CHAPTER - I

SYNTHESIS AND CHARACTERISATION OF

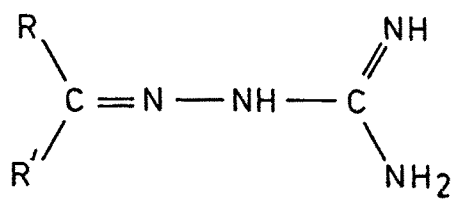
CINNAMALDEHYDE GUANYLHYDRAZONE

1.1 INTRODUCTION

Spectrophotometric methods are particularly useful when the insufficient sample is present for the gravimetric and titrimetric methods. For the determination of trace amounts of metal ions, spectrophotometric method is often preferred. Although interferences by other metal ions is often a serious problem, suitable systems can be developed for the analysis of metal ions in presence of impurities. The rapid development both in science and technology stresses the need for the production of pure materials. Hence the development of new techniques for the determination of trace impurities in highly pure materials is desirable. New analytical methods are based on instrumental techniques.

The organic reagents find extensive applications in spectrophotometry. The study of organic reagents still attracts many chemists, because these reagents allow development of highly sensitive, selective and rapid methods for the analysis of variety of materials. Solvent extraction and simultaneous spectrophotometric determination of metals has proved to be most useful as it helps to improve sensitivity or selectivity or both.

Metal complexes of Schiff's bases have occupied a central role in the development of coordination chemistry. Schiff's bases are interesting as analytical reagents. Hydrazones, thiosemicarbazones and oximes have been most widely studied, but guanylhydrazones have not previously been studied as analytical reagents. Guanylhydrazones are first synthesized by Thiele and Dralle[1]. Their importance is due to their pharmacological properties. Their general structure is



where R and R' are H or any organic radical. The analytical properties of the guanylhydrazone depend on the structural features of both R and R'.

Guanylhydrazones have a similar structure to thiosemicarbazones. The great affinity to sulphur for coordination of metal ions poses a serious hindrance in the use of thiosemicarbazones as analytical reagents, and hence it makes selective methods difficult to establish. The replacement of the sulphur atom of the thiosemicarbazones by the imine group of the guanylhydrazones can increase the selectivity and sensitivity.

and oral disinfectants[9] and are used as antiseptics for foods[10].

Several steroid guanylhydrazones were prepared[11,12]. Inhibitory effect of these compounds are shown on in-vitro growth of some dermatophytes. They are also useful in waste water purification, precipitation of organic anions, especially dyes from waste water.

Some aminoguanidine derivatives are used in photographic materials and for paper treatment[13], useful as cationic agents for retention of dyes and pigments on cellulose fibres and provides dry and wet strength in paper.

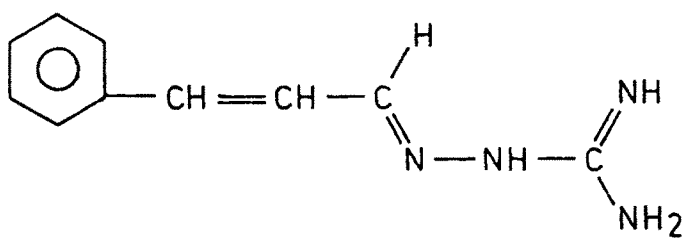
Some guanylhydrazone compounds possess antileukemic activity, antihistamine activity[14], antiviral activity[15] and also antimalarial activity. Several quanylhydrazone complexes have antifungal activity[16] and act as anticancer and antiflammatory agents[17].

These studies have been very much useful in the chemistry of guanylhydrazone complexes. The properties of the complexes and the reactions of the ligands and complexes have been studied in this dissertation.

The reactivity of Schiff's bases is also dependent on the structural characteristics of the aldehyde or ketone which is condensed with the amine. Aldehydes and ketones give easily crystallizable guanylhydrazone derivatives and this property is used for the identification of the compounds with C=O function.

