

8-Quinoliny-Ethylphosphate

I) 8-Quinoliny Mono-ethyl Ortho-phosphate And Its Complexes With Some Transition Metals.

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Summary: Oxine is usually used for accurate determination of most metals specially in acidic solutions. The present work was directed towards the complexing of both oxine and phosphate to get a more powerful chelating agent. The complexing of metals from the first transition series with this oxine derivative was studied with the effect of pH on its stability. The confirmation of the structures were done using IR, UV, NMR and the Mass spectra. The limits of pH at which the transformation between the keto- to enol form occurs has been given.

Introduction

8-Hydroxyquinoline(oxine) is by far the most frequently employed extracting agent for group separation.¹ Oxine was first introduced in quantitative analysis in 1927 by R. Berg who used it for accurate determination of most metals². Derivatives of oxine are found to be more selective toward metal ions because the number of reacting metal ions is restricted, owing to the steric effect, to those having a large enough ionic radius. Also the substituents on the parent compound could participate in bonding to the metal ion. This enhanced selectivity of the derivatives is manifested in higher values of dissociation constant compared with that of the parent compound, therefore these derivatives extract metal ions from more acidic solutions³. For these reasons oxine and its derivatives have been extensively studied over many decades as an important chelating and analytical reagent⁴. With special regards to the azo derivatives, they are considered as valuable dyes and metalochromic indicators^{5,6}.

Our interest in the study of the above mentioned compound was initiated by the desire to investigate the effect of combining the two complexing groups, oxine and phosphate in one molecule. The primary intention was to seek a more powerful chelating agent which could also be more specific towards certain metals than oxine itself.

Information from visible-ultraviolet spectra was used to establish the molecular structure of this compound. In the present work some complexes

with metals from the first transition series were prepared and their spectra were examined primarily for proof of chelation. Stability constants and thermodynamic properties of these complexes will be discussed in another publication.

The halochromic properties of the mentioned oxine derivative under study were investigated in detail since complexation and stability of complexes is greatly affected by changes in the pH. Studying the halo-chromism of the compound helped to identify the type of molecular structure available for complexation at different pH values. On the other hand, colours produced due to the halochromic shifts were not intense enough to encourage the use of the compound under study either as an analytical reagent or as an indicator.

Experimental

Apparatus: The vis-uv absorption spectra were measured with a Beckman Spectrophotometer Model Acta M VII. The ir were run on a Beckman Spectrophotometer model IR 4240. The desired pH value of a solution was adjusted by the use of a Pye-Unicam Potentiometer model 292 MK 2 and solutions of sodium hydroxide and nitric acid solutions. All solutions were prepared with a conductivity water (resistivity one mega ohm) ligand solutions otherwise indicated, contained 57 mg/l of the compound under study i.e. 1.5×10^{-4} molar. Complexation of this

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compound with metal was achieved by the mixing of 1:1 solutions of the metal nitrate and the ligand solution both having the final concentration of 0.75×10^{-4} molar. 8-Hydroxyquinoline solution was 1.4×10^{-4} molar and is prepared from material purchased from the Koch-light laboratories Ltd., England, and was further purified by double recrystallization from 80% ethanol.

Preparation of 8-quinolinyl monoethyl ortho-phosphate:

0.1 Mole (6.8 g) of sodium ethoxide (i.e. 2.3 g Na + 4.6 g absolute C_2H_5OH) was added dropwise with occasional stirring to 0.1 mole (37 g) of diquinolinyl phosphorochloridate which had been cooled in an ice bath. The reaction took three hours to completion. The product was then extracted with ether, and the ethereal phase was washed several times to remove the NaCl formed in the reaction. The ether extract was subsequently dried over anhydrous Na_2SO_4 , filtered and evaporated under vacuum to obtain the crude product. Recrystallization from absolute ethyl alcohol gave pale yellow crystals (85% yield) m.p. $229^\circ C$, yellows at $200^\circ C$.

It was necessary to filter the aqueous solutions of the prepared compound in order to remove a few white colloidal particles.

All other chemicals were analytical reagents and were used as received. All glassware was calibrated. In performing the optical measurements, solutions containing the same amounts of reagents except the oxine ester were used as blanks.

