

Synthesis, Characterization and Analytical Applications of Copper(II) N-Hydroxyamidines Complex

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Copper(II) reacts with N-hydroxy-N-(*o*-chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride and forms buff precipitate in the pH range 2.5–10.0, which is insoluble in water and most of the organic solvents. The reaction is highly selective at pH 3.0–4.5. The analytical data indicate metal to ligand ratio 1 : 2. The conversion factor 0.0837 is very small, which makes the method applicable for the determination of micro quantity of copper(II). Most of the common ions including Mn(II), Ni(II), etc., do not interfere with the determination. The method has been successfully applied for the determination of copper(II) in alloys and biological samples.

Key Words: Copper(II), Gravimetric Reagent, N-Hydroxyamidines.

INTRODUCTION

In recent years, a series of hydroxyamidines have been synthesized. They constitute an interesting and versatile class of chelating agents capable of co-ordination with metal ions and giving soluble and insoluble complexes¹⁻⁵. Chatterji *et al.*⁶ reported the behaviour of chelating agents is considerably affected on substitution in phenyl ring or replacement of phenyl group by naphthyl group. On this basis five new hydroxy-amidines have been synthesized and their reaction with copper(II) has been studied. It was found that all the five hydroxyamidine hydrochlorides synthesized in the present investigation react in a similar way. N-hydroxy-N-(*o*-chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride was used due to better yield of the reagent.

EXPERIMENTAL

A single pan semimicro balance Dona Analytical (sensitivity 0.01 mg) was used for weighing purpose. The pH of the solution was measured with Systronics pH-meter type 322. BDH AnalaR copper metal in dilute nitric acid was dissolved. The solution was boiled to expel oxides of nitrogen. The solution was standardized volumetrically using iodometric method⁷ and gravimetrically using salicylaldoxime. 1% solution of N-hydroxy-N-(*o*-chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride in alcohol was used for precipitation purpose.

Procedure: Copper ion solution containing 10 : 15 mg of the metal was diluted to about 150 mL with distilled water and the pH was adjusted in between 3.5–5.0 by adding the acetate buffer. 1% (w/v) solution of the reagent was added with constant stirring. A buff coloured precipitate separated out. It was digested on a water bath at 60–70°C for about 30–40 min. The precipitate was filtered in a sintered crucible C-4, washed repeatedly with 40% aqueous alcohol, dried at 110–120°C and weighed as $(C_{21}H_{18}N_2OCl)_2Cu$.

Copper complex is precipitated immediately when N-hydroxy-N-(*o*-chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride solution is added to copper solution at pH 2.5 to 10.0. The buff coloured complex is insoluble in water and most of the organic solvents like ethanol, carbon tetrachloride, chloroform, etc. TGA curve confirms that the complex is stable up to 200°C; the m.p. is 198°C. The results of elemental analysis are given in Table-1.

TABLE-1
ANALYTICAL DATA OF COPPER(II) COMPLEXES OF HYDROXYAMIDINES

S. No.	Compounds	m.p. (°C)	Analysis % found (Calcd.)			
			C ₁	C	H	N
1.	N-Hydroxy-N-(<i>o</i> -chloro)phenyl N'-(2,6-dimethyl)phenyl benzamidine hydrochloride copper chelate	210	8.29 (8.37)	65.90 (66.34)	4.65 (4.73)	7.12 (7.36)
2.	N-Hydroxy-N-(<i>o</i> -chloro)phenyl N'-(2,5-dimethyl)phenyl benzamidine hydrochloride copper chelate	202	8.32 (8.37)	66.12 (66.34)	4.59 (4.73)	7.10 (7.36)
3.	N-Hydroxy-N-(<i>o</i> -chloro)phenyl N'-(2,4-dimethyl)phenyl benzamidine hydrochloride copper chelate	208	8.19 (8.37)	65.98 (66.34)	4.32 (4.73)	7.06 (7.36)
4.	N-Hydroxy-N-(<i>o</i> -chloro)phenyl N'-(2-methyl-5-chloro)phenyl benzamidine hydrochloride copper chelate	198	7.82 (7.91)	59.68 (59.73)	3.01 (3.13)	6.66 (6.96)
5.	N-Hydroxy-N-(<i>o</i> -chloro)phenyl (α -naphthyl) benzamidine hydrochloride copper chelate	212	7.92 (7.88)	66.32 (68.42)	3.85 (3.96)	6.88 (6.94)

Effect of pH: For adjustment of the pH, acetic acid, dilute ammonia and ammonium acetate were used. The reaction is quantitative in the pH range 3.5 to 9.8 though precipitation starts at pH 2.5. Above 11.0 pH complex is not formed. The selectivity of the reagent is more at low pH 4.0 to 5.0.

