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SYNTHESIS, CHARACTERIZATION & ANTIBACTERIAL STUDIES ON MIXED LIGAND Cu (II) COMPLEXES WITH POLYDENTATE LIGANDS

Chemistry

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ABSTRACT

Mixed ligand Cu (II) complexes of the type [M (Q) (L).2H2O] have been synthesized using 8-hydroxyquinoline (HQ) as a primary ligand and N- and/or O-donar amino acids (HL) such as L-valine, L-asparagine, L-glutamine, L-arginine and L-methionine as a 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 DMSO (dimethyl sulphoxide) in 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 transition & d-d transition. The thermal analysis data of the complexes indicate the presence of crystallized water molecules. The agar cup method & tube dilution method have been used to study the antibacterial activity of the complexes against the pathogenic bacteria S.aureus, C.diphtheriae, S.typhi & E.coli. The results have been compared with those of control tetracycline, which was screened simultaneously & indicated mild antibacterial activity of the complexes.

KEYWORDS

Mixed ligand copper complexes, synthesis, antibacterial study.

Many researchers have studied characterization, antimicrobial & toxicological activity of mixed ligand complexes of transition metal (1-6). The role of mixed ligand complexes in biological process has been well recognized (7, 8). It has been found that a majority of the metal complexes with 8-hydroxyqunoline process biological activity (9-11). Amino acids are well known for their tendency to form complexes with metals having biological significance & metabolic enzymatic activities (12). Antitumor activity of some mixed ligand complexes has also been reported (13, 14). The antibacterial & Anti-fungal properties of a range of copper (II) complexes have been evaluated against several pathogenic bacteria & fungi (15-16).

Therefore, it was considered to study the complexation & to determine the biological activity copper complexes. The present paper reports synthesis. Characterization & antibacterial studies of the mixed ligand Cu (II) complexes prepared with 8-hydroxyqunoline (HQ) as a primary ligand & amino acids (HL) such as L-valine, L-asparagine, L-glutamine, L-arginine and L-methionine as a secondary ligands. The metal complexes have been characterized by elemental analysis & various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic spectra, IR spectra and thermal studies.

EXPERIMENTAL

Materials

Analytical grade copper (II) chloride dehydrate was used as such without further purification L-valine, L-asparagine, L-glutamine, L-arginine and L-methionine & 8-hydroxyqunoline were obtained from S.D. Fine chemicals, Mumbai, India. Solvents like, ethanol, dimethyl sulphoxide & laboratory grade chemicals, whenever used were distilled & purified according to standard procedures (17,19).

Preparation of Mixed ligand Complexes

Mixed ligand Cu (II) were prepared from copper (II) chloride dihydrate, 8-hydroxyquinoline (HQ) as a primary ligand & different amino acids (HL) such as L-valine, L-asparagine, L-glutamine, L-arginine and L-methionine as a secondary ligands.

To an aqueous solution ($10cm^3$) of copper (II) chloride dehydrate (170mg, 1mmol) was mixed with ethanolic solution ($10cm^3$) of 8-hydroxyqunoline (145mg, 1mmol) was added. The mixture was stirred and kept in boiling waterbath for 10 min. To this hot solution, an aqueous solution ($10cm^3$) of amino acids (1mmol) was added with constant stirring. The mixture was again heated in a water bath. The complexes were obtained by raising p^H 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 vaccum.

Instrumentation

The complexes were analyzed for C,H, N & S contents on Thermo Finnigan Elemental Analyzer, Model No. FLASH EA 1112 Series at Department of Chemistry, I.I.T., Mumbai. Metal content was estimated complexometrically by standard procedure (20, 21).

The Molar Conductance values were measured in DMSO (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= $1.0cm^{-1}$).

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

The electronic absorption spectra of all the complexes in DMSO solution (10^{-3}M) in the ultraviolet & visible region were recorded on Shimadzu UV/VIS-160 spectrometer using a quartz cell of 1cm optical path at GNIRD, Mumbai.

