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Preparation and Characteristics of N-Hydroxyamidines

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ABSTRACT:- *The Preparation and characteristics of five new N-Hydroxyamidines using 4-fluoro benzaanilide have been described, 4-fluoro-aniline was treated with Benzoyl chloride to get crystals of anilide. The Pure aniline was converted into imidoyl chloride by heating with thionyl chloride. Equimolor quantities of (4. fluoro) phenyl benzamidoyl chloride when reacted with N-aryl hydroxylamine, in diethyl ether solution at 0^{0}-5^{0} C, white shining crystals of N-Hydroxyamidine hydrochloride were obtained. These were characterised on the basis of M.P, elemental analysis, UV and IR spectra.*

The ultraviolet absorption spectra of N-Hydroxyamidine hydrochloride in ethanol shows three district absorption band attributed to π- π transitions. The band observed at around 207 nm, 250-260 nm and 300-322 assigned as electron transfer band.*

The IR spectra were taken in the region 3700-400un^{-1}. The characteristic bands associated with hydroxyamidine functional group are due to C=N, -NH, O-H…N and N-O group which have been assigned in these IR spectra.

On the basis of the colour reaction of N-Hydroxyamidine a simple rapid selective and sensitive method has been proposed for extraction spectrophotometric determination of Iron transition metals like Iron, Molybdenum, Vanadium, from their, slag, soil and geological materials. This method has been successfully applied for gravimetric estimation of copper using N-Hydroxyamidines which is very simple and rapid.

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I. INTRODUCTION

Organic chelating agents have great practical importance, chelate are ligand has various sites for donation. Binding of a multidentate Ligand chelate to a metal ion results in an increased stability of the complexes as compared to monodentate analog (chelate effect). Some of the most frequently used chalating agents include ethylene diamine tetracetic acid (EDTA) oxalic acid, &-Hydroxyquinoline, dimethyl glyoxime etc.

Complex compounds formed by central ion with two or more different ligands are known as mixed ligands or complexes. These complexes are readily extracted by organic solvents, so that extraction photometric methods of analysis can be developed[1-4].

The absorption spectra of these mixed ligand complexes differ from those of the corresponding single ligand complexes[5-8] in both position and height of absorption maxima.

The increased interest in mixed ligand complex has stimulated development of new methods of analysis and on analytical applications.

N-Hydroxyamidines preparation used by Ley and other[9-10] played important role they reacted N-aryl-benzimidoyl chloride with N-arylhydroxylamine in ether at low temperature. But these studies were principally concerned with the the isomerism and reduction of Hydroxyamidines K. Satyanarayan and R.K. Mishra[11] discussed for the first time in analytical chemistry of Hydroxyamidine Hydrochloride. The complexing properties of the reagents[12] are modified by substitution in reagent molecule, hence a new N-Hydroxyamidine hydrochloride has been prepared and characterised by elemental analysis, m.p, IR & UV spectra.

The introduction of Hydroxyamidine hydrochloride as a new type of metal chalating agents, opens a new field, both of synthetic as well as of analytical interest. The special feature of those reagents are.

a) These have three sites for substitution with various groups and a better understanding of the influence of the substituents in the aromatic system.
b) These reagents form intensely coloured and easily extractable mixed complexes with various metal ions in presence of several complexing agents.
c) These colour reaction have been found to be highly sensitive and selective for estimation of those ions.

Thus an important line of approach in developing more sensitive and selective methods of determining ions is the use of mixed ligand complexes.

Geological samples, ores, alloys contain low to high concentration of transition metal like Fe, V, Mo, Cu, etc, their analysis requires analytical methods of high sensitivity, selectivity and control of interference effect[94]

II. EXPERIMENTAL

PREPARATION AND CHARACTERISTICS:-

The preparation and characteristic of five new N-Hydroxyamidines using 4-fluoro aniline have described, anilide prepared from 4-fluoro aniline for this 4-fluoro aniline with sodium hydroxide and Benzoyl chloride shaken vigrously white crystals formed. This anilide was heated with thionly chloride at high temp to get imidoyl chloride it is suggested by wallach and his student[13,14]. Then N-phenyl hydroxylamine[15] was prepared by reducing nitrobezene with zinc dust in aqneous medium. Lastly N-Hydroxyamidine hydrochloride is prepared by condensation of imidoylchloride and N-phenyl hydroxylamine. In ether at 0^0-5^0C. The crystals were recrystallised using absolute alcohol.

The Five N-Hydroxyamides Were Prepared, Elemental Analysis.

These are as follows -

1. N- Hydroxy - N - phenyl - N' (4-fluoro) phenyl benzamidine hydrochloride.

   Analysis - Calculated for $C_{19}H_{16}N_2$ OF Cl.

   Calculated - C = 66.56 H = 4.67 N = 8.17

   found - C = 66.62 H = 4.72 N = 8.22

   Yield = 80% m.p = 166 ^{0}C

2. N-Hydroxy - N - (2 methyl) phenyl N' (4-fluoro) benzamidine hydrochloride

   Analysis - Calculated for $C_{20}H_{18}N_2$ OF Cl.