Guanylhydrazones react as chelating ligands and form complexes with transition metal ions. Cinnamaldehyde guanylhydrazone has been used extensively.

The structure of cinnamaldehyde guanylhydrazone (CAG) is



Guanylhydrazone compcunds are cardioactive substances[2,3] and are used as new pharmaceuticals[4]. Several such compounds are useful as bactericides and insecticides[5-7], in treating heart insufficiency and hypersensitivity[8] in normal leukemia bearing mice as grown inhibitors. Some of these compounds have extremely high bacterial activity and are suitable as internal, external

Cinnamaldehyde guanylhydrzone (CAG) can be used for the determination of Cu(II), Ni(II), Co(II) and Pd(II) and also for the simultaneous determinations of Co(II) and Pd(II).

1.2 EXPERIMENTAL

1.2.1 Apparatus :

The absorbance measurements were done on a spectronic-20-Bausch and Lomb, equipped with matched pair of glass test tubes.

For pH measurements, Digital pH meter ELICO, model LI-120, having glass-calomel combination electrodes was used. The pH meter was standardized by using 0.05 M potassium hydrogen phthalate (pH = 4.01) and 0.01 M borax (pH = 9.18) buffers.

All the measurements were done at room temperature $\sim$ 25 to 30^{o}C

1.2.2 Reagents :

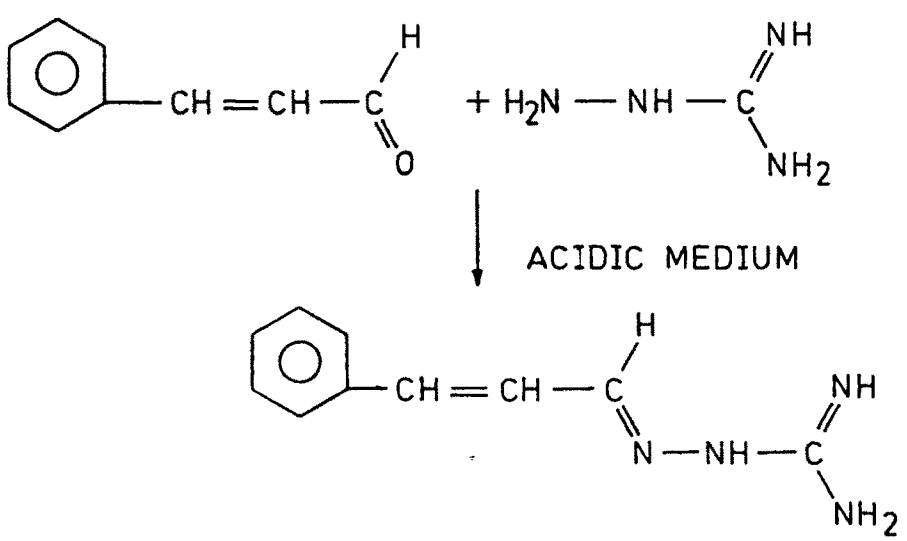
All solvents and reagents were of analytical reagent grade.

Glass distilled conductivity water was used throughout the work.

1.2.3 Synthesis of CAG :

Cinnamaldehyde guanylhydrazone (CAG) has been synthesized as per recommended procedure[18]. Aminoguanidine bicarbonate was used instead of aminoguanidine dihydrochloride which simplified the synthesis and gave much better yield.

A mixture of 1.32 g (1.3 ml) cinnamaldehyde, 1.36 g aminoguanidine bicarbonate, and 2 ml ethyl alcohol was acidified and was heated for 10 min. Then 100 ml of water was added and was made slightly alkaline to give shining yellowish white crystals of cinnamaldehyde guanylhydrozone (1.48 g) M.P.= 194° ±1° C. The compound is quite stable for months. The reaction is



1.2.4 Solubility :

The reagent is soluble in ethyl alcohol, methyl alcohol, acetone, chloroform and acetic acid but insoluble in water, benzene and carbon tetrachloride.

