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Synthesis and spectral studies of transition metal complexes supported by NO-bidentate Schiff-Base ligand

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ABSTRACT

In present paper, transition metal complexes derived from 2-((3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl)methylene amino) phenol were synthesized. The general composition of the complexes is $[M(L)_2 \cdot nH_2O]$, where $M = Cu(II), Co(II), Ni(II)$, and $n=2$. The ligand acts as a bidentate ligand. The ligand was characterized by Mass, IR, ¹H-NMR and ¹³C-NMR spectral studies. Complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility, Mass, ¹H-NMR, IR, UV/visible, spectral techniques and TGA studies.

Keywords: Schiff base, Metal complexes, Pyrazole aldehyde, Spectral techniques.

INTRODUCTION

Schiff bases named after *Hugo Schiff* described the condensation between an aldehyde and an amine. Schiff base ligands are able to coordinate metals through imine nitrogen and another group usually linked to aldehyde. Schiff bases are an important class of ligands in coordination chemistry and find extensive application [1-2]. Schiff bases are straightforward to prepare thus being versatile [3]. Modern chemists still prepare Schiff bases. In present time active and well-designed Schiff base ligands are considered to be privileged ligands [4] due to their ability to form complexes with a wide range of transition metal ions. These complexes have played an important role in the development of coordination chemistry [5]. Schiff bases are considered to be very good chelating agents [6], specially when -OH functional group closed with azomethine group. In recent years, there has been enhanced interest in the synthesis and characterization of transition metal complexes containing Schiff bases as ligands due to their importance as catalysts in many reactions [7-12]. The chemistry of metal complexes including ordinary complexes, chelates and mixed ligand complexes has been extensively studied till date for their bioinorganic relevance as well as a wide range of physicochemical properties [13-14]. In this work, we report the results of our studies on the synthesis, spectral properties of Co(II), Ni(II) and Cu(II) complexes of Schiff base of Pyrazole aldehyde with 2-aminophenol.

MATERIALS AND METHODS

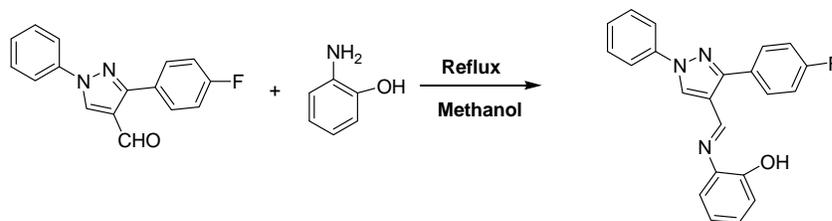
All the chemicals used were of AR grade. Cobalt (II), Nickel (II) and Copper (II) used as acetate salts were of Merck. Pyrazole aldehyde was synthesized by very well-known *Vilsmeier-Haack* [15] reaction and purified by usual separation methods.

Elemental analyses were carried out on EURO EA-3000 RS-232. IR spectra were recorded on 8400 FTIR Simadzu Spectrometer. ¹H-NMR spectra of the ligand and complexes in DMSO-d₆ were recorded on a Bruker Advance II 400 Spectrometer at room temperature using TMS as internal standard. UV-Visible spectra were recorded on

Shimadzu, Pharmaspec UV-1700, UV visible spectrometer. Mass spectra of ligands were recorded on GC-MS QP-2010 spectrometer, The ESI mass spectra of metal complexes were carried out using a micromass Q-ToF Micro spectrometer. Thermal analyses have been carried out by using Shimadzu (TGA-50H) from room temperature to 1000°C under heating rate of 15°Cmin⁻¹.

Synthesis of 2-((3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl) methylene amino) phenol

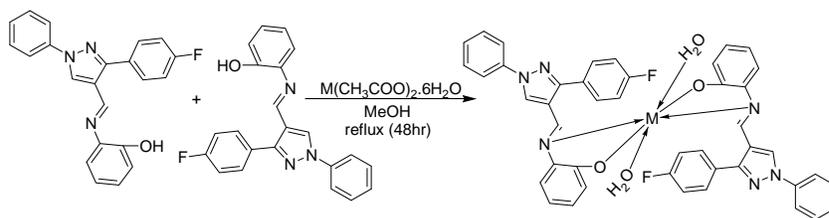
Schiff base was synthesized by using a synthetic approach. A methanolic solution of *o*-amino phenol (0.01M) was added to the solution of Pyrazol aldehyde (0.01 M, 30ml Methanol). The resulting reaction mixture was reflux for 8 hours. The progress of reaction was monitored by TLC (solvent system, benzene: acetone- 8:2). After completion of the reaction, the reaction mixture was poured into crushed ice. The separated solid product was filtered and washed with cold saturated sodium bisulphate solution and recrystallized with ethanol.



