

MAGNETIC AND SPECTRAL STUDIES OF Ni(II), Cu(II) AND Pd(II) CHELATES OF LIGANDS DERIVED FROM 2-HYDROXY-1-NAPHTHAL-DEHYDE AND SOME DIAMINES

RECENTLY Holm *et al.*^{1,2} have reviewed the metal chelates of Schiff bases. A perusal of the literature has indicated that no studies have been carried out on the metal chelates of Ni(II), Cu(II) and Pd(II) with N-N'-ethylene or propylene bis-(2-hydroxy-1-naphthalidimine) and, the same has now been undertaken.

These chelates were prepared by two techniques. (i) The preformed Ni(II), Cu(II) or Pd(II) chelates of 2-hydroxy-1-naphthaldehyde were refluxed with an excess of ethylenediamine or propylenediamine and their respective chelates were obtained in which the two $-NH_2$ groups of the diamines condensed with the two aldehydic groups, giving rise to tetradentate chelates. (ii) By refluxing 2-hydroxy-1-naphthaldehyde with the metal diamines, the chelates were obtained.

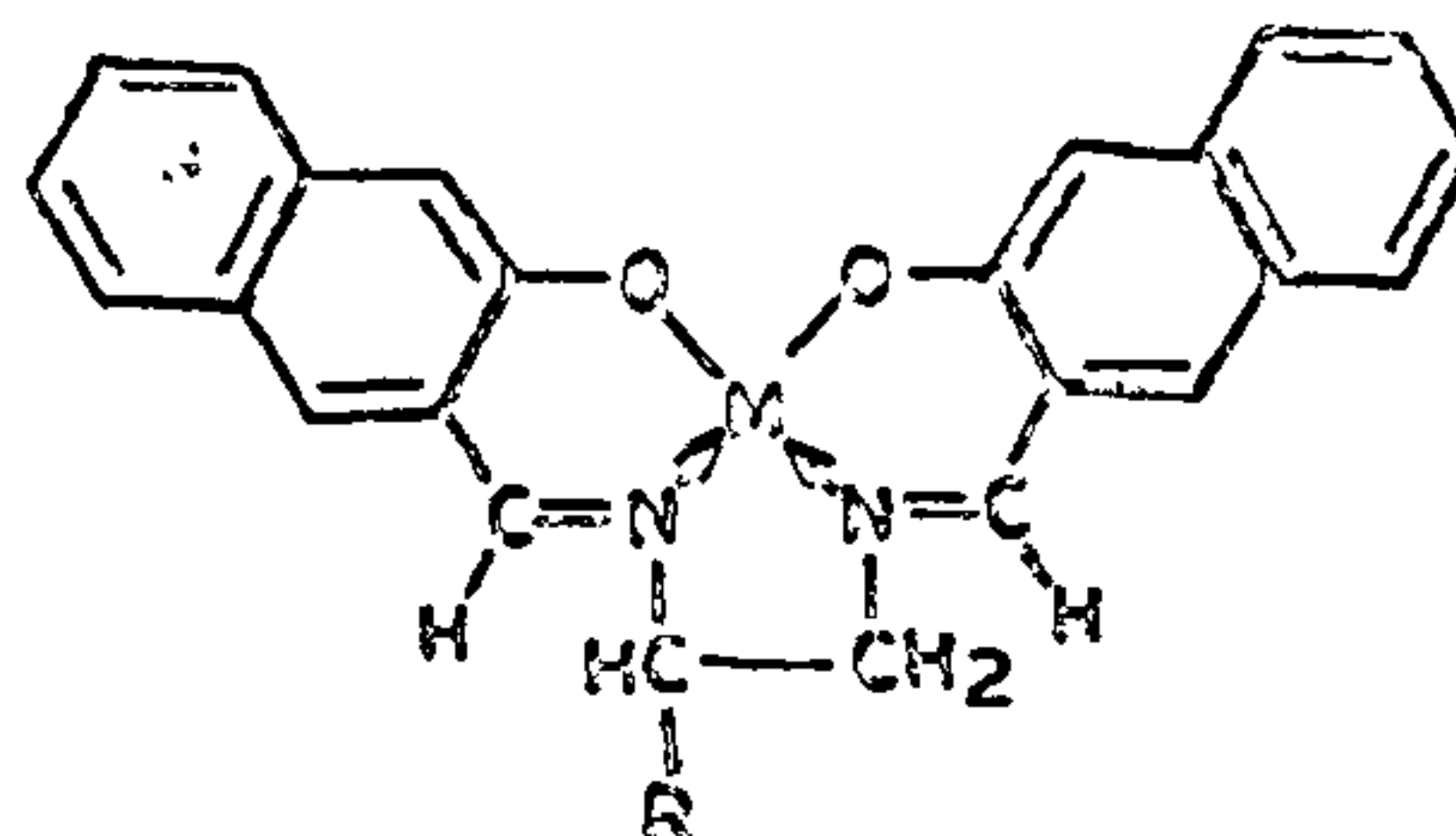
The solid chelates were recrystallised from chloroform. These chelates are stable at room temperature but decompose on heating to above 210°. These compounds are insoluble in water but soluble in chloroform and other organic solvents.

