

Asian Resonance

Studies on Coordination Compounds of Some Pyrazoline-5-One Derivative

Abstract

Some tridentate ligands were synthesized by the reaction of ethyl 2-phenylhydrazono-3-oxobutyrates and its derivative with isoniazid by the method reported in literature.

The hexacoordinated complexes of Cu(II) and Ni(II) ions with these ligands were synthesized, and characterised on the basis of their electronic, IR absorption properties and magnetic properties. The composition of the complexes were found as $[ML_2]$. The analysis shows that after mono deprotonation the ligand 1-isonicotinoyl-3-methyl-4-(phenylhydrazono)-2-pyrazoline-5-one (HL), their methyl derivative HL' and methoxy derivative HL'' behaved as tridentate N,N,O donor ligand.

The structural studies of metal complexes revealed that each metal ion is hexacoordinated. The electronic spectral band and IR spectral bands have been interpreted.

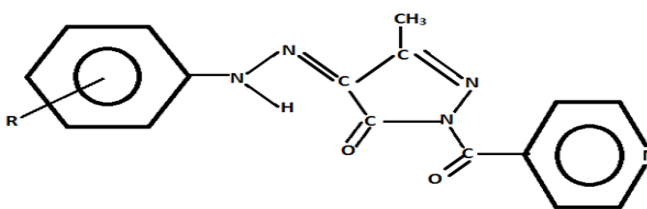
Keywords: Pyrazoline, Isoniazid, Coordination compounds, hydrazone.

Introduction

Diversely substituted pyrazolines and their derivatives embedded with variety of functional groups are important biological agents and significant amount of research activities have been directed towards such class of compounds. In particular they are used as antitumour¹, antibacterial², antifungal³, antiviral⁴, antiparasitic, antitubercular and insecticidal agents⁵. Some of these compounds have also been used as antiinflammatory⁶⁻⁹, antidiabetic, anaesthetic¹⁰⁻¹³ and analgesics.

Pyrazoline-5-one derivatives are biologically active compound¹⁴ and also finds application in photography¹⁵ and dyes¹⁶. Furthermore isoniazid is a well known drug and it is also well accepted that incorporation of hydrazono¹⁷ group enhances the biological activity of the heterocycles¹⁸.

Further It is an accepted result that metal ion incorporation usually enhances the biological activity of such molecule. In this paper we describe the synthesis, structural determination and coordination chemistry of ligands containing hydrazono group, isoniazid moiety alongwith pyrazoline unit. We have synthesized the ligand having formula (I) and characterized their Cu(II), Ni(II) complexes.



(I)

Where R = H (HL)

R = CH₃ (HL')

R = OCH₃ (HL'')

Experimental

All the chemicals used were of AR grade. Their purity has been examined by TLC and melting point. The infra red spectra of complexes were recorded in KBr pellet on Perkin Elmer 1000 FTIR spectrophotometer. Electronic spectra were recorded in the range 200-850nm on Perkin Elmer Lambda-15 UV VIS spectrophotometer. The Magnetic susceptibility of complexes were measured by Gouy method at room temperature.

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Preparation of Ligands

The ligands HL, HL' and HL'' were synthesized by adding the solution of ethyl-2-phenylhydrazono-3-oxobutyrates and its para substituted phenylhydrazono derivatives (0.002 mol) in 10-15 ml acetic acid into solution of isoniazid (0.002 mol) in 15-20 ml of acetic acid. The mixture was refluxed for 6 hours and allowed to stand overnight. Yellow crystals were obtained.

Preparation of Coordination Compounds

The hot solution of ligand (0.005 mol) and aq. solution of metal acetate/chloride were mixed and refluxed for two hours. The insoluble product was filtered out, washed with water, hot benzene and recrystallized from methanol.

