Acta Ciencia Indica, Vol. XL C, No. 2, 63 (2014)

SYNTHESIS AND CHARACTERISATION OF N-HYDROXY-N-(4-CHLORO)PHENYL-N′-(4-FLUORO) PHENYL BENZAMIDINE HYDROCHLORIDE

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RECEIVED : 17 April, 2014

N-Hydroxyamidines are organic reagents used for detection and determination of transition metal ions. The selectivity and sensitivity can be suitably altered by changing the substituent groups attached to the functional group. This paper describes the synthesis of new N-Hydroxyamidine by the condensation of N-Hydroxy-N-(4-chloro) phenyl hydroxyamidine with-N(4-fluoro) phenyl benzamidoyl chloride in ether solution at 0^0 – 5^0C. White crystals of N-Hydroxy-N-(4-chloro) phenyl N'(4-fluoro) phenyl benzamidine Hydrochloride separate out. The compound was recrystallised with absolute alcohol. Melting point of the compound is 165°C. It is neither hygroscopic nor decompose upto 165°C. It is soluble in alcohol, chloroform, benzene but insoluble in ether.

The elemental analytical data confirms its molecular formula [$C_{19}H_{15}N_2Cl_2OF$]. The UV spectra of the compound in ethanol shows three distinct absorption bands attributed to π–π* transitions. The infrared spectra of hydroxyamidine hydrochloride have been examined and principal bands associated with O – H----N, C= N^+H, and N – O stretching vibrations have been located. The colour reactions of the compound with various transition metal ions have been studied. These studies confirm that the compound is suitable for gravimetric determination of Cu(II), Ni(II), Mo(VI) and extraction and spectrophotometric determination of V(V), Fe(III) etc.

KEYWORDS : N-Hydroxyamidines, Imidoyl chloride IR-Spectra UV Spectra.

INTRODUCTION

N-Hydroxyamidines are monobasic and bidentate chelating reagent having the functional grouping.

$$\begin{array}{l} -C=N- \\ \quad | \\ -N-OH \end{array}$$

They form five membered ring on chelation with metal ion. These compounds are stable towards light and heat and can be easily synthesised. These are appreciably soluble in various organic solvents. The solution of these compounds can be stored for a long time without

detorioration. The synthesis of seven hydroxyamidines of the general formula was reported by Ley and Holzweissig [1-2].

$$\begin{array}{l} Ar' - C = N - Ax \\ \qquad\quad | \\ Ar'' - N - OH \end{array}$$

Their studies were mainly concerned with the isomerism and reduction of hydroxyamidines.

Recently number of hydroxyamidines have been synthesised by Mishra *at al* [3-10]. These have been found to be excellent reagents for gravimetric and spoectrometric determination of some metal ions. These reagents reacts with metal ions in presence of various complexing agent like carboxylic acids phenols, aldehydes, azides, thiourea etc. giving coloured mixed complexes which can be extracted into organic solvents hence useful for extraction spectrophotometric determination of metal ions.

As compared to the established reagents such as oxine, cupferon, oximes, hydroxamic acid, hydroxytrizine and dithizone, Hydroxyamidines have wider scope as analytical reagents. Hydroxyamidine functional grouping has three sites for substitution with various groups and better understanding of the influence of substituents in aromatic system of the reagent will help greatly in carrying out systematic research for improvement of this class of reagent.

EXPERIMENTAL

Reagent and Chemicals :

All the chemical used were of A.R. grade. 4-fluoro aniline, thionyl chloride, 4-chloronitrobenzene. Zinc dust Ammonium chloride, alcohol ether etc.

Method :

Synthesis of N-Hydroxy-N-(4-chloro) phenyl-N'-(4-fluoro) phenyl benzamidine hydrochloride involves four steps.

Step-1 :

Preparation of (4-chloro) phenyl-(4-fluoro) benzanilide - It was done by schotten Baumann reaction [13]. The anilide was purified by recrystallization with 90% alcohol. The white crystals were dried in oven at 90°C-100°C.

Step-2 :

Preparation of N-(4-chloro) phenyl hydroxylamine [14]. 4-Chloro nitrobenzene was reduced by zinc dust in neutral alcoholic aquous solution to N-(4-chloro) phenyl hydroxylamine. The yellow crystals obtained were dissolved in little benzene and petroleum ether was added to the solution. Yellow shining crystals of N-(4-chloro) phenyl hydroxylamine were formed which were dissolved in ether.

