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Preparation and Characterization of Adduct Complexes of Copper (II) with α-Picolinic Acid

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Abstract

Adduct complexes of Copper (II) with α-picolinic acid (α-picH) of composition [Cu(α-pic)$_2$NN] were prepared with NN=ethylenediamine (en), o-phenylenediamine (opd), 4-methyl-o-phenylenediamine (mopd), α,α'-dipyridyl (α,α'-dipy) and 1,10-phenanthroline (phen). The complexes show electronic absorption spectra similar to octahedral structure. The infrared spectral studies indicate deprotonation of carboxylic acid OH in complexes.

Keywords

Adduct complexes, α-picolinic acid, Copper (II).

Methods and Materials

The ligands were obtained from E. Merck and I.R. spectra were determined on KBr disc in the range of 400-4000 cm^{-1} at I.I.T. Guwahati. Ultra-violet and visible (U–V) spectra were recorded in ethanol at N.I.T. Patna. The magnetic susceptibility values were determined by Gouy method in Patna university, Patna.[8]

Introduction

The complexes of α-picolinic acid are known and reported by different workers.[1-8]

Experimental

Preparation of adduct complexes: [Cu(α-pic)$_2$(NN)]

where, NN = en, opd, mopd, α,α'-dipy and phen

Procedure:

The complex bis(α-picolinato) copper(II) was prepared by reacting a hot ethanolic solution of α-picolinic acid (0.02 mole) and copper(II) chloride (0.01 mole) in 30 ml aqueous ethanol by adjusting pH near 8-9 by adding dilute ammonia. The resulting complex was taken in a round-bottomed flask in 30 ml ethanol and refluxed for one hour. The resulting solutions were concentrated to 5–10 ml and cooled over night, when crystalline adduct complex separated. The products were filtered, washed with a few drops of cold methanol, and dried in a desiccator over KOH. The results of elemental analysis of Copper (II) and Nitrogen are recorded in Table-A.

Table A

Compound	% Element Found (Calculated)	
	Cu	Nitrogen
[Cu(α-pic)$_2$(en)]	17.21 (17.29)	15.13 (15.24)
[Cu(α-pic)$_2$(opd)]	15.12 (15.29)	13.32 (13.48)
[Cu(α-pic)$_2$(mopd)]	14.61 (14.79)	13.13 (13.04)
[Cu(α-pic)$_2$(α,α'-dipy)]	13.62 (13.71)	11.89 (12.08)
[Cu(α-pic)$_2$(phen)]	13.09 (13.06)	13.40 (13.43)

Results and Discussion

The results of elemental analysis of complexes (Table-A) correspond to composition [Cu(α-pic)$_2$(NN)], where, NN = en, opd, mopd, α,α'-dipy and phen.

The complexes are soluble in ethanol, methanol, and dioxane but highly soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The DMF solution at 30°C shows negligible electrical conductance values (8-10 ohm^{-1}mol^{-1}cm^{2}), suggesting their non-ionic character.

Infrared Spectra

The I.R. spectrum of α-picolinic acid shows a strong broad band at 2600 cm^{-1} suggesting strong intramolecular hydrogen bonding. The broad band disappears in all complexes indicating deprotonation of α-picolinic acid in all adduct complexes. The ν(NH$_2$) stretching frequency of ethylenediamine (en), o-phenylenediamine (opd), and 4-methyl-o-phenylenediamine (mopd) coordinated in adduct complexes occurs near 3340–3320 cm^{-1}. The δ(NH$_2$) of the amines located near 1540–1550 cm^{-1} occurs at a higher frequency in complexes. The ν(C=N) of α,α'-dipyridyl (α,α'-dipy) and 1,10-phenanthroline(phen) observed at 1595–1620 cm^{-1} shifts to lower frequency. In adduct complexes on coordination, the ν(C=O) of free α-picolinic acid is found at 1690 cm^{-1} and near 1660–1680 cm^{-1} in complexes. The carboxylic acid ν(C–O) observed at 1080 cm^{-1} shifts to higher wave number and occurs near 1160–1185 cm^{-1}, supporting deprotonated carboxyl oxygen (C–O)[9-10].

The diagnostic I.R. bands of complexes are recorded in Table B.

