

The Absorption Characteristic of Ruthenium Dipyridyl and Ortho-Phenanthroline Derivatives

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Summary: Ten Pyridyl-substituted Pyrazine ligands containing ferrioin atomic grouping have been examined as complexing reagents for ruthenium (ii) and their molar absorptivities at their respective λ_{\max} have been reported. The effect of methyl substitution on absorption maxima and molar absorptivities are established.

Introduction

Ruthenium exhibits many chemical properties much similar to that of iron, including their colour reactions towards ferrioin type reagents. But little attention has been paid in exploring the possibility of determining the ruthenium by the methods commonly used for iron with ferrioin type reagents. The probable explanation is, that ruthenium compounds are infrequently encountered in practical problems; moreover ruthenium exists as coloured ionic compounds, thus needing no special method for studying it spectrophotometrically. However Bank and O'Laughlin¹, found, ruthenium (iii) in presence of hydroxylammonium chloride, reacting with 1,10-phenanthroline to give intense orange yellow tris (1,10-phenanthroline) ruthenium (ii) complex. The reaction being

slow at room temperature but sufficiently rapid at elevated temperature. A similar but more sensitive method based on the use of bathophenanthroline has also been described by Vita and Trivisonno² for the determination of ruthenium in uranium compounds. Recently Hashmi³ has proposed the use of 2,4,6-tripyridyltriazine for the determination of ruthenium. But no work has been reported on the pyridyl-substituted pyrazine ligands, containing α,α -diimine reactive atomic grouping with ruthenium. The reagents (I to X) (Fig. 3, Table No. 1) react with ruthenium in presence of excess of hydroxylammonium chloride to form coloured complexes. The reactions are slow but gradual at room temperature and requires a maximum of five days for colour development.

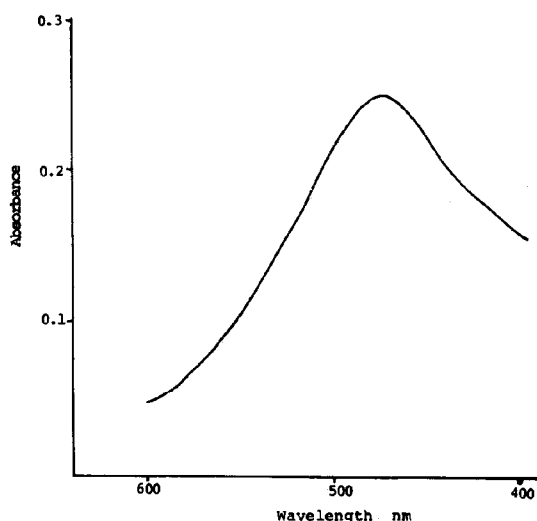


Figure No. 1: Absorption Spectrum of 8 $\mu\text{g/ml}$ Ruthenium (II) Complex with 2,3-Bis (2-pyridyl)-5,6-dihydropyrazine in water.

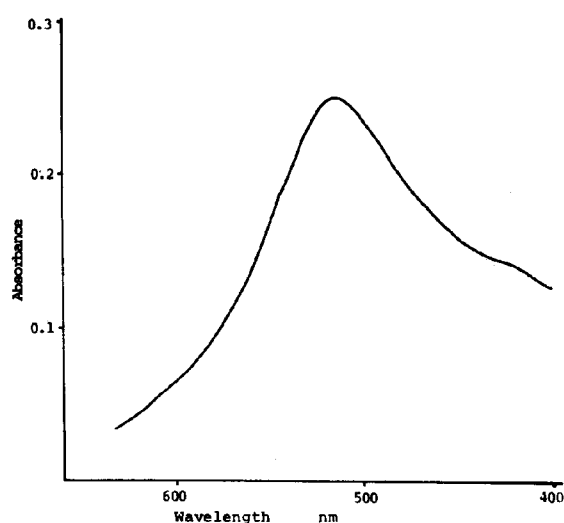


Figure No. 2: Absorption Spectrum of 10 $\mu\text{g/ml}$ Ruthenium (II) Complex with Bis (2-pyridyl) pyrazine in water.

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Table 1.

Reagents	R ₁	R ₂	R ₃	R ₄
I. 2,3-Bis (2'-pyridyl)-5,6-dihydropyrazine.	H	H	H	H
II. 2-(2'-pyridyl)-3-[2''-(6''-methylpyridyl)] -5,6-dihydropyrazine.	H	CH ₃	H	H
III. 2,3-Bis (2'-pyridyl)-5-methyl-5,6-dihydropyrazine.	H	H	CH ₃	H
IV. 2-(2-pyridyl)-3-[2''-(6''-methylpyridyl)] -6-methyl 5,6-dihydropyrazine.	H	CH ₃	H	CH ₃
V. 2,3-Bis (2'-pyridyl)-5,6-dimethyl -5,6-dihydropyrazine.	H	H	CH ₃	CH ₃
VI. 2,3-Bis (2'-pyridyl)-5,5-dimethyl 5,6-dihydropyrazine.	H	H	(CH ₃) ₂	H
VII. 2,3-Bis (2'-pyridyl) pyrazine	H	H	H	H
VIII. 2-(2'-pyridyl)-3-[2''-(6''-methylpyridyl)] Pyrazine.	H	CH ₃	H	H
IX. 2,3-Bis (2'-pyridyl)-5-methylpyrazine.	H	H	CH ₃	H
X. 2-(2-pyridyl)-3-[2''-(6''-methylpyridyl)] -5-methylpyrazine.	H	CH ₃	CH ₃	H

Experimental

Goodwin and Lions⁴ prepared (I) and (VII) and reported their complex formation abilities with iron (II), while Stephen⁵ studied their potentials for quantitative determination of iron (II). The preparations of (III) and (IX)⁶ and II, IV, V, VI, VII and X for the quantitative determinations of iron and copper are also reported⁷.