Step-3 :

Preparation of Imidoyl chloride - The N-(4-chloro) phenyl (4-fluoro) benzanilide was mixed with 3.0 to 5.0 ml thionyl chloride and refluxed at 130°C – 140°C for three hours. The excess of thionyl chloride was removed by vaccum distillation. The yellow oil obtained was dissolved in absolute ether and solution was cooled to 0°C to 5°C [15].

Step-4 :

Preparation of N-Hydroxy (4-Chloro) phenyl N'-(4-fluoro) phenyl benzamidine hydrochloride. - N-4 chloro phenyl hydroxylamine was mixed with N'-(4-fluoro) phenyl benzamidoyl chloride in ether at low temperature (0°C – 5°C) dropwise, with constant shaking. White crystals separate out after about 30 minutes, these were filtered and recrystallise with absolute alcohol.

Characterisation of the Compound :

N-Hydroxy N-(4-chloro) phenyl-N'(4-fluoro) phenyl benzamidine hydrochloride is a white crystalline solid. It is soluble in almost all organic solvents except diethyl ether. Melting point in 1650C. Elemental analysis data. are in good agreement with the proposed formula $C_{19}H_{15}N_2Cl_2OF$.

Calculated % C = 60.47, H = 3.97, N = 7.42

Found % C = 60.20, H = 3.80, N = 7.32,

The UV spectra was recorded in alcohol. Three distinct bands appear at λ max 200-220 nm, another peak at λ max 250-270 nm and third at λ max 310-330 nm. The IR spectra of the compound gives C-H stretching band at 3040 cm^{-1}, C=NH band at 1580 cm-1 and N-O band at 940 cm^{-1} [16].

The compound gives violet complex with Fe(III) which is soluble in alcohol. When potassium thiocyanate is added to it, orange red complex is formed which can be extracted in toluene. The compound gives buff precipitate with copper (II) which is insoluble in 60% alcohol. The suitable pH range for quantitative precipitation of copper (II) is 2.5 to 10.8. On this basis a gravimetric method can be developed for separation and estimation of copper (II) in ores and alloys.

The colour reaction with some metal ions are given in Table -1.

Table – 1. Analytical data on reaction of N-Hydroxy amidine with various metal ions.

Metal Ion	Complexing agent	Approximate pH/Acidity	Characterisation of Complex
Iron (III)	Thiocyanate	0.20 - 0.55 M HCl	Orange - red complex, extractable in to benzene, ε, 11470 at 460 nm.
Iron (III)	Benzoic acid	2.8 - 6.0	red - purple complex, extractable in to benzene, ε, 3210 at 520 nm.
Vanadium (V)	Acetic acid	1.5 - 8.0	Blue - violet complex, extractable in to chloroform, ε, 4100 at 560 nm.
Vanadium (V)	Thiocyanate	0.6 - 2.2	Deep green complex, extractable in to chloroform, ε, 3400 at 580 nm.
Vanadium (V)	Benzaldehyde	1.5 - 4.0	Greenish blue complex, extractable in to chloroform, ε, 3500 at 560 nm.

Vanadium (V)	Salicylaldehyde	2.5 - 5.0	Green - blue complex, extractable in to chloroform, ε, 5000 at 590 nm.
Vanadium (V)	4 - Hydroxy benzaldehyde	2.0 - 2.2	Greenish blue complex, extractable in to chloroform, ε, 8160 at 560 nm.
Mo (V)		2.0 - 5.0	Yellow precipitate soluble in common organic solvent
Mo (V)	Thiocyanate	1.5 - 2.9 M HCl	Orange - red complex, extractable in to benzene, ε, 3760 at 460 nm.
Ni (V)		6.0 - 8.5	Yellow precipitate insoluble in 60% ethanol.
Copper (II)		2.5 - 10.8	Buff coloured complex insoluble in hot water and common organic solvent.

Conclusion

N-Hydroxy(4-chloro) phenyl hydroxylamine reacts with N-(4-fluoro) benzamidoyl chloride in ether medium at 0°C – 5°C and forms white crystals of N-Hydroxy (4-Chloro) phenyl-N'-(4-fluoro) phenyl benzamidine hydrochloride. The compound is thermally stable and soluble in most of the organic solvents except in ether. It forms chelate with Cu(II), Ni(II) which are insoluble. The reaction is quantitative. Its colour reaction with Fe(III), V(V) Mo(V) etc. make it a sensitive and specific reagent for detection and spectrophotometric determination of these ions.

Acknowledgement

Authors are thankful to the Principal Dr. R. N. Singh Government Post Graduate College, Rajnandgaon (C.G.) and Dr. Alok Mishra Head of Chemistry Department for providing laboratory facilities for the present work.

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