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Synthesis of *N*-Hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)benzamidine Hydrochloride and Its Reactions with Various Metal Ions#

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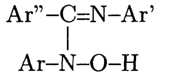
A new reagent *N*-hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)benzamidine hydrochloride, has been synthesized and is characterized on the basis of mp, elemental analysis, IR and UV spectra. The reactions of the reagent with metal ions suggest that new methods can be developed for gravimetric and extraction spectrophotometric determination of metal ions. The reagent has been successfully used for the extraction-spectrophotometric determination of vanadium(V) in presence of phenol. Many common ions including Co^{2+}, Zn^{2+}, Ag^{+}, Mn^{2+}, etc. do not interfere in the determination. The method has been applied for the determination of vanadium in steel samples.

Recently*N*-hydroxy-*N*,*N*′-diarylbenzamidine, monobasic and bidentate chelating agents have been used as versatile reagents for determining metal ions.$^{1-5)}$ The synthesis of only seven *N*-hydroxyamidines was first reported by Ley and Holtzweissing$^{6,7)}$ but their studies were concerned with kinetics of hydrolysis of *N*-hydroxyamidine hydrochloride, their isomerism and reduction. Only few investigations regarding synthesis and analytical applications of hydroxyamidine have been carried out. The analytical potentialities of these organic reagents can be modified by proper substitution in the phenyl groups attached to the coordinating nitrogen.



$$\begin{array}{l}\mathrm{Ar''{-}C{=}N{-}Ar'}\\ \quad\;|\\ \mathrm{Ar{-}N{-}O{-}H}\end{array}$$

In this connection a new hydroxyamidine *N*-hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)benzamidine hydrochloride has been prepared and characterized on the basis of mp, elemental analysis, IR and UV spectra. Its reactions with various metal ions have been studied. A new method has been developed for the extraction-spectrophotometric determination of vanadium(V) using this reagent in the presence of phenol. *N*-Benzoyl-*N*-phenyl-*N*-hydroxylamine (PBHA) is commonly used as a selective reagent for vanadium but suffers from number of draw backs,$^{8-10)}$ which are successfully eliminated in the proposed method. No partial reduction of vanadium is observed and hence the extraction is quantitative. Cr^{3+}, Mn^{2+}, Ti^{4+}, Zr^{4+}, Zn^{2+} do not interfere. The method is accurately applied for the determination of vanadium in BCS steels.

Experimental

All the reagents used were of A.R. grade. *p*-Anisidine was purified by crystallization from absolute ethanol.

Apparatus: A systronic pH meter type 321 was used for pH measurements. A Carl Zeiss Jena SPEKOL was employed for spectrophotometric measurements.

Preparation: *N*-(*p*-Methoxyphenyl)benzimidoyl chloride was prepared from *N*-benzoyl-*p*-anisidine by the action of thionyl chloride at 100—110 °C. Excess thionyl chloride was removed by distillation under reduced pressure. *o*-(Chlorophenyl)hydroxylamine (0.05 mol) was dissolved in diethyl ether and was placed in 500-ml conical flask equipped with a dropping funnel. To this, *N*-(*p*-methoxyphenyl)benzimidoyl chloride (0.05 mol) dissolved in the same solvent was added dropwise during the course of 5 to 10 min while stirring the solution with a glass rod. Stirring and shaking were continued for one and half hour till white shining crystals were formed. The crystals were filtered off and washed with ether. The crude product was crystallized with absolute ethanol. Yield, 60%, mp 135 °C. Analysis. Calcd for $C_{20}H_{18}N_2O_2Cl_2$: C, 61.69; H, 4.60; N, 7.19%. Found: C, 61.42; H, 4.31; N, 6.93%.

Characterization and identification of newly synthesized compound was obtained by UV and infrared spectra. The ethanolic solution of the compound gives three bands in the region 200 to 400 nm. Strong band at 210 nm is assigned as a local excitation band of phenyl chromophore on the basis of similar assignments in various aromatic Schiff's bases. The band at 260 nm is very weak band, the band at 310 nm is electron transfer band.$^{11)}$ The infrared spectra were recorded in KBr on a Perkin–Elmer model 221 equipped with sodium chloride optics in the region 3700—400 cm^{-1}. The band due to free OH group is absent while the bands due to C=N, =NH were observed at 1620 and 2550 cm^{-1}. The band for N–O was observed at 930 cm^{-1}.$^{12)}$

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Table 1. Analytical Data on Reaction of *N*-Hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)benzamidine Hydrochloride with Various Metal Ions