Scheme I: Synthesis of ligand

Synthesis of Cu (II), Ni (II) and Co (II) complexes

A solution of the metal (II) acetate (0.005 M) in minimum amount of ethanol was added to an ethanolic solution of the ligand (0.01M, 20 ml). The mixture was refluxed for 48 hr on a boiling water bath. The volume was reduced to half and precipitated complex washed with water then recrystallized from hot methanol and dried in vacuum.



M= Cu, Co, Ni

Scheme II: Synthesis of metal complexes

RESULTS AND DISCUSSION

Physical and spectral characterization of Schiff base 2-((3-(4-fluorophenyl)-1-phenyl-1H-pyrazol-4-yl) methylene amino) phenol

Colour: off white, Yield 85%, melting point 144°C, elemental analysis calculation for C₂₂H₁₆FN₃O Calculated; C, 74.36; H, 5.27; N, 11.56; O, 8.81; Found: C, 74.47; H, 5.20; N, 11.52; O, 8.21; Elemental analyses of the ligand reflected that the ligand has the molecular formula given.

¹H-NMR and ¹³C-NMR of ligand

¹H-NMR of ligand showed the exchangeable signals at 9.91 and 9.28 ppm for the protons of the phenolic OH and azomethine proton -CH=N. The signals at 9.21 ppm were attributed to the proton of pyrazole, a multiplet at 6.8-8.5 ppm showed the aromatic protons of Schiff base ligand. ¹³C-NMR of ligand showed the following signals: A signal appeared at 183 δ is attributed to azomethine carbon, F-CH₃ at 150 δ, Phenolic carbon at 151δ, phenyl rings of ligand showed the following signals, 115.37 δ, 115.48 δ, 115.58 δ, 118 δ, 118.62 δ, 119.32δ, 120.91δ, 126.91δ, 127.11 δ, 128.51 δ, 129.41 δ, 129.71 δ, 130.42 δ, 130.50 δ, 137.23 δ, 151.25 δ.

Characterization of metal complex

Metal complexes were characterized by ESI Mass, IR, UV/visible, TGA spectral techniques and magnetic susceptibility measurements. Physical characteristics of metal complexes mentioned in table I.

Table I. Physical characteristics and analytical data of the complexes

Compound	Formula	Colour	M.P/D.P (°C)	Yield (%)	Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
[Cu(L) ₂ .2H ₂ O]	C ₄₄ H ₃₄ CuF ₂ N ₆ O ₄	brown	344	70%	3.52
[Co(L) ₂ .2H ₂ O]	C ₄₄ H ₃₄ CoF ₂ N ₆ O ₄	Brick red	335	69%	3.45
[Ni(L) ₂ .2H ₂ O]	C ₄₄ H ₃₄ NiF ₂ N ₆ O ₄	Yellowish green	346	64%	4.24

Mass Spectra

The ESI mass spectra of the ligand and its metal complexes were used to compare their stoichiometric composition. The Ligand [L] showed a molecular ion peak [M⁺] at m/z 356. Which show the molecular wt. of ligand. The mass spectra of Cu (II) complex showed a molecular ion peak [M⁺] at m/z = 811 weight of the respective compound. Co (II) complex showed a peak at m/z = 808 which corresponds to [M+1] molecular ion peak. Weight of the respective compounds while that of Ni(II) complex shows m/z=809 which corresponds to [M+1] molecular ion peak. These peaks supported the structure of the complexes and confirmed the stoichiometry of metal chelates as ML₂ type.

Infrared spectra

The spectrum of ligand showed the characteristic ν (HC=N) at 1627cm⁻¹, ν (-OH) at 3356 cm⁻¹, ν (-C=C), ν (-C=N), ν (-N-N) of pyrazole at 1454, 1485, 1053cm⁻¹ respectively, aromatic ν (-C-H) and ν (-C=C) bands due to stretching at 3122 - 2895 cm⁻¹ and 1508-1502 cm⁻¹ respectively. ν (-C=N) bands at 1627 cm⁻¹, which were shifted to a lower frequency (10-60cm⁻¹) due to the coordination of the nitrogen atom of the azomethine group in the spectra of all the metal complexes (1564-1614 cm⁻¹) [16-17]. The sharp band due to ν (-OH) stretching vibration disappeared in complex formation. IR spectrum of all the complexes has a broad band in the region 3200-3453 cm⁻¹ were assigned to the ν (-OH) of water indicated the presence of lattice or coordinated water molecule [18], water content was also identified by thermal analyses. All complexes exhibit C-F stretching band in the region 1000-1100cm⁻¹. The low frequency region of the spectra revealed the presence of medium intensity bands in the region 455-569cm⁻¹ due to ν (M-O) and ν (M-N) vibrations [19]. All the IR data suggested that the metal was bonded to the Schiff bases through the phenolic oxygen and the imino nitrogen [20].