   Calculated - C = 67.32 H = 5.04 N = 7.85

   found - C = 67.52 H = 5.16 N = 7.92

   Yield = 62% m.p = 152 ^{0}C

3. N-Hydroxy-N - (3 methyl) phenyl N' (4-fluoro) phenyl benzamidine hydrochloride

   Analysis - Calculated for $C_{20}H_{18}N_2$ OF Cl.

   Calculated - C = 67.32 H = 5.04 N = 7.85

   found - C = 67.82 H = 5.12 N = 7.95

   Yield = 71% m.p = 159 ^{0}C

4. N-Hydroxy- N- (4 methyl) phenyl N' (4-fluoro) phenyl benzamidine hydrochloride

   Analysis - Calculated for $C_{20}H_{18}N_2$ OF Cl.

   Calculated - C = 67.32 H = 5.04 N = 7.85

   found - C = 67.52 H = 5.14 N = 7.88

   Yield = 82% m.p = 142 ^{0}C

5. N-Hydroxy- N- (4 chloro) phenyl N' (4-fluoro) phenyl benzamidine hydrochloride

   Analysis - Calculated for $C_{19}H_{15}N_2$ OF Cl.

   Calculated - C = 60.47 H = 3.97 N = 7.42

   found - C = 60.37 H = 3.91 N = 7.38

   Yield = 45% m.p = 179 ^{0}C

ULTRA VIOLET SPECTRA OF HYDROXYAMIDINES -:

Ultra violet spectra of newly synthesised hydroxyamidines have studied in alcohol. It shows absorption band in π- π* transition at 207 nm local excitation band of phenyl chromophore other too bands around 250-260 nm and 300-322 nm assigned as electron transfer bands. The UV absorption bands for five hydroxyamidines are discussed in Table -1.

Table - 1 Ultra Violet Absorption characteristics of Hydroxyamidines

S.N.	N-Hydroxyamidines	λMax	Ɛ $Mole^{-1} cm^{-1} x 10^{-4}$	λMax nm	Ɛ $1Mole^{-1} cm^{-1}$	λMax	Ɛ $1Mole^{-1} cm^{-1}x10^{-4}$
(1)	N-Hydroxy N phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	207	3.20	256	1.16	310	1.20
(2)	N-Hydroxy N (2 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	208	3.10	256	1.35	310	1.56
(3)	N-Hydroxy N (3 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	210	3.10	258	1.72	310	1.72
(4)	N-Hydroxy N (4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	208	3.20	258	1.60	310	1.62
(5)	N-Hydroxy N (4 chloro) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	206	3.30	256	1.24	320	1.24

INFRA-RED SPECTRA OF N-HYDROXYAMIDINES -:

The infra red absorption spectra of newly synthesised hydroxyamidines have studied in the region 3700 - 400 cm^{-1}. The characteristic bands associated with N-Hydroxyamidine functional grouping are due to C=N, NH-OH…C-H, - N - O group IR stretching frequencies of Hydroxyamidine hydrochloride are given in Table - 2.

Table - 2 Infra red Stretching Frequencies (cm^{-1}) of Hydroxyamidines Hydrochloride

S.N.	N-Hydroxyamidines	λMax	Ɛ $Mole^{-1} cm^{-1} x 10^{-4}$	λMax nm	Ɛ $1Mole^{-1} cm^{-1}$	λMax	Ɛ $1Mole^{-1} cm^{-1}x10^{-4}$
	N-Hydroxyamidines	O-H	Ar-H	= N-H	C=NH	C=N	N…..O
(1)	N-Hydroxy N phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	___	3040	2550	1628	___	940
(2)	N-Hydroxy N (2 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	___	3030	2580	1620	___	930
(3)	N-Hydroxy N (3 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	___	3040	2560	1620	___	930
(4)	N-Hydroxy N (4 methyl) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	___	3030	2560	1620	___	930
(5)	N-Hydroxy N (4 chloro) phenyl N' (4 fluoro) phenyl benzamidine hydrochloride	___	3030	2560	1620	___	930

REACTION OF N-HYDROXY AMIDINES WITH TRANSITION METAL IONS -:

S.n.	Element	Mixed Reagent	Colour / Precipitate	pH/Acidity	λMax	E mol cm^2
(1)	Fe (III)[14-15]	SCN ⁻	Orange red soluble in benzene, Toulene, chloroform etc	0.2-0.7 M Hcl	470 nm	12400
(2)	Mo (V)[16]	SCN ⁻	Brown-red soluble in benzene, Toulene, etc	2.2-3.5 M Hcl	470 nm	6114
(3)	V (V)[17]	SCN ⁻	Blue - Violet complex	1.0 - 3.2 M Hcl	590 nm	Quantitative analysis
(4)	C_4(II)[18-21]		Buff precipitate in soluble in 80% alcohol	2.0-11.PH	Quantitative analysis	
(5)	Ni (II)		Yellow ppt.	4.0 -7.0 PH	Quantitative analysis	Quantitative

III. CONCLUSION

N-Hydroxyamidines are highly sensitive, reagents suitable for the detection and determination of transition metal ion in geological materials. A new research field is opened for synthesis and characterisation of these new chelating agents whose several properties are not explored.

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