Results and Discussion

The structure of the compound was confirmed with its IR, UV, NMR, and Mass spectra. In the IR spectrum, Fig. 1, the bands indicative of an hydroxyl group are absent in the region $3200 - 3600 \text{ cm}^{-1}$. Vibrations due to the aromatic ring⁷ appear as three strong peaks at 1625, 1595 and 1550 cm^{-1} . These bands are common in the spectra of quinoline derivatives⁸. The P = O stretching mode is displayed in the strong absorption of 1295 cm^{-1} and other stretching frequencies of the $[PO_4]^{3-}$ group absorbs intensely in the $1100 - 1000 \text{ cm}^{-1}$ region. Two peaks appear in the region $600 - 500 \text{ cm}^{-1}$ which could be assigned to the P - O deformation modes of the

$[PO_4]^{3-}$ ion. The monosubstituted pattern of the aromatic ring is exhibited in the single sharp band of 620 cm^{-1} .

The fact that the compound is partially ionic is indicated by its high melting point ($229^\circ C$) as compared to the melting point of oxine ($75^\circ C$)⁹. Furthermore, its solubility in highly polar solvents such as alcohols, dimethyl sulphoxide, water etc., and its insolubility in non-polar organic solvents like benzene, petroleum ether, carbon tetrachloride, strengthen the view that the compound is partially ionic.

8-Quinolinyl monoethyl phosphate is presumably having the structure shown in Fig. 2 with phosphorus atom hexa coordinated in an octahedral site symmetry. The second possibility could be that P is being tetrahedrally bonded to oxygen atoms only.

The effect of pH (Halochromic effect)

Electronic spectra of aqueous solutions of the compound under study at different pH values, Fig. 3, showed similarity to those of oxine¹⁰. Absorbance curves join at two distinct isosbestic points namely at 321 and 334 nm. This is indicative of change in the molecular structure concurrent with the change in the pH of the solution. These structures have to be produced by the mechanism of ketoenol tautomerism in the molecule. This process is illustrated in Fig. 4.

Because of the acidic nature of the ligand solution, structure (A) is the one prevailing in the solution until the addition of an alkali. The stability of structure (A) is enhanced by the nature of tautomeric equilibrium which favours the formation of a weaker acid, i.e., the keto-form that has the hydrogen atom bonded to a carbon rather than a more negative atom¹¹. As a result of its stability, structure (A) will persist in solution until the pH value exceeds 4.5 units, Fig. 3.

On reaching the pH value of 6.2, structure A is completely converted to the enol form, structure B, and this is apparent from the disappearance of the band of 357 nm which is attributed to the carbonyl group¹⁰. In Fig. 3 the lowest curve (5a), of pH 4.4, runs parallel to those of the acidic media. Curve (5a) is the spectrum of the initial solution prior to adding either acid or base. Their addition changes the shape of the curve drastically. Consequently, spectrum (5a) is suggestive of low-level dissociation of the ester in

