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Synthesis and spectral characterization of Co (II) and Ni (II) complexes of salicylidimine-(2-hydrazono)-benzimidazole

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Abstract : Metal complexes of Co (II) and Ni (II) with a novel Schiff base [{2-(2-(1*H*-benzimidazol-2-yl) hydrazinylidene) methyl} phenol] were synthesized successfully. The resulting complexes were characterized by elemental analysis, magnetic moment measurements, conductivity measurements, IR, UV-VIS, ^{1}H NMR and ^{13}C NMR spectral studies. According to these data, we propose distorted octahedral geometry to both the metal complexes. Hydrazonyl Schiff bases and their Cobalt and Nickel complexes have a variety of applications in biological, clinical and analytical fields.

(Keywords: Schiff base, salicylaldehyde, benzimidazole, hydrazine, transition metal complex)

Introduction

The chemistry of the transition metal complexes of Schiff-base ligands has played an important role in the development of coordination chemistry as a whole[1]. The field of Schiff base metal complexes is fast developing on account of the wide varity of possible structurs, and they have been studied extensively because of their fascinating physiochemical properties and for their numerous applications in different scientific areas[2, 3]. The Schiff bases are more effective as chelating agents when they have supporting and stabilizing moiety like –OH in the vicinity of >C=N group. Metal complexes with Schiff base ligands have been studied for their application in biological, clinical, analytical and pharmacological areas[4]. Chelating ligands containing N, N, and O donor atoms show broad biological activity and are of special interest because of the ways in which they are bonded to the metal ions[5]. It was seen that the biological activity of Schiff bases increase upon complexation with metal ions[6]. Recently there has been a considerable interest in the coordination chemistry of transition metals especially, Cobalt and Nickel with O and N donor hydrazone ligands because of their potential biological and pharmacological applications[7].

Heterocyclic benzimidazoles, their derivatives and their transition metal complexes have received considerable attention in coordination chemistry because it was found that such complexes showed larger biological activities than the free ligands[8].

The ligands bearing both hard and soft donors receive much attention because of their versatility in coordination along with remarkable catalytic and biological applications. Salicylaldehyde is converted to chelating ligands by condensation with amines, generally known as salicylaldimine. Such systems have also contributed in the progress of chemistry of co-ordination complexes of transition metal ions. The steric factors and electronic properties of salicylaldimine Schiff bases can be easily tuned by altering the salicylaldehyde substrates[9]. In this paper efforts were taken for the synthesis and characterization of transition metal complexes of the tridentate ligand which coordinates through two nitrogen of the hydrazone moiety and the oxygen of salicylaldehyde ring.

2. Experimental

All the chemicals used in the present investigation were of analytical grade and used without further purification**.** 2-marcepto benzimidazole, salicylaldehyde, DMF and DMSO was of Sigma Aldrich chemicals. Nickel acetate and Cobalt acetate were of E merck chemicals.

2.1 Material and Methods

The percentage compositions of C, H and N of complexes were determined by using micro analytical methods of Thermo finning FLASH EA 1112 series elemental analyzer. The elemental analysis of cobalt and nickel were carried by following standard gravimetric methods. Infrared spectra of ligands and their complexes were recorded on Bruker 3000 Hyperion spectrometer in KBr pellets in the range of (4000-450 cm^{-1}). The UV-Visible spectra were recorded on a Schimadzu UV spectrometer in the wavelength range 200-1100 nm, at SAIF, IIT Bombay. The ^1H NMR spectra was recorded on Bruker Av-III HD 400 MHz spectrometer by employing TMS as internal standard. Melting points of the ligand and decomposition temperature of complexes were determined on Polmon instrument (model No.MP-96). The Molar conductance measurements were carried out in DMF (10^{-3} M) using Digisun Electronic Digital conductivity meter of model: DI-909. The Magnetic susceptibilities of complexes were determined on Gouy's balance model 7550 at 23°C.

2.2 Synthesis

2.2.1 Synthesis of 2-hydrazinyl-1H-benzimidazole

2-hydrazinobenzimidazole synthesized from 2-mercaptobenzimidazole and hydrazine hydrate. 2- Mercaptobenzimidazole (0.01 mol) was suspended in hydrazine hydrate (0.02 mol) in R.B. flask and was heated in an oil bath at 120°C, till removal of H_2S is complete (tested with lead acetate paper). The white crystalline solid thus obtained was filtered and washed with water and recrystallized from 50% ethanol in 75% yield, m. p. above 300°C[10].

