{N}_2$	342.71	Light green	313	6.95
2	$[\text{Ni}(\text{Q})(\text{Iso}) \cdot 2\text{H}_2\text{O}]$	$\text{NiC}_{15}\text{H}_{22}\text{O}_5\text{N}_2$	368.71	Light green	321	6.29
3	$[\text{Ni}(\text{Q})(\text{Pro}) \cdot 2\text{H}_2\text{O}]$	$\text{NiC}_{14}\text{H}_{18}\text{O}_5\text{N}_2$	352.71	Light green	286	6.48
4	$[\text{Ni}(\text{Q})(\text{HPro}) \cdot 2\text{H}_2\text{O}]$	$\text{NiC}_{14}\text{H}_{18}\text{O}_6\text{N}_2$	368.71	Light green	306	6.58
5	$[\text{Ni}(\text{Q})(\text{Thr}) \cdot 2\text{H}_2\text{O}]$	$\text{NiC}_{13}\text{H}_{18}\text{O}_6\text{N}_2$	356.71	Light green	287	6.14

<sup>a</sup>Q represents the deprotonated primary ligand 8-hydroxyquinoline, whereas Ser, Iso, Pro, HPro and Thr represent deprotonated secondary ligands L-serine, L-isoleucine, L-proline, 4-hydroxy-L-proline and L-threonine.

Table 2. Elemental analysis data, molar conductance and magnetic moment of nickel complexes

No.	Complex	Elemental analysis Found (Calculated)				Molar conductance (Mhos cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M.)
		% M	% C	% H	% N		
1	[Ni(Q)(Ser)·2H <sub>2</sub> O]	16.76 (17.13)	41.61 (42.01)	4.43 (4.66)	7.92 (8.17)	0.031	3.08
2	[Ni(Q)(Iso)·2H <sub>2</sub> O]	15.71 (15.92)	48.59 (48.81)	5.71 (5.99)	7.25 (7.59)	0.031	2.96
3	[Ni(Q)(Pro)·2H <sub>2</sub> O]	16.19 (16.64)	50.61 (51.03)	4.87 (5.10)	7.52 (7.93)	0.039	3.17
4	[Ni(Q)(HPro)·2H <sub>2</sub> O]	15.62 (15.96)	45.41 (45.68)	4.23 (4.62)	7.57 (7.61)	0.032	3.08
5	[Ni(Q)(Thr)·2H <sub>2</sub> O]	16.14 (16.45)	43.34 (43.73)	4.77 (5.04)	7.65 (7.84)	0.031	3.12

Table 3. Thermal data of nickel complexes

No.	Complex	Temperature range (°C)	% Weight loss due to water		% Weight loss due to 8HQ and amino acid	
			Found	Calculated	Found	Calculated
1	[Ni(Q)(Ser)·2H <sub>2</sub> O]	107-185	9.75	10.50	76.58	72.36
2	[Ni(Q)(Iso)·2H <sub>2</sub> O]	108-167	10.30	9.76	81.78	74.31
3	[Ni(Q)(Pro)·2H <sub>2</sub> O]	93-174	10.76	10.20	79.89	73.14
4	[Ni(Q)(HPro)·2H <sub>2</sub> O]	93-167	10.84	9.73	76.78	74.24
5	[Ni(Q)(Thr)·2H <sub>2</sub> O]	104-175	9.93	10.09	73.60	73.44

A broad band observed in the region between 3300-3196 cm<sup>-1</sup> due to asymmetric and symmetric O-H stretching modes and a weak band in the range 1577-1575 cm<sup>-1</sup> due to H-O-H bending vibrations, indicating presence of a coordinated water molecule (38-40), was further confirmed by thermal studies. The N-H asymmetric and N-H symmetric vibrations observed at ~3040 and ~2960 cm<sup>-1</sup>, respectively, in the free amino acids are shifted to higher wave numbers, i.e. in the range 3192-3088 cm<sup>-1</sup> and 3059-3057 cm<sup>-1</sup>, respectively, in the spectra of the complexes, suggesting coordination of the amino group through nitrogen with the metal ion. The  $\nu_{\text{asymmetric}}$  (COO) band of the free amino acids i.e. ~1590 cm<sup>-1</sup> is shifted to higher wave number, i.e. in the range 1607-1604 cm<sup>-1</sup> and the  $\nu_{\text{symmetric}}$  (COO) mode observed at ~1400 cm<sup>-1</sup> in the spectra of the free amino acids is shifted to lower wave number, i.e. 1373-1371 cm<sup>-1</sup>, in the spectra of complexes, indicating the coordination of the carboxylic acid group via oxygen with the metal ion. The difference ( $\nu_{\text{asymmetric}} - \nu_{\text{symmetric}}$ ) in the range 233-231 cm<sup>-1</sup>, indicates that the M-O bond is purely covalent (41, 42).