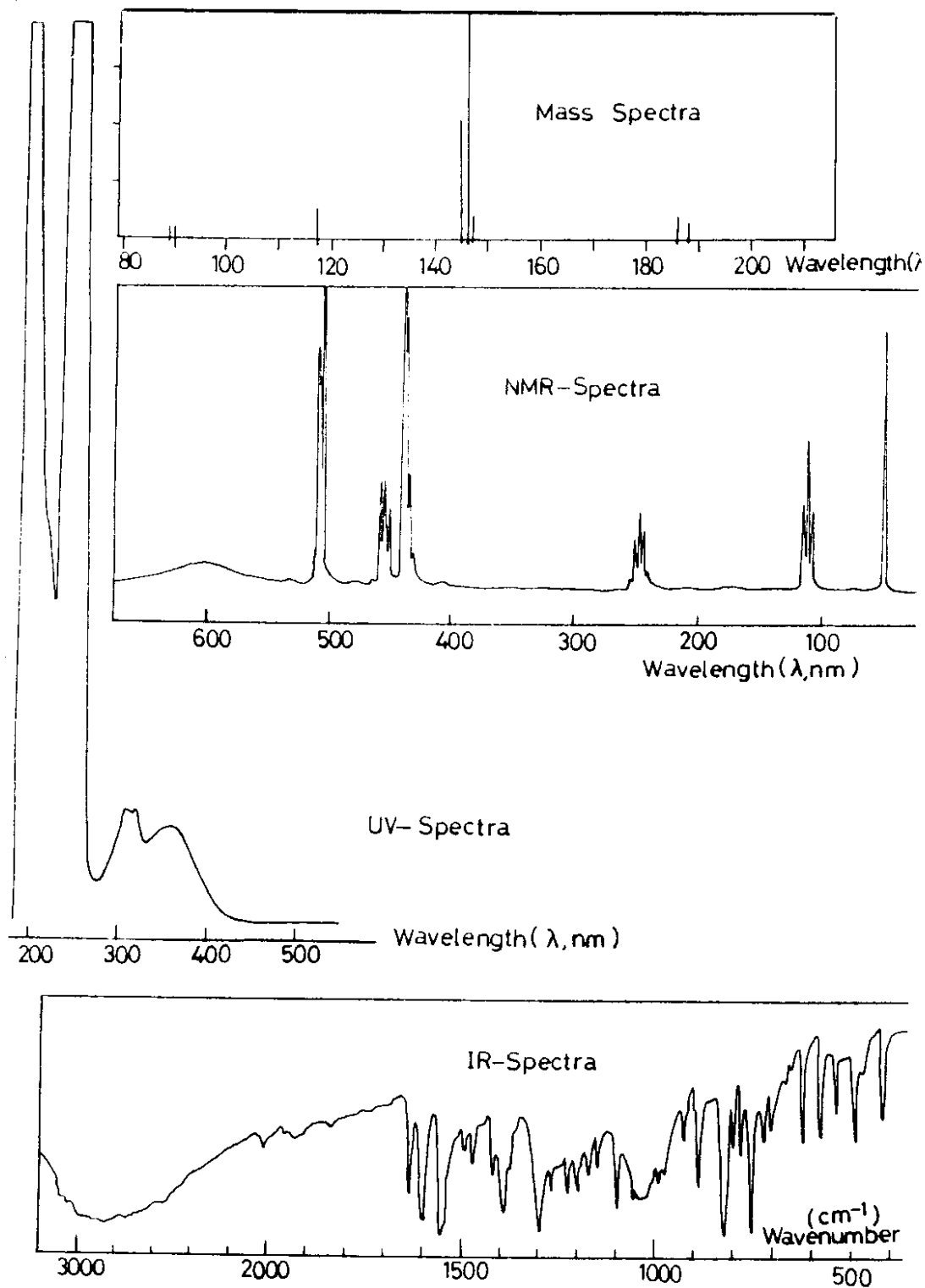


Fig. 1. The IR, UV, NMR and Mass Spectra of 8-Quinolinyl-Mono-ethyl-Orthophosphate.

solution rather than a different structural form.

The band of 310 nm, considered to be a heterocyclic transition¹², is most prominent in the vicinity of the neutral region (pH = 7, ± 2). This has been explained on the grounds of the auxochromicity of the hydroxyl group of structure B. Another explanation of the intensity enhancement is the availability of the non-shared electrons of the pyridinic nitrogen to enrich the π -electronic system. At more basic conditions this band diminishes rather too rapidly. In our opinion, this extensive loss of energy could not be explained merely by the disappearance of the

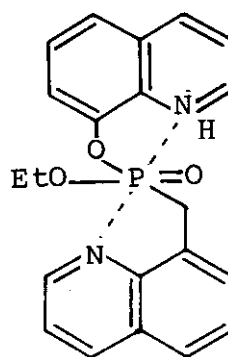


Fig. 2. Structure of 8-Quinolinily-Monoethyl-Orthophosphate.