Table B

Compound	ν(NH$_2$) ν(C-H)	ν(C=O)	ν(C=N)	δ(NH$_2$)	ν(C-N)	ν(C-O) (carboxylic)	δ(C-H)
[Cu(α-pic)$_2$(en)]	3320 m 3010 m	1672 str	1591 m	1574 m	1270 m	1210 m	748 str
[Cu(α-pic)$_2$(opd)]	3245 m 3010 m	1665 str	1591 m	1515 m	1275 m	1190 m	752 str
[Cu(α-pic)$_2$(mopd)]	3310 m 3015 w	1672 str	1501 m	1545 m	1230 m	1201 m	742 str

	2912 sp						
[Cu(α-pic)$_2$(α,α'-dipy)]	3015 m	1662 str	1595 m	-	1225 m	1215 m	740 str
[Cu(α pic)$_2$(phen)]	3010 m, sp	1675 str	1591 m	-	1240 m	1190 m	742 str

m = medium, str = strong ,w = weak , sp =sharp

Ultra-violet spectra:

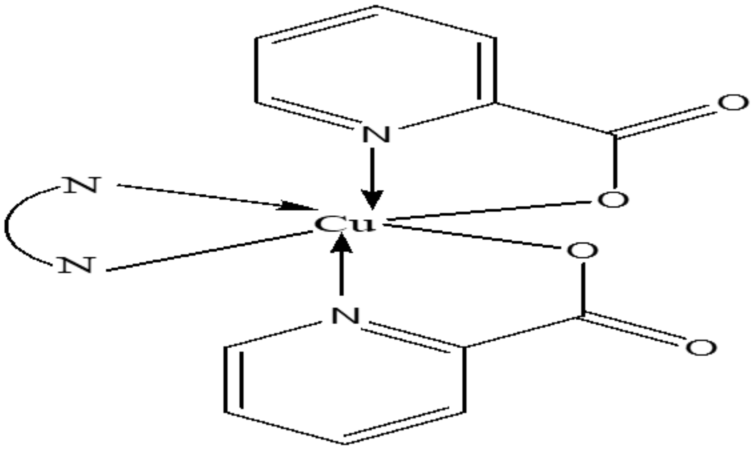
The UV spectra of complexes show ligand vibration in the violet region attributed to, $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, and ν(N-O) vibrations.

The d-d transitions in complexes (Table C) are observed as a medium band at 440-460 nm and a broad band at 650-720 nm assigned to $B_{1g} \rightarrow A_{1g}$ and $B_{1g} \rightarrow B_{2g}$, E_g transitions in a distorted octahedral field[11].

Table C

Complex	Band Position in nm	Probable Assignment
[Cu(α-pic)$_2$(opd)]	385 nm, very strong	Charge Transfer (C-T)
	460 nm, medium	$^2B_{1g} \rightarrow {}^2A_{1g}$
	640-670 nm, broad	$^2B_{1g} \rightarrow {}^2B_{2g} + {}^2E_g$
[Cu(α-pic)$_2$(mopd)]	390 nm, very strong	C-T
	455 nm, shoulder	$^2B_{1g} \rightarrow {}^2A_{1g}$
	630-670 nm, medium, broad	$^2B_{1g} \rightarrow {}^2B_{2g} + {}^2E_g$
[Cu(α-pic)$_2$(α,α'-dipy)]	390 nm, very strong	C-T
	460 nm, shoulder	$^2B_{1g} \rightarrow {}^2A_{1g}$
	645-675 nm, medium, broad	$^2B_{1g} \rightarrow {}^2B_{2g} + {}^2E_g$
[Cu(α-pic)$_2$(phen)]	400 nm, very strong	C-T
	440 nm, shoulder	$^2B_{1g} \rightarrow {}^2A_{1g}$
	640-675 nm, medium, broad	$^2B_{1g} \rightarrow {}^2B_{2g} + {}^2E_g$
[Cu(α-pic)$_2$(en)]	370 nm, strong	C-T
	440 nm, shoulder	$^2B_{1g} \rightarrow {}^2A_{1g}$
	640-665 nm, medium, broad	$^2B_{1g} \rightarrow {}^2B_{2g} + {}^2E_g$

From results of Infra -red, ultra-violet and magnetic susceptibility measurement, the following probable structure of [Cu (α-pic)$_2$ (NN)] are suggested:



Where, [NN = ethylenediamine (en), o-phenylenediamine (opd), 4-methyl-o-phenylenediamine (mopd), α,α′-dipyridyl (α,α′-dipy), 1,10-phenanthroline (phen)].

Conclusion

Both amines and α-picolinic acid coordinate as bidentate ligands, and α-picolinic acid is a monobasic chelating agent.

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