Infrared spectra of all the ligands & their metal complexes were recorded in KBr disc on a Perkin-Elmer FTIR spectrophotometer model 1600 in the region 4000-400 cm^{-1} at Department of Chemistry, I.I.T., Mumbai. The pellets were prepared 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 (22).

The Thermogravimetric (TG) & Differential Thermal Analysis (DTA) measurements 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 900^0C at heating rate of 10^0C/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 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 & the plate was incubated at 37^0C for 24h. The extent of growth inhibition from the

edge of the cup was considered as 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 test compounds were subjected to in vitro screening against Staphylococcus aureus, Corynebacterium diphtheriae, Salmonella typhi & Escherichia coli using Muller Hinton broth as the culture medium.

The test compound (10mg) was dissolved in DMSO (10cm^3) so as to prepare a stock solution of concentration 1000 µg/mL. From this stock solution, aliquots of 50 to 1000 µg/mL were obtained in test broth.

Bacterial inoculums were prepared in sterilized Muller Hinton broth and incubated for 24hrs. at 370C. They was dispersed (5cm3) in each borosilicate test tube (150×20mm). The test sample solution was added in order to attain final concentration at 50 to 1000 µg/mL. The bacteria inoculums 0.1cm^3 of the desire bacterial strain (S. aureus,C.diphtheriae, S. typhi & E.coli) containing 106 bacteria/cm^3 was inoculated in the tubes. The tubes were incubated at 370C for 24hrs. & then examine for the presence or absence of growth of the test organism.

The lowest concentration which showed no visible growth was noted as minimum inhibitory concentration (MIC).

Tetracycline was used as standard drug against Gram-positive and Gram-negative bacteria by similar screening procedure. The solvent DMSO was also tested as control to see that it did not affect the growth of the culture. MIC of tetracycline was found to be MIC of tetracycline was found to be 1.5 µg/cm3 against S. aureus, 2.0 µg/cm3 against C. diphtheriae, 1.5 µg/cm^3 against S. typhi and 2.5 µg/cm^3 against E. coli.

RESULT & DISCUSSION

Characterization of Metal Complexes

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

$$CuCl_2.2H_2O + HQ + HL \quad Cu(Q)(L).2H_2O] + 2HCl$$

where, Q is deprotonated N and O donor primary ligand, 8-hydroxyquinoline and L is deprotonated N and / or O donor secondary ligands, different amino acids .

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 ethyl alcohol, acetone etc., but are fairly soluble in DMSO.The elemental analysis data (Table 2) of metal complexes are consistent with their general formulation as 1:1:1 mixed ligand complexes of the type [Cu(Q)(L).2H2O]. The molar conductance values of the complexes in DMSO at 10-3 M concentration are low (< 1) indicating their non-electrolytic nature (23).

Magnetic studies

The magnetic moments of the metal complexes were calculated from the measured magnetic susceptibilities after employing diamagnetic correction and revealed their para -magnetic nature. The observed values for effective magnetic moment (µeff) in BM, in Table 2 are in the range 1.73 to 1.97.

It suggest the square planar geometry for copper complexes, the magnetic moments of the compounds investigated support the conclusions.

Electronic absorption spectra

The electronic spectra of metal complexes in DMSO were recorded in the UV-visible region. The spectra show three transitions in the range 272-280 nm (36765- 35714cm-^{1}) , 333-339 nm (30030-29499 cm-^{1}) and 388-398 nm (25773-25126 cm-1) ascribed π π* , n π* and the charge transfer transitions (LMCT) from the ligands to the metal, respectively (24) As the term implies, these transitions involve electron transfer from one part of the complex to another which are fully allowed and hence give rise to much more intense absorption.

