

## NOTE

## Hydroxyamidine Hydrochloride as a Spectrophotometric Reagent for Iron(III)<sup>†</sup>

SHAHBAZ KHAN and HEM LATA MOHABEY\*

*Department of Chemistry**Government Digvijay Postgraduate College, Rajnandgaon, India*

The preparation and properties of five new hydroxyamidine hydrochlorides have been described. Equimolar quantities of N-aryl hydroxylamine and N-aryl-imidoyl chloride were reacted in diethyl ether. All the isolated compounds have been characterised on the basis of m.p., elemental analysis, ultraviolet and infrared spectra. All the hydroxyamidines react with iron(III) forming blue alcohol soluble complex at 2.2 to 4.0 pH and above 4.5 pH colour changes to violet. In presence of thiocyanate a hyperchromic and hypsochromic effect is observed. The orange-red complex which can be extracted into benzene absorbs strongly at 460 nm. Thus a new method can be developed for extraction-spectrophotometric determination of iron(III).

**Key Words:** Hydroxyamidine hydrochlorides, Spectrophotometric reagent, Iron(III).

N-Hydroxyamidines are recently used as a spectrophotometric reagent for the determination of transition metal ions<sup>1-5</sup>. The complexing properties of the reagents can be modified by different modes of substitution. Therefore, five new hydroxyamidine hydrochlorides have been synthesized and characterized on the basis of melting point, elemental analysis, ultraviolet spectra and IR spectra. The reaction of these synthesized hydroxyamidine hydrochlorides with iron(III) has been studied. It was found that all the five hydroxyamidine hydrochlorides synthesized in the present investigation behave in a similar manner and are useful for extraction, spectrophotometric determination of iron(III) in soil samples, water samples, vegetable plants, etc.

All the reagents used were of analytical grade. Ultraviolet spectra of the newly synthesized compounds were recorded in ethanol. The infrared spectra were recorded in KBr on Perkin-Elmer 1800 (FTIR) spectrophotometer equipped with sodium chloride optics. Procedure for the preparation of hydroxyamidine hydrochloride N-(O-chloro) phenyl hydroxylamine was dissolved in diethyl ether and was placed in a 500 mL conical flask. To this equimolar quantity of N-aryl-p-

<sup>†</sup>Presented at the 90th annual session of the Indian Science Congress Association-2003, Bangalore, India.

toluimidoyl chloride dissolved in same solvent was added slowly with constant shaking during the course of 5 to 10 min. The solution was stirred continuously with a glass rod. After 1 h white shining crystals were formed which were filtered and washed with ether. These were recrystallized from hot alcohol.

The ultraviolet spectra of ethanolic solution of hydroxyamidine hydrochloride in the region 200–400 nm show three intense bands. The assignment of electronic transition associated with the bands has been obtained on the basis of available data on Schiff's bases and amidines<sup>6-9</sup>

The infrared spectra of hydroxyamidine hydrochlorides have been recorded in KBr on Perkin-Elmer 1800 FTIR spectrophotometer in the range 4000–400  $\text{cm}^{-1}$ .

In the IR spectra of hydroxyamidine hydrochloride a band is observed at 1630–1610  $\text{cm}^{-1}$ . This band is due to C=NH absorption. The shift of C=N absorption band from 1600  $\text{cm}^{-1}$  to higher frequencies is due to salt formation<sup>10,11</sup>. All the hydroxyamidine hydrochlorides show strong broad ammonium band =N<sup>+</sup>H at 2600–2550  $\text{cm}^{-1}$ . A sharp band at  $930 \pm 10 \text{ cm}^{-1}$  is due to N—O stretching<sup>12</sup>. The hydroxyamidines examined here show C—H stretching vibrations in the region  $3030 \pm 30 \text{ cm}^{-1}$  which is in support of the fact that aromatic C—H stretch appears near 3030  $\text{cm}^{-1}$ . A representative infrared spectrum is presented in Fig. 1.

All the hydroxyamidine hydrochlorides react with iron(III) in the pH range 2.2–4.5 forming blue complex in alcohol. This blue solution shows maximum absorbance at 580–590 nm. In presence of thiocyanate, orange-red complex is formed which can be extracted into benzene. This coloured extract absorbs strongly at 460 nm having molar absorptivity  $11000 \pm 1000 \text{ mole}^{-1} \text{ cm}^{-1}$  at  $\lambda_{\text{max}}$ . This colour reaction can be applied for the determination of iron(III) in iron ores, soil samples, water samples and biological materials.