The solution of the reagent in ethanol was stable for months without any deterioration.

1.2.5 Characterisation of CAG :

CAG is stable in air. There is no action of light on the reagent. So, no special care is required to protect it from light.

The microelemental analysis of the chromatographically purified reagent confirmed the formula $C_{10}H_{12}N_4$ (Molecular weight = 188.0). Calculated percentage of elements are C = 63.83 % H = 6.38 % and N = 29.79 %. Experimentally found percentage of elements are C = 63.56 %, H = 6.43 % and N = 30.01 %

1.2.6 Ultraviolet spectra of the reagent (CAG) :

Fig 1.1 shows the ultraviolet absorption spectra of the reagent (CAG) in ethanol (1.0×10^{-4}M) at different pH values.

Absorption maxima and molar extinction coefficients of the reagent at different pH values are given in table 1.1.

Table 1.1 : Spectral characteristics of the reagent (CAG)

pH	Absorbance at λ		Molar extinction coefficients, ϵ l mole^{-1} cm^{-1} at λ	
	305 nm	335 nm	305 nm	335 nm
4.0	0.71	0.17	0.71×10^4	0.17×10^4
6.0	0.68	0.20	0.68×10^4	0.20×10^4
7.0	0.63	0.23	0.63×10^4	0.23×10^4
8.0	0.53	0.28	0.53×10^4	0.28×10^4
9.0	0.45	0.33	0.45×10^4	0.33×10^4
10.0	0.41	0.46	0.41×10^4	0.46×10^4
11.0	0.38	0.74	0.38×10^4	0.74×10^4
12.0	0.34	0.95	0.34×10^4	0.95×10^4
13.0	0.28	1.12	0.28×10^4	1.12×10^4

