

Studies on Coordination Behavior of Co (II) and Ni (II) Complexes of Pyrazolone

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ABSTRACT: Complexes of N-(3-Methyl-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene-N'-(4'-antipyrine)hydrazine (HATP) and N-(3-Methyl-1-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene)-N'-(4'-benzothiazole)hydrazine (HBTP) with Co(II) and Ni(II) metal ions have been prepared and characterized by their elemental analysis, molar conductance values, magnetic susceptibilities, UV, IR and NMR spectral studies. The chemical studies and spectral data indicate that the ligands are in hydrazone form. Complexes are six coordinated with O_h symmetry. These are paramagnetic. HATP behaves as neutral tetradentate ligand. Antibacterial activities of the synthesized complexes and ligands against gram (+)ive and gram (-)ive bacteria have also been studied.

KEYWORDS: Co(II), Ni(II), HATP, HBTP, UV, IR, NMR, Gram(+)ive, Gram(-)ive.

I. INTRODUCTION

Hydrazones of pyrazolone derivatives are of much interest due to their high chelating ability and applications in analytical chemistry.^{1,2} Also, Azo hydrazone tautomerism of aryl azo derivatives of β -dicarbonyls, naphthols and 2-pyrazolin-5-ones has provided controversy and interest both in the past.^{3,4} These have varied ligational behavior towards different metal ions and have created specific structural features in their metal complexes⁵.

In the present work we report the synthesis, characterization and antibacterial screening of metal complexes of Co(II) & Ni(II) with Pyrazolones i.e, HATP and HBTP. We are in process of synthesizing and study with other Lanthanide(III) ions also⁶.

II. EXPERIMENTAL

- Materials & Methods:** Thiosemicarbazide and 2-Aminobenzothiazole were purchased from Loba. 4-Aminoantipyrine were purchased from Fluka. All other chemicals, solvents and metal salts used were of AR Grade and were purchased from Hi-Media.
- Synthesis of HATP :** 3-Methyl-1-thiocarbamyl-2-pyrazolin-5-one (MTP) has been prepared by as in literature⁶. 4-Aminoantipyrine (10 gm, 0.05 mole) was diazotized and the diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of (0.05 mol 7.85 gm) MTP. This mixture was kept in an ice-bath for ~ 1 hr with occasional stirring.
Bright red crystals of HATP separated. It was filtered under suction, washed with ether and then recrystallized from ethanol. The purity of the compound was checked by TLC using silica gel plate and its elemental analysis. Its m.pt. was found to be 210⁰C.
- Synthesis of HBTP :** 0.05 mol., 10 gm of 2-Aminobenzothiazole was diazotized and diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of MTP (7.85gm, 0.05 mol). The mixture was kept in ice for ~40 minutes, fine yellowish brown crystals of HBTP separated out. It was filtered under suction washed

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Vol. 5, Issue 5, May 2016

with ether and then recrystallized from ethanol. The purity was checked by TLC and its elemental analysis. Its melting point was 195^oC.

4. **Synthesis of Complexes** :Complexes were prepared by refluxing aqueous ethanolic solution of metal salts (0.05 mol) and ligands (0.06 mol) in ethanol for one hour on a water thermostat. On cooling the solid complexes separated. These were filtered and washed with ethanol to remove excess ligand if any and then with benzene. It was now dried over P₄O₁₀.

Metal contents were estimated by usual procedure after digesting the complexes with conc. H₂SO₄. Chloride in the complex was estimated by *Volhards Method*⁷. Nitrogen content was determined using elemental analyser *Heraeus Carlo Erba-1108* at CDRI Lucknow.

Magnetic moments of the complexes were determined in *Gouy Balance Calibrated* using [HgCo(NCS)₄] at room temperature in *Inorganic Research Laboratory. P.G. Deptt. Of Chemistry, L.N.M.U Darbhanga*. Molar conductance of the complexes was measured by digital conductance meter systronics model 304.

Analytical data, decomposition, temperature conductance, color and μ_{eff} values are listed in Table-1.

IR spectra of the ligand and complexes were recorded on a *Perkin Elmer IR spectrometer* using *KBr Pellet method*.

¹H NMR spectra were recorded on JEOLGSX 400 NMR spectrometer from CDRI Lucknow.

Table-1: Color, Molar Conductance, Magnetic Susceptibility, Decomposition Temperature and Elemental Analysis of Metal Complexes.

Complex	Color	Molar Conductance (ohm ⁻¹ cm ² mol ⁻¹)	μ_{eff} . (BM.)	Decomposition temp.	Metal Content (%) Obs./Cal.
1. [Co(HATP)Cl ₂]	Grey	1.47	5.12	327	9.92/9.87
2. [Ni(HATP)Cl ₂]	Deep Green	2.18	4.43	324	9.78/9.71
3. [Co(HBTP)H ₂ O.Cl ₂]	Deep Grey	1.79	5.17	372	12.35/12.29
4. [Ni(HBTP)H ₂ O.Cl ₂]	Light Green	1.99	4.45	312	12.17/12.10

5. **Antibacterial Assay:** The bacterial activity of HATP and HBTP and their Co(II) & Ni(II) complexes were tested against gram (+)ive bacteria *Staphylococcus aureus* and gram (-)ive bacteria *Pseudomonas aeruginosa*, *E. Coli* and *Klebsiella pneumonia* by *Disc-Diffusion Method* using *Agar Nutrient* as medium and *Ofloxacin* as control⁸.

