

NOTE

N-Hydroxy-N-p-Tolyl-N'-β-Naphthyl Benzamidine Hydrochloride as a Gravimetric Reagent for the Determination of Copper(II)

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N-Hydroxy-N-p-tolyl-N'-β-naphthyl benzamidine hydrochloride has been used as a new reagent for gravimetric determination of Cu(II). The proposed reagent forms a buff coloured precipitate with Cu(II) in the pH range 2.5 to 10.8. The precipitate can be dried up to 200°C without decomposition. The solid copper complex has been characterised on the basis of m.p., elemental analysis, magnetic measurements, infrared, TGA and DTA.

Key Words: N-Hydroxy-N-p-tolyl-N'-β-naphthyl benzamidine hydrochloride, Gravimetric, Copper(II).

Several methods have been proposed for the determination of copper¹⁻⁶, but all these suffer from experimental limitation such as instability of the complex, temperature limitation, etc. A simple, rapid and sensitive method has been proposed for the gravimetric determination of Cu(II) with a new hydroxyamidine, N-hydroxy-N-p-tolyl-N'-β-naphthyl benzamidine hydrochloride. The conversion factor $63.7/765.6 = 0.0830$ is very small, hence a very small quantity of copper up to 2 mg can be determined with the proposed method. Most of the common ions generally associated with copper alloys do not interfere in the determination. Therefore the method has been successfully applied for the determination of copper in different ores and alloys.

All the chemical, used were of analytical grade. N-Hydroxy-N-p-tolyl-N'-β-naphthyl benzamidine hydrochloride was prepared by the condensation of equimolar quantities of N-p-tolyl-hydroxylamine and β-naphthyl benzimidoyl chloride in ether medium at 0–5°C. The white crystals were recrystallised with absolute alcohol (m.p. 154°C, yield 40%).

Copper(II) Solution: A stock solution of copper(II) was prepared by dissolving BDH AnalaR copper metal in dil. nitric acid and the solution was standardised (i) gravimetrically using salicyldoxime⁷ and (ii) volumetrically using iodometric titration.

Synthesis of the complex: Copper solution containing 10–210 mg of copper was taken in a 400 mL beaker and diluted to 150 mL. pH of the solution was kept 3.5 to 10.0 using acetic acid and ammonia. Warmed the solution to 60–70°C and added 1% reagent solution (20–30 mL per 15 mg Cu) dropwise with stirring, till complete precipitation and digested over a boiling water bath for 20

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min with occasional stirring. It was filtered while hot through a weighed G-3 sintered glass crucible. The precipitate was washed with hot water and then with 60% alcohol till the washings gave no colour with ferric chloride. Dried the precipitate at 130–140°C to constant weight and weighed as $(C_{24}H_{19}N_2O)_2Cu$. The complex is stable up to 215°C. % Analysis, found (calcd.): C = 75.03 (75.23) H = 4.56 (4.96), N = 6.98 (7.31) and Cu = 8.12 (8.30).

Infrared spectra of the ligand and copper complex were studied in KBr in the region 4000–400 cm^{-1} . The free ligand consists of a weak band at 2550 cm^{-1} confirming the presence of protonated azomethine nitrogen in the hydroxy amidine hydrochloride. The strong band at 1610 cm^{-1} due to $-C=N^+H$ in the free ligand lowered and appeared at 1580 cm^{-1} in the spectrum of the complex. This band shifts to lower frequency by 30 cm^{-1} on complexation due to reduction of electron density in the azomethine linkage confirming the formation of $C=N \dots Cu$ coordinate bond⁸. The N—O stretching mode appears at 960 cm^{-1} in copper complex which was at 930 cm^{-1} in the free ligand. Replacement of proton of $-N-OH$ group by copper to higher frequency supports N—O—Cu bond in the complex.

A sharp exothermic peak is observed at about 220°C in copper complex which may be due to the transition from one state to another state of the chelate.⁹ Broad exothermic peak was observed about 300°C corresponding to rapid mass-loss in TG curve which may be due to oxidation-reduction reaction. Sheshagiri *et al.*¹⁰, Sheshadri *et al.*¹¹ and other workers¹² reported the thermal stability of metal chelates of oxime.

The magnetic measurements suggest paramagnetic nature of the complex, *i.e.*, presence of one unpaired electrons is shown.

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