Results and Discussion**Characterization of the ligands**

Elemental analysis of ligand shows that molecular formula of the ligands were C₁₆H₁₃N₅O₂(HL), C₁₇H₁₆N₅O₂(HL'), C₁₇H₁₆N₅O₃(HL''). Appearance of IR band at 1730 cm⁻¹ in all ligands indicated the presence of exocyclic >C=O group while appearance of band at about 1630 cm⁻¹ indicated the presence of conjugated >C=O group. In all the ligands an IR band is observed at 1520 cm⁻¹ which is assigned to C=N group. The presence of IR band at 3240 cm⁻¹ indicated N-H group in the ligand. The UV absorption bands at 245 nm and 395 nm are indicative of C=N group and N=N=C groups respectively. All these observations support the tentative structure (I) for ligands.

Characterization of Complexes

The results of elemental analysis of complexes corresponds to general formula [ML₂], where M= Cu and Ni. L= L, L', L''.

All complexes are found to be insoluble in water and common organic solvents like benzene, chloroform, alcohol, acetone, dimethylformamide etc., therefore their conductivity measurement could not be possible.

Magnetic Properties

The all copper complexes are paramagnetic with magnetic moment in the range of 1.8 – 2.0 (table -2). Although the magnetic moment at different temperature were not carried out, it is reasonable to conclude that the complexes were monomeric and in (+2) oxidation state.

Magnetic moment of all nickel complexes were in the range 3.12-3.14 BM. The Paramagnetic behavior of Nickel complexes were attributed to the (+2) oxidation state with distorted octahedral geometry.

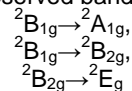
IR Spectral Studies

A close examination of table-3 reveals that an IR peak around 3240 cm⁻¹ was present in the ligands but on complexation with the metal ions this peak disappeared. It is inferred the coordination through phenylhydrazone nitrogen after deprotonation. This was further confirmed by the IR peak around 425±5 cm⁻¹ which was assigned for M-N bond in the complexes. It was also inferred that a

peak around 1730 cm⁻¹ in the ligand which was assigned for conjugated >C=O group disappears on complex formation with metal ions. This indicated the coordination of conjugated carbonyl group with metal. The presence of IR peak at around 455±5 cm⁻¹ confirmed presence of M-O bonds. The retention of >C=N band at 1520 cm⁻¹ in the complexes were suggestive of the fact that >C=N group remains unaffected during complex formation.

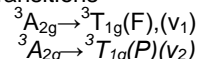
Electronic Spectral Studies

All complexes of copper (II) ion display three bands i.e. at 790 nm, 650 nm and 430 nm. These bands appeared to arise due to d-d transition. Copper (II) ions having d⁹ configuration exhibits Jahn Teller distortion and the observed bands were assigned as



The UV spectral bands of nickel complexes are broad and in the region 240 to 800 nm. A close examination of the table -4 indicate about the occurrence of two bands at 675 nm, 403 nm.

The electronic spectrum may be interpreted in terms of distorted octahedral geometry of donor atoms around metal ions and the bands were considered to arise due to the transitions



The ligand field parameters of the complexes were calculated on the basis of method provided by Lever¹⁹ at all and reported in table-5. The 10Dq values were in the range of 9174.83±165 cm⁻¹ and the complexes were found having approximately 20% covalent character. The v₂/v₁ value also supports the distorted octahedral geometry.

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Ligand	Formula of Ligand	Melting point	Color	Yield	N- analysis		IR- bands				UV-bands	
					observed	calculated	V _{N-H}	V _{C=O}		V _{N=C}		
								exocyclic	Conjugated			
HL	C ₁₆ H ₁₃ N ₅ O ₂	198°C	Yellow	70%	22.8%	22.2%	3240cm ⁻¹	1730cm ⁻¹	1640cm ⁻¹	1520cm ⁻¹	245nm	395nm
HL	C ₁₇ H ₁₆ N ₅ O ₂	201°C	Yellow	68%	21.7%	20.8%	3240cm ⁻¹	1730cm ⁻¹	1640cm ⁻¹	1522cm ⁻¹	245nm	395nm
HL	C ₁₇ H ₁₆ N ₅ O ₃	206°C	Yellow	67%	20.7%	19.9%	3245cm ⁻¹	1732cm ⁻¹	1645cm ⁻¹	1525cm ⁻¹	245nm	395nm