All these compounds give satisfactory carbon, hydrogen, nitrogen and metal analyses which suggest 1:2 metal-ligand stoichiometry. Magnetic susceptibility measurements were carried out using Gouy apparatus with mercury(II) tetrathiocyanatocobaltate as the reference³. The magnetic moment of Cu(II) chelate was found 1.86 B.M. at 303° A whereas Ni(II) and Pd(II) chelates were found diamagnetic.

The chloroform solution of the copper(II) chelate gives one broad band at 570 nm while that of nickel(II) chelate gives two shoulders at 660 nm and 560 nm assignable to the transitions $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1B_{3g}$. Palladium(II) chelate consists of two absorption bands with their peaks at 450 nm and 373 nm which are assigned to the transitions $^1A_{1g} \rightarrow ^1B_{1g}$ and $^1A_{1g} \rightarrow ^1E_{1g}$ respectively. Thus the electronic spectra supported by the magnetic data suggest a square-planar configuration of the metal chelates under investigations. This configuration is further supported by the i.r. spectra given below.

The i.r. spectra of these chelates were recorded in nujol mull using sodium chloride prism. The i.r. spectra of the ligand consist of two sharp bands at 3600 and 1640 cm^{-1} which may be due to νOH and $\nu C=N$, respectively. Two more bands at 1200 and 1030 cm^{-1} due to C-N and C-C stretchings have also been observed. In the case of metal chelates the bands due to νOH disappeared and

the $\nu C=N$ frequency was lowered to 1610 cm^{-1} suggesting the co-ordination of azomethine nitrogen to the metal atom. The bands at 670 and 600 cm^{-1} represent metal-oxygen and metal-nitrogen stretchings respectively. Thus the chelates may have the structure as shown in Fig. 1.



Where M = Cu(II), Ni(II) or Pd(II) and
R = H or CH_3

FIG. 1. Metal chelates of N-N' ethylene or propylene bis-(2-hydroxy-1-naphthalidimine).

Authors are thankful to CSIR (India), for the award of fellowship to one of them (BRS).

Department of Chemistry,
University of Jodhpur,
Jodhpur,

B. R. SINGHVI,
M. R. MALI
R. K. MEHTA.

February 3, 1977.

1. Cotton, F. A., *Prog. Inorg. Chem.*, 1966; **7**, 88.
2. Lyapina, S. S., Mishchenko, V. V., Trailina, E. P., Savich, I. A. and Spitsyn, V. I., *Dokl. Akad. Nauk., S.S.S.R.*, 1970, **190**, 593.
3. Mehta, R. K. and Gupta, R. K., *Indian J. Chem.*, 1973, **11**, 56.

A COLORIMETRIC METHOD FOR THE ESTIMATION OF AMPICILLIN

Introduction

INDIAN Pharmacopoeial and British Pharmacopoeial procedures for the estimation of ampicillin are based upon the conversion of ampicillin to penicillenic acid whose absorbance is measured. British Pharmaceutical Codex procedure for the estimation of ampicillin in syrups and tablets is based on the reaction of hydroxylammonium hydrochloride and ferric chloride with ampicillin both before and after treatment with sodium hydroxide solution. Various analytical methods¹ based on titrimetric, microbiological, uv spectrophotometric, fluorimetric and colorimetric are described by earlier authors. Most of the methods reported earlier are time consuming.

The α -amino group of ampicillin is reported to play a significant role in its broader antibacterial activity². Keeping this in view an attempt was made to use the

amino group for developing a colorimetric method for the estimation of ampicillin. Ampicillin reacts with 4-dimethylaminocinnamaldehyde to form an orange coloured Schiff's base with an absorbance maximum at 480 nm. This forms the basis for the determination of ampicillin by the colorimetric method reported in this paper. The method is simple, accurate and has been successfully utilised for the estimation of ampicillin and its dosage forms.