Infra –red spectra

The FTIR spectra of the metal complexes were recorded in KBr discs over the range 4000-400 cm- 1 These spectras of metal complexes were complicated due to the presence of numerous bands with varying intensities making, interpretation task quite 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-donar ligands, 8-hydroxyquinoline and their metal complexes (25-28).

An important features of infrared spectra of the metal complexes is the absence of band 3440 cm-1 due 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 takes place to form M-O bond.

A strong ν (CO) band observed in the range 1111-1105 cm-1 indicates the presence of oxime moiety in the complexes coordinated through its nitrogen and oxygen atoms as uninegative bidentate ligand.

The ν (C=N) mode observed at 1580 cm-1 in the spectra of free HQ ligand is found to be shifted to lower wave number in the range of 1500-1460 cm-1 in the spectra of complexes, which indicates the coordination through tertiary nitrogen donor of HQ. The coordination through ring nitrogen atom of HQ with the metal has been confirmed on the basis of bands observed at the range of 508-504 cm-1 and 791-780 cm-1 that corresponds to in plane and out of plane ring deformation modes respectively. (9,10,25).

By comparing the spectra of free amino acids, it has been proved that there is decrease in the N-H stretching frequency on complex formation (26, 27). Character and strength of the M-N bond has been correlated to the shift of N-H stretching band (28).

A (29-31),broad band observed in the region between 3300-3194 cm-1 due to asymmetric and symmetric O–H stretching modes and a weak band in the range 1578-1570 cm-1 due to H–O–H bending vibrations indicating presence of water molecules further confirmed by thermal studies.

Broad bands observed at range 3193-3086 cm-1 and 3060-3052 cm-1 are assigned to N-H (asymmetric) and N-H (symmetric) vibrations respectively. In case of IR spectra of free amino acid these bands appear at the range of 3040 and 2960 cm-1. This shift of N-H vibrations to higher wave numbers, suggest that in the formation of metal complexes, nitrogen atom of amino group coordinate to metal ion.

Co-ordination through the amino group of the amino acids has been further confirmed by the C-N symmetrical stretching frequency. It is observed at 950 cm-1 in the spectra of free amino acids and found to be shifted to lower wave numbers in the range of 914-910 cm-1 in the spectra of the complexes. The coordination of carboxylic acid group via oxygen with the metal ion may be indicated by the interpretation of the asymmetric and the symmetric mode of vibration of (COO-) band. The asymmetric (COO-) band of free amino acids i.e. 1610-1590 cm-1 is shifted to higher wave number, in the range 1643-1602 cm-1 and the symmetric (COO-) mode observed at 1400 cm-1 in the spectra of free amino acids is found to be shifted to lower wave number in the range of 1373-1370 cm-1, in the spectra of complexes.

The difference (vasymmetric ¬¬¬¬-¬ vsymmetric) is in the range 270-232 cm-1 indicating that the M-O bond is purely covalent (32,33). Some new bands of weak intensity observed in the regions of 615-600 cm-1 and at 410 cm-1 may be ascribed to the M-O and M-N vibrations respectively(10,32,33). It may be noted that these vibrational bands are absent in the infra-red spectra of HQ as well as amino acids. The M-O bond has much less covalent character than the M-N bond so the stretching bands of the former appear in low frequency region.

Table1. Empirical formula, molecular weight, colour, decomposition temperature & PH of the Copper complexes studied

Sr. No.	Complex	Empirical Formula	Molecular Weight	Colour	Decomposition Temperature ()	pH
1	[Cu(Q)(Val)].2 H_2O	$CuC_{14}H_{20}O_5N_2$	359.85	Green	250	6.99
2	[Cu(Q)(Asp].2 H_2O	$CuC_{13}H_{13}O_6N_3$	374.82	Green	263	6.98

3	[Cu(Q)(Glu)].2H_2O	$CuC_{14}H_{19}O_6N_3$	388.85	Green	246	7.01
4	[Cu(Q)(Arg)].2H_2O	$CuC_{15}H_{23}O_5N_5$	416.90	Green	260	6.99
5	[Cu(Q)(Met)].2H_2O	$CuC_{14}H_{20}O_5N_{2S}$	391.91	Green	258	7.00

Q represents the deprotonated primary ligand-8-hydroxyquinoline, where as Val , Asp, Glu, Arg & Met represent deprotonated secondary ligands: L-valine, L-asparagine, L-glutamine, L-arginine and L-ethionine respectively.