2.2.2 Synthesis of Schiff base salicylidimine-(2-hydrazono)-benzimidazole (HL) (SHBI)

To a warm ethanolic solution of 2-hydrazinobenzimidazole (0.01 mol in 20 mL) an ethanolic solution of salicylaldehyde (0.01 mol in 20 mL) was added and the mixture was refluxed for about 4 hours on a water bath, when brown colored precipitate was obtained. It was filtered, washed and recrystallized from ethanol.

Structure of the Schiff base is shown below

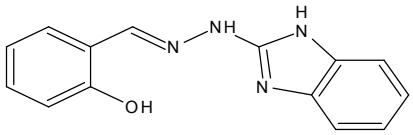

Fig 1: [{2-(2-(1*H*-benzimidazol-2-yl) hydrazinylidene) methyl} phenol] (SHBI)

2.2.3 Synthesis of metal complexes

To the hot ethanolic solution of ligand HL (0.86 mmol) the hot ethanolic solution of acetates of Co (II) (0.43 mmol) or Ni (II) (0.43 mmol) was added drop wise and the resulting mixture was refluxed for 2–4 h, kept reaction in basic condition. The solid product obtained was separated, washed thoroughly with ethanol and dried in vacuum. The colored complexes were filtered and washed with warm water, aqueous ethanol and finally with acetone. The purity of the complexes was checked by TLC.

3. Results and Discussion

3.1 Physical properties

All the complexes are stable at room temperature and are non-hygroscopic. On heating, they decompose at high temperatures. The complexes are insoluble in water but are soluble in DMSO. The molar conductance of metal complexes was measured using 10^{-3}M DMF as solvent. The molar conductance Co (II) complex showed values 2.8 $\Omega^{-1}cm^{-2}mol^{-1}$ while Ni (II) complex exhibit 10.8 $\Omega^{-1}cm^{2}mol^{-1}$. These values suggest that both the complexes are non-electrolytes[11, 12].

3.2 Elemental analysis

The elemental analysis data (Table-1) revealed that the stoichiometry of the Co (II) and Ni (II) complexes is 1:2 (metal: ligand). The composition assigned to the ligand and its complexes may, therefore be formulated.

Table - 1
Physical characterization, molar conductance, magnetic moment data of the Schiff's base and its complexes

Compounds	Mol. Wt.	μ_{eff} (BM)	Λ_M	Elemental analysis (%) Found(Calc.)			
				C	H	N	M
Ligand(BHMP) $[C_{14}H_{12}N_4O]$	252	-	-	66.63 (66.67)	4.75 (4.76)	22.18 (22.20)	–
Co-SHBI $[CoC_{28}H_{22}N_8O_2]$	560.93	4.58	2.8	59.61 (59.90)	3.81 (3.92)	19.83 (19.97)	10.50 (10.51)
Ni-SHBI $[NiC_{28}H_{22}N_8O_2]$	560.69	3.09	10.8	59.80 (59.93)	3.87 (3.92)	19.83 (19.98)	10.33 (10.47)

3.3 NMR spectra of Schiff's base

The ligand SHBI shows a singlet at 11.92 ppm due to phenolic OH. The sharp singlet at 8.81 attributed to azomethine proton (-CH=N-) confirms the formation of the ligand as proposed. The signals obtained at 6.9-7.66 ppm are due to protons of aromatic rings.

^{1}H NMR (DMSO-d_6): δ (ppm) 11.92 (b, 1H, OH), 8.81 (s, 1H, -CH=N), 6.9-7.42 (m, 4H), 7.66 (d, 1H, aromatic), 7.01 (m, 3H, aromatic), 9.76 (b, 1H, -NH imidazole), 6.35 (s, 1H, -NH)

^{13}C NMR (DMSO-d_6)**:** δ (ppm) 113.2, 122.5, 119.2, 116.6, 154.7, 122.5, 145.2, 158.1, 131.8, 136.1, 131.6, 113.8, 117.2, 136.8.

3.4 Infrared spectra of the Schiff base and its complexes

In order to study the bonding mode of Schiff base to the metal complexes, the IR spectrum of the free ligand was compared with the spectra of the complexes. The main IR bands and their assignments are given below:

HL^a- IR (ν_{max} /cm^{-1}): 3375 (νO-H—N) Phenolic (bonded), 2830 & 2745 (νC-H str (CHO)), 1622 (νC=N Azomethine group), 1553 (νC=N (imidazole)) 1350 (νC-N (cyclic)), 1260 (νC-O Phenolic), 3081 (νAr C-H stretching), 1590 (ν Ar-C=C stretching), 3290 (N-H stretching).

Co-SHBI - IR (ν_{max} /cm^{-1}): 2849 & 2725 (νC-H str (CHO)), 1610 (νC=N Azomethine group), 1525 (ν C=N (imidazole)) 1349 (νC-N (cyclic)), 1293 (ν C-O Phenolic), 3060 (νAr C-H stretching), 1587 (ν Ar-C=C stretching), 3289 (N-H stretching), 636 (ν Co-O stretching), 550 (νCo-N stretching).