Amount of Reagent: To study the effect of amount of reagent on gravimetric determination of copper, varying amounts of 1% reagent solution were added to 12 mg copper. The final volume of the solution was made to 150 mL. The pH of the solution was adjusted to 4.0. It was found that 15 mg of the reagent was sufficient for complex precipitation of 1 mg of copper. 20 mL of 1% alcoholic solution was used for precipitation of 5 mg of copper.

Excess reagent caused no adverse effect as it could be washed out easily with 60% ethanol (Table-2).

TABLE-2
DETERMINATION OF COPPER IN ALLOYS

Sample No. and name	Copper found (%)	Average value	Certified value	Standard deviation
Brass	70.11	70.11	70.03	± 0.01936
	70.14			
	70.10			
	70.10			
	70.12			
5f brass	70.76	70.78	70.80	± 0.02
	70.76			
	70.78			
	70.80			
	70.80			
Gun metal	87.86	87.86	87.90	± 0.015
	87.86			
	87.84			
	87.84			
	87.87			
White metal	4.08	4.10	4.10	± 0.028
	4.12			
	4.12			
	4.06			
	4.08			

Digestion: The digestion of the precipitate was done on a water bath at 70–80°C for 20–30 min till the mother liquor was clear; prolonged digestion for 3 h caused no adverse effect.

Filtration and washing: The precipitate was filtered immediately after digestion while hot to prevent post-precipitation and co-precipitation through a preweighed sintered glass crucible (porosity G-4). It was washed with 60% hot alcoholic solution till no blue colour was obtained when ferric chloride solution was added to the washing.

Drying the precipitate: The precipitate was dried at 100–120°C and weighed as $(C_{21}H_{18}N_2OCl)_2Cu$. The m.p. of the complex was 198°C; from thermogravimetric analysis it was clear that the complex decomposes when heated above 200°C.

Accuracy and precision: Reproducibility studies were carried out on 10 independent solutions each containing 10.5 mg copper(II). The standard deviation was ± 0.006663 while the relative standard deviation was ± 0.0628. Thus the proposed method is accurate and precise.

Applications

An accurately weighed amount of alloy containing 10–15 mg of copper in 25 mL aliquot of the final solution was dissolved in 40% nitric acid in a 400 mL beaker. The solution was evaporated to near dryness to remove oxides of nitrogen. It was diluted and filtered to remove the insoluble matter. The insoluble matter was thoroughly washed with dilute nitric acid. The filtrate was again evaporated to near dryness and diluted with water. The solution was transferred to a 250 mL volumetric flask and diluted to volume. The amount of copper was determined following the recommended procedure. The results of the analysis are summarized in Table-3.

RESULTS AND DISCUSSION

N-hydroxy-N-(*o*-chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride has been proposed as a highly selective and sensitive reagent for the gravimetric estimation of copper(II). The conversion factor (metal/metal complex) for copper (0.0837) is favourable for the determination of small quantities of the metal (*ca.* 2 mg) can be determined with the proposed method. Several methods have been proposed for the gravimetric determination of copper¹² but all these suffer from experimental limitations like instability of the complex, temperature, conditioning solubility of the complex, etc.

The comparative study of the proposed method with some important methods is summarized in Table-3.

Infrared Spectra of Copper Complex: The ligand molecule consists of a broad band at 2550 cm^{-1} confirming the presence of azomethene nitrogen in hydroxyamidine hydrochloride¹⁵. This band is absent in the spectra of copper complex indicating deprotonation of azomethene nitrogen. A strong band at 1610 cm^{-1} is observed in the spectra of the free ligand which is due to $\text{C}=\overset{+}{\text{N}}\text{H}$, which appears at 1580 cm^{-1} in the spectra of copper complex. This band shifts to lower frequency by 30 cm^{-1} on complexation due to reduction of electron density in the azomethene linkage. The formation of $\text{C}=\text{N}\cdots\text{Cu}$ coordinate bond¹⁶ is confirmed. The N—O stretching mode appears at 960 cm^{-1} in copper complex. This supports N—O—Cu bond in the complex.

