

In the A - X system of InI molecule, (0, 0), (0, 1) and (1, 0) bands degraded to violet were analysed. These bands reveal the presence of single P and R branches of which P is the head forming branch (Fig. 1). The rotational analysis has been carried out by standard methods (Herzberg⁴, 1955 and Younger and Winans⁵, 1960). Analysis of (0, 1) band at 4072.7 Å was carried out by comparing the combination relations for the common upper and lower state respectively of (0, 0) band at 4098.5 Å. The rotational constants for the three bands of A → X system obtained in the present work are given below:

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Band	ν cm ⁻¹	B' cm ⁻¹	B'' cm ⁻¹	D' cm ⁻¹	D'' cm ⁻¹
(1, 0)	24548.535	0.0374 ₂	0.0368 ₁	0.12 × 10 ⁻⁷	0.087 × 10 ⁻⁷
(0, 0)	24393.853	0.0377 ₂	0.0368 ₂	0.087 × 10 ⁻⁷	0.075 × 10 ⁻⁷
(0, 1)	24216.705	0.0376 ₁	0.0364 ₁	0.1 × 10 ⁻⁷	0.06 × 10 ⁻⁷

Molecular constants of InI molecule obtained from the present analysis are given below along with the microwave data.

State	B _e cm ⁻¹	r _e Å	ΔG ₃ cm ⁻¹	a _e cm ⁻¹
A ³ Π ₀	0.0376 ₂	2.710 ₂	155.7 ₂	0.6 × 10 ⁻⁴
X ¹ Σ ⁺	0.0362 ₂	2.770 ₁	176.1 ₂	1.3 × 10 ⁻⁴
	*0.0368	*2.754	—	1.04 × 10 ⁻⁴

The ground state configuration of Indium moniodide molecule can be written as $zo^2 y\sigma^2 w\pi^4 x\sigma^2$ analogous to those of halides of the same group (InCl, InBr, InI) giving rise to ¹Σ⁺ ground state. The excited electron configuration is $zo^2 y\sigma^2 w\pi^4 x\sigma\pi$ which gives rise to ¹Π or ³Π state. ¹Π—¹Σ⁺ transition is attributed to C → X system which is analogous to those of similar molecules. However ¹Π state is repulsive in the case of InI molecule which gives a continuum at 3180 Å. The ³Π state belongs to Hund's case (a) due to its large coupling constant (648.9 cm⁻¹). Hence ³Π₀, ³Π₁ and ³Π₂ states are analogous to ¹Σ, ¹Π and ¹Δ states respectively. ³Π₂ → X¹Σ⁺ transition is a forbidden one whereas ³Π₁ → ¹Σ⁺ has been ascribed to the B → X system. Hence ³Π₀ → ¹Σ⁺ transition may be attributed to the A - X system of InI molecule. The appearance of single P and R branches in case of (0, 0), (0, 1) and (1, 0) bands confirms this assignment.

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*Microwave data (1958).

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COPPER COMPLEXES OF PHTHALHYDRAZIDE-5-AZO-2-NAPHTHOL

Our previous work on metal chelates of o-hydroxyazo compounds¹ led us to a tridentate ligand, phthalhydrazide-5-azo-2-naphthol, which unlike the bidentate o-hydroxyazo compounds, forms stable metal chelates with a variety of metal ions. Complexes of this tridentate ligand with Copper (II), wherein the fourth co-ordination position of the metal ion is occupied by ammonia or a heterocyclic base (pyridine or α, β or γ-picoline) have been characterised.

Experimental

Phthalhydrazide-5-azo-2-naphthol was prepared as follows: 3-Nitrophthalic anhydride was treated with hydrazine sulphate in presence of sodium acetate. The resulting 5-nitrophthalhydrazide was reduced with ammonium sulphide to yield pale yellow 5-aminophthalhydrazide (luminol) in 90% yield². This was diazotised and coupled with β-naphthol when phthalhydrazide-5-azo-2-naphthol³ resulted in 70% yield. Recrystallised from ethyl alcohol m.p. 305–307° C.

