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2,6-Di(2'-Pyridyl)-3,5-di[2''-(6''-methylpyridyl)] Pyrazine as a New Spectrophotometric Reagent for Iron (II)

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Introduction

Japp and Wilson [1] and Leuckart [2] reported th preparation of 2,3,5,6-tetraphenylpyrazine by heating benzoin and ammonium formate or acetate. Goodwin and Lions [3] and Stephen [5] described the synthesis of 2,3,5,6-tetrakis (2'-pyridyl)pyrazine (TPP) and 2,3,5,6-tetrakis [2'-(6'-methylpyridyl)] pyrazine (TMPP) and examined their copper(I), nickel (II), cobalt(II), iron(II) and ruthenium(II) complexes. Pflam et al. [4] have applied TPP for the quantitative determination of iron(II). Khuhawar et al have used TPP iron(II) complex for the indirect determination of sulphite and sulphide. Here the same reaction has been applied on 6-methyl-2,2'-pyridoin for the preparation of DPMPP.

Experimental

Preparation of 2,6-DI(2'-pyridyl)-3,5-di[2''-(6''-methylpyridyl)]-pyrazine (DPMPP)

Freshly prepared 6-methyl-2,2-pyridoin [6] (4.4 g) and ammonium acetate (7g) were heated together till 6-methyl-2,2-pyridoin melted (82°C) and the temperature of the liquid rose to 120°C. The temperature was maintained for 10 min and 20 ml of water was added to homogenous dark coloured liquid. The mixture was cooled to 5°C overnight. Precipitate was filtered and washed with little water and recrystallised from a mixture of benzene-petroleum spirit (60-80°C). m.p. 184-85, $C_{26}H_{20}N_6$ require % C = 75.00, H = 4.8 N = 20.2; found % C = 75.0, H = 4.7, N = 19.91.

Solutions

Solutions containing 1mg/ml of cation and anion were prepared from AR $CuCl_2.2H_2O$, $(NH_4)_2$ $(Fe(SO_4)_2$, $6H_2O$, $MnSO_4$. $4H_2O$. $ZnSO_4.H_2O$. $Co(NO_3)_2.6H_2O$, $Cr(NO_3)$. $9H_2O$, $CdSO_4$. $8H_2O$, $NiCl_2.6H_2O$, $RuCl_3$ $5H_2O.Na_2HPO_4$, sodium citrate and sodium tartrate.

Analytical Procedure

Solution 1.0 ml containing 2.5-100 ug of iron (II) was transferred to 25 ml volumetric flask, followed by 1 ml of freshly prepared 1% ascorbic acid, 2 ml of buffer solution ($PH_{4.6}$) and 4 ml of organic reagent (0.2%) in ethanol:water (1:1). The volume was adjusted with ethanol or water. The absorption spectrum was measured against solvent. The solvent extraction in 1,2-dichloroethane was carried out as under:

The iron (II) solution was added in the separating funnel followed by other reagents as above. Sodium perchlorate 2g was added and the complex extracted twice with 1,2-dichloroethane. Ethanol 2 ml was added before dilution to volume with 1,2-dichloroethane.

All the absorbances were measured with cecil CE-505 spectrophotometer in conjunction with recroder CE-500 with 1 cm silica cells.

Results and Discussion

The reagent reacts with iron (II), copper(I), copper(II), cobalt(II), ruthenium (II) to form red violet, purple, green, brown and purple red respectively complexes in aqueous-ethanolic solution immediately, except ruthenium takes 2-3 days for its maximum colour development at room temperature (20°C). The colour reaction towards iron(II) is highly sensitive with molar absorprivity of 2.09×10^{4} at 575 nm in aqueous solution. The iron(II) complex is extractable in 1,2-dichloroethane as perchlorate ion association complex, with slight decrease in sensitivity with molar absorptivity of 1.84×10^{4} $1\ mole^{-1}\ cm^{-1}$ at 572 nm. The copper (I), copper (II), cobalt (II) and ruthenium (II) complexes absorb maximally at 510 nm, 680 nm, 530 nm and 524 nm with molar absorptivites of 3400, 108, 1200, 1900 $1.\ mole^{-1}\ cm^{-1}$ respectively.

The effect of variation of pH on the formation of iron(II) complex in aqueous solution was investigated using conventional buffer in the pH range of 1-10 at unit interval and the absorbance was measured at 575 nm. The colour of the complex failed to develop in strongly acidic or alkaline solution and reaches and remains maximum between pH 3-7, and the acetate acetic acid buffer pH 4.6 covered pH range satisfactorily.

The colour of the complex obeys the Beer's law over the 0.1-4.0 µg/ml of iron (II) in aqeuous solution and the percentage error for the analysis of iron test soltuions was found within ± 0-1.2%.

Copper (I) and cobalt (II) interfere due to the formation of coloured compounds, but nickel (II) and ruthenium (II) could be tolerated upto 1 µg/ml. Mn(II), Cr(II), Zn(II), Cd(II), Pb(II), Bi(II), Citrate, tartrate and phosphate did not interfere when present ten times the concentration of iron (II).

The reactions of the reagent DPMP towards iron (II) and copper(I) shows molar absoptivities of 2.09×10^{4} and 3.5×10^{3} at 575 and 510 nm respectively in aqueous solution, which compares very well with the iron (II) complex of TPP and copper (I) complex of TMPP with molar absorptivities of 2.06×10^{4} and 4.2×10^{3} at 575 and 520 nm respectively. It is therefore infered that the favourable properties of the TPP and TMPP reagents in terms of their reactions towards iron (II) and copper(I) are combined in reagent DPMPP due to asymmetric methyl substitution.

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