

# Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol. 24, No. 2, April 1981

## SOME NEW ORGANIC REAGENTS FOR COPPER AND IRON

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(Received April 7, 1980; revised February 28, 1981)

The new compounds, benzil-N-phenylamino-ethaneimine, 2,2'-pyridil-N-phenylaminoethaneimine, and 6,6'-dimethyl-2,2'-pyridil-N-naphthylamino-ethaneimine, have been prepared by condensation of the appropriate  $\alpha,\alpha'$ -diketone and N-aryl substituted 1,2-diaminoethanes. The compounds have been characterized and their reactions with copper(I) and iron(II) ions have been investigated spectrophotometrically. These compounds behave as typical ferrioxin – and cuprioxin – type ligands towards these ions.

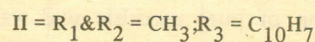
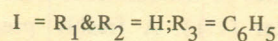
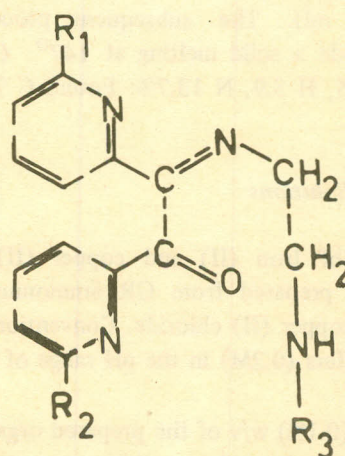
### INTRODUCTION

It is well recognised that more organic reagents are available for the determination of copper and iron than for any other metal. In general, those reagents of the cuprioxin and ferrioxin type are preferred because of the ease with which they form stable copper(I) and iron(II) chelate compounds which are readily extracted by water-immiscible solvents. The high selectivity of these reactions is a further significant feature in the use of these reagents in chemical analysis, and many applications are reported in the literature [1].

Certain aliphatic compounds such as glyoxalbis(methylimine) and diacetylbis(methylimine) [2] which contain the same sequence of atoms comprising the well-known ferrioxin functional grouping present in 2,2'-bipyridine and 1,10-phenanthroline, form iron(II) complexes with similar absorption spectra to those of the classical iron(II) ligands, but of considerably lower stability. Bush and Bailar [3] have prepared Pyridinal(methylimine) which contains the  $\alpha,\alpha'$ -diimine structural unit partially incorporated in the aromatic ring, and this gives an iron(II) complex with enhanced stability in solution.

The Schiff's bases obtained by the condensation of N-phenylethylene-diamine and N(1-naphthyl)ethylene-diamine with the 1,2-diketones, 2,2'-pyridil and 6,6'-dimethyl-2,2'-pyridil, provide a structural link between the purely aromatic ligands such as 2,2'-bipyridine and

the simple aliphatic compounds containing the  $\alpha,\alpha'$ -diimine grouping. In such compounds (I and II), the pyridine ring provides the aromatic contribution while the imine linkage in the side chain corresponds to the aliphatic part of the ligand molecule the fact that these compounds exhibit a striking similarity in their behaviour towards iron(II) and copper(I) as 2,2'-bipyridine indicates that the same functionality is present.





## EXPERIMENTAL

## Preparation of Reagents

*Benzil-N-phenylaminoethaneimine* (*Benzoyl-phenyl-N-[(β-N-phenylamino)-ethyl] methineimine*) N-Phenylethylene-diamine (0.7g) dissolved in dry ether (15 ml) was slowly added to a solution of benzil (1.05g) in ethanol (15 ml). The solution was refluxed for 2 hr and the solvent was allowed to evaporate spontaneously at room temperature. The gummy mass so obtained was extracted several times with 10 ml-portions of n-hexane. Partial evaporation of the solvent at room temperature gave an orange-coloured precipitate, which was recrystallized from n-hexane to give a solid (m.p. 81–82°).  $C_{22}H_{20}N_2O$  requires: C 80.5, H 6.1, N 8.5%. Found: C 80.7, H 6.37, N 8.5%.

*2,2'-Pyridil-N-phenylaminoethaneimine* (*2-Pyridylketone-2-pyridyl-N-[(β-N-phenylamino)ethyl] methineimine*) N-Phenylethylene-diamine (0.7g) dissolved in dry ether (15 ml) was slowly added to a refluxing solution of 2,2'-pyridil (1.06g) (Aldrich Chemical Co) in ethanol (15 ml). The subsequent procedure was similar to the above to provide a solid (m.p. 98.9°).  $C_{20}H_{18}N_4O$  requires: C 72.73, H 5.45, N 16.9%. Found C 72.9, H 5.7, N 16.9%.

