

## Some new Pyridyl-Substituted Pyrazine Ligands for Copper

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**Summary:** The new cuproin ligands 2-(2-pyridyl)-3,5,6-triphenyl-5, 6-dihydropyrazine and 2-(2-pyridyl)-e,5,6-triphenylpyrazine closely related to 2,2-bipyridine and 1,10-phenanthroline have been synthesized by simple synthetic routine. The ligands react with copper(I) to form coloured complexes, which are easily extractable in water-immiscible organic solvents. The molar absorptivities are also reported.

In the field of reagent chemistry, recent developments involving 1,10-phenanthroline and 2,2-bipyridine have proved interesting and practically fruitful. Their complex forming properties were discovered and extensively studied by Blau<sup>1</sup>. Although Blau's classic work on the behaviour of these compounds remained dormant for about 40 years, their analytical uses were then exploited in several directions, specially in the field of colorimetry and redox titrimetry. The earlier applications of 1,10-phenanthroline led to renewed interest in this type of reagents. It was observed quite earlier that compounds having bulky substituents adjacent to nitrogen donor atom do not form tris-complexes with iron(II), but these substitution did not hinder the formation of corresponding copper(I) complex where only two molecules of the ligands are attached to the central atom in tetrahedral symmetry, forming two five membered rings with two heterocyclic nitrogen atoms.

The present work underlines the preparation of bi-dentate 2-(2-pyridyl) substituted pyrazine ligands containing bulky phenyl groups neighbouring the imine nitrogen, from a diketone. The report explores the potentialities of using these ligands for the spectrophotometric determination of copper.

A number of pyridyl-substituted pyrazine ligands containing feroin and cuproin functionalities were first reported by Goodwin and Lions<sup>2</sup>. They observed their complexation of iron(II), ruthenium(II), nickel(II) and copper(II), but ignoring their possible uses as analytical reagent. While Stephen<sup>3</sup> carried out comparative studies of six bidentate and tridentate pyridyl-substituted pyrazine ligands as chromogenic reagent for copper and iron.

Since then, a number of pyridyl-substituted

pyrazine ligands have been synthesized to study the effect of methyl-substitution on complex formation for exploiting them as analytical reagents.<sup>4,7</sup>

### Experimental

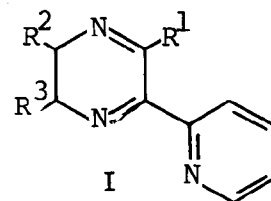
#### *Preparation of reagents.*

Hydrobenzamide was prepared by condensing benzaldehyde with ammonia, isomerized to amarin on heating for 5 hours at 120°C. Amarin was acetylated to meso-N-benzoyl-N-acetyl-1, 2-diphenyl-1,2-diaminoethane, which was hydrolysed with (1:1) sulphuric acid to obtain meso-1,2-diphenyl-1,2-diaminoethane<sup>5</sup>

The micro-analysis of the samples was carried out at the department of chemistry, University of Birmingham and Elemental Micro-analysis Limited, U.K.

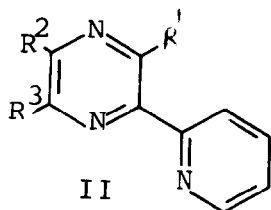
The I. R. spectra of the compounds were recorded on Unicam SP 1025 I.R. Spectrophotometer.

The absorption spectrum of all the solutions in visible region was recorded with double beam Beckman BD prism specgrophotometer.



*Preparation of 2-(2-pyridyl)-3,5,6-triphenyl-5,6-dihydropyrazine.*

Meso-1,2-diphenyl-1,2-diaminoethane (2.1g) dissolved in 10 ml of ethanol was slowly added to the refluxing solution of 1,2-dioxo-1-phenyl-2-(2-pyridyl) ethane (2.1g) in 15 ml of ethanol. Solution was refluxed for 30 minutes and allowed to cool. The precipitate was filtered and recrystallised from ethanol to give solid melting at 251°C. A sample of compound submitted for analysis ( $C_{27}H_{21}N_3$  requires % C=83.75, H=5.43, N=10.85; found % C=85.8, H=5.2, N=10.9). The I. R spectrum of the compound in Nujol shows peaks at 690, 700, 747, 755, 768, 787, 800  $cm^{-1}$  for C-H and at 1560 and 1580  $cm^{-1}$  for C=C and C=N bands.



*Preparation of 2-(2-pyridyl)-3,5,6-triphenyl-pyrazine.*

To 2-(2-pyridyl)-3,5,6-triphenyl-5,6-dihydropyrazine (1.0g) dissolved in 15 ml of mesitylene was added palladium-charcoal (0.1 g) (Pd, 10%). The reaction mixture was refluxed for 36 hours and filtered while hot. The solution was cooled over night to 0°C. The precipitate was filtered and recrystallised from benzene-petroleum spirit (40-60°) to obtain a solid melting at 248°C. The analysis report of the sample shows ( $C_{27}H_{19}N_3$  requires % C=84.16, H=4.8, N=10.78; found % C=84.34, H=4.8, N=10.78). The I.R spectrum of the compound in Nujol indicates the peaks at 705, 755, 770, 792, 807  $cm^{-1}$  for C-H and at 1560 and 1580  $cm^{-1}$  for C=C and C=N bands.