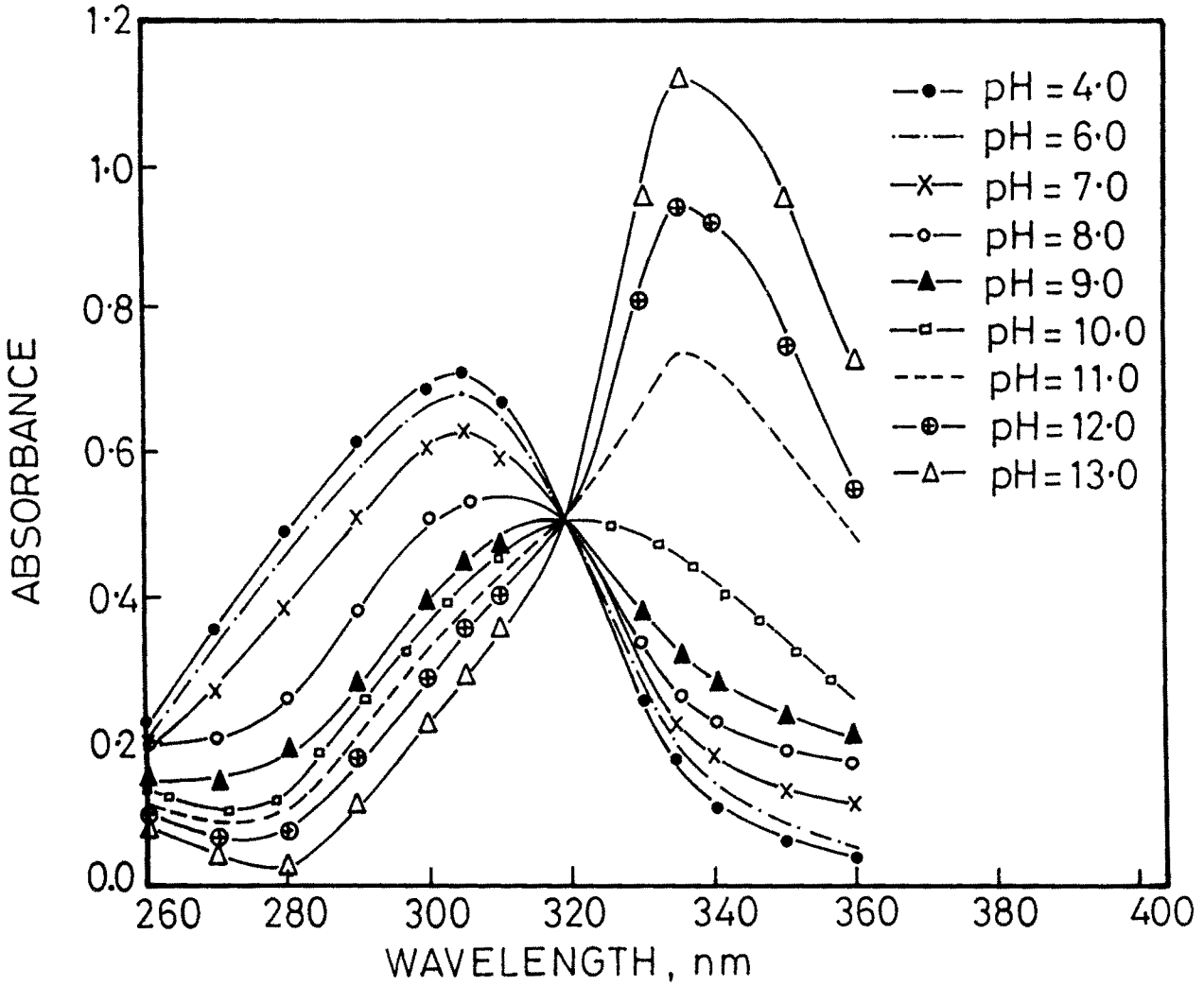


FIG. 1·1 – ULTRAVIOLET SPECTRA OF REAGENT (CAG).