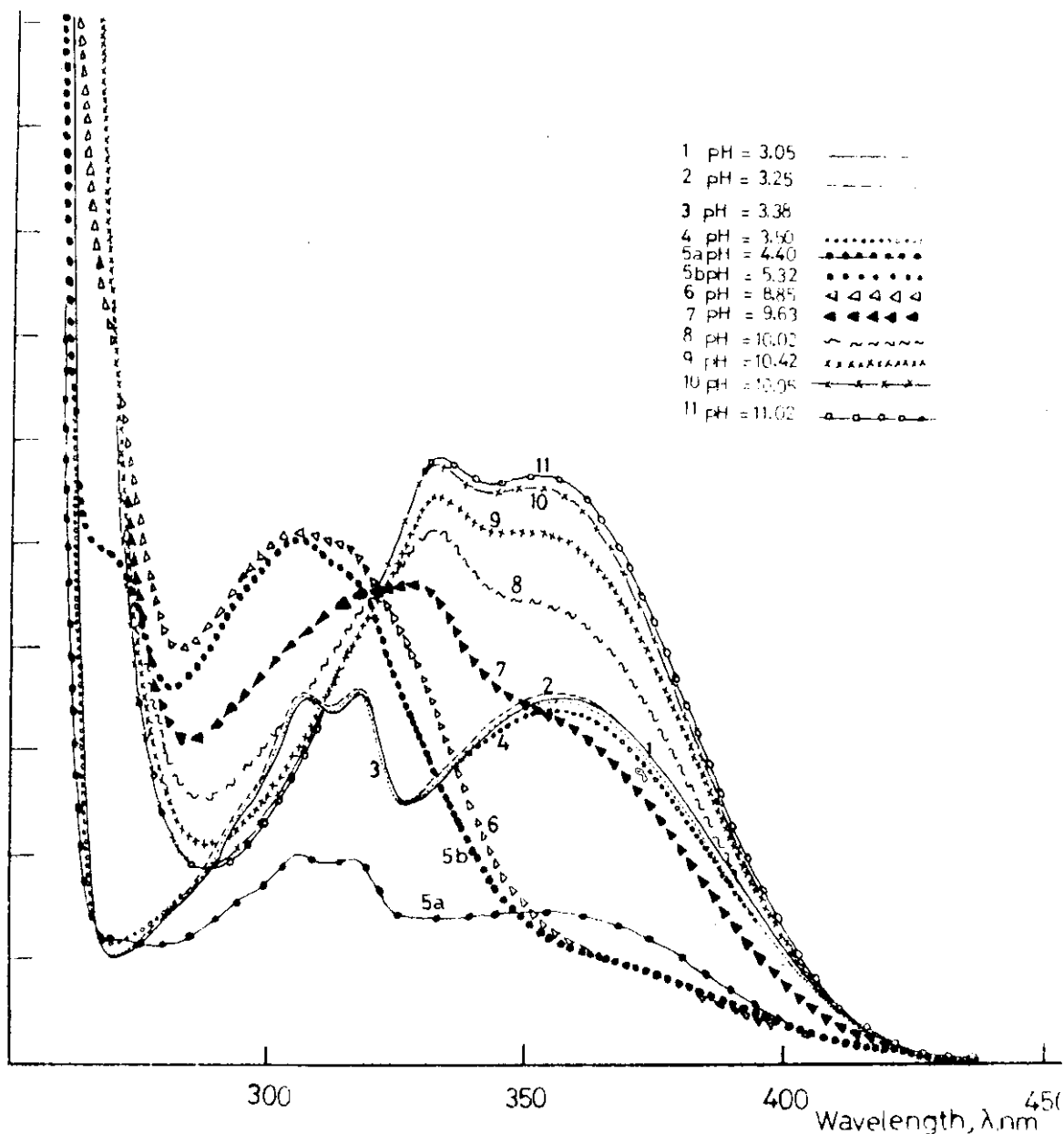


Fig. 3. Electronic Spectra of 8-Quinolinily-Monoethyl-Orthophosphate at Different PH-Values.

