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Cu(II), Cd(II) and Ni(II) Complexes of 5-Bromosalicylaldehyde-4-hydroxybenzhydrazone: Synthesis and Spectral Studies

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Abstract

Four complexes of 5-bromosalicylaldehyde-4-hydroxybenzhydrazone were synthesized and characterized by elemental analyses, electronic, and infrared spectra. In all complexes, hydrazone exists either in the neutral form, deprotonated monoanionic form or in dideprononated dianionic form. Structures were assigned to all the complexes based on the physico-chemical studies.

Keywords: 5-Bromosalicylaldehyde-4-hydroxybenzhydrazone, Coordination Chemistry, Aroylhydrazone, Ligand

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1. Introduction

Aroylhydrazones are a group of compounds having –C=N- linkage. They are important in coordination chemistry because of their simple synthetic strategy, easily tunable steric, electronic properties and denticity. They can act as a neutral or monoanionic bidentate or tridentate ligand depending on the substituents and the reaction conditions.

The coordination chemistry and biochemistry of aroylhydrazones have attracted increasing interest due to their chelating ability and their pharmacological applications.[1] The pharmacological activity is found to be more in the case of metal complexes when compared to the free ligand and some side effects may decrease upon complexation.[2] The metal complexes have been extensively used as biological probes [3], DNA cleaving agents [4], catalysts [5,6], sensing materials [7,8] and corrosion inhibitors.[9] The biological activity of these complexes has been found to be highly dependent on the coordination behavior of metal ions and the binding sites on the ligands.[10]

In the present paper we report the synthesis and characterization of a new aroylhydrazone ligand from 5-bromosalicylaldehyde and 4-hydroxybenzhydrazide and also the chelating behavior of this ligand towards different transition metals such as copper, nickel and cadmium.

2. Experimental

All details about the synthesis of Cu(II), Cd(II) and Ni(II) complexes of 5-bromosalicylaldehyde-4-hydroxybenzhydrazone are given below.

2.1 Materials and Techniques

The solvents methanol, dimethylsulfoxide etc. were purchased from Merck. For the synthesis, the reactants, 4-hydroxybenzhydrazide, 5-bromosalicylaldehyde, glacial acetic acid, copper(II) sulfate pentahydrate, nickel(II) acetate tetrahydrate, cadmium(II) acetate dihydrate etc. were procured from Sigma

Aldrich Ltd. The carbon, hydrogen and nitrogen analysis were carried out using Vario EL III elemental analyzer. The IR absorption spectra were performed with a JASCO FT-IR-5300 spectrometer in the 4000 – 400 cm^{-1} region by making their KBr discs. The electronic spectra were taken on a spectro UV-Visible double beam UVD-3500 spectrometer in the 200 – 900 nm range.

2.2 Synthesis of 5-bromosalicylaldehyde-4-hydroxybenzhydrazone (H_2L)

The hydrazone is synthesized by adapting the reported procedure in [11] and [12].

The ligand (H_2L) was prepared by the condenzation of 5-bromosalicylaldehyde and 4-hydroxybenzhydrazide in acid medium (Scheme 1). A methanolic solution (20 ml) of 5-bromosalicylaldehyde (0.201 g, 1 mmol) was added to a solution of 4-hydroxybenzhydrazide (0.152 g, 1 mmol) in 20 ml methanol and reaction mixture was refluxed for 1 hour after adding 2 drops of glacial acetic acid. On cooling yellow crystals were separated and dried. The yield is 74 %.

Scheme 1 Synthesis of ligand (H_2L)

2.3 Syntheses of Complexes

2.3.1. Syntheses of $[CuL]_2 \cdot DMSO \cdot H_2O$, $[Ni(HL)_2] \cdot DMSO \cdot CH_3OH$ and $[CdL]_2$

All the three complexes are synthesized by the general procedure in which methanolic solution of copper(II) sulfate pentahydrate (0.124 g, 0.5 mmol) / nickel(II) acetate tetrahydrate (0.124 g, 0.05 mmol) / cadmium(II) acetate dehydrate (0.133 g, 0.5 mmol) were added to a stirred solution of H_2L (0.156 g, in 0.5 mmol) in methanol. Resultant solution was refluxed for 2 hours. The precipitates obtained were filtered washed and recrystallized from DMSO and acetonitrile mixture.

2.3.2. Synthesis of $[Cu_3(H_2L)_3(\mu\text{-}NCS)_2\text{-}(\mu\text{-}SO_4)_2] \cdot 3DMSO \cdot H_2O$

Aqueous solution of copper(II) sulfate pentahydrate (0.124 g, 0.5 mmol) was added to a stirred mixture of H_2L (0.156 g, 0.5 mmol) and potassium thiocyanate (1 ml) in methanol. Resultant solution was refluxed for 2 hours. The sandal coloured product obtained was filtered, washed and recrystallized from DMSO and acetonitrile mixture.

