

Preparation, Characterization and Structural Aspect of Zn (II) Complexes

*Anurag, Asha Kumari

*anurag100895@gmail.com

Department of Chemistry, Patna University, Patna

Abstract

The mixed ligand complexes of Zinc(II) with α -picolinic acid (α -picH) and α -Quinaldinic acid (α -QuinaldH) as basic coordinating agent and o-nitrophenol (onphH), α -Nitroso- β -Naphthol (HaN β N) and 8-hydroxyquinoline (8HQ) as secondary ligand molecules in complexes having composition: [Zn(α -pic)(onph)], [Zn(α -pic)(α N β N)], [Zn(α -pic)(8Q)], [Zn(α -Quinald)(onph)], [Zn(α -Quinald)(α N β N)] and [Zn(α -Quinald)(8Q)] were prepared and characterized by elemental analysis, electrical conductance value and Infra-red spectral studies.

Keywords:

The mixed ligand complexes of Zinc (II) using α -picolinic acid and α -Quinaldinic acid as basic ligand.

Introduction

Except Iron, Calcium, Sodium and Potassium, Zinc (II) is most vital element for physiological system and their coordination complexes have most widely and extensively been studied¹⁻⁹. Zinc(II) enzymes like hydrazinase, carbonic dehydratase and others are most essential substance for development and growth of physiological system.¹⁻⁶ Zinc (II) compounds are also the most vital element for plant growth.⁷⁻⁸

Experimental

Materials and methods

The organic ligand α -picolinic, α -Quinaldinic acid, o-nitrophenol, α -Nitroso- β -Naphthol, 8-hydroxyquinoline used were obtained from E. Merck, B.D.H., Aldrich-chem and Sigma H. The Zinc (II) metal salts are E. Merck extra pure or B.D.H. Anal-R quality reagent.

Physical investigations: magnetic susceptibility values were determined in own department using Gouy method at 301°K. Electrical conductance values in dimethylformamide (DMF) were determined at 30-31°C on sytonic conductivity meter bridge. The elemental analysis and infrared spectra were determined at I.I.T. Guwahati. Electronic absorption spectra of ligand and complexes were recorded at N.I.T. Patna.

Method of Preparation of Complexes

Procedure:

Molar solution each about (0.01 mol) of Zinc(II) acetate, α -picolinic acid or α -Quinaldinic acid with o-nitrophenol, α -Nitroso- β -Naphthol and 8-hydroxyquinoline were mixed in 50 % ethanol and refluxed on magnetic stirrer for 1-2 hours and the pH of mixed solutions were raised and adjusted to 8-9 by adding NH_4OH . The resulting Zinc(II) complexes were collected and washed with a little ethanol and finally dried at 50-60 °C. The result of elemental analysis corresponds to formula in Table A.

Table A

Elemental analysis of complexes

Compound	% Element Metal	Found (Calculated) Nitrogen
$[\text{Zn}(\alpha\text{-pic})(\text{onph})]$	19.72 (20.08)	8.51 (8.60)
$[\text{Zn}(\alpha\text{-pic})(\alpha\text{N}\beta\text{N})]$	18.01 (18.19)	7.86 (7.78)
$[\text{Zn}(\alpha\text{-pic})(8\text{Q})]$	20.11 (20.35)	8.61 (8.71)
$[\text{Zn}(\alpha\text{-Quinald})(\text{onph})]$	17.12 (17.23)	7.28 (7.39)
$[\text{Zn}(\alpha\text{-Quinald})(\alpha\text{N}\beta\text{N})]$	15.31 (15.33)	6.49 (6.51)
$[\text{Zn}(\alpha\text{-Quinald})(8\text{Q})]$	17.73 (18.09)	7.63 (7.75)

Results and Discussion

The mixed ligand complexes of α -picolinic acid or α -Quinaldinic acid with Zinc(II) of o-nitrophenol, α -Nitroso- β -Naphthol and 8-hydroxyquinoline are yellow to orange yellow in colouration. All the complexes are stable in dry air e.g. over anhydrous CaCl_2 in desiccator. These complexes are soluble in methanol, ethanol and dimethyl formamide (DMF) but are insoluble in water and non-polar solvents like benzene, toluene and ether. In DMF at 30°C all the complexes show negligible electrical conductance value ($12\text{-}15 \text{ ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$) suggesting non conducting neutral nature of complexes. All these complexes having composition $[\text{Zn}(\alpha\text{-pic})(\text{onph})]$, $[\text{Zn}(\alpha\text{-pic})(\alpha\text{N}\beta\text{N})]$, $[\text{Zn}(\alpha\text{-pic})(8\text{Q})]$, $[\text{Zn}(\alpha\text{-Quinald})(\text{onph})]$, $[\text{Zn}(\alpha\text{-Quinald})(\alpha\text{N}\beta\text{N})]$ and $[\text{Zn}(\alpha\text{-Quinald})(8\text{Q})]$ undergo decomposition on heating which is considerably higher than the melting point of free ligands (Table-B).

