



Studies on Copper(II)Complexes of Some PolymericResins.

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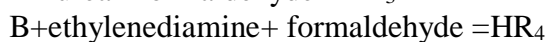
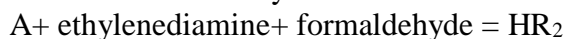
Abstract: Some polymeric resins were synthesized by the condensation reaction of ketoximes (derived from acetophenone /benzophenone derivatives) with urea / ethylenediamine and formaldehyde. The resins were used as ligands to synthesize copper(II) complexes. The resins and their complexes were characterized by elemental analysis, IR and UV spectral studies.

KEYWORDS: Ketoxime, Polymeric resin, Coordination Compounds.

Introduction:

Coordination polymers of metal ions with polymeric ligands containing chelating groups have been subject of attention to the chemist since last few decades. The metal selectivity of polychelates of schiffs base ligand have been recently reported to possess unusual electric properties and dielectric constants. Prasad and co-workers[1] using some coupling products have isolated metal complexes of the type [CuL(OH)(H₂O)] [NiL(OH)(NH₃)₂H₂O] and [ZnL(OH)(H₂O)], (where L is hydrazone type ligand) the donor sites of the coupling product being ketonic oxygen and phenylamino nitrogen in deprotonated form. These compounds have subsequently been used to synthesize polymeric complexes.

Recently "Srivastava and coworkers"[2-7] have prepared thiozole derivatives and their Cu(II) and Ni(II) complexes have been synthesized and characterized. In continuation of the above work, we herein report the synthesis of some polymeric resins derived by the condensation of some ketoximes with urea or ethylenediamine in presence of formaldehyde. The sequence of the reactions are as follows-



These resins were characterized with the help of elemental analysis, U.V. and I.R. spectral analysis.

They are subsequently used as ligand and their Cu(II) complexes were also synthesized. The complexes were characterized by I.R., U.V and elemental analysis.

EXPERIMENTAL

Materials and methods

All the chemicals used were of AR grade. Their purity has been examined by TLC and melting point. The infrared spectrum of complexes were recorded in KBr pallet on PerkinElmer 1000 FTIR spectrophotometer. Electronic spectra of ligands were recorded in the range of 200 to 850nm on Perkin Elmer lambda- 15 UVVIS spectrophotometer. The magnetic susceptibility of complexes were measured by Gouy method at room temperature.

Preparation of Oxime:

0.5 gram of hydroxylaminehydrochloride and 0.5 gram of hydrated sodium acetate was dissolved in 3 ml. of water and then 0.5 gram of the 2-hydroxy-4 methylacetophenone/ 2-hydroxy-benzophenone was added and mixture was heated on water bath, ethanol was added dropwise with shaking until a clear solution was obtained. The reflux was continued until a sample of the reaction mixture gave a clear solution on addition to a little 2N sodium hydroxide solution. The product was cooled when the derivative was crystallised out, recrystallisation was done with ethyl alcohol, aqueous ethanol or petroleum ether.

Preparation of Resins

A mixture of corresponding oximes (0.05 mol.) urea/ ethylenediamine (0.05 mol.) and formaldehyde (0.1 mol.) in the presence of 5% NaOH was heated at 55°C, for 3 hours in a water bath. The separated brown coloured resin was washed with hot water and dried. The dried resin was repeatedly washed several times with solvent ether to remove unreacted resin and purified by dissolving in 8% NaOH, reprecipitating by dropwise addition of 1:1 (v/v) HCl. It was again washed with boiling water and dried.

Preparation of copper(II) complex

The resin(1.50gm) was dissolved in DMF(100ml) containing a slight amount of water. To it copper(II) nitrate was added slowly with constant stirring. A green solid was precipitated out at 6.5 pH when an aqueous saturated solution of sodium acetate was added. The product was digested for sometime on water bath. It was filtered and washed with DMF, hot water and dried at 60°C.

Results and Discussion

The physical constants and major IR spectral bands and UV spectral bands regarding the synthesized polymeric resin are presented in table I and II.