The copper complex containing ammonia was prepared as follows: Copper(II) chloride dihydrate (0.85 g; 0.005 mole), dissolved in the minimum amount of water, was added with stirring to a

solution of the ligand (1.65 g; 0.005 mole) in liquor ammonia (50 ml). The mixture was stirred for half an hour, then cooled, filtered, and the crystalline residue washed with water. Yield: 1.6 g. Complexes containing the heterocyclic bases were prepared similarly, by using 150 ml. of the base in place of liquor ammonia. The mixed solutions in these cases were also warmed to about 50°, before cooling. Yields are noted in Table I. Since the complexes are only sparingly soluble in common organic solvents, they could not be recrystallised, but were washed with hot alcohol, before sucking dry. The compounds did not melt or decompose until 330°.

Carbon and hydrogen contents of the ligand and the complexes were determined microanalytically, and metal content of the complexes by usual gravimetric procedure, after decomposing them with concentrated sulphuric-nitric acid mixture. A list of complexes prepared and their analytical data are given in Table I.

considerably low, and is at about 1615 cm⁻¹ in a variety of *o*-hydroxyazo compounds. There are also strong evidences to show that phthalhydrazide exists almost entirely in the monohydroxy form^{6,7}. On the basis of such evidences the ligand, phthalhydrazide-5-azo-2-naphthol can be represented by structures A and B in Fig. 1. In view of the tautomerism shown, the amide carbonyl stretching frequency would also be expected to be low. In conformity with the above two structures, the ligand shows two strong absorptions in the double bond region at 1630 and 1615 cm⁻¹, assignable to the amide carbonyl and quinone carbonyl respectively of the ligand.

As should be expected from the hydrogen bonded structure, a strong and considerably broad band extending from 3500 to 2400 cm⁻¹ (maximum at 3000 cm⁻¹) is observed in the spectrum of the ligand. Although O-H, N-H and the intramolecularly hydrogen bonded N-H-O group, all, could be contributing to this band, only the last

TABLE I

Sl. No.	Compounds	Yield %	Colour	C	Analytical data* H	Cu
1.	Phthalhydrazide-5-azo-2-naphthol (H ₂ L)	65	deep red	66.65 (67.05)	3.18 (3.32)	
2.	[CuL(NH ₃)]	80	brownish violet	51.89 (52.62)	3.62 (3.65)	15.20 (15.45)
3.	[CuL(pyridine)]	75	black	59.18 (58.41)	3.75 (3.60)	12.98 (13.45)
4.	[CuL(α -picoline)]	70	brown	58.28 (59.21)	3.71 (3.90)	12.58 (13.06)
5.	[CuL(β -picoline)]	70	brown	57.97	3.65	12.30
6.	[CuL(γ -picoline)]	70	brown	57.26	3.84	12.71

* Calculated values are in parentheses.

Thermograms were obtained on a Stanton recording thermobalance. A pye-Unicam U.V.-Visible spectrophotometer was used for recording U.V. spectra in DMF. Infrared spectra of KBr pellets were recorded using a Perkin Elmer Model 337 spectrophotometer.

Results and Discussion

The complexes prepared are non-conducting in DMF, and do not contain the counter anion of the copper salt used for synthesising the complexes. On the basis of their analytical data these complexes are represented in Table I. The complexes have been further characterised on the basis of infrared spectral evidence.

Investigations in the past have revealed that *o*-hydroxyazo compounds (for example phenylazo- β -naphthol) exist predominantly in their quinone-hydrazone form, which is intramolecularly hydrogen bonded^{4,5}. Due to this strong hydrogen bonding the quinone carbonyl stretching frequency remains

mentioned can be responsible for the observed extension of the band to such low wave numbers⁸.