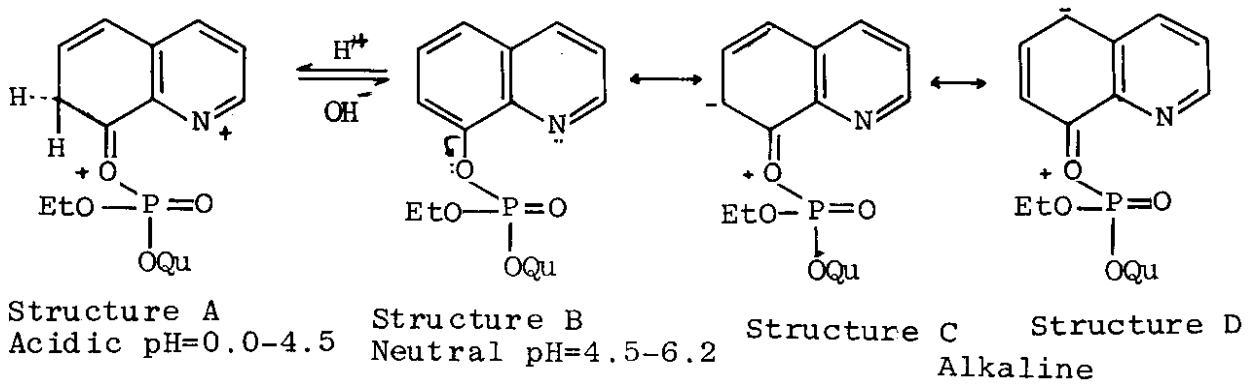


Fig. 4. Effect of PH-Value on the Molecular Structure.

Table 1. Absorption maxima (λ_{\max}) for oxine ethyl phosphate and its metal complexes in water

Transition*	Ligand I	Co ⁺⁺	Ni ⁺⁺	Cu ⁺⁺	Cr ⁺⁺⁺	Fe ⁺⁺⁺
	198			192 _{vs}		
(¹ B _b ← ¹ A ₁)		207			195 _{vs}	
(¹ E _u ← ¹ A _{1g})	207	216 _{vs}	218 _{vs}	202 _{vs}		192 200
	246			245		254
(¹ B _b ← ¹ A ₁)	253	254 _s	256 _s	252	350 _{vs}	
(¹ E _{1u} ← ¹ A _{1g})				260		
				263		
(¹ L _a ← ¹ A ₁)	306	306	307 _m	305	295shd	
	318	312	318 _m	318	308 _m	307
¹ B _{1u} ← ¹ A _{1g})		320		331	320 _m	318
		349				
(¹ L _b ← ¹ A ₁)	357	356	355 _w	360	358 _m	360
						455
¹ B _{2u} ← ¹ A _{1g})					575 _w	610
		205 _{vs}				
		301 _s				
Metal ion absorptions		480 _m	302 _s	200	300	
		510 _m	393 _m	210	407	300
		615 _w	655 _w	300	572	
			720 _w	800		

vs = very strong, s = strong, m = medium w = weak, shd = shoulder

*Ref. 12,13 Because the authors of those articles used the older system of spectroscopic symbols, we have cited them between brackets alongside the new symbols.