TABLE-1  
KEY INFRARED BANDS ( $\text{cm}^{-1}$ ) OF HYDROXYAMIDINES

Hydroxyamidine	$\nu(\text{O—H})$	$\nu(\text{Ar—H})$	$\nu(\text{NH})^+$	$\nu(\text{C=NH})^+$	$\nu(\text{N—O})$
N-Hydroxy-N-( <i>o</i> -chloro) phenyl-N'-(2-methyl) phenyl- <i>p</i> -toluamidine hydrochloride	—	3060	2565	1618	940
N-Hydroxy-N-( <i>o</i> -chloro) phenyl-N'-(3-methyl) phenyl- <i>p</i> -toluamidine hydrochloride	—	3040	2560	1620	930
N-Hydroxy-N-( <i>o</i> -chloro) phenyl-N'-(4-methyl) phenyl- <i>p</i> -toluamidine hydrochloride	—	3050	2550	1620	930
N-Hydroxy-N-( <i>o</i> -chloro) phenyl-N'-(2-chloro) phenyl- <i>p</i> -toluamidine hydrochloride	—	3040	2560	1620	930
N-Hydroxy-N-( <i>o</i> -chloro) phenyl-N'-(4-chloro) phenyl- <i>p</i> -toluamidine hydrochloride	—	3040	2560	1620	930

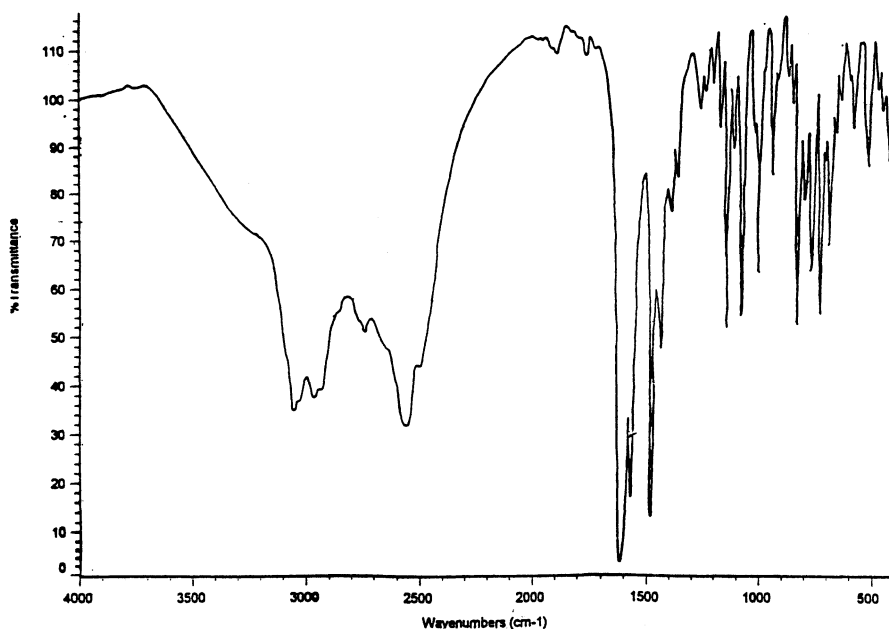


Fig. 1. IR spectra of 6-N-hydroxy-N-(*o*-chloro) phenyl-N'-(2-methyl) phenyl-*p*-toluamidine-hydrochloride

### ACKNOWLEDGEMENTS

Authors are thankful to the director, CDRI Lucknow and RSIC Nagpur for providing elemental analysis, spectral data and academic resource inputs for the present work.

### REFERENCES

1. K. Satyanarayna and R.K. Mishra, *Anal. Chem.*, **46**, 1605 (1974).
2. K.S. Deb and R.K. Mishra, *Curr. Sci. (India)*, **47**, 341 (1978).
3. H. Mohabey, P.K. Sharma and R.K. Mishra, *Proc. Indian Acad. Sci.*, **89**, 95 (1980).
4. H. Mohabey and R.K. Mishra, *J. Indian Chem. Soc.*, **57**, 142 (1980).
5. I. Mishra and H. Mohabey, *Bull. Chem. Soc. (Japan)*, **66**, 1533 (1993).
6. H.H. Jaffe and M. Orchin, *Theory and Application of Ultraviolet Spectroscopy*, John Wiley & Sons Inc., p. 284 (1964).
7. *UV Atlas of Organic Compounds*, Vol. III, Butterworths, London and Verlag-Chemie, Weinheim (1967).
8. E.S. Hand and W.P. Jencks, *J. Am. Chem. Soc.*, **84**, 3505 (1962).
9. A.I. Scott, *Interpretation of the Ultraviolet Spectra of Natural Products*, Pergamon Press, Inc., New York, p. 122 (1964).
10. H.A. Szymanski, *Theory and Practice of Infrared Spectroscopy*, Plenum Press, New York, p. 291 (1963).
11. R.D. Brown and A. Penfold, *Trans Faraday Soc.*, **53**, 397 (1957).
12. A.T. Pillipenko, E.A. Shapk and I.L. Shevchenko, *Zhur Neorg Khim.*, **121**, 463 (1967).