Table B

Compound	Colour	Melting point/Decomposition temp.
α -picH	White	135 m
α -QuinaldH	White	155 m
[Zn(α -pic)(onph)]	Yellow	219 t
[Zn(α -pic)(α N β N)]	Yellow	280 d
[Zn(α -pic)(8Q)]	Yellow	280 d
[Zn(α -Quinald)(onph)]	Brown	222 t
[Zn(α -Quinald)(α N β N)]	Brown	270 d
[Zn(α -Quinald)(8Q)]	Orange	275 d

m = melting, d = decomposition and t= transition

Infrared Spectra

Infrared spectral measurement of the ligands and their Zn (II) complexes were recorded between 4000–650 cm^{-1} in KBr disc. The I.R. data of the complexes are shown in Table C. The broad band at 2600 cm^{-1} in the spectrum of the α -picolinic acid(α -picH) points to strong intermolecular hydrogen bonding in free ligand. The spectra of mixed ligand complexes of α -picolinic acid and α -Quinaldinic acid with Zn (II) derivatives of organic acids show a number of I.R. bands. The -OH stretching frequency of the ligand in complexes disappear indicating deprotonation of carboxylic (OH) or phenolic (OH) of ligands in bond formation in complexes. The band at 3000-3100 cm^{-1} in ligands and their complexes are attributed to (C-H) stretch of phenyl ring (C-H) frequency⁹. The (C-O) hydroxy group I.R. band of ligands are shifted to higher frequency, supporting the bonding of phenolic (C-O) oxygen in coordination to all complexes.

Table C

IR Bands of complexes

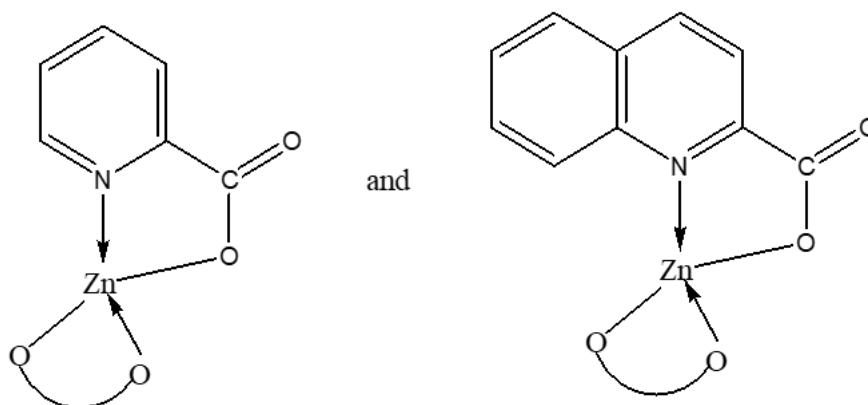
Compound	$\nu(\text{OH}) + \nu(\text{CH})$	$\nu(\text{CO})$ (carbonyl)	$\nu(\text{C}=\text{N})$	$\nu(\text{NO}_2)$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$ (phenolic)	$\delta(\text{C}-\text{H})$
α -picH	3118 m 2600 br	1710 m	1617 m	-	1144 str	1062 str	741 str
α -QuinaldH	3420 br 3013 m	1627 m	1601 m	-	1157 m	1048 str	788 str
$[\text{Zn}(\alpha\text{-pic})(\text{onph})]$	3012 w	1680 str	1601 m	1543 str	1142 m	1167 m	755 m
$[\text{Zn}(\alpha\text{-pic})(\alpha\text{N}\beta\text{N})]$	3025 m 3005 m	1693 str	1602 m	-	1181 str	1226 str	748 str
$[\text{Zn}(\alpha\text{-pic})(8\text{Q})]$	3013 m 2938 m	1692 str	1595 str	-	1156 str	1215 str	748 str
$[\text{Zn}(\alpha\text{-Quinald})(\text{onph})]$	3015 m	1662 m	1602 m	1542 str	1148 m	1192 m	756 m
$[\text{Zn}(\alpha\text{-Quinald})(\alpha\text{N}\beta\text{N})]$	3021 m	1672 m	1601 str	-	1148 m	1172 m	747 m
$[\text{Zn}(\alpha\text{-Quinald})(8\text{Q})]$	3042 m	1656 m	1597 str	-	1152 m	1185 m	744 m

m = medium, str = strong, shp = sharp, br = broad

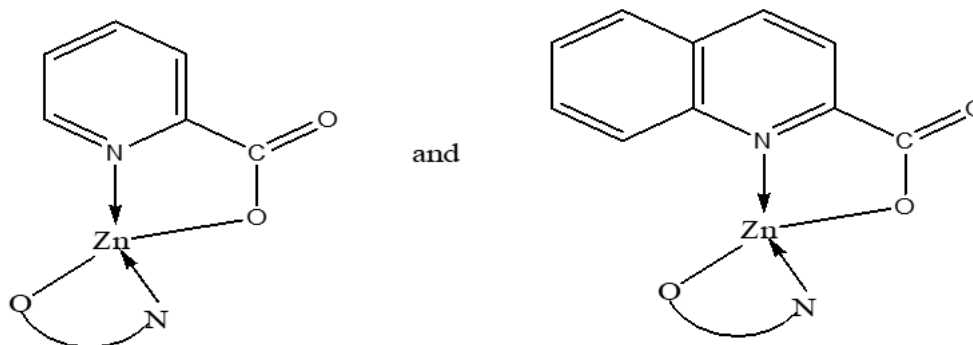
Ultra-Violet Spectra

UV-spectra of Zinc (II) complexes do not show d-d transition as Zinc(II) is d^{10} electronic system.

From the studies of physical measurements, analytical values of the complexes, the following probable structures of complexes are shown below:



Where O-O = Deprotonated o-nitrophenol (onph)



Where O-N = Deprotonated α -Nitroso- β -Naphthol (α N β N) and 8-hydroxyquinoline (8Q)

Conclusion

In complexes the ligands are bidentate monobasic chelating agents. Since Zinc (II) has $3d^{10}$ electronic configuration and four coordinated and tetrahedral structure.

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