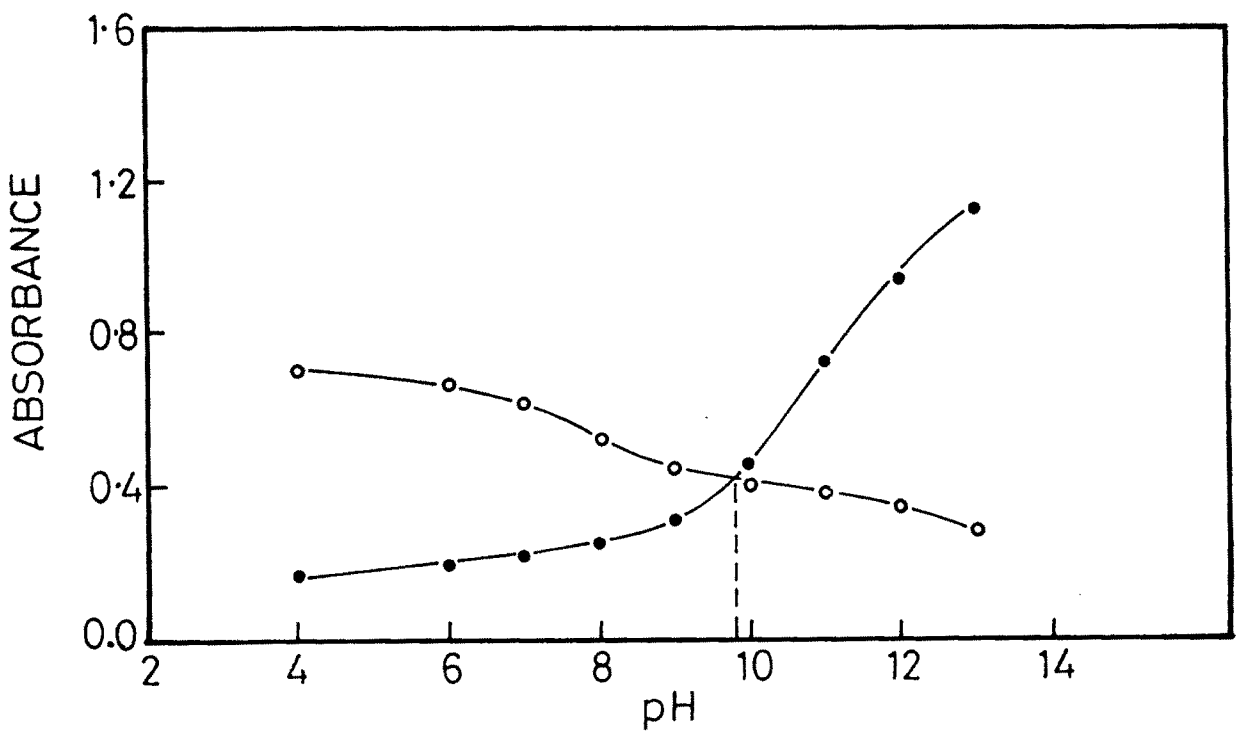


FIG. 1·2 — DETERMINATION OF pK .
o——o 305 nm, •——• 335 nm .

1.2.7 Infrared spectrum of the reagent (CAG) :

Infrared absorption spectrum in the range 4000 to 200 cm^{-1} was run on Perkin Elmer 221 IR spectrophotometer in KBr pellets (Fig. 1.3). The characteristic absorption bands were observed as follows :

3450 cm^{-1}	---------->	KBr band
3400 cm^{-1}	---------->	NH stretch
3200-3100 cm^{-1} (broad)	----->	NH_2 stretching
3040-3010 cm^{-1}	---------->	CH stretching -CH=CH-
2950 cm^{-1}	---------->	=N- vibrations
2940 cm^{-1}	---------->	Overtone pattern
2850 cm^{-1}	---------->	
2320 cm^{-1}	---------->	
2020 cm^{-1}	---------->	
1860 cm^{-1}	---------->	
1780 cm^{-1}	---------->	
1700 cm^{-1}	---------->	
1680-1600 cm^{-1}	---------->	NH_2 deformtion, complicated pattern
1670-1500 cm^{-1}	---------->	$N_2C=N$ absorption due to guanidines and due to NH deformation and CN stretching vibrations.
1460, 1440 cm^{-1}	---------->	Aromatic band, phenyl ring
800, 745, 725 cm^{-1}	---------->	5 adjacent H wag.