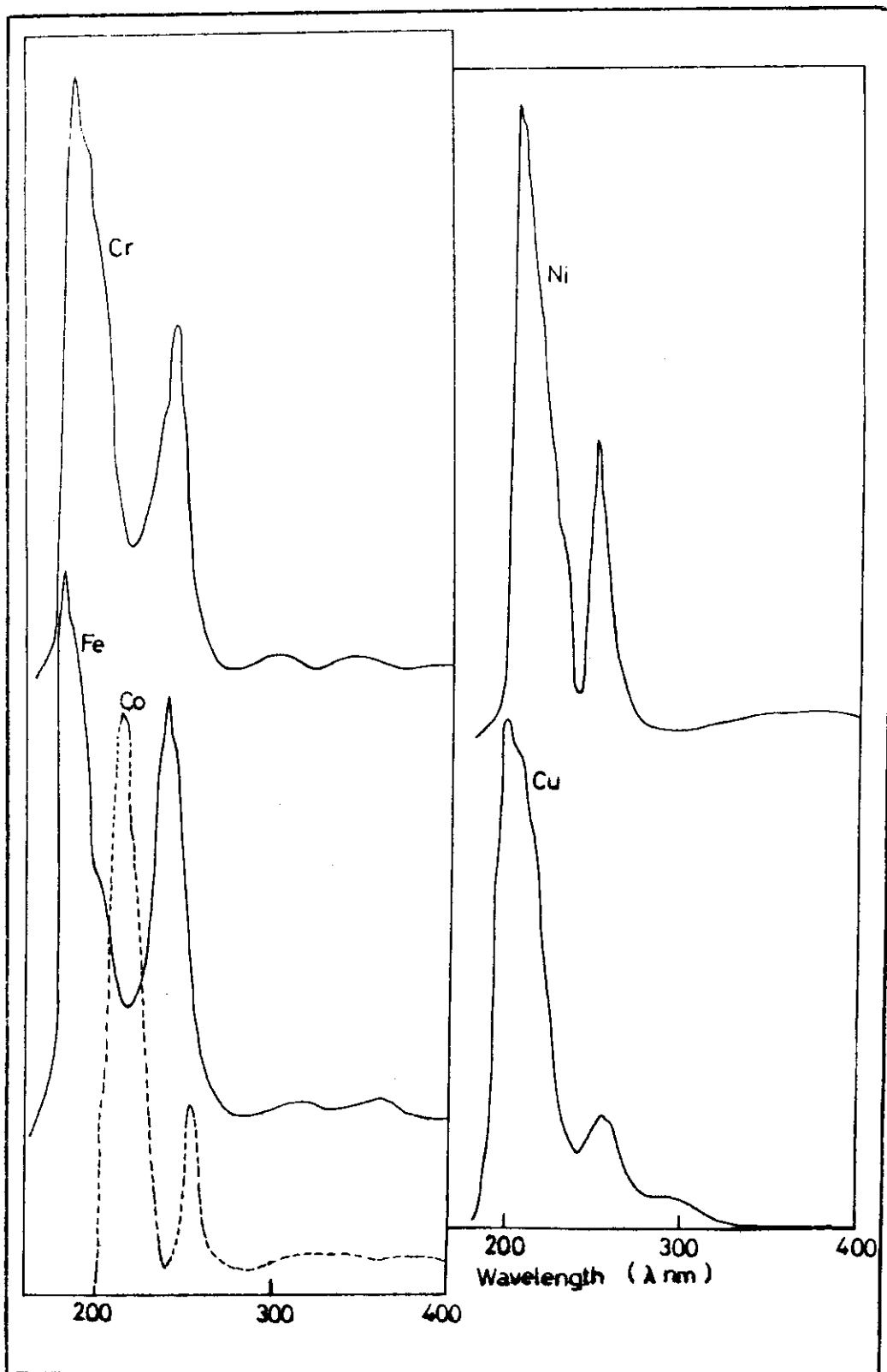


Fig. 5. Electronic Spectra of some Metal-Oxine Complexes.

auxochromic OH group (on passing from structure B to those of C and D). This might be explained by supposing that the band has simply shifted bathochromically because of the resonance and conjugation associated with the newly formed keto-structure, thus becoming buried within the strong absorption of 350 nm. A protrusion at 330 nm is probably due to the tip of this hidden band.

In the present work the compound under study was used to complex the metal ions of cobalt, nickel, copper, iron and chromium from their nitrate solutions. Complex formation was concluded from changes in the position and absorptivity of the ligand peaks, (Fig. 5). Table 1 gives the absorbance maxima (λ_{\max}) for these complexes. The assignments of these absorptions are in accord with previous studies^{12,13} on similar quinoline derivatives.

In table 1, the absorption of a complex is compared with those of both metal and ligand. It is apparent that the original ligand bands which appear at 198 and 207 nm are shifted to 207 and 216 nm respectively. While the cobalt nitrate has absorptions at 205 and 301 nm. Since the complex has absorptions differing from either its metal ion or the ligand, we conclude that the complex has formed and is stable in its aqueous solutions as a complex and not as individual ligand and metal ion.

Conclusion

The molecular structure of oxinmonoethylphosphate has been confirmed on the basis of spectral information. The optical halochromism of the compound under study has helped to throw light on its structure. Five metal complexes were prepared and proofs of their complexation were obtained from potentiometric titrations¹⁴ and electronic spectroscopy. The halochromic shifts of the complexes are not far enough in the visible region to produce intense colours. Therefore, the possibility of the tested compound to be utilized as a metalochromic indicator or as a complexometric analytical reagent is rather limited.

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