Some new bands of weak intensity observed in the regions around 615-605 cm<sup>-1</sup> and 410 cm<sup>-1</sup> may be ascribed to the M-O and M-N vibrations, respec-

Table 4. Antibacterial activity (mm) of nickel complexes by agar cup method

No.	Complex	Test	
		<i>C. diphtheriae</i>	<i>S. aureus</i>
1	[Ni(Q)(Ser)·2H <sub>2</sub> O]	9	16
2	[Ni(Q)(Iso)·2H <sub>2</sub> O]	11	19
3	[Ni(Q)(Pro)·2H <sub>2</sub> O]	12	20
4	[Ni(Q)(HPro)·2H <sub>2</sub> O]	13	25
5	[Ni(Q)(Thr)·2H <sub>2</sub> O]	14	21

tively (11, 43, 44). It may be noted that these vibrational bands are absent in the infra-red spectra of HQ as well as amino acids.

### Thermal studies

The TG and DTA studies of the complexes have been recorded in the nitrogen atmosphere at the constant heating rate of 10°C/minute.

Thermal study on the mixed ligand nickel complexes in controlled nitrogen atmosphere was carried out to understand the stages and temperature range of decomposition.

The most probable decomposition pattern of the complexes is proposed on the basis of the care-

Table 5. MIC ( $\mu\text{g/mL}$ ) data of nickel complexes

No.	Complex	<i>C. diphtheriae</i>	<i>S. aureus</i>	<i>C. albicans</i>
1	[Ni(Q)(Ser)·2H <sub>2</sub> O]	300	150	200
2	[Ni(Q)(Iso)·2H <sub>2</sub> O]	400	100	150
3	[Ni(Q)(Pro)·2H <sub>2</sub> O]	400	300	350
4	[Ni(Q)(HPro)·2H <sub>2</sub> O]	400	200	300
5	[Ni(Q)(Thr)·2H <sub>2</sub> O]	200	100	150
6	Tetracycline	2.0	1.5	1.5

ful examination of TG and DTA curves. The thermo analytical data are summarized in Table 3.

The TG of the complexes shows that they are thermally quite stable but to varying degree. The complexes show gradual loss in weight due to decomposition by fragmentation with increasing temperature. The complexes with L-serine, L-isoleucine, L-proline, 4-hydroxy-L-proline and L-threonine show similar behavior in TG and DTA studies. The thermogram of these complexes shows the loss in weight corresponding to two water molecules in the temperature range 93-185°C, followed by weight loss in the range 286-522°C which is approximately equal to algebraic sum of weight loss due to both amino acid and 8HQ moieties (45, 46).

The DTA of the complexes display an endothermic peak in the range 143-150°C, indicating the presence of coordinated water molecules and a single exothermic peak in the range 380-430°C indicates that there may be simultaneous decomposition of amino acid and 8HQ moieties. A constant weight plateau after 700°C indicates the completion of reaction (47-50).

However the weight losses observed in the decomposition reaction were slightly higher due to uncertainty in the formation of final residue. Thermal decomposition of metal complexes in inert atmosphere produces finely divided metal powder (51) which gets transformed to metal oxide spontaneously even in the presence of traces of oxygen present in nitrogen gas used in the experiment (52). Therefore, the decomposed residue may contain a mixture of finely divided metal powder along with metal oxide.

On the basis of the physico-chemical studies, the octahedral geometry is proposed for nickel complexes.

The bonding and structure for the metal complexes may be represented as shown in Figure 1.

#### Biological studies

All the metal complexes were screened against *Corynebacterium diphtheriae*, *Escherichia coli*,

*Staphylococcus aureus*, *Candida albicans* and *Salmonella typhi*.