Table II: Selected IR frequencies of ligands and their metal complexes.

Compound	ν (H ₂ O)	ν (C=N)	ν (OH)	ν (C-F str.)	ν (M-N)	ν (M-O)
L(ligand)		1627	3356	1153	-	-
Cu(L) ₂	3410	1564	-	1030	516	488
Co(L) ₂	3439	1614	-	1105	592	455
Ni(L) ₂	3417	1581	-	968	569	478

Electronic absorption spectra

The UV-Visible spectra of the ligand and its complexes were recorded in DMF at room temperature. The electronic spectrum of ligand showed only one intense band at 292 nm, which was assigned to n→ π^* transition of the C=N chromophore. On complex formation this was shifted to higher wavelength, suggested the coordination of azomethine nitrogen. Selective electronic spectral bands of metal (II) complexes are given in table III. UV of copper complex (fig-1) showed two bands, one at 434 nm may exhibited the charge transfer band (L→M) and the other band at 728 nm assigned to ²E_g → ²T_{2g} which was characteristic of distorted octahedral geometry [21]. The cobalt (II) complex exhibited four bands having λ_{max} at 328, 368, 432 and 440 nm (fig-2). The band at 328 assigned to Charge transfer band and last three bands could be assigned for corresponding d-d transitions, which justified the octahedral geometry of Co complex. Ni (II) complex showed bands each at 380, 426, 444 and 734 nm (fig-3). the band at 380 showed Charge transfer band last three band assigned to ³A_{2g}(F) → ³T_{2g}(F), ³A_{2g}(F) → ³T_{1g}(F), ³A_{2g}(F) → ³T_{1g}(P) transitions respectively. This result suggested octahedral geometry of Ni complexes.

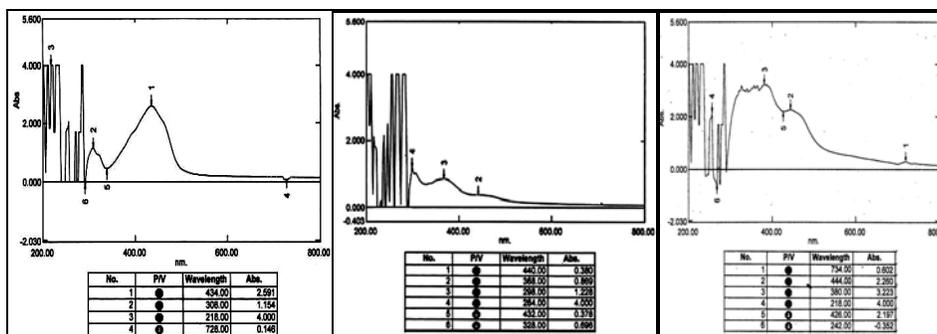


Fig-I

Fig-II

Fig-III

Table III: Electronic transition and magnetic moments of the complexes.

Complex	Spectral bands (nm)	Assignment	μ_{eff} (298K) (BM)
Cu(II)	728	${}^2E_g \rightarrow {}^2T_{2g}$	1.61
	434	Charge transfer	
Co(II)	440	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$	4.81
	432	${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$	
	368	${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$	
	328	Charge transfer	
Ni(II)	734	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$	2.8
	444	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$	
	426	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$	
	380	Charge transfer	

Magnetic susceptibility measurement

The most probable stereochemistry of the synthesized Cu(II), Ni(II) and Co(II) complexes was given by its magnetic moment. The effective magnetic moments of Cu (II), Co (II) and Ni (II) complex were measured in DMF solution at room temperature. The effective magnetic moment (μ_{eff}) of Cu (II) complex was seen 1.61 B.M. corresponding to one unpaired electron with a slight orbital contribution to the spin-only-value and the absence of spin-spin interactions. On the basis of electronic spectra and magnetic susceptibility measurements, a distorted octahedral geometry [22] around Cu (II) is suggested. The value of magnetic susceptibility (μ_{eff}) of Co (II) complex was 4.81 BM which suggested the high spin six-coordinated octahedral arrangement of ligand molecules around the metal ion [23-24]. The Ni (II) complex has effective magnetic moment (μ_{eff}) value of 2.8 BM indicating a spine free octahedral [25-26] configuration. These geometries were also supported by electronic transitions.

