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For Spectrophotometric Determination Of Copper (II)

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SUMMARY

A systematic spectrophotometric study is carried on the complexation of cupric ions with metformin hydrochloride. Physicochemical studies on the chelate in both solution and solid state are performed. The optimum conditions for formation of the chelate are reported. Spectrophotometric measurements are applied to deduce the composition, structure and mode of chelation. Chelate formation has been utilised for the determination of copper (II).

INTRODUCTION

Metformin hydrochloride is a member of biguanides (1,1- dimethyl biganide) which have a great importance in the clinical field. Metformin lowers the blood sugar level to the minimum physiological limit, and destroys the malarial parasites indirectly by attract ion. It is used as antidiabetic, antimalarial and analgesic. Metformin have been found to give rise to numerous compounds with many bivalent metals. The bivalent copper as usual combines with two molecules of metformin to form complexes. Similarly, copper has been reported to form a 1:2 complex with biguanide.

EXPERIMENTAL

Materials:

All the essential materials used in the present investigation were of the chemically pure grade (AR or RP) which were used as such without any further purification.
Standard copper - A standard copper solution was prepared by dissolving 1.96458 gm of copper sulphate in previously boiled and cold redistilled water and standardised colorimetrically with sodium diethyl-dithiocarbamate by a standard procedure. A stock 0.1 M solution of the ligand was prepared by dissolving 1.655 gm. From the salt in redistilled water to give 100 ml solution. Solutions of lower concentrations were prepared as needed by further dilution with redistilled water.

Apparatus:

Spectrophotometric measurements in the visible and ultraviolet range were recorded on a Unicam Sp 6—400 recording spectrophotometer, with matched 1 cm fused silica cells.

The IR spectra (KBr) were recorded on a "Pye Unicam" SP 1100 recording spectrophotometer.

The pH values were measured by the use of a Beckman expanded scale pH meter.

Procedure:

To 1 ml of the standard copper solution containing 10⁻² M² Cu²⁺, the calculated amount of metformin hydrochloride was added to give the fixed concentration 3 x 10⁻² M ligand. The required volume of sodium hydroxide solution was added to adjust the pH at about 11, then the total volume of solution was made up to the mark in 10 ml volumetric flask. The absorbance of the purple colour of copper bis-metformin was measured at 520 nm against blank. The stoichiometric ratio of the complex formed is solution was investigated spectrophotometrically.

RESULTS AND DISCUSSION

The bivalent copper combines with two molecules of metformin to form four coordinated planer complex. In the same way as in copper biguanide there arises the question of deciding between the two possible different structure of a metal meformin complex, due to a different in the position of metal metformin bonds. This is evident from the following representation of the structure suggested for the copper metformin structure a or b.
In order to show further light on this problem a methanolic solution of copper salicylidene complex\textsuperscript{8} was added to the biguanide complex where a secondary crystalline complex separated. This reaction is characteristic for amino function. Consequently structure (a) seemed more likely. Structure (a) was thus suggested for this complex.
The linkage of copper with the substituted nitrogen can be understood in terms of the fact that tertiary nitrogen is the most basic center in the molecule. Reaction takes place by coordination in contrast to reports by biguanides.

On examining the IR spectrum of the complex in comparison to that of metformin hydrochloride, it was found that the spectrum of the complex showed absorption similar to that of the metformin HCl with slight shifts and in some regions a wide broadening. The main shift can account for the complex deformation is in the N-H stretching region, where broadening and quenching of the band was observed indicating involvement of this function in chelation.9,10 Whereas the metformin showed C=NH at 1620—1650 cm⁻¹, its complex with copper revealed a red shift in this region11, and very weak broad absorption peaks in the range 1630—1600 cm⁻¹ was observed.

The electronic absorption spectrum of metformin hydrochloride in methanol showed no absorption in the visible range, however, mixtures containing the ligand and copper (II) were found to exhibit an absorption of which proved to be highly dependent on pH (cf. Fig. 1) and is presumably assigned as of π—π* transitions.12 The electronic spectrum of copper metformin complex showed no maximum at pH ≤ 3. At pH ≥ 3 a maximum absorption at wavelength of 620 nm corresponding to copper mono-metformin was observed. As the pH increases the wavelength for the maxima exhibited blue shifts and in faintly alkaline pH the maxima are shifted to new position and became of higher intensity indicating that in this pH range a new species is formed in the solution. Thus, it may be suggested that the complex formed in solution in the pH range 4—7 is different than that existing at pH ≥ 7. Thus, it may be suggested that in pH range 4—7 1:1 complex is formed and, that the bis-metformin chelates is formed in pH ≥ 7. In order to provide evidence for these suggestions the stoichiometric ratio of the complex formed in solutions was investigated spectrophotometrically at pH 11. The results are presented graphically in Figs. (2 and 3). For this purpose the molar ratio was utilized. The continuous variation method at different concentrations at λmax 520 nm was also utilized. The two methods indicate that 1:1 and 1:2 complexes were formed.

The stability constant of the bis-metformin copper complex was determined following the spectrophotometer method of Harvey and
The stability constant was $1.143 \times 10^{16}$ compare to copper biguanide $^{16,17}$ ($1.50 \times 10^{11}$).

The reaction of copper (II) and metformin has been used for the spectrophotometric determination of copper (II). The optimum conditions for the determination have been studied. The optimum pH for the formation of the copper (II) chelate was 10.5—11. Accordingly, all the experiments were performed at pH = 11.

Experiments on the effect of time proved that the complex is formed instantaneously and is stable for 10 minutes. The structure of the complex was found to be independent on the ionic strength of the medium within the studied range (0.1—0.5).

The recommended sequence of addition for copper (II) and metformin is either Metal-Ligand-alkali or ligand-metal-alkali.

A systematic study of the influence of interfering ions lead to conclusion that the presence of the following ions in 10-fold amounts relative to copper (II) do not interfere: Li$^+$, Na$^+$, K$^+$, Rh$^{3+}$, Ir$^{3+}$, Al$^{3+}$, Fe$^{3+}$, Au$^{3+}$, Mo$^{6+}$, Os$^{8+}$, SO$_4^{2-}$, CN$^-$ and Cl$^-$. Co$^{2+}$, Ni$^{2+}$, Fe$^{2+}$ and amino acids such as glycine do interfere.

It was found that Beer’s law is obeyed in the range 2-20 ppm copper in methanol solvent. The present method for determination has the advantages of being sensitive to determination of copper, fairly reproducible and precise as indicated by the low value of the standard deviation (0.05) calculated for 10 ppm copper (10 determination), and rapid solvent extraction is unnecessary.

**Suggested Method For the Determination Of Copper (II):**

To an aliquot solution containing 20 to 200 µg of copper in a 10 ml measuring flask, 2 ml of $10^{-2}$ M metformin were added followed by adding a known volume of the fixed final alkalinity, then 5 ml of acetone (or ethanol). The total volume of solution was made up to the mark in a 10 ml measuring flask, with redistilled water. Mix well and measure the absorbance at 520 nm against blank. Compute the concentration by extrapolation from a calibration graph prepared in the same manner.
Fig. (1) Effect of pH on Absorption spectra of Copper Metformin.
Fig (2), Continuous Variation Method of copper Metformin Complex.
[Metformin] = 2 \times 10^{-2} \text{ M}

[Cu}^2] = 0.2 \times 10^{-2} \text{ M} - 3 \times 10^{-2} \text{ M}

\lambda = 520 \text{ m}\mu

pH = 11

Fig (3), Molar Ratio Method for Copper Metformin Complex.
REFERENCES