

Synthesis and spectral characterization of Co(II), Ni(II) and Cu(II) mixed ligand complexes of schiff base derived from 3-Phenylimino-2-Indolinone

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ABSTRACT

Biologically important Schiff base ligand 3-phenyl imino 2-indolinone hydrazone (PIIH) have been synthesized by condensation of 3-phenyl imino-2-indolinone with hydrazone hydrate. The metal chelates of PIIH with bivalent transition metal ions. Cu(II), Ni(II) and Cu(II) have been synthesized. The structure of Schiff base and their metal chelates have been characterized by elemental analyses, molar mass, IR and electronic spectra, magnetic susceptibility and molar conductivity values. These studies indicate that the compound PIIH acts as neutral bidentate ligand and coordination proposes through indoline N and azomethine N of hydrazone moiety. The rest of coordination position of metal ions are satisfied by neutral ligands such as ammonia, pyridine, α -picoline, β -picoline and γ -picoline. The chelates of Co(II), Ni(II) and Cu(II) proposed to be octahedral in geometry.

Key words: Schiff base/ PIIH/ Co(II), Ni(II) and Cu(II) Complexes/ Hydrazone

INTRODUCCION

Carbonyl compound derivatives such as hydrazones are important masked organic compounds¹⁻². Hydrazone are highly crystalline and are used for characterization and purification of carbonyl compounds.³⁻⁴ Regeneration of carbonyl compounds from prepared hydrazones have received a significant attention in recent years⁵⁻⁹ within the framework of Green chemistry¹⁰, a noticeable improvement provided by the association of solvent free techniques¹¹ and microwave activation¹². Keeping these facts in mind and in continuation of our earlier work¹³⁻²⁰ on metal chelates of Schiff base ligand, in this communication we wish to report synthesis, characterization and antimicrobial activity of some bivalent metal chelates of Co(II), Ni(II) and Cu(II) with 3-phenyl imino 2-indolinone hydrazone [PIIH]

EXPERIMENTAL

Material and Methods

The compound 3-phenyl imino 2-indolinone was prepared according to earlier reported²¹ method. All other chemicals were reagent grade and be used without further purification.

Preparation of ligand [PIIH]

The ligand 3-phenyl imino 2-indolinone hydrazone [PIIH] was prepared by condensing equimolar quantities of 0.01 M of 3-phenyl-imino 2-indolinone dissolved in ethanol with ethanolic solution of hydrazine hydrate. The reaction mixture was refluxed for 3 h on water bath and the resulting mixture was poured in crushed ice whereby precipitate was obtained. It was filtered off, washed several times with water, recrystallized from ethanol and finally dried in electric oven (yield-55-60%).

Preparation of the complexes

The complexes of Co(II), Ni(II) and Cu(II) complexes were prepared by refluxation precipitation procedure. The hot ethanolic solution of ligand PIIH (0.02 M) were condensed with ethanolic solutions of acetate of Co(II), Ni(II) and Cu(II) (0.01 M). The resulting mixture of the solution was refluxed on water bath for 1 h. It was cooled and treated with liquor ammonia/pyridine/ α -picoline/ β -picoline/ γ -picoline separately. The mixture of the solution was again refluxed on water bath for 1 h. It was then cooled, filtered and washed thoroughly with ethanol. The procedure carried out in each case were similar with slight variation of timing of reflux. Yield in all cases 70-75%.

The metal content of all the complexes were analysed using Perkin Elmer-2400 elemental analyzer. The electronic spectra were recorded on Cary 2390 spectrophotometer. Magnetic susceptibility were measured by Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. Molar conductance were recorded on Systronics conductivitymeter model-303 using DMF as a solvent. The IR spectra of ligand and their metal complexes were recorded on Perkin Elmer-577 spectrometer in the range 4000-200 cm^{-1} using KBr disc.