The studies based on agar cup method revealed that the complexes are sensitive against *S. aureus*, less sensitive against *C. diphtheriae* and resistive against *E coli* and *S. typhi* (Table 4).

The minimum inhibitory concentration (MIC) of complexes (Table 5) ranges between 100-450  $\mu\text{g/mL}$ . The complexes are found to be more active against *S. aureus* as compared to *C. albicans* and *C. diphtheriae*. As compared to standard antibacterial compound tetracycline, the complexes show moderate activity against the selected strains of microorganisms (53).

The studies on antifungal activity (Table 6) revealed that all the metal complexes show moderate activity against the selected strains of microorganisms. When compared to standard antifungal compound, amphotericin, the complexes show less activity against the selected strains (53).

#### CONCLUSIONS

The higher decomposition temperatures of the complexes indicate a strong metal-ligand bond and electrical conductance studies show non-electrolytic nature of the complexes, respectively. Magnetic studies indicate paramagnetic nature of the complexes. The IR spectra show bonding of the metal ion through N- and O- donor atoms of the two ligands. Thermal analysis confirms the presence of

Table 6. Antifungal activity (mm) – percentage inhibition data of nickel complexes

No.	Complex	<i>A. niger</i>
1	[Ni(Q)(Ser)·2H <sub>2</sub> O]	28
2	[Ni(Q)(Iso)·2H <sub>2</sub> O]	35
3	[Ni(Q)(Pro)·2H <sub>2</sub> O]	22
4	[Ni(Q)(HPro)·2H <sub>2</sub> O]	30
5	[Ni(Q)(Thr)·2H <sub>2</sub> O]	49
6	Amphotericin	1.5

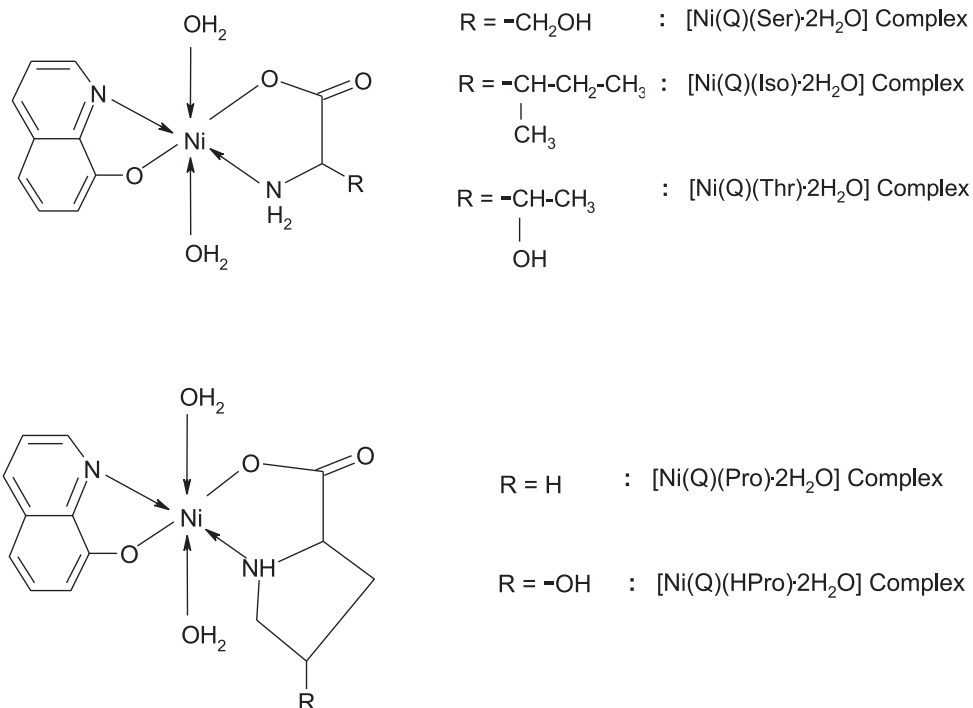


Figure 1. The structures of nickel complexes

coordinated water molecules. On the basis of these results an octahedral structure is proposed for nickel complexes under study.

The biological study shows that complexes are found to be more active against *S. aureus* as compared to *C. albicans* and *C. diphtheriae*. Compared to standard antibacterial compound, tetracycline, the complexes show moderate activity against the selected strains of microorganisms.

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