3. Results and Discussion

3.1 Elemental Analysis

The elemental analysis values showed that the found and calculated values are in close agreement with the proposed formula of the complexes. We denote $[CuL]_2 \cdot DMSO \cdot H_2O$, $[Ni(HL)_2] \cdot DMSO \cdot CH_3OH$, $[CdL]_2$ and $[Cu(H_2L)_3(\mu\text{-}NCS)_2\text{-}(\mu\text{-}SO_4)_2] \cdot 3DMSO \cdot H_2O$ as C1, C2, C3 and C4, respectively. The elemental analysis data are given in Table 1.

Compound	**Colour (Yield)**	Λ_M	**Found %**			**Calculated %**			**Proposed Geometry**
			C	H	N	C	H	N	
H_2L	Yellow (74%)		49.87	3.52	8.20	50.17	3.31	8.36	
C1	Dark green (46%)	26	39.23	2.59	6.19	39.04	2.57	6.50	Square Planar
C2	Brown (44%)	15	43.46	3.43	6.74	43.05	3.24	7.25	Octahedral
C3	Yellowish brown (53%)	11	38.14	2.50	6.70	37.74	2.04	6.29	Square Planar
C4	Green (55%)	23	31.11	1.87	6.44	31.60	2.47	6.70	Octahedral

Table 1 Colour, conductivity, elemental analysis and proposed geometry of complexes

3.2 Electronic Spectrum Analysis

The significant absorption bands in the electronic spectra of aroylhydrazone and its complexes recorded in DMF are presented in Table 2. Bands in the wavelength region 280–340 nm are attributed to π→π* and n→π* transition (Figure 1)

In the electronic spectra of copper(II) complexes **C1** and **C4**, intraligand bands in the range 280-330 nm assigned to n→π* and π→π* transitions of the aroylhydrazone moiety are present (Figure 2). It is observed that n→π* and π→π* transitions of hydrazones suffered a marginal shift up on complexation. The shift of the bands due to intraligand transitions is the result of the weakening of the C=N bond and extension of conjugation upon complexation. The charge transfer bands are observed as intense bands in the 400-410 nm region and the broadness of these bands is due to the combination of O →Cu and N →Cu LMCT transitions [13]. The visible spectra of the complexes were recorded in DMF and exhibit d-d bands in the wavelength 630 nm in case of complex **C1** and in case of complex **C4** the d-d transition is observed at 690 nm. This may due to change of environment of metal atom due to coordination.

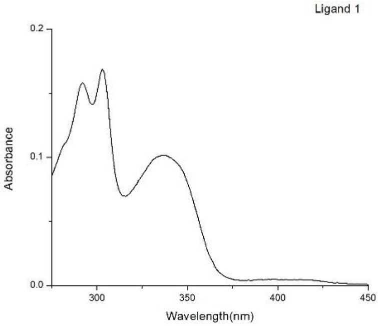

Figure 1 Electronic spectrum of H_2L

In complex **C2** electronic spectra give insight into the coordination geometry of nickel(II) ion. The bands 276 and 290 nm, 303, 320 and 333 nm correspond to π→π* and n→π* transitions. It shows an observable shift in the intraligand transitions. The charge transfer bands are observed as intense bands in the 400-420 nm region (Fig. 3). The d-d bands are masked by strong charge transfer absorption.

Complex **C3** shows n→π* and π→π* transitions at 278, 289, 300, 320 and 332 nm wavelength. The cadmium complex shows its charge transfer band spectra at 400-420 nm (Figure 3). Due to d^{10} configuration of cadmium(II) ions no appreciable absorptions are observed in the visible region.