Experimental

Reagent solution.—Dissolve 0.1 gm of 4-dimethylaminocinnamaldehyde (GR) in 100 ml isopropanol. The reagent can be preserved in a refrigerator for one week.

Standard and Sample Preparation.—All the samples of ampicillin and its formulations used in the analysis were diluted with a mixture of acetic acid and isopropanol (1:1:5) to give a concentration of 1 mg/ml.

Assay.—Pipette out 1 ml aliquots each of the standard and sample preparations into separate 25 ml standard flasks and make up to the mark with isopropanol. Transfer one ml of these solutions to 10 ml standard flasks, add 1 ml reagent followed by 1 ml acetic acid. Keep the flasks in the boiling water-bath for 2 minutes, allow to cool and dilute to the mark with isopropanol. Measure the absorbance at 480 nm within 15 minutes against reagent blank.

Results and Discussion

Ampicillin was found to react with 4-dimethylaminocinnamaldehyde to produce a Schiff's base. This aldehyde was preferred as a chromogenic agent over vanillin and 4-dimethylaminobenzaldehyde, as deeper colour was obtained. After several experiments isopropanol and glacial acetic acid were found to be the most suitable solvent and acid respectively for optimum colour development. To arrive at an absorbance with less photometric error the reagent requirement was fixed as 1 ml of 0.1% reagent for the range 0.5–12.5 µg of ampicillin per ml.

The colour developed was stable for 15 minutes. The orange coloured chromogen had an absorbance maximum at 480 nm. The colour obeys Beer's law in the concentration range 0.5–12.5 µg per ml of ampicillin. A standard was prepared simultaneously with each experiment to minimise the error.

Several samples of ampicillin, its tablet, capsule, injection and syrup were analysed by the present method and the official methods. The values obtained by the proposed method differ from those of the official methods by a maximum of $\pm 0.6\%$, whereas the results obtained by earlier colorimetric method³ for ampicillin differed by $\pm 2.0\%$.

The proposed method is accurate and is suitable for a quick analytical control of ampicillin and its dosage forms.

Quality Control Laboratories, G. RAMANA RAO.*
Indian Drugs and GEETA KANJILAL.
Pharmaceuticals Ltd., K. RAMA MOHAN.
Hyderabad 500 037, India,
April 21, 1977.

* To whom all enquiries should be directed.

1. Klaus Florey, *Analytical Profiles of Drug Substances*, Academic Press, New York and London, 1973, 2, 1.
2. Wilson, C. O., Gisvold, O. and Doerge, R. F., *Text Book of Organic Medicinal and Pharmaceutical Chemistry*, Pitman Medical Publishing Co. Ltd., London, Fifth Edition, 1966, p. 331.
3. Chowdhury, C., *Indian Journ. of Pharm.*, 1976, 38, 124.

MERCURIC NITRATE AS A SIMPLE AND NEW CHROMOGENIC SPRAY REAGENT FOR THE DETECTION OF OPIUM AND ITS ALKALOIDS

VARIOUS chromogenic spray reagents for the detection of opium and its alkaloids on thin layer plates have been described in literature¹⁻⁴, the most widely used being the Iodoplatinate reagent and Dragendorff's reagent. The iodoplatinate reagent though effective and widely used involves the use of costly platonic chloride. The Dragendorff reagent does not give clear differentiation of the spot from background when the alkaloid is present in low quantities. During the present investigations, mercuric nitrate has proved to be a sensitive chromogenic spray reagent for the detection of opium alkaloids on t.l.c. plates.

Glass plates of size 20 × 20 cm were coated with silica Gel G (E/M) to a thickness of 250 µm and the plates after air drying, were activated in an air oven at 110° for one hour. Then plates were cooled in a desiccator. Methanolic solution of morphine and chloroform solution of codeine, narcotine, papaverine and thebaine were spotted on the plate, and the plate developed in a solvent mixture of benzene: methanol (8:2). After the solvent front had moved to a distance of 10–12 cm, the plate was taken out and dried and sprayed with 4% solution of mercuric nitrate in 3% dil HNO₃ and the plates were heated at 110° for 15 minutes.

Results and Discussion

Reddish-brown to yellow spots appeared after heating the plates. Morphine, thebaine, papaverine and narcotine could be detected even at 2 µg level but the minimum detection limit for codeine is 10 µg. The colours of the spots are given in Table I. Hg²⁺ is a well-known electron acceptor⁵. The alkaloids having a lone pair of electrons on the nitrogen atom function as electron