Table-I
Elemental analysis and U.V. spectral date of polymeric resin.

Resin	Elemental Analysis		U.V Spectral Band
	C	N	
V Calculated for C ₁₂ H ₁₆ N ₃ O ₃	57.50% (57.60%)	16.50% (16.80%)	215nm, 256nm
VI Calculated for C ₁₃ H ₂₀ N ₃ O ₂	62.00% (62.40%)	16.50% (16.80%)	214nm
VII Calculated for C ₁₆ H ₁₆ N ₃ O ₃	64.00% (64.42%)	14.00% (14.09%)	213nm, 256nm
VIII Calculated for C ₁₇ H ₂₀ N ₃ O ₂	68.00% (68.45%)	14.00% (14.09%)	214nm

(The calculated values are given in brackets)

Table -II
I.R.spectral bands of polymeric resins

Resin	ν_{O-H}	$\nu_{C=N}$	ν_{N-O}	$\nu_{\overset{O}{\parallel}{C}-NH}$	ν_{CH_2} bridging
V	2725 cm^{-1} (sharp & intense)	163 cm^{-1} (sharp & intense)	930-990 cm^{-1} (m)	1475 and 1450 cm^{-1} (m)	2800-3100 cm^{-1} (weak & broad)
VI	2718 cm^{-1} (sharp & intense)	1629 cm^{-1} (sharp & intense)	928-990 cm^{-1} (m)	_____	2799-3100 cm^{-1} (weak & broad)
VII	2715 cm^{-1} (sharp & intense)	1630 cm^{-1} (sharp & intense)	929-990 cm^{-1} (m)	1474 and 1450 cm^{-1} (m)	2798-3100 cm^{-1} (weak & board)
VIII	2720 cm^{-1} (sharp & intense)	1630 cm^{-1} (sharp & intense)	928-990 cm^{-1} (m)	_____	2800-3100 cm^{-1} (weak & broad)

- The elemental analysis corresponds to the general molecular formula of the resin Figure-1. The resins were found insoluble in common organic solvents such as; benzene, ether, nitrobenzene T.H.F.,(tetrahydrofuran) etc. It suggests that resins were polymeric in nature

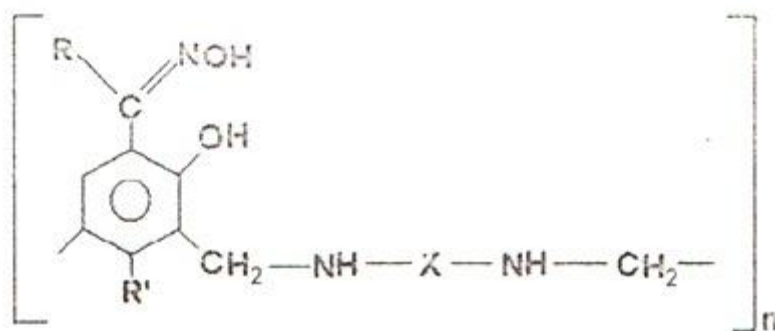
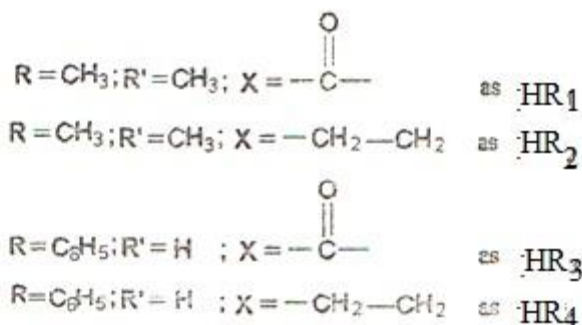


Figure:- 1

Where



U.V. Spectral Study:

The U.V. spectral data of the resins display a broad and intense peak near 214 ± 1 nm which may safely be assigned to $n \rightarrow \pi^*$ transition in $>C=N-OH$ group of keto oximes. Further the peak around 256 nm which was found to be present in compound HR_1 and HR_3 and absent in the compound HR_2 and HR_4 are assigned to arise due to $n \rightarrow \pi^*$ transition in $>C=O$ group.