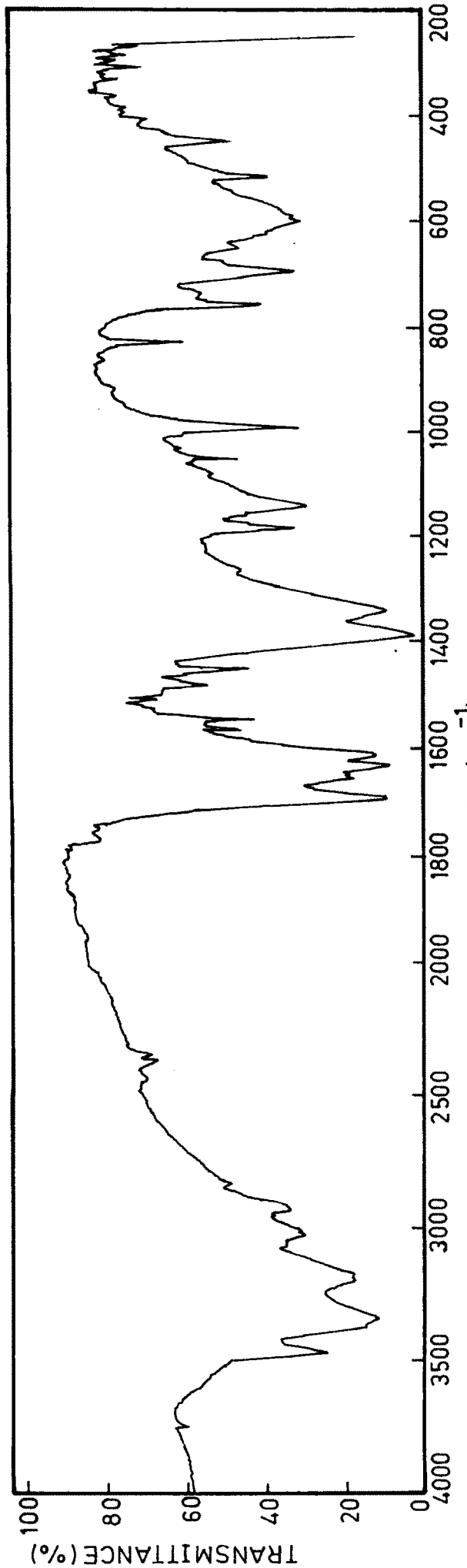


FIG. 1·3 — INFRARED SPECTRUM OF REAGENT (CAG).

1.2.8 Determination of ionization constant of CAG :

The ionization constant of the reagent (CAG) was obtained both by spectrophotometric method and by pH-metric method.

a) **By Spectrophotometric Method :**

The ultraviolet spectra of the reagent are shown in fig 1.1. At pH 4.0, the reagent shows the absorption band with λmax at 305 nm, which lowers in intensity as pH increases. With increasing value of pH, the absorbance at longer wavelength increases, and at pH 13.0, highest intensity band with λmax at 335 nm appears. All the spectral curves pass through the isosbestic point at 317 nm, thereby indicating a dynamic equilibrium between ligand and its deprotonated species, assuming that at pH 4.0, the molecular form of the ligand is exclusively present and the deprotonated species is absent and that at pH 13.0, the deprotonated species is present exclusively and the molecular form is absent. By using Henderson equation and also from the half height[19] of the sigmoid curve (Fig. 1.2), the pK value for the deprotonation of the ligand is found to be 9.86.

b) **By pH-metric Method :**

5.0 ml of 0.01 M CAG was taken in a thermostated titration vessel at 30 $\pm 1^{o}C$ containing 20.0 ml distilled water. The solution was titrated with 0.1 M NaOH. An ELICO Digital pH meter with pH readable to $\pm$ 0.01 was used. The pH meter was calibrated with pH 4.01 and 9.18 by phthalate and borax buffers respectively. The ionization constants were calculated from the pH values. The pK was determined by using the formula

$$pK = pH + \log \frac{[HA]}{[A^-]}$$

HA represents the reagent, CAG. The log $[H^+]$ values were read from the pH meter.

The titration was repeated until two sets of values differeing within $\pm$ 0.01 pH units were obtained. The results of study are summarised in table 1.2 which show that the pK is 9.86 for cinnamaldehyde guanylhydrazone (CAG).

Table 1.2 : Determination of ionization constant of CAG at 30± 1°C

[CAG] = 0.01 M; NaOH = 0.1 M.

NaOH ml	pH	Stoichiometric concentration		log [HA]/[A⁻]	pK
		HA	A⁻		
0.5	8.15	0.018	0.002	0.954	9.10
1.0	9.68	0.016	0.004	0.602	10.28
1.5	9.90	0.014	0.006	0.367	10.27
2.0	10.03	0.012	0.008	0.176	10.22
2.5	10.09	0.010	0.010	0.000	10.09
3.0	10.15	0.008	0.012	-0.176	9.97
3.5	10.21	0.006	0.014	-0.367	9.84
4.0	10.25	0.004	0.016	-0.602	9.65
4.5	10.31	0.002	0.018	-0.954	9.36
					Mean pK = 9.86

1.2.9 Complex formation :

The reagent (CAG) forms complexes with Cu(II), Ni(II), Co(II) and Pd(II). A detailed account of the complex formation with these four metals is discussd in the following chapters. Simultaneous determinations of Co(II) and Pd(II) are also discussed in this dissertation.

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