DMSO was used as solvent for making test solutions of all the compounds studied. The paper disc (6mm) containing the compound (100µg/disc) was placed on the surface of the nutrient agar plate previously spread with 0.1 ml of sterilised culture of micro-organism. These were incubated at 37^oC for two days. The diameter of inhibition zone around the paper disc was measured (Table-2).

Table-2: Antibacterial activities of the ligands & complexes (Zone formation in mm)

Compound	<i>Pseudomonas Aeruginosa</i>	<i>S. Aureus</i>	<i>E. Coli</i>	<i>Klebs.</i>
Control (<i>Ofloxacin</i>)	25	26	19	22
HATP	17	15	18
[Co(HATP)Cl ₂]	23	17	14	15
[Ni(HATP)Cl ₂]	24	22	16	18
HBTP	19	14
[Co(HBTP)Cl ₂]	22	18	21
[Ni(HBTP)H ₂ O]	23	24	19	25

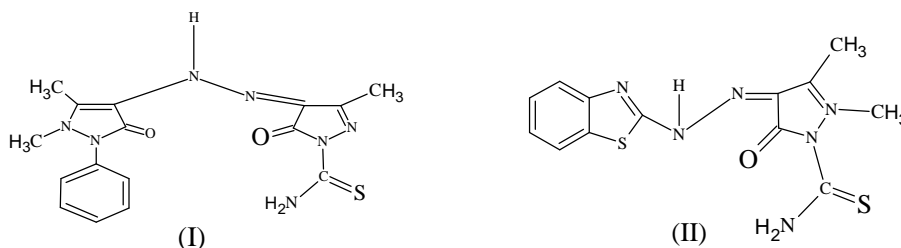
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III. RESULTS & DISCUSSION

The complexes are non-hygroscopic, almost colored and are soluble in DMSO & DMF. They decompose above 300^o C. The molar conductance values show their non-electrolytic nature. IR spectra of the ligands shows a band at 1665 cm⁻¹ assignable to $\nu_{C=O}$ of thiocarbamyl pyrazolone⁹. The band at 1640 cm⁻¹ in the spectra of HATP is due to $\nu_{C=O}$ of antipyrine¹⁰. The bands at 1627 & at 1572 cm⁻¹ can be due to C=N mode of HATP & HBTP respectively¹¹. A weak band at ~3100 cm⁻¹ can be assigned to stretching frequency of intramolecularly hydrogen bonded NH in HATP and the band at 3175cm⁻¹ in the spectrum of HBTP is due to NH of hydrazone part¹². The ν_{NH_2} & $\nu_{C=N}$ appeared at 3360 cm⁻¹ & 1160cm⁻¹ respectively¹³. The -N=C=S ring stretching frequency in HBTP is observed at 2020cm⁻¹. The ¹H NMR spectra of ligands are recorded in DMSO. δ^s and peaks are observed at 7.3-7.7 δ and 7-7.9 δ . These are assigned to aromatic C-H of the ligands HATP showed low field signal for the hydrazone proton at 13.5 δ .¹⁵ This low field shift is due to intramolecular hydrogen bonding. The hydrazone proton of HBTP appears at 8.4 δ . The signals at 2.3 δ -(6H), 2.5 δ (3H) and 3.1 δ (2H) may be due to two identical C-CH₃, N-CH₃ and NH₂ protons respectively. NMR & IR Spectra of ligands reveals that coupling of 4-Diazoantipyrine & 2-Diazobenzothiazole with 3-Methyl-1-thiocarbamyl-2-pyrazolin-5-one at its 4th position has resulted in the production of a hydrazone via rearrangement^{16,17} I & II.



In the IR spectra of HATP metal complexes we find a shift in the ν_{N-H} mode of NH₂ to 3300 from 3360cm⁻¹, it reveals the coordination of N-atom of NH₂. Also, stretching frequencies of C=O & C=N bonds are lowered by 40-60cm⁻¹. So, in addition of coordination via NH₂, both Carbonyl oxygen atoms and azomethine nitrogen atoms are coordinated to the metal ions. Thus HATP acts as tetradentate of N₂O₂ type ligands. Similar negative shift in the frequencies of $\nu_{C=O}$, $\nu_{C=N}$ & ν_{N-H} of NH₂ is found in the spectra of HBTP metal (II) complexes revealing the coordination through carbonyl oxygen, azomethine nitrogen & amino nitrogen atoms, so that HBTP acts as ONN donor ligand. The bands around 3300-3500cm⁻¹ & 800-830cm⁻¹, found in the HBTP metal(II) complexes indicate the presence of coordinated water molecule. Presence of coordinated water molecule is further confirmed by TG analysis¹⁹. The presence of additional non-ligands band in the spectra of the all metal complexes around 530-570cm⁻¹ and 440-390cm⁻¹ are assignable to M-N & M-O stretching frequencies²⁰. Thermal studies of the metal-complexes were carried under static air condition. The thermogram of HBTP metal(II) complexes indicate two clear cut stages, first corresponding to the dehydration of the coordinated water molecule and second to the decomposition process²¹.

IV. CONCLUSION

On the basis of above discussion Coordination no. Six for all the prepared complexes has been suggested. A comparison of the diameters of inhibition zone of compounds investigated shows that Ni(II) complexes exhibit higher antibacterial activity against *Pseudomonas* & *Klebsiella* than even the control ofloxacin at the same concentration and identical conditions. The complexes are more antibacterial than the respective ligands against all the bacteria studied.

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