I.R.Spectral Study:

The I.R. spectral data of polymeric resin and the ir tentative assignments are given in table II. From the table it appears that all resins exhibit a sharp band of medium intensity around $2720 \pm 5 \text{ cm}^{-1}$. This band may be attributed to phenolic OH group and the OH group of oxime. The lowering in the frequency of -OH band of oxime is expected due to hydrogen bonding with the -NH group preferably, (the hydrogen bonding with C=O group is not favourable).

The peak at around 1450 and 1475 cm^{-1} in compound HR_1 and HR_3 are arising due to $-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}$ group which was found absent in compound HR_2 and HR_4 . The lowered value than expected for $>\text{C}=\text{O}$ group was due to the partial double bond character of the carbonyl compound. The $>\text{C}=\text{N}$ of oxime group displayed a sharp and intense band around 1627 cm^{-1} . In all the compounds there were a weak and broad band near $2800-3300 \text{ cm}^{-1}$, which was indicative of the presence of $>\text{CH}_2$ bridging group.

Thus on the basis of I.R. spectra it was concluded that the oxime group and $-\text{CH}_2$ bridging group was present in all the compounds and the keto-oxime group was present in only compound HR_1 and HR_3 but absent in HR_2 and HR_4 . However the $>\text{NH}$ group could not be ascertained separately because of the presence of -OH and $-\text{CH}_2$ bridging group. Which overlapped after the lowering due to the hydrogen bonding.

Characterization of Polychelates of Copper (II) Ions:

The physical characteristics of complexes and element analysis of copper and nitrogen are given in table III. The result of the element analysis of the complexes corresponds to the general formula $\text{MR}_2(2\text{H}_2\text{O})$ where R = resin and $\text{M}=\text{Cu}$ and thus all complexes are biligated. The complexes were found to be insoluble in water and common organic solvent, like benzene, chloroform, alcohol, acetone etc. therefore electrical conductivity.

Table - III
Magnetic moments, physical constants and analytical data of Cu(II)

Name of Complexes	μ_{eff} at 298°K in B.M.	Decomposition Temperature	% Yield	Colour	% N	% Cu
$[\text{Cu}(\text{R}_1)_2(2\text{H}_2\text{O})]$	1.83	280°C	70	Dark Green	14.0 (14.9)	5.1 (5.16)
$[\text{Cu}(\text{R}_2)_2(2\text{H}_2\text{O})]$	1.83	280°C	70	Dark Green	14.5 (14.97)	5.0 (5.16)
$[\text{Cu}(\text{R}_3)_2(2\text{H}_2\text{O})]$	1.87	280°C	45	Black	4.3 (4.41)	12.5 (12.7)
$[\text{Cu}(\text{R}_4)_2(2\text{H}_2\text{O})]$	1.90	230°C	65	Deep Brown	15.1 (15.35)	5.0 (5.30)

During the present investigation the magnetic moment values observed for Cu (II) complexes were found in the range 1.80-2.00 B.M. which is characteristic of copper in +2 oxidation state. The higher magnetic moment value over spin only value 1.73 B.M. complexes can be attributed to spin orbit coupling and T.I.P. contributions.

(I) **I.R. Spectral Studies:**

The I.R. spectral bands of the complexes of copper (II) are recorded in table IV.

Table - IV

Complexes	$\nu_{\text{O-H}}$	ν_{CH_2} bridging	$\nu_{\text{C=N}}$	$\nu_{\text{C-NH}}$ $\begin{array}{c} \text{O} \\ \\ \text{C-NH} \end{array}$	$\nu_{\text{N-O}}$ bridging
[Cu(R ₁) ₂ (2H ₂ O)]	3250- 3400 (b & m)	2800- 3100 (w & b)	1590- 1600 (S)	1475-1450 (m)	960-1000 (m)
[Cu(R ₂) ₂ (2H ₂ O)]	3248- 3400 (b & m)	2799- 3100 (w & b)	1589- 1600 (S)	-	958-1000 (m)
[Cu(R ₃) ₂ (2H ₂ O)]	3248- 3400 (b & m)	2799- 3100 (w & b)	1590- 1600 (S)	1474-1450 (m)	957-1000 (m)
[Cu(R ₄) ₂ (2H ₂ O)]	3250- 3400 (b & m)	2798- 3100 (w & b)	1588-1600 (S)	-	960-1000 (m)