Table IV: Thermo analytical results of metal complexes

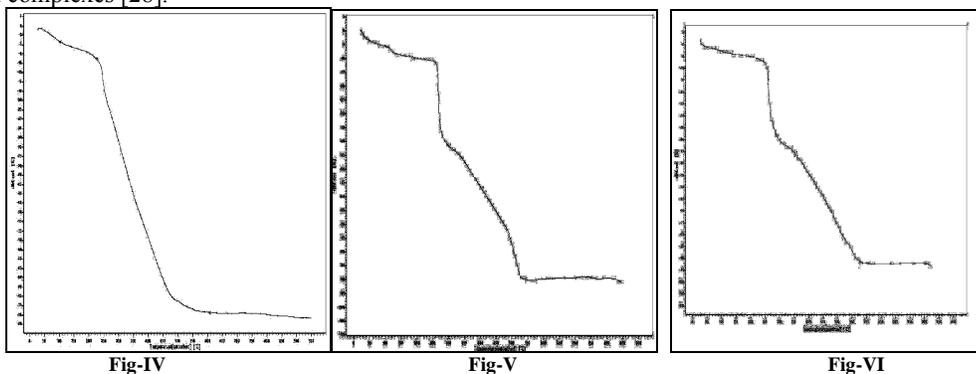
Complexes	Temperature of TGA (°C)	Weight loss (%)		Assignment
		Calc.	Found	
C ₄₄ H ₃₄ CuF ₂ N ₆ O ₄	101.7	4.4	4.2	Loss of two lattice water molecule.
	224.6	4.4	4.5	Loss of two coordinated H ₂ O molecule
	600	82.07	71.8	Material decomposition, forming of CuO
C ₄₄ H ₃₄ NiF ₂ N ₆ O ₄	80	4.4	4.9	Loss of two lattice water molecule.
	250	4.4	4.0	Loss of two coordinated water.
	280	30.1	29.55	Elimination of C ₁₆ H ₁₁ FN ₂ .
	550	52.71	50	Complete decomposition and formation of NiO
C ₄₄ H ₃₄ CoF ₂ N ₆ O ₄	250	4.46	5.1	Loss of two coordinated water molecule.
	340	42.13	39.9	Elimination of C ₂₂ H ₁₅ N ₃ F.
	585	44.11	47.5	Complete decomposition of material and formation of CoO.

Thermal analysis of metal complexes

Thermo gravimetric analysis (TGA), coupled with spectroscopic measurements could elucidate the structure of the compounds. The thermal behavior of complexes was summarized in table IV. TGA of metal complexes was performed in the range of 50-1000 °C under nitrogen.

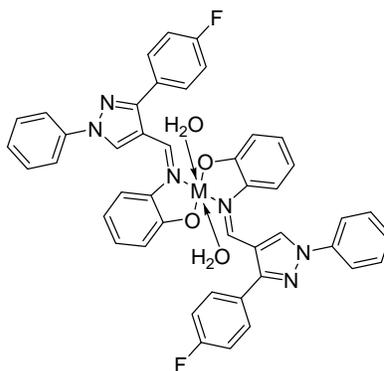
Thermogram of Cu- complex (fig-4) indicated the total weight loss of 79.9% up to 1000°C, which observed in three steps, (i) A small weight loss at 101.7°C was 4.2% (calculated value 4.4%) which is assigned to the loss of lattice water, (ii) weight loss in the range of 224.6-494.4°C was 4.5% (cal.4.4%) which corresponds to the loss of coordinated water.(iii) Maximum weight loss 71.8% (cal.82.07%) in the range of 494.5°C -800 °C corresponds to

complete decomposition of ligand moiety around the metal ion and the formation of metal oxide (CuO) [27]. Thermogram of Ni complex (fig-5) indicates total weight loss 90.6% up to 1000°C, which was observed in three steps (i) small weight loss 4.9% (calculated value 4.4%) at 80°C, which corresponds to loss of lattice water, (ii) weight loss in the range of 250-280°C was 4.0% (cal.4.4%) corresponds to the loss of coordinated water (iii) weight loss 29.55% (cal.30.1%) in the range of 250°C-280°C can be assigned to decomposition of one ligand (iv) weight loss 50% (cal.52.7%) in the range 280-550 corresponds to complete decomposition and formation of metal oxide. Thermogram of Co complex (fig-6) indicated the total 92.5% up to 1000°C, (i) weight loss 5.1% (cal.4.46%) in range of 200°C -250°C, which corresponds to coordinated water molecules (ii) weight loss in the range 250-340°C was 39.9% (42.13%) which can be assigned as decomposition of ligand (iii) weight loss 47.57% (cal.44.11%) in the range of 340°C -585°C showed the complete decomposition and formation of metal oxide. The thermo gravimetric analysis (TGA) provides authentic information regarding the presence of water molecules in the coordination sphere of the all complexes [28].



CONCLUSION

The complexes were coloured and the ratio of metal to ligand are 1:2 in all complexes. Conductance value indicates the non-electrolytic nature of complex [29]. TGA of metal complexes indicated the presence of two coordinated water molecule. The value of magnetic susceptibility, electronic spectral data and TGA analysis suggested a plausible octahedral structure around the metal ions as shown in the proposed structure.



Proposed structure metal (II) complexes

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