Table 2. Elemental analysis data, molar conductance & magnetic moments of Copper complexes.

Sr. No.	Complex	Elemental Analysis Found(Calculated)					Molar conductance (Mhos cm^2 mol^{-1})	μeff. (B.M.)
		% M	% C	% H	% N	% S		
1	[Cu(Q)(Val)].2H_2O	17.60 (17.66)	46.69 (46.73)	05.60 (05.61)	07.78 (07.78)	---	0.021	1.94
2	[Cu(Q)(Asp].2H_2O	16.94 (16.95)	41.63 (41.65)	04.56 (04.58)	11.21 (11.21)	---	0.019	1.97
3	[Cu(Q)(Glu.].2H_2O	16.31 (16.34)	43.23 (43.24)	04.94 (04.94)	10.80 (10.81)	---	0.020	1.90
4	[Cu(Q)(Arg)].2H_2O	15.22 (15.24)	43.19 (43.21)	05.56 (05.57)	16.79 (16.80)	---	0.022	1.89
5	[Cu(Q)(Met)].2H_2O	16.21 (16.22)	42.89 (42.90)	05.13 (05.15)	07.15 (07.15)	08.16 (08.18)	0.013	1.73

Abbreviations see Table 1.

Table 3. Thermal data of Copper complexes

Sr. No.	Complex	Temperature range for loss of water molecules ( )	Weight loss due to water	Temperature range for loss of 8HQ & amino acid ( )		Weight loss due to 8HQ & amino acid	
			Found	Calculated		Found	Calculated
1	[Cu(Q)(Val)].2H_2O	33-88	10.22	10.00	249-541	72.45	72.33
2	[Cu(Q)(Asp].2H_2O	34-87	10.01	09.60	245-540	73.63	73.44
3	[Cu(Q)(Glu].2H_2O	33-80	09.35	09.26	248-545	74.52	74.39
4	[Cu(Q)(Arg)].2H_2O	32-90	08.98	08.63	250-530	76.15	76.12
5	[Cu(Q)(Met)].2H_2O	32-89	09.25	09.19	260-543	74.75	74.60

Abbreviations see Table 1.

Table 4. Antibacterial activity (mm)of copper complex by agar cup method

Sr. No.	Complex	Test			
		S.aureus	*C.diphtheriae*	*S. typhi*	*E.coli*
1	[Cu(Q)(Val)].2H_2O	23	13	22	13
2	[Cu(Q)(Asp].2H_2O	22	14	20	12
3	[Cu(Q)(Glu.].2H_2O	25	12	24	11
4	[Cu(Q)(Arg)].2H_2O	21	18	20	12
5	[Cu(Q)(Met)].2H_2O	26	17	23	12
6	Tetracycline	30	25	26	26

Abbreviations see Table 1.

Table 5. MIC(mg/ml)data of copper complexes.

Sr. No.	Complex	*S.aureus*	*C.diphtheriae*	*S. typhi*	*E.coli*
1	[Cu(Q)(Val)].2H_2O	50	100	50	100
2	[Cu(Q)(Asp].2H_2O	50	100	100	100
3	[Cu(Q)(Glu].2H_2O	50	150	50	250
4	[Cu(Q)(Arg)].2H_2O	100	100	50	150
5	[Cu(Q)(Met)].2H_2O	50	100	50	100