I.R.Spectral Bands of Copper(II) Complexes in cm⁻¹

The comparison of the IR spectrum of resins and its complexes revealed that a band of medium intensity appears around 3250-3400 cm⁻¹ in complexes and it was assigned to coordinated water molecule in the

complexes. The ν_{C} bridging and $\nu_{\text{C-NH}}$ bands in ligands remain intact in the complexes which suggest that the bridging group of two aryl ring of the ligands did not involve in the coordination. The OH group which absorbed around 2725 cm⁻¹ in ligands were found absent in the complexes. It was suggestive of the deprotonation of the phenolic group. The oxime-OH overlapped in CH₂ bridging group, therefore it could not be separately identified. The $\nu_{\text{C=N}}$ absorption which were found in ligands around 1627 cm⁻¹ suffers a blue shift and absorbed around 1590-1600 cm⁻¹ in complexes which was attributed to the involvement of the N-atom of oxime group in coordination. The conclusion is further supported by the increase in N-O frequency in all complexes. In all complexes a new band around 420 cm⁻¹ can safely be assigned to arise due to Cu-N bond.

(ii) Electronic Spectral Studies:

During the present course of investigation electronic spectra of all copper (II) complexes have been recorded using diffuse reflectance techniques taking barium sulphate as standard in the region 200-1100 nm.

The position and their tentative assignment for copper(II) complexes are given in table-V.

Table - V**Electronic Spectral Bands of Copper(II) Complexes**

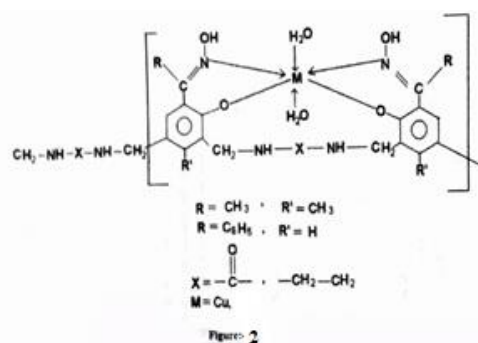
Name of Complexes	Internal Ligand transition	U.V. Spectral Data	${}^2B_{1g} \rightarrow {}^2B_{2g}$		${}^2B_{1g} \rightarrow {}^2E_g$	
			In nm	in cm^{-1}	In nm	in cm^{-1}
[Cu(R ₁) ₂ (2H ₂ O)]	210nm, 251nm	210nm, 251nm, 440nm, 650nm	650	15384	440	22727
[Cu(R ₂) ₂ (2H ₂ O)]	209nm	209nm, 440nm, 650nm	645	15503	435	22988
[Cu(R ₃) ₂ (2H ₂ O)]	210nm, 251nm	210nm, 252nm, 440nm, 650nm	655	15267	440	22727
[Cu(R ₄) ₂ (2H ₂ O)]	208nm	208nm, 440nm, 650nm	650	15384	440	22727

The spectra of all copper (II) polychelates gave bands around 210 nm and in case of complexes with ligands HR₁ and HR₃ bands around 250 nm also. The peaks were considered to arise due to inter-ligand transition.

The broad electronic reflection band located around 650 ± 5 nm along with a weak shoulder around 440 nm may be attributed to arise due to d-d transition and may be considered as arising due to ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^3B_{1g} \rightarrow {}^2E_g$ transitions in pseudo octahedral geometry.

Conclusion:

On the basis of above discussion it was concluded that the copper (II) polychelates synthesized from resin HR₁ to HR₄ have the following structures.



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