*Preparation of Solutions*

Solutions of copper(II) and iron(II) containing

1mg/ml were prepared from pure copper(II) chloride and ammonium iron(II) sulphate. Conventional acetate-acetic acid buffer solutions pH 3-6 were used throughout investigation.

Solutions (0.005M) of the organic reagent were prepared by suspending the requisite amount in small volume of ethanol, to which 5M Hydrochloric acid was added dropwise till the dissolution was complete. The solution were then diluted to volume with ethanol. Freshly prepared 1% w/v solution of pure ascorbic was used for reduction of copper(II). Pure solid sodium nitrate was used in the extraction studies described below.

*Qualitative Studies:*

To each of several semi-micro test tubes were added in turn one drop of Mn(II), Fe(II), Cu(II), Zn(II), Co(II), Cr(III), Cd(II) metal ions solutions, 2 drops of 1% w/v ascorbic acid, 5 drops of organic reagent solution and 10 drops of buffer solution (between pH 3-6). The formation of any colour and its variation with pH were noted. Chloroform and 1,2-dichloroethane were used to assess the extractability of the complexes.

*Quantitative Studies.*

Exactly 1.0 ml of metal ion solution was transferred to 25 ml volumetric flask and 1ml of 1% w/v freshly prepared ascorbic acid and 5ml of organic reagent were added, followed by 2ml of acetate-acetic acid buffer pH=5. The contents were diluted with ethanol.

Extractions were carried out as follows:

The metal ion solution (1.0 ml) was placed in a 250 ml separating funnel followed by other reagents as above; 7-8 ml of extracting solvent were then added and contents were thoroughly mixed. The organic layer was collected in 25ml volumetric flask and extraction was repeated with 7-8 ml of solvent (in case of 1,2-dichloroethane and chloroform 1-2 ml of ethanol was added to the flask before dilution to volume).

Spectra of all the solutions were recorded against reagent blank in the appropriate solvent.

**Results and Discussion**

The spectrophotometric data are summarized in

Table 1. Quantitative Spectrophotometric Studies of The Copper(I) Reactions.

Reagent	Solvent	$\lambda$ - max nm	$\epsilon$ - l mole <sup>-1</sup> cm <sup>-1</sup>	Stability
2-(2-pyridyl)-3,5,6-triphenyl-5,6-dihydropyrazine	Ethanol	570	3.6x10 <sup>3</sup>	> 2 hr
	1,2-dichloroethane	570	3.5x10 <sup>3</sup>	> 2 hr
2-(2'-Pyridyl)-3,5,6-triphenylpyrazine	Ethanol	565	4.7x10 <sup>3</sup>	> 2 hr
	1,2-dichloroethane	560	4.0x10 <sup>3</sup>	> 2 hr

table I. The reagents only react with copper(I) in the characteristic fashion of cuproin type reagents and their reactions towards iron(II) are sterically hindered because of the bulky phenyl groups substituted near the imine nitrogen in pyrazine ring. This behaviour is analogous to the behaviour of better known bidentate ligands 6,6-dimethyl-2,2-bipyridine and 2,9-dimethyl-1,10-phenanthroline - one of the selective reagents for copper.

2-(2-pyridyl)-3,5,6-triphenyl-5,6-dihydropyrazine reacts in weakly acidic medium to form a complex soluble in ethanol. The spectrum of copper(I) chelate shows a broad band with a maximum at 570 nm and molar absorptivity of  $3.6 \times 10^3$  l. mole<sup>-1</sup> cm<sup>-1</sup> in an ethanol-water mixture. The complex is easily extractable in chloroform and 1,2-dichloroethane from a aqueous solution containing appreciable concentration of sodium perchlorate or sodium nitrate, with reasonable solution stability.

2-(2-pyridyl)-3,5,6-triphenylpyrazine which also contain cuproin functionalities showed reasonably promising as copper(I) reagent. Addition of an excess of the reagent to ethanol-water solution of copper(I) salt in weakly acidic media (pH=4-7) develops red purple colour immediately. The complex in ethanol-water mixture absorbs maximally at 565 nm with molar absorptivity of  $4.6 \times 10^3$  l. mole<sup>-1</sup> cm<sup>-1</sup>.

The complex is easily extractable in chloroform and 1,2-dichloroethane in the presence of sodium nitrate and sodium perchlorate as an ion-association complex. The reagent shows reasonable solution stability for qualitative and quantitative determination in aqueous solution.

The red-purple chelate is only formed with a ligand: copper(I) ratio of more than 2:1; less than this leads to the formation of a blue colour. Therefore it is expected that the red-purple colour is due to bis complex of copper (I)  $[\text{Cu}(\text{lig})_2]^+$  and blue colour may be of  $[\text{Cu}(\text{lig})(\text{solvent})_2]^+$ ,  $(\text{Cu}(\text{lig})(\text{Solvent})\text{cl})^0$  species. Similar species have been reported by the previous investigators.<sup>3,6</sup>

#### Conclusion

The main objective of these studies is to develop new sensitive cuproin type ligands and study the effect of phenyl substitution on complexation. Although the ligands reported here for the first time are not as sensitive and stable as expected, however the ease of preparation, selectivity and reasonable stability enable their recommendation as analytical reagent for qualitative determination of copper.

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