Ni-SHBI- IR (ν_{max} /cm^{-1}): 28556 & 2722 (ν C-H str (CHO)), 1606 (ν C=N Azomethine group), 1512 (ν C=N (imidazole)) 1352 (ν C-N (cyclic)), 1288 (ν C-O Phenolic), 3051 (νAr C-H stretching), 1589 (ν Ar- C=C stretching), 3388 (N-H stretching), 646 (ν Ni-O stretching), 555 (ν Ni-N stretching).

➢ The formation of the Schiff base is confirmed by the presence of a band at 1626cm^{-1} due to νC = N stretching vibration[13], a down field absorption in complexes at 1610 and 1606 cm^{-1} respectively, indicating coordination through N-atom of azomethine group[14]. This is further supported by the appearance of medium intensity

band at 550-555 cm^{-1} which is assigned to ν (M-N) vibration.

➢ The observed decrease in the position of C=N (imidazole) band may be due to chelation of ring-N to the M (II) ion. This fact is further supported by the appearance of medium intensity band at 550-555 cm^{-1}, assigned to (νM-N) vibration.

➢ Schiff bases give a broad weak band near 3375 cm^{-1} assigned due to ν (O-H…..N) vibration were not observed in the spectra corresponding M (II) complexes. This indicates the deprotonation of phenolic –OH and subsequent bonding of its oxygen with M (II) during complex formation[15].

➢ The upward shift of C-O frequency in M (II) complex than the corresponding free ligand 1260 cm^{-1} suggest the bonding of phenolic oxygen with M (II) during complexation, which is further supported by a new band around 636-646 cm^{-1} due to ν(M-O)[16,17].

3.5 Magnetic moments & electronic spectral data

The electronic spectral studies of the metal complexes of Co (II) and Ni (II) with Schiff bases were carried out in DMSO solution. The Co (II) ion in complex has d^7 configuration. In octahedral field, the ground state $^4T_{1g}$ is three-fold orbitally degenerate state and causes an orbital contribution to the magnetic moment data of Co (II) complexes indicate the presence of three unpaired electrons was found to be 4.58, which is in the expected range (4.3–5.2 BM) of octahedral complexes. The absorption spectrum of the Co(II) complex exhibit two bands at 9965 and 22, 105 cm^{-1} which are attributed to $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)$ (ν_1) and $^4T_{1g}(P)\rightarrow{}^4T_{1g}(F)$ (ν_3) transitions respectively, that are characteristic of octahedral configuration[18]. Along with these transitions the spectra also has two shoulders at 1700 and 21045 cm^{-1}. The shoulder appearing at 21,045 cm^{-1} may be due to $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$ (ν_2) transition. Further known that the shoulder occurring near 17,000 cm^{-1} is not due to ν_2 transition but is due to spin for bidden $^4T_{1g}(F)\rightarrow T_{2g}(G)$ transition[19].

Ni(II) complex exhibits 3 electronic spectral bands at 9680, 16580 and 23970 cm^{-1} can be assigned to $^3A_{2g}\rightarrow{}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (ν_2) and $^3T_{2g}\rightarrow{}^3T_{1g}(P)$ (ν_3). The Ni (II) complex has magnetic moment 3.09 BM, which is in the usual range of reported octahedral complexes[20].

Table - 2 Ligand field parameters of complexes

Complex	Dq (cm^{-1})	B (cm^{-1})	β	υ_2/υ_1
Co-SHBI	1125.7	895	0.92	2.13
Ni-SHBI	968	767	0.74	1.71

The ligand field parameters (Dq, B, β) have also been calculated using standard methods. The value of Racah parameter (B) was less than respective free ion values, indicating the orbital overlap and delocalization of d-electron on the ligand. The nephelauxetic ratio (β) was found to be less than one, which reveals the partial covalent nature of metal ligand bonds. All the parameters for Co (II) and Ni (II) complexes are in good agreement with the distorted octahedral geometry [21].

4. Conclusion

The SHBI ligand and its Co (II) and Ni (II) complexes have been structurally characterized. The analytical data show that the metal ligand stoichiometry in both the complexes is 1:2. Both the complexes are non-electrolytes in DMF. The magnetic and spectral data show that the ligand is tridentate which coordinated through the nitrogen of the azomethine group, imidazole ring of benzimidazole and phenolic oxygen, forming a distorted octahedral chelate ring structure. Based upon magneto-chemical studies and electronic spectral data, it can safely be concluded that Co (II) and Ni (II) ions in the present complex exist in the distorted octahedral environment.

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