Table 1:- Physical constants, analytical data & Spectral bands of Ligands

Complexes	Magnetic moment	Melting Point	Percentage yield	Color	Metal-analysis		Nitrogen analysis	
					Observed	Calculated	Observed	Calculated
[CuL ₂]	1.83BM	228°C	65%	Dark green	9.3%	8.98%	20.6%	20.1%
[CuL' ₂]	1.80BM	230°C	66%	Dark green	9.1%	8.9%	20.2%	19.8%
[CuL'' ₂]	1.80BM	234°C	70%	Dark green	8.9%	8.7%	19.77%	19.5%
[NiL ₂]	3.12BM	224°C	60%	Purple	8.6%	8.3%	20.83%	20.1%
[NiL' ₂]	3.12BM	226°C	65%	Purple	8.4%	8.0%	20.3%	19.7%
[NiL'' ₂]	3.12BM	231°C	65%	Purple	8.2%	7.8%	19.9%	19.0%

Table -2:- Physical Constants, analytical data of Complexes.

Complexes	V _{C=N}	V _{M-O}	V _{M-N}	V _{C=O}
[CuL ₂]	1580cm ⁻¹	450cm ⁻¹	420cm ⁻¹	1650cm ⁻¹
[CuL' ₂]	1580cm ⁻¹	455cm ⁻¹	425cm ⁻¹	1650cm ⁻¹
[CuL'' ₂]	1580cm ⁻¹	460cm ⁻¹	430cm ⁻¹	1650cm ⁻¹
[NiL ₂]	1580cm ⁻¹			1650cm ⁻¹
[NiL' ₂]	1580cm ⁻¹			1650cm ⁻¹
[NiL'' ₂]	1580cm ⁻¹			1650cm ⁻¹

Table- 3:- IR-Spectral bands of Complexes.

Complexes	² B _{1g} → ² A _{1g}	² B _{1g} → ² B _{2g}	² B _{1g} → ² E _g	³ A _{2g} → ³ T _{1g} (F)	³ A _{2g} → ³ T _{1g} (P)
[CuL ₂]	790nm	650nm	430nm		
[CuL' ₂]	795nm	655nm	480nm		
[CuL'' ₂]	795nm	655nm	430nm		
[NiL ₂]				670nm	403nm

[NiL ₂]				675nm	390nm
[NiL' ₂]				676nm	420nm

Table - 4 Electronic Bands of Complexes.

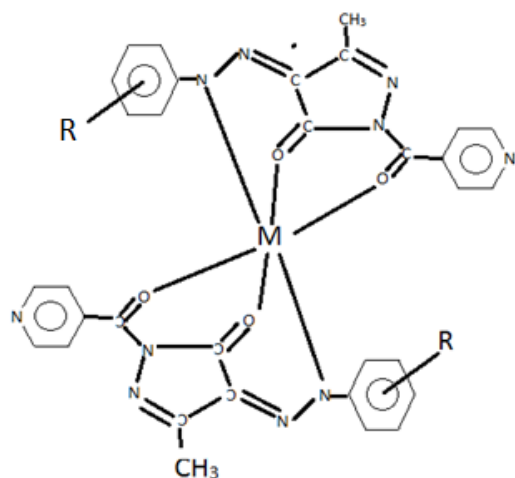
Name of complex	v ₃ /v ₂	10Dq /ln cm ⁻¹	B'	β	β ⁰ percentage	v ₂ /v ₁
[NiL ₂]	1.663	9193.3	806.4	0.76	24	1.62
[NiL' ₂]	1.731	8990.5	899.0	0.85	15	1.65
[NiL'' ₂]	1.609	9340.7	710.3	0.67	23	1.58

Table-5 Field parameter

Conclusion

On the basis of observations and results it is inferred that the ligand is coordinated through exocyclic >C=O and hydrazone nitrogen atom and the geometry of the complexes were distorted octahedral. The following tentative structures were proposed.

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Where R= H, CH₃, OCH₃
M = Cu and Ni

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