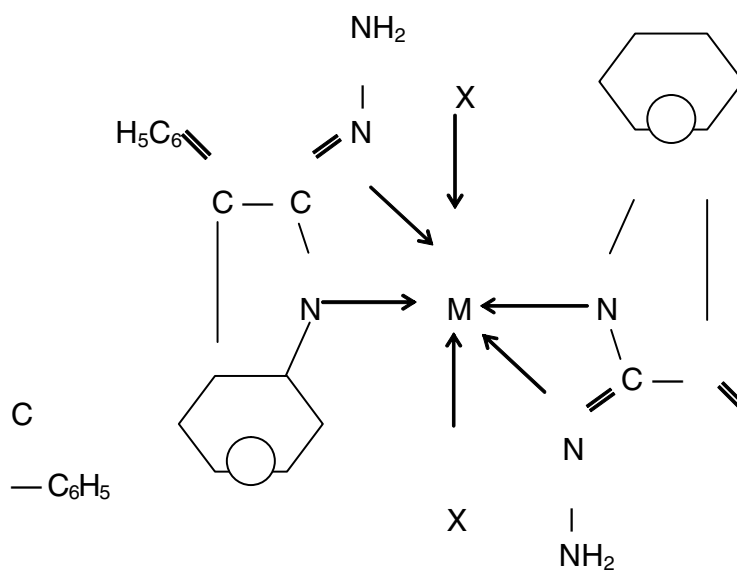
RESULTS AND DISCUSSION

The IR spectrum of the ligand PIIH exhibits a broad band at 3260 cm^{-1} which assigned^{22,23} to $\nu_{\text{N-H}}$ vibration. In the spectra of the complexes this band shows red shift indicating coordination takes place through N atom of secondary amino group of the indoline ring. The next IR spectrum of the ligand exhibits a strong broad band at 1640 cm^{-1} assigned^{22,24} to $\nu_{\text{C=N}}$. This band is shifted to lower frequency region with slightly reduced intensity suggesting coordination of azomethine N of the hydrazone moiety. The linkage with azomethine N is confirmed by the appearance of a far ir band at 460-420 cm^{-1} which may be assigned^{22,25-27} to $\nu_{\text{M-N}}$.

The other band in the region 1200-1800 cm^{-1} remain practically unchanged and assigned due to phenyl ring vibrations. The spectra of the pyridine adducts shows an additional bands near 650 cm^{-1} and have been assigned due to pyridine ring. These assignments is established from literature²⁷⁻²⁹.

Electronic spectra and magnetic susceptibility of the complexes

The electronic spectra of Co(II) complexes exhibits three bands in the region 11600-10100,



M = Co(II), Ni(II) and Cu(II); X = NH_3 , $\text{C}_6\text{H}_5\text{N}$, α -picoline, β -picoline and γ -picoline

Fig.1: $[\text{M}(\text{PIIH})_2\text{X}_2]$

Table 1: Analytical, colour, molar mass, magnetic susceptibility, conductivity measurement and decomposition temperature of ligand PIH and its metal complexes