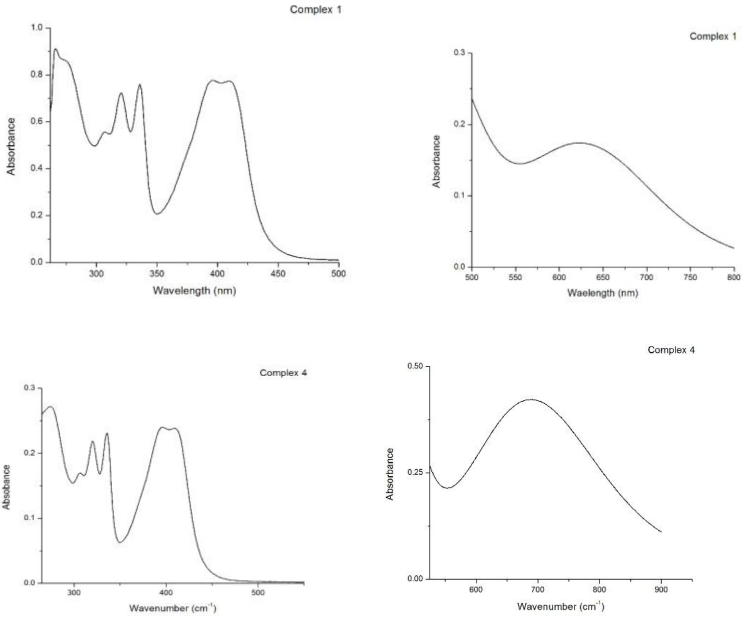

Figure 2 Electronic spectra of complex **C1** and **C4**

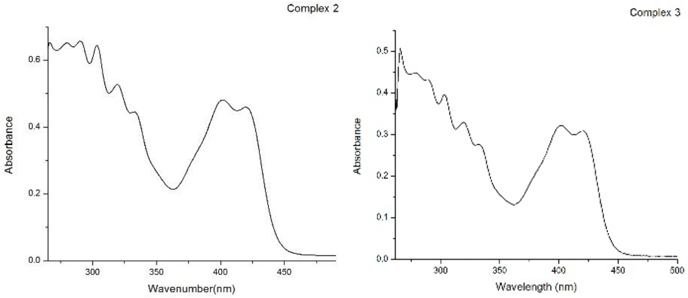

Figure 3 Electronic spectra of complexes **C2** and **C3**

Electronic spectra of all the complexes (**C1-C4**) (combined) are shown in Figure 4.

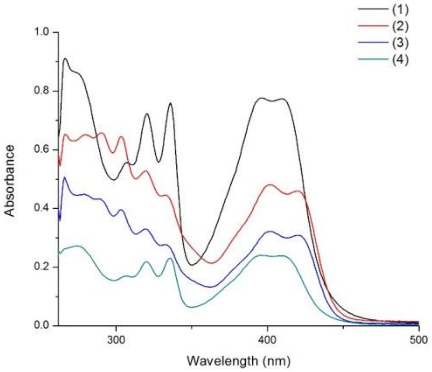

Figure 4 Combined electronic spectra of all the complexes

Compound	π→π*	n→π*	CT	d-d
H_2L	280	290, 340		
C1	276	310, 320, 335	390, 410	620
C2	279, 290	303, 320,333	402, 419	-
C3	278, 289	300, 320, 332	401, 420	-
C4	274	305, 320, 335	393, 410	690

Table 2 Electronic spectral assignments for ligand and complexes

3.3 Infrared Spectral Analysis

Infrared spectra of the aroylhydrazone is recorded on a JASCO FT-IR-5300 spectrometer in the 4000-400 cm^{-1} range using KBr pellets. The significant bands observed in the IR spectra of the aroylhydrazone along with their relative assignments are presented in the Table 3. FT-IR spectral data of the compounds are in accordance with their molecular structure. In the IR spectra of aroylhydrazone, v(C=N) band is observed at 1612 cm^{-1} indicates the condenzation of hydrazide and the aldehyde/ketone moiety and it is in agreement with the literature reports of aroylhydrazone.[14,15] In the IR spectrum of H_2L, the v(C=O) stretching vibration is observed at 1658 cm^{-1} suggesting that the hydrazone exists in the amido form in the solid state. This is further supported by the medium band in 3241 cm^{-1} due to v(O-H) vibration.

The spectrum of the proligand showed v(C=N) band at 1612 cm^{-1} region which is shifted to lower frequencies in the spectra of the complexes (1495-1611 cm^{-1}) indicating the involvement of azomethine nitrogen in coordination to the metal ion. The v(C=O) band present in the IR spectrum of hydrazone is absent in complexes **C1** and **C3** but a new band appears in the 1237-1283 cm^{-1} region due to v(C–O) stretching vibration, indicating that the deprotonated ligand is in the iminol form in the complexes. In the case of free hydrazone a broad band at 3241 cm^{-1} is due to the stretching mode of phenolic O–H group.

Compound	v(C=N)	v(C=N)^a	v(C=O)/v(C–O)	v(N–N)	v(O-H)	v(N-H)
H_2L	1612	---	1658	1177	3241	---
C1	1606	1533	1237	1168	---	---
C2	1557	1567	1599	1170	---	3358
C3	1611	1559	1283	1176	---	---
C4	1485	1386	1598	1198	3195	3403

^{a} - newly formed C=N

Table 3: Infrared spectral assignments of ligand and complexes

This band is found to be absent in all the complexes except complex **C4**, indicating deprotonation of phenolic –OH and its coordination to the central metal ion. In complex **C1**, a broad band at 3397 cm^{-1} is due to the presence of lattice water. The v(N-N) bands of complexes have appeared in the region 1168-1198 cm $^{-1}$.

In complexes **C2** and **C4**, the v(C=O) at 1599 and 1598 cm^{-1} and v(N–H) at 3358 and 3403 cm^{-1} indicate that the ligand exists in amido-form. In complex **C2**, a broad band at 3358 cm^{-1} is due to the presence of methanol in lattice.

4. Conclusion

The ligand 5-bromosalicylaldehyde-4-hydroxybenzhydrazide was prepared by the condensation reaction in acidic medium. They generally exist in the amido form in the solid state and in solution, they tend to exist as an equilibrium mixture of amido and iminol forms. The synthesized complexes are studied by different analytical techniques.

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