In the infrared spectra of copper complex synthesized in the present investigation M—N band was observed at 467 cm^{-1} which is in support of Nakamoto's assignment. (Cu—O) band absorbs in low frequency region due to low bond order and relatively heavy mass of copper. In the present complex this band appears at 430 cm^{-1} . The comparison of the spectra of free ligand and copper complex suggests that the band due to $\overset{+}{\text{N}}\text{—H}$ stretching disappears while bands due to $\text{C}=\text{N}$, N—O shift on chelation with copper. The $\nu(\text{C}=\text{N})$ of the free ligand in the region 1605 cm^{-1} to lower frequency region ($\Delta\nu = 20\text{ cm}^{-1}$) in the complex indicates coordination of azomethine nitrogen with copper. The N—O stretching mode appears at high frequency suggesting N—O—Cu bond in the complex¹⁶. The method has been successfully applied for the determination of copper in alloys.

TABLE-3
DIFFERENT GRAVIMETRIC REAGENTS FOR THE DETERMINATION
OF COPPER(II) IONS

Reagent	Conversion factor	Interference	Remarks
8-Hydroxy Quinoline ⁷	0.18059	Mn, Fe(II, III) interfere	The reagent forms a green complex with copper, pH 5.3–14.0, but it is not very specific reagent. Shik ⁵ claims an error of 0.4–0.6% in the determination of copper from pure salt solution or in presence of Ca(II), Mg(II) and Mn(II).
Rubeanic acid ⁸	—	Co, Ni, Zn and many common ions	It is one of the most sensitive reagents so far known but the olive green to black powder obtained in alkaline pH cannot be directly weighed due to the presence of certain adhering impurities.
α -Nitroso- β -naphthyl amine ⁹	—	Many metals interfere	The reagent forms a chocolate brown complex in presence of tartrate or acetate which is directly weighable but due to the precipitation on alkaline side it has limited specificity.
Salicyldoxime ^{10, 11}	0.18922	Fe(II), V(V), Pd(III), Au(III), Zn(II), Co(II) and Ni(II)	The reagent gives green complex with copper. It decomposes in the reaction media above 80° to give unremovable products which get contaminated with copper complex. Complex is soluble in ethanol and, therefore, it is difficult to remove excess of reagent completely. The selectivity of the reagent is also poor.
α -Benzoin oxime ^{12, 13}	0.22002	W(VI), V(V), large amounts of Fe(II), Zn(II) and ammonium salts	The ignition of the complex has to be done very slowly, otherwise graphite will be formed. Azzalin ²⁰ has reported that excess of reagent cannot be reported completely. Shik ¹⁹ has reported the precipitation of CuO before the addition of reagent in strongly ammonical solution. The reagent itself is photosensitive and darkens on exposure to light.
3-Hydroxy-1,3-diphenyl triazine ¹⁴	0.1303	V(V), Ag(I), Au(III), excess of reagent	The reagent behaves like a reducing agent. The process of filtration takes time.
Quinaldinic acid	0.14919	Fe(III), Zn(II)	The sensitivity and specificity of the reagent is low. Moreover, the complex is soluble at low pH at which it is used.
N-Hydroxy-N-(<i>o</i> -chloro)phenyl-N'-(2,6-dimethyl)phenyl benzamidine hydrochloride	0.0837	—	The complex is insoluble in 70% hot alcohol, hence adhering reagent can easily be washed out. Process of filtration is fast. Interference due to Fe(II), V(V), Bi(III), Ti(IV) can be eliminated by masking with tartaric acid.

The thermal dissociation data including initial decomposition temperature (T_a), inflexion point temp. (T_b) and weight loss (% w) due to oxidation reduction are 230°, 480° and 540°C. It is obvious from the TGA curve that no loss in weight is observed when the chelate is heated up to 230°C indicating the absence of coordinating water molecules in the coordination sphere of the metal¹⁷. It was confirmed by the absence of a peak around 3500 cm^{-1} in the IR spectra of the complex. Initial decomposition temperature is 230°C and inflexion temperature is 480°C. The initial decomposition temperature is frequently used to define the thermal stability of metal chelates.

The appearance of a sharp exothermic peak in the temperature range 220–230°C may be due to transition from one state to another state of the chelate. Broad exothermic peak was observed in the temperature range 450–480°C corresponding to rapid mass loss in TG curve which may be due to oxidation-reduction reaction.

The exothermic peaks were preceded by broad endothermic peaks. It has been demonstrated by Dollimore and Griffiths that exothermic breakdown of the copper complex leads to the endothermic decomposition of the copper complex¹⁷. The exothermic nature of the decomposition in air is the result of the oxidation-reduction reactions.

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