Metal ion	Complexing agent	pH/acidity range	Characteristic of the complex
Cu(II)	—	3.0 to 10.5	Buff colored precipitate, insoluble in water, ethanol or alcohol and common organic solvents.
Ni(II)	—	7.0 to 10.0	Yellow precipitate insoluble in 60% ethanol, stable towards heat up to 180 °C.
Mo(VI)	—	3.0 to 6.0	Yellow precipitate soluble in organic solvents, stable up to 105 °C.
Fe(III)	—	3.0 to 4.6	Blue complex soluble in ethanol ε=3600 at 590 nm.
Fe(III)	—	5.0 to 10.0	Red-purple complex ε=4000 at 540 nm.
Fe(III)	Thiocyanate	0.3 to 0.6 M[a] HCl	Orange red complex extractable into benzene ε=12000 at 460 nm.
Fe(III)	Benzoic acid	3.0 to 5.3	Purple complex extractable into benzene ε=3200 at 530 nm.
Fe(III)	Salicylic acid	2.5 to 4.8	Purple complex extractable into benzene, ε=3600 at 540 nm.
Mo(V)	Thiocyanate	2.0 to 4.0 M HCl	Orange red complex extractable into benzene ε=3600 at 470 nm.
V(V)	Thiocyanate	1.5 to 5.0	Green complex extractable into chloroform ε=5200 at 590 nm.
V(V)	Phenol	1.2 to 3.0	Deep blue complex extractable into chloroform ε=5000 at 600 nm.
V(V)	Acetic acid	1.2 to 10.0 M	Blue violet complex extractable into chloroform ε=4000 at 580 nm.

a) 1 M=1 mol dm^{-3}.

Reactions of *N*-Hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)benzimidine Hydrochloride with Various Metal Ions. The reactions of the reagents towards the metal ions were studied using the procedure described by West.[13)]

General Procedure: 1 ml of the solution containing 5 mg of metal ion under study, was taken in a 100-ml beaker and diluted to 50 ml. To this solution of the reagent in ethanol was added dropwise with constant stirring. The pH of the solution was adjusted with acetic acid and then was slowly increased by addition of ammonia. The initial pH, at which precipitation or coloration commenced was recorded. The colored species was extracted with chloroform alone or with the aid of another complexing agents. The absorption spectra were recorded against reagent blank.

Results and Discussion

N-Hydroxy-*N*′-(*p*-methoxyphenyl)benzamidine hydrochloride reacts with copper(II) producing heavy granular buff colored precipitate which is insoluble in hot water and many organic solvents. The reaction is quantitative at pH 3.0 to 10.2. The complex is thermally stable and can be dried at 100—170 °C without decomposition. Nickel(II) forms yellow precipitate at pH 7.0—10. The precipitate can be dried at 100—180 °C. Molybdenum(VI) gives deep yellow insoluble complex with ethanolic solution of the reagent at pH 3.0—6.0. The complex can be dried at 100 °C without decomposition. Thus the reagent can be used for the gravimetric determination of copper(II), nickel(II), and molybdenum(VI).

Vanadium(V), iron(III)molybdenum(V) react with *N*-hydroxy-*N*-(*o*-chlorophenyl)-*N*′-(*p*-methoxyphenyl)-benzamidine hydrochloride in the presence of phenol, thiocyanate, carboxylic acids, azide etc. and form colored mixed complexes (Table 1). These colored species can be extracted with various water immicible organic solvents like chloroform, carbon tetrachloride, benzene etc. and show promise of using the reagent for selective extraction and spectrophotometric determination of these metal ions.

Extraction- Spectrophotometric Determination of Vanadium(V) Using *N*-Hydroxy-*N*-(*o*-chlorophenyl)- *N*′- (*p*- methoxyphenyl)benzamidine Hydrochloride and Phenol. An aliquot of vanadium solution containing 100 µg of the metal ion was placed in a 100-ml separatory funnel. The pH of the solution was adjusted to 2.5±0.5 with hydrochloric acid and ammonia. Now added chloroform solution of HCPABH and phenol and shaked vigorously for two minutes. Separated the organic phase and dried over anhydrous sodium sulfate. Now transferred it into 25-ml volumetric flask and diluted with chloroform to the mark. Measured the absorbance at $\lambda_{\max}$ (600 nm) against reagent blank.

Effect of Variables: Vanadium formed blue green complex with HCPABH and phenol which is extractable into chloroform, toluene, carbon tetrachloride. Chloroform was found to be the best because the complex is more readily extractable in this solvent. The extraction is quantitative at pH 2.0 to 3.1. The wavelength of maximum absorbance is 600 nm with molar absorbance of 5900 dm^3 mol^{-1} cm^{-1}. Five fold molar excess of the reagent and 200 fold molar excess of phenol are adequate for complete extraction of vanadium(V). The colored system follows Beer's law in the range 0.8—4.8 ppm. The standard deviation of the method was found to be 0.5%.

Most of the common ions including Co^{2+}, Zr^{4+}, Ti^{4+}, Zn^{2+}, Ag^{+} do not interfere with determination. The method have several advantages over the commonly used PBHA method. No partial reduction of vanadium(V) is observed hence the reaction is quantitative. The method has been successfully applied for the determination of vanadium in BCS steel samples (Table 2).

Table 2. Determination of Vanadium in BCS Steels

Alloy	Vanadium found % (n=5)[a]	Certified value %	C.V. %
64a alloy steel	$1.55_2\pm0.005$	1.57	0.32
252 low allow steel	$0.45_2\pm0.006$	0.46	1.33

a) Average of five determinations.

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