*6,6'-Dimethyl-2,2'-pyridil-N-naphthylaminoethaneimine* (*6-Methyl-2-pyridylketone-6-methyl-2-pyridyl-N-[(β-N-naphthylamino)ethyl] methineimine*) -N-Naphthylethylene-diamine hydrochloride (0.75g) dissolved in distilled water (10 ml) was neutralized with 0.1N sodium hydroxide and extracted twice with ether. The ether extract was dried over anhydrous sodium sulphate and was slowly added to a refluxing solution of 6,6'-dimethyl-2,2'-pyridil [4] (0.7g) in ethanol (15 ml). The subsequent procedure was as above to provide a solid melting at 147°.  $C_{26}H_{24}N_4O$  requires: C 76.5, H 5.9, N 13.7%. Found C 76.3, H 5.8, N 13.2%.

## Preparation of Solutions

Solutions of Iron (II) and copper (II) containing 1mg/ml were prepared from GR ammonium iron (II) sulphate and copper (II) chloride. Conventional acetate-acetic acid buffers (0.2M) in the pH range of 3 to 6 were used.

Solutions (0.1%) w/v of the prepared organic reagents were made by dissolving the requisite amount in sufficient ethanol. The volumes of the solutions were then made up with ethanol: water (1:1). A freshly prepared 1% w/v aqueous solution of pure ascorbic acid was used for the reduction of copper (II) and any iron (III) present in the iron (II) solution. Pure solid sodium nitrate was required for the extraction studies described below.

## Spectrophotometric Studies

The metal ion solution (1.0 ml) was transferred to a 25-ml volumetric flask, and 1 ml of 1% w/v ascorbic acid solution (1 ml) and the organic reagent solution (5 ml) were added, followed by sufficient acetate-acetic acid buffer solution to give pH 5. The contents were diluted to volume with ethanol or water, and the absorption of the solution in the visible region was measured with a Beckmann DB Prism spectrophotometer with 1 cm silica cells.

When measurements were done in solvents other than water-ethanol, the following procedure was used. The metal ion solution (1.0 ml) was placed in 50-ml separating funnel followed by the other reagents as above; 7–8 ml of extracting solvent were then added and contents were mixed well. The organic layer was collected in 25-ml volumetric flask and the extraction was repeated with a further 7–8 ml of solvent (in the case of 1,2-dichloroethane, 1–2 ml of ethanol was added to the flask before dilution to volume with 1,2-dichloroethane).

Absorbances of all solutions were measured against reagent blanks in appropriate solvents.

IR Spectra of the reagents in the range 625 to 3800  $cm^{-1}$  were recorded with a Unicam 1025 spectrometer using nujol mulls.

## RESULTS AND DISCUSSION

The microanalyses indicate the presence of oxygen in all three reagents, but their IR spectra provide diagnostic information concerning the presence of N-H and C=O vibrations (Table 1) in the molecules. These spectra show that only one of the ketonic groups in each of the  $\alpha,\alpha'$ -

Table 1. IR absorptions ( $cm^{-1}$ ) of reagents in nujol.

	N-H	C=O	C=N	C=C	C-H
2,2'-Pyridil-N-phenylaminoethaneimine(I)	3360	1685	1600	1575 1500	730, 695 750
6,6'-Dimethyl-2,2'-pyridil-N-naphthylaminoethaneimine (II)	3350	1680	1630	1580 1520	785, 770 750, 740
Benzil-N-phenylaminoethaneimine	3360	1660	1610	1600	755, 725 700



Table 2. Absorption studies with iron(II) and copper(I).

Reagent	Metal	Medium	$\lambda$ -max (nm)	$\epsilon$ (1 mole <sup>-1</sup> cm <sup>-1</sup> )	Time of development	Stability
2,2'-Pyridil-N-phenylaminoethaneimine	Fe(II)	Water	560	9.0 x 10 <sup>3</sup>	immediate	15 min
		Ethanol	565	1.3 x 10 <sup>4</sup>	"	1 hr
		1,2-dichloroethane	575	1.5 x 10 <sup>4</sup>	"	>1 hr
	Cu (I)	Ethanol	470	8.8 x 10 <sup>3</sup>	"	15 min.
6,6'-Dimethyl-2,2'-pyridil-N-naphthylamino ethaneimine	Cu (I)	Water	483	5.6 x 10 <sup>3</sup>	"	>1 hr
Benzil-N-phenyl aminoethaneimine	Fe (II)	Water-ethanol	500	6.1 x 10 <sup>3</sup>	3 hr	—

diketonic compounds (2,2'-pyridil, 6,6'-dimethyl-2,2'-pyridil and benzil) is involved in the condensation process with the N-aryl substituted diamine.