In the spectra of the metal complexes, the two carbonyl bands of the ligand, are shifted to about 1660 and 1575 cm⁻¹. Metal ligand bonding, as in structure C in Fig. 1, can adequately explain the shift in the carbonyl stretching frequencies. The quinone carbonyl of the ligand, perturbed through co-ordination to the metal, shows a depressed carbonyl stretching frequency at about 1575 cm⁻¹. On the other hand metal chelation fixes the tautomeric form A of the ligand, thus strengthening its amide carbonyl (by obviating tautomerism involving structure B) and consequently raising its stretching frequency to about 1660 cm⁻¹. Spectra in the 3500-2400 cm⁻¹ region also support the structure, since in the place of the very broad band of the ligand, a considerably narrower band (3500-2900 cm⁻¹) with maximum at about 3300 cm⁻¹ occurs in the spectra of the complexes. Structure C

would demand such a change, since the chelated hydrogen of the ligand has been replaced by the metal atom (together with the O-H hydrogen) and hence the band is now caused only by the N-H group which, from the breadth of the band, appears to be involved in weak intermolecular hydrogen bonding.

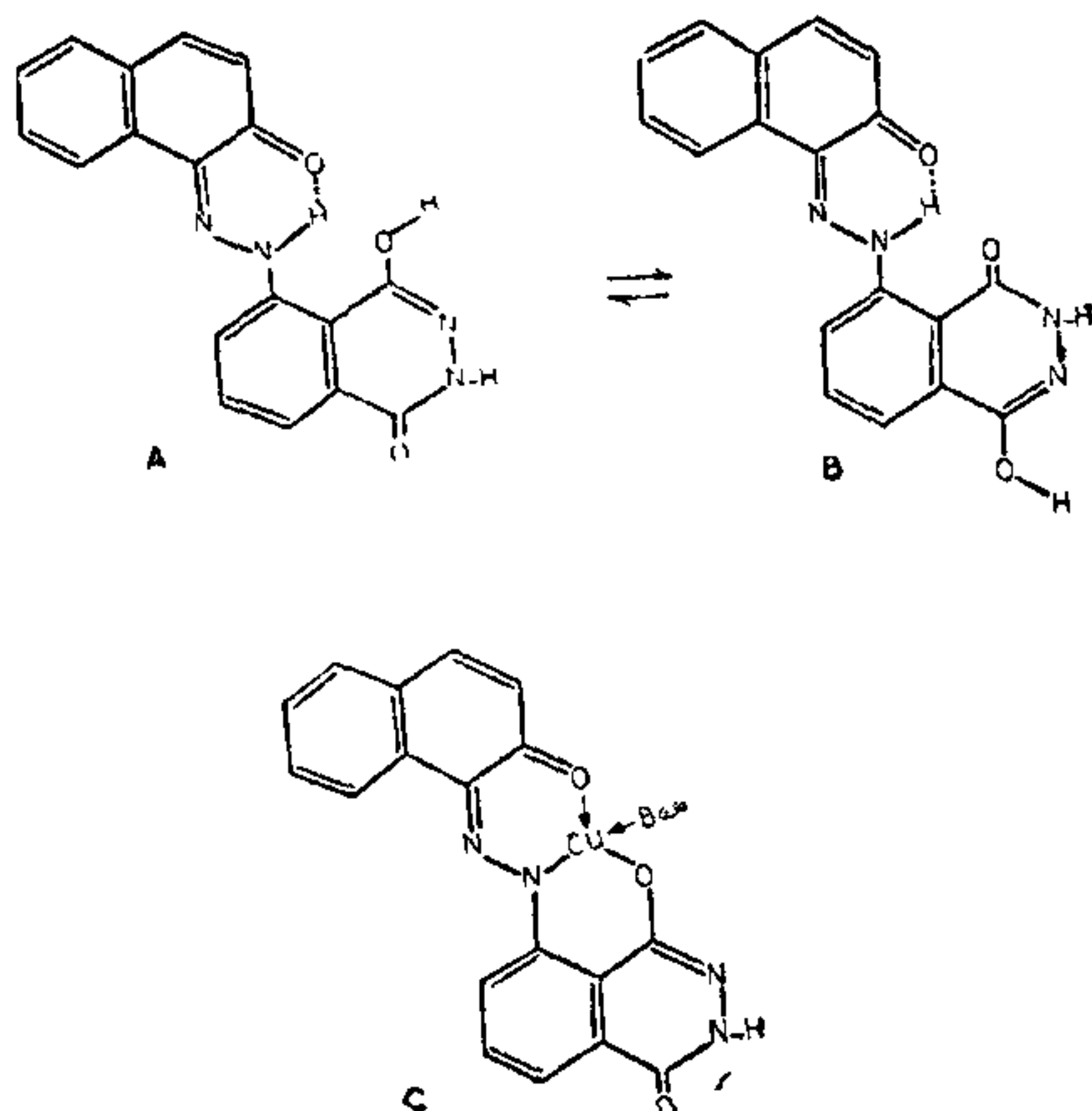


FIG. 1

The complex, $[\text{CuL}(\text{NH}_3)]$, when boiled with caustic alkali liberated the expected amount of ammonia. Thermograms of the complexes $[\text{CuLB}]$ ($\text{B} = \text{base}$) reveal that the heterocyclic base is expelled preferentially and quickly in a single step at about 340°C , after which the rest of the molecule decomposes slowly.

The U.V. spectrum of the complex $[\text{CuL}(\text{NH}_3)]$ is very similar to that of the ligand. Hence it is evident that no rearrangement of the ligand occurs during chelation.

A copper chelate of the N-methyl derivative of the title ligand has been previously reported⁹. Although no structural study was attempted, the chelate has been assumed to have an analogous structure shown in Fig. 1 C.