| Compounds (Colour) | Molar mas | % Analysis found (calculated) | | | | μ_{eff} B.M | λ_{max} electronic cm ⁻¹ | Ω_m ohm ⁻¹ cm ² mol ⁻¹ | DT °C |
|---|-----------|-------------------------------|------------------|--------------------|------------------|---------------------------|---|--|----------|
| | | M | C | N | H | | | | |
| PIH | 249 | | | | | | | | |
| (Colourless) | | | 72.10 | 22.26 | 5.07 | | | | |
| [Co(PIH) ₂ (NH ₃) ₂] | 590.93 | 9.84 (9.97) | 72.28 (60.67) | (22.48) (18.73) | (5.22) (4.28) | 4.94 | 10300 16600 | 9.7 | 227 |
| (Brown) | | | (60.92) | (18.95) | (4.39) | | 23700 | | |
| [Co(PIH) ₂ (C ₆ H ₅) ₂] | 738.93 | 7.83 (7.97) | 48.43 (48.71) | 15.02 (15.15) | 3.35 (3.51) | 4.91 | 10600 16900 | 9.4 | 216 |
| (Dark brown) | | | (48.71) | (15.15) | (3.51) | | 23200 | | |
| [Co(PIH) ₂ (a-pic) ₂] | 742.93 | 7.86 (7.93) | 48.30 (48.56) | 15.00 (15.07) | 3.38 (3.49) | 4.97 | 10400 16700 | 9.3 | 232 |
| (Reddish brown) | | | (48.56) | (15.07) | (3.49) | | 24000 | | |
| [Co(PIH) ₂ (b-pic) ₂] | 742.93 | 7.80 (7.93) | 48.41 (48.56) | 14.96 (15.07) | 3.36 (3.49) | 5.01 | 10100 17400 | 9.8 | 216 |
| (Light brown) | | | (48.56) | (15.07) | (3.49) | | 23900 | | |
| [Co(PIH) ₂ (g-pic) ₂] | 742.93 | 7.85 (7.93) | 48.32 (48.56) | 14.92 (15.07) | 3.35 (3.49) | 5.03 | 10500 1770 | 9.1 | 230 |
| (Light brown) | | | (48.56) | (15.07) | (3.49) | | 238000 | | |
| [Ni(PIH) ₂ (NH ₃) ₂] | 590.71 | 9.80 (9.93) | 60.53 (60.94) | 18.79 (18.96) | 4.28 (4.40) | 3.16 | 12900 18700 | 10.3 | 214 |
| (Grey) | | | (60.94) | (18.96) | (4.40) | | 25400 | | |
| [Ni(PIH) ₂ (C ₆ H ₅) ₂] | 738.71 | 7.79 (7.94) | 48.45 (48.73) | 15.07 (15.16) | 3.40 (3.51) | 3.17 | 12800 18500 | 10.8 | 212 |
| (Deep grey) | | | (48.73) | (15.16) | (3.51) | | 25300 | | |
| [Ni(PIH) ₂ (a-pic) ₂] | 742.71 | 7.75 (7.90) | 48.26 (48.47) | 14.93 (15.07) | 3.39 (3.50) | 3.12 | 12600 18300 | 11.2 | 203 |
| (Deep grey) | | | (48.47) | (15.07) | (3.50) | | 25600 | | |
| [Ni(PIH) ₂ (b-pic) ₂] | 742.71 | 7.80 (7.90) | 48.30 (48.47) | 15.00 (15.07) | 3.38 (3.50) | 3.21 | 13200 19000 | 11.1 | 197 |
| (Deep grey) | | | (48.47) | (15.07) | (3.50) | | 25700 | | |
| [Ni(PIH) ₂ (g-pic) ₂] | 742.71 | 7.69 (7.90) | 48.37 (48.47) | 14.87 (15.07) | 3.39 (3.50) | 3.19 | 13000 19100 | 10.9 | 201 |
| (Deep grey) | | | (48.47) | (15.07) | (3.50) | | 25100 | | |
| [Cu(PIH) ₂ (NH ₃) ₂] | 595.54 | 10.52 (10.66) | 60.40 (60.44) | 18.61 (18.80) | 4.29 (4.36) | 1.85 | 15800 17900 | 7.8 | 240 |
| (Blue) | | | (60.44) | (18.80) | (4.36) | | 15900 17800 | 7.3 | 238 |
| [Cu(PIH) ₂ (C ₆ H ₅) ₂] | 743.54 | 18.42 (18.54) | 47.85 (48.41) | 14.84 (15.06) | 3.36 (3.49) | 1.81 | 15900 17800 | 7.3 | 238 |
| (Greenish blue) | | | (48.41) | (15.06) | (3.49) | | 16300 18300 | 8.4 | 236 |
| [Cu(PIH) ₂ (a-pic) ₂] | 747.54 | 8.39 (8.49) | 47.80 (48.15) | 14.99 (14.98) | 3.38 (3.47) | 1.83 | 16300 18300 | 8.4 | 236 |
| (Deep blue) | | | (48.15) | (14.98) | (3.47) | | 16100 18200 | 8.8 | 237 |
| [Cu(PIH) ₂ (b-pic) ₂] | 747.54 | 8.36 (8.49) | 47.93 (48.15) | 14.73 (14.98) | 3.30 (3.47) | 1.84 | 16100 18200 | 8.8 | 237 |
| (Deep blue) | | | (48.15) | (14.98) | (3.47) | | 16200 18100 | 7.9 | 222 |
| [Cu(PIH) ₂ (g-pic) ₂] | 747.54 | 8.30 (8.49) | 47.49 (48.15) | 14.69 (14.98) | 3.33 (3.47) | 1.85 | 16200 18100 | 7.9 | 222 |
| (Deep blue) | | | (48.15) | (14.98) | (3.47) | | | | |

DT = Decomposition Temperature

17700-16600, 24000-23200 cm^{-1} assignable to ${}^4\text{T}_{2g}$ $\leftarrow {}^4\text{T}_{1g}$ (F), ${}^4\text{A}_{2g}$ (F) $\leftarrow {}^4\text{T}_{1g}$ (F), ${}^4\text{T}_{1g}$ (P) $\leftarrow {}^4\text{T}_{1g}$ (F) respectively, suggesting octahedral^{30,31} geometry for the complexes. Octahedral geometry of Co(II) complexes is further supported^{32,34} by magnetic susceptibility values in the range 4.91-5.03 B.M. The Ni(II) complexes exhibit three bands in the regions 13200-12600, 19100-18300 and 25700-25100 cm^{-1} which are assigned to ${}^3\text{T}_{2g}$ (F) $\leftarrow {}^3\text{A}_{2g}$ (F), ${}^3\text{T}_{1g}$ (F)