The results of the qualitative studies for the reactions of these compounds with metal ions are given in Table 2. The metal ions iron(II) and copper (I) give reactions of possible analytical interest with these reagents. Moreover, the reactions occur in a predictable trend. 2,2'-Pyridil-N-phenylaminoethaneimine reacts with both iron (II) and copper (I) in a manner characteristic of ferrioin type reagents, while 6,6'-dimethyl-2,2'-pyridil-N-naphthylaminoethaneimine shows only the cuproin reaction as expected. Benzil-N-phenylaminoethaneimine which lacks the characteristic  $\alpha, \alpha'$ -diimine ( $-\text{N}=\text{C}-\text{C}=\text{N}-$ ) functional grouping, surprisingly develops a purple colour with iron (II) which gradually reaches a maximum in about 3 hr at room temperature (30<sup>o</sup>). The reaction time can, however, be reduced at elevated temperature.

**2,2'-Pyridil-N-phenylaminoethaneimine.** This compound coordinated readily with iron(II) and copper (I) salts to give intensely coloured violet and brown complexes in weakly acidic medium. The iron(II) and copper (I) complexes are easily extractable as the nitrate ion association complexes in 1,2-dichloroethane with absorption maxima at 575 nm, and 470 nm and molar absorptivities of  $1.5 \times 10^4$  and  $8.8 \times 10^3$  respectively. The molar absorptivities of the iron (II) and copper (I) complexes compare well with the

values of  $1.1 \times 10^4$  and  $7.2 \times 10^3$  for the respective complexes of 1,10-phenanthroline, but the present complexes are not sufficiently stable in aqueous media for spectrophotometric applications. However, the iron(II) complex with nitrate as ion association complex is highly soluble in organic solvents and leads to an appreciable increase in sensitivity with reasonable solution stability. The sensitivity of the solvent extraction procedure makes this a particularly useful analytical reagent.

**6,6'-Dimethyl-2,2'-pyridil-N-naphthylaminoethaneimine.** This compound reacts with copper (I) in weakly acidic solution in the characteristic fashion of cuproin type reagents to give a purple complex in aqueous-ethanol solution. The spectrum of the copper (I) complex has a maximum at 483 nm with a molar absorptivity of  $5.6 \times 10^3$  in aqueous-ethanol medium. The complex is slightly less sensitive than the better-known 2,2-biquinoline ( $\epsilon = 6.1 \times 10^3$ ). The decrease in sensitivity may probably arise from the presence of the large naphthyl group at the end of the chain, which might distort the planarity of the heterocyclic nitrogen atoms.

**Benzil-N-naphthylaminoethaneimine.** This reagent, which does not contain the typical ferrioin functionality forms a purple complex on addition of an excess of the reagent to an aqueous-ethanol solution of iron (II) in weakly acidic media. The colour development is fairly slow at room temperature, but at elevated temperatures

(80°) the maximum colour develops within an hour and subsequently a brown precipitate is formed. The spectrum of the complex shows it to absorb maximally at 500 nm with a molar absorptivity of  $6.1 \times 10^3$ , but the exact nature of the complex is yet to be determined.

#### CONCLUSION

Few organic reagents have been so thoroughly investigated as the ferroin- and cuproin-type reagents. These studies have produced many extraordinarily sensitive and selective colorimetric reagents of this class. Therefore, it is doubtful that the reagents reported for the first time in this work will find practical applications for the quantitative determination of copper and iron. Nevertheless, the ease of their preparation and the simplicity of the reaction conditions for the complex formation are advantages for the qualitative analysis of iron and copper in aqueous solutions, and lend support to the structural

requirements for molecules to react as ferroin- and cuproin-type ligands.

*Acknowledgement.* Thanks are due to I. Arain, Director, Institute of Chemistry and G.H. Kazi, Director, National Centre of Excellence in Analytical Chemistry, University of Sind, for their encouragement during this work.

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