Solutions (0.2%) of the ligands (I to X) were prepared in water: ethanol (1:1).

Stock solutions of ruthenium containing 1 mg/1 ml, hydroxylammonium chloride 10% w/v and conventional acetate-acetic buffer solutions pH 3-6 were prepared from appropriate reagent grade RuCl₃·5 H₂O, hydroxylammonium chloride, sodium acetate and acetic acid.

Exactly 0.20-0.25 ml metal ion solution containing 1 ml/ml of ruthenium was transferred to a 25 ml volumetric flask. 2 ml of 10% w/v hydroxylammonium chloride and 5 ml of organic reagent solution were added,

followed by 2 ml of particular buffer solutions. The volume was made up with ethanol or water and the solution was allowed to stand at room temperature (20-25°) for five days.

The absorption spectrum of the solution was recorded with Cecil CE 505 spectrophotometer in conjunction with a recorder CE 500, against reagent blank in 1 cm silica cells.

Results and Discussion

The results of qualitative studies are given in table 2. The ruthenium metal ion, not surprisingly shows reactions of possible analytical interest with ten reagents. Moreover, the complex formation occurs slowly, but once formed; is stable for more than a month without change in absorbance. This behaviour of these bidentate ligands, is analogous to the behaviour of the better known bidentate ligands 1,10-phenanthroline and 2,2'-bipyridine⁸.

Table 2.
Investigation of complex Formation of Ligands with
Ruthenium (II) in Aqueous Solution at pH=5

Reagent	$\lambda_{\max_{nm}}$	ϵ -l. mole ⁻¹ cm ⁻¹
I	475	3133
II	470	2779
III	465	2122
IV	460	2274
V	465	1389
VI	433	2337
VII	513	2506
VIII	510	1667
IX	502	2122
X	502	1819

The absorption data (table 2) indicates that methyl substitution in the pyridyl, pyrazine and dihydropyrazine rings leads to a decrease in absorbance with blue shift. Presumably, methyl substitution introduces a measure of steric hindrance or disturbs the coplanarity of hetrocyclic rings, which accounts for lower molar absorptivities. For example reagents II and III are less sensitive than I for their reactions with ruthenium, inspite of expected higher basicities of donor nitrogen atoms in II and III ligands owing to alkyl substitution. Finally, ruthenium complexes with dihydropyrazine ligands (I to VI) are comparatively more sensitive than corresponding pyrazine ligands as previously observed for copper and iron⁷.

Although this study is intended only as a comparison of the chromogenic properties of pyridyl-substituted pyrazine ligands containing bidentate methine chromophore with ruthenium, but the results indicate that even simple compounds of this type can lead to some selective analytical reactions.

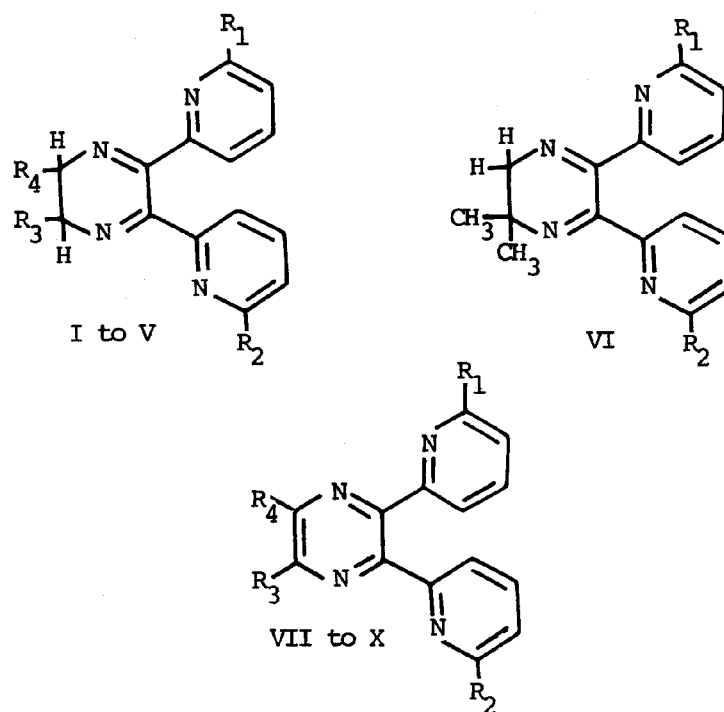


Figure No. 3: Structural formulae of ligands (I to X).

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