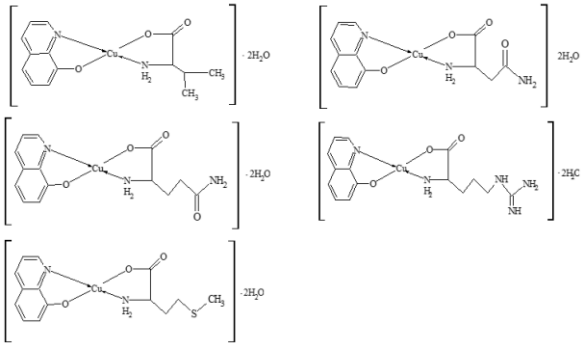
Abbreviations see Table 1.

Thermal studies

The TG and DTA studies of the complexes have been recorded in the nitrogen atmosphere at the constant heating rate of 10^0C/ min. The TG of the complexes shows that they are thermally quite stable to varying degree. The complexes shows gradual loss in weight due to decomposition by fragmentation with increasing temperature as presented in Table 3. All the copper (II) complexes show similar behavior in TG and DTA studies. The TG-DTA curves of these complexes show the loss in weight corresponding to two crystallized water molecules in the temperature range 32-90^{0}C, followed by simultaneous weight loss due to amino acid and 8-hydroxyquinoline moieties in the range 245-545^{0}C.

The DTA of the complexes display an endothermic peak in the range 27-90^{0}C, which indicates the presence of crystallized water molecules. As the temperature is raised, the DTA curve shows a broad exothermic in the range 245-545^{0}C attributed to simultaneous decomposition of amino acid and 8-hydroxyquinoline moieties present in the complexes. The formation of broad exothermic is possibly due to simultaneous decomposition of ligand moieties and their subsequent oxidation to gaseous products like CO_2 and H_2O. A constant plateau after 600-700^{0}C indicates the completion of reaction. (34-37).

Like most of the metal organic complexes also decomposes to a fine powder of metal oxide i.e., CuO. The constant weight plateau in TG above 610^{0}C indicates completion of the reaction. The CuO formed was confirmed by X-ray diffraction pattern of the decomposed product (38).



Biological studies

All the metal complexes were screened against *Staphylococcus aureus*, *Corynebacterium diphtheriae*, *Salmonella typhi* and *Escherichia coli*. The studies based on agar cup method revealed that the complexes are sensitive against *S. aureus* and *S. typhi* as compared to *C. diphtheria* and *E. Coli*

The minimum inhibitory concentration (MIC) of metal complexes ranges between 50-250 μg/cm^3. The results show that, as compared to the activity of metal salts and free ligands the metal complexes (Table 5.3) show higher activity (Table 5.4 to 5.5).

The activity of metal complexes is enhanced due to chelation (22). The chelation reduces considerably the polarity of the metal ions in the complexes, which in turn increases the hydrophobic character of the chelate and thus enables its permeation through the lipid layer of microorganisms. As compared to standard antibacterial compound, tetracycline, the complexes show minor activity against selected strains of microorganisms (39). Minor activity of these complexes is due to bulky structure of the complexes.

On the basis of the physico-chemical studies, the bonding and structure for the copper complexes may be represented as shown in figure 1.

CONCLUSIONS

The higher decomposition temperature of the complexes indicate a strong metal –ligand bond and electrical conductance studies show non-electrolytic nature of the complexes. Magnetic studies indicate paramagnetic nature of the complexes. Electronic absorption spectra of the complexes show intra-ligand and charge transfer transitions. IR spectra show bonding of the metal ion through N-and O-donar atoms of the two ligands. Thermal analysis confirms the presence of crystallized water molecules. On the basis of above results, square planar structure is proposed for copper complexes under study.

The antibacterial study shows that complexes are found to be more active against S.aureus and P.aeruginosa as compared to C.diphtheria and E.coli compared to standard antibacterial compound, tetracycline, the complexes show minor activity against selected strains of microorganisms.**Acknowledgments:**

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