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Ni(II), Cu(II) AND Pd(II)-CHELATES OF N-HYDROXYETHYLPYRROLIDENEIMINE SCHIFF BASE

N-HYDROXYETHYLPYRROLIDENEIMINE (abbr. H_2P) acts as a bidentate Schiff base and forms solid chelates with Ni(II), Cu(II) and Pd(II). The chelates have been characterised by elemental analysis, magnetic susceptibility measurements, electronic and infrared spectra.

H_2P was synthesised by refluxing an equimolecular mixture of ethanolamine and pyrrole-2-carboxaldehyde in benzene for an hour at 110°C . Water was removed azeotropically with benzene. After distilling out the benzene a yellow solid m.p. 72° was obtained. It gave satisfactory C, H and N analysis.

The metal chelates were prepared by refluxing a mixture of hydrated metal (II)-acetates and H_2P in 95% ethanol for two hours. The solid material formed was filtered, washed with ethanol, dried and recrystallised from methanol. The metal chelates gave satisfactory elemental analysis and display 1 : 2 metal-ligand stoichiometry.

Cu(II)-chelate was found paramagnetic (μ_{eff} 1.87 B.M. at 303°K) while Ni(II)- and Pd(II)-chelates diamagnetic.

The electronic absorption spectra of Ni(II)-chelate in methanol exhibit two bands at around 16200 and 17500 cm^{-1} suggesting the square-planar configuration of the Ni(II)-chelate¹. The Cu(II)-chelate solution in methanol consist of two broad bands at 16700 and 24200 cm^{-1} which indicate the square-planar geometry of its molecule². Pd(II)-chelate greatly favours a square-planar configuration². Solution spectra of Pd(II)-chelate indicate three bands at 22200 , 26400 and 30500 cm^{-1} assignable to the transitions $^1\text{A}_{1g} \rightarrow ^1\text{B}_{1g}$; $^1\text{A}_{1g} \rightarrow ^1\text{E}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$, respectively which reveal a square-planar configuration of the compound. Thus H_2P functions as a bidentate ligand in all the three metal chelates of interest.

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