$\leftarrow {}^3\text{A}_{2g}$ (F) and ${}^3\text{T}_{1g}$ (P) $\leftarrow {}^3\text{A}_{2g}$ (F) respectively. The electronic spectral data suggest an octahedral^{31,35,36} geometry for Ni(II) complexes, which is further supported^{32,33,37} by magnetic susceptibility values in the range 3.21-3.12 B.M. The electronic spectra of Cu(II) complexes exhibits two bands in the region, 16700-15900 and 18300-17800 cm^{-1} which are assigned to the transitions ${}^2\text{T}_{2g}$ (F) $\leftarrow {}^2\text{E}_g$ and charge transfer bands. The electronic spectral data

Table 2: Key IR spectral bands (cm^{-1}) of ligand PIIH and its metal complexes

| Compounds | $\nu_{\text{N-H}}$ | $\nu_{\text{C=N}}$ | $\nu_{\text{M-N}}$ |
|--|--------------------|--------------------|--------------------|
| PIIH | 3260 s,b | 1640 s,b | |
| [Co(PIIH) ₂ (NH ₃) ₂] | 3235 m,b | 1620 m,b | 440 m |
| [Co(PIIH) ₂ (C ₆ H ₅) ₂] | 3230 m,b | 1625 m,b | 435 m |
| [Co(PIIH) ₂ (α -pic) ₂] | 3230 m,b | 1615 m,b | 440 m |
| [Co(PIIH) ₂ (β -pic) ₂] | 3235 m,b | 1615 m,b | 430 m |
| [Co(PIIH) ₂ (γ -pic) ₂] | 3230 m,b | 1620 m,b | 440 m |
| [Ni(PIIH) ₂ (NH ₃) ₂] | 3230 m,b | 1610 m,b | 450 m |
| [Ni(PIIH) ₂ (C ₆ H ₅) ₂] | 3230 m,b | 1610 m,b | 450 m |
| [Ni(PIIH) ₂ (α -pic) ₂] | 3235 m,b | 1610 m,b | 460 m |
| [Ni(PIIH) ₂ (β -pic) ₂] | 3235 m,b | 1620 m,b | 460 m |
| [Ni(PIIH) ₂ (γ -pic) ₂] | 3230 m,b | 1620 m,b | 455 m |
| [Cu(PIIH) ₂ (NH ₃) ₂] | 3235 m,b | 1610 m,b | 425 m |
| [Cu(PIIH) ₂ (C ₆ H ₅) ₂] | 3230 m,b | 1610 m,b | 430 m |
| [Cu(PIIH) ₂ (α -pic) ₂] | 3235 m,b | 1610 m,b | 420 m |
| [Cu(PIIH) ₂ (β -pic) ₂] | 3230 m,b | 1615 m,b | 425 m |
| [Cu(PIIH) ₂ (γ -pic) ₂] | 3230 m,b | 1620 m,b | 430 m |

m = medium, s = strong, b = broad

indicates distorted octahedral^{31,38} geometry for Cu(II) complexes. The magnetic moment values of copper(II) complexes lie in the range 1.86-1.81 B.M.^{32,33,39}

Antifungal activity

The ligand PIIH and its complexes of Co(II), Ni(II) and Cu(II) complexes have been screened antifungal activity against *Aspergillus niger* and *Penicillium expansum* by disc diffusion technique⁴⁰ using DMF as solvent at concentration of 50 mg. It was observed that fungicidal effect of the complexes is more effective than free ligand. This is due to chelation which reduces the polarity of metal ion due to partial sharing of its positive charge with ligand⁴¹.

Molecular conductivity

Molar conductance data were recorded on systronics conductivity meter model 303 using DMF as a solvent. All the complexes were found to be non electrolytic⁴² in nature giving conductivity value in the range 6.3-11.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. The molar conductance value of the complexes also supported the assigned structure on the basis of elemental analyses, spectral data, magnetic susceptibility measurements.

CONCLUSION

Based on stoichiometries and spectrochemical studies it is proposed that PIIH behave as bidentate ligand and

coordination takes place through azomethine N, indoline N atom and N atoms of NH₃/ pyridine and different picolines. The structure of the complexes of Co(II), Ni(II) and Cu(II) are proposed octahedral in geometry as shown in Fig. 1.

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