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Synthesis and Characterization of Transition Metal Complexes of 2-Benzoylpyridine benzoylhydrazone

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Abstract

Cobalt(II), zinc(II) and mercury(II) complexes have been synthesized by the reaction of cobalt chloride, zinc chloride, zinc bromide and mercuric chloride with 2-benzoylpyridine benzoylhydrazone and characterized by analytical and spectral studies.

Keywords: Co^{II} complexes; Zn^{II} complexes; Hg^{II} complexes; 2-benzoylpyridine benzoylhydrazone.

Introduction

Coordination chemistry is a challenging field in inorganic chemistry and has evolved as an important subject area in current research activities. Coordination compounds have been known for well over a century and the scientific interest in these compounds increased dramatically. Coordination complexes show diversity in structures depending on the metal ion, its coordination number and the denticity of the ligands used. The presence of nitrogen and oxygen atoms attached to ligands increases their denticity and thereby enhancing coordinating possibilities. Moreover, presence of these atoms in the coordination sphere leads to their biological activity. Hence the coordination chemistry of nitrogen-oxygen donor ligands is an interesting area of research. In this aspect, a

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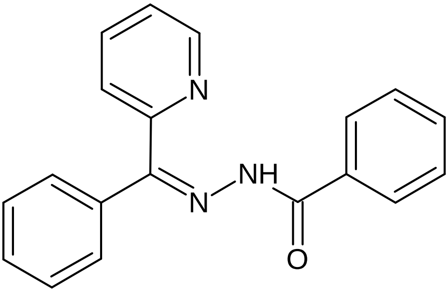
great deal of attention has been focussed on the complexes formed by transition metal ions with acylhydrazones. In view of their applicability in various fields, acylhydrazones, with triatomic >C=N–N< linkage, takes the forefront position in the development of coordination chemistry.

Many hydrazone derivatives have been found to possess anti-inflammatory activities [1]. 3-N-Methyl-N-(4-chloro-1-phthalazinyl) and 3-N-methyl-N-(4-xro-1-phthalazinyl) hydrazones possess anthelmintic activity. The biological results revealed that some of the hydrazones have prominent anti-convulsant activity [2,3]. The antibacterial and antifungal properties of 2,6-diacetylpyridine bis(acylhydrazones) and a series of metal complexes were investigated by Carcelli *et al* [4]. Recently Affan *et al* have reported the cytotoxicity and anti-termitic property of thiophene-2,2-carboxaldehyde benzhydrazone and its tin complexes [5]. Hydrazone complexes show remarkable catalytic activity in various organic reactions [6].

Many Zn^{2+} fluorescent sensors have been reported, exhibiting high selectivity and sensitivity over other biologically essential metal ions in specific ranges of concentration [7, 8]. Mercury and its compounds have been used in medicine, although they are much less common today than they once were, now that the toxic effects of mercury and its compounds are more widely understood.

In this work we report the syntheses and spectral characterization of cobalt, zinc and mercury complexes of 2-benzoylpyridine benzoylhydrazone (HBPB). Structure of the hydrazone is shown below.



2-Benzoylpyridine benzoylhydrazone (HBPB)

Results and Discussion

Syntheses of cobalt (II), zinc(II) and mercury(II) complexes

The analytical data of the compounds prepared are presented in Table 1. The results of elemental analyses show that the complexes have the molecular formulas [Zn(BPB)Cl], [Zn(BPB)Br], [Co(BPB)Cl]·CH_3OH and [Hg(BPB)Cl]. All the five complexes are colored. The complexes are soluble in DMF. The molar conductivity values of the compounds in DMF show that they are non-conductors [9].

Table 1. Elemental analysis and molar conductance

Compound	**Colour**	**Elemental Anal. Found (Calcd)**			**λ_m#**
		C	**N**	**H**	
HBPB	Colour less	75.77 (75.73)	13.88 (13.94)	4.89 (5.02)	···
[Zn(BPB)Cl]	Yellow	56.46 (56.88)	10.28 (10.47)	3.39 (3.52)	7.7
[Zn(BPB)Br]	Yellow	51.12 (51.21)	9.27 (9.43)	3.11 (3.17)	2.1
[Hg(BPB)Cl]	Yellow	42.40 (42.55)	7.87 (7.83)	2.55 (2.63)	6.1
[Co(BPB)Cl] ·CH_3OH	Brown	56.32 (56.29)	10.33 (9.85)	4.69 (4.25)	3.5

= Molar conductivity in (mho cm^2 mol^{-1}) taken in 10^{-3} M DMF

Infrared Spectral Analyses

In IR spectrum of HBPB, strong bands due to the υ(N−H) and υ(C=O) modes at 3063 and 1678 cm^{-1}are observed. It suggests that the hydrazone exists in the amido form in the solid state [10,11]. The formation of azomethine bond is confirmed by the presence a prominent band at 1571 cm^{-1} due to azomethine υ(C=N) stretching [12]. A comparison of the IR spectra of ligand and metal complexes shows that significant variations have occurred in the characteristic frequencies upon complexation. In all complexes, it was found that the characteristic spectral bands for υ(N–H) and υ(C=O) stretches of the hydrazone appearing at 3063 and 1678 cm^{-1} respectively disappear on complexation, which supports the coordination *via* iminolate form instead of amido form, formed during tautomerization process [13,14]. The imine stretching frequency of the uncoordinated ligand, shifts towards higher frequency on complexation with the metal, suggesting coordination to the metal through imine nitrogen [15,16]. In the complex [Zn(BPB)Cl], the azomethine band appears at 1591 cm^{-1}. On complexation a new band appears at 1521 cm^{-1} [17, 18]. A band at 1358 cm^{-1} indicates the coordination of the (C–O) group. The υ(N–N) stretching appears at 1149 cm^{-1}. In the complex [Zn(BPB)Br], the deprotonation of the ligand and coordination of the enolate oxygen is evident from the bands at 1513 and 1345 cm^{-1} due to the newly formed C−N and C−O bonds respectively. The azomethine bond is shifted and observed at 1596 cm^{-1}. A peak at 1150 cm^{-1} is due to v(N−N). In the complex [Hg(BPB)Cl], the presence of band at 1577 cm^{-1} indicates the shift of azomethine band upon complexation. On complexation a new band due to v(C=N) is resolved at 1513 cm^{-1}, which confirms the coordination of the ligand through imine nitrogen. A peak at 1353 cm^{-1} corresponding to υ(C−O) indicate the oxygen coordination. The υ(N−N) band appears at 1143 cm^{-1}. On complexation a band at 1378 cm^{-1} assignable to υ(C–O) stretching vibration is seen in complex [Co(BPB)Cl]·CH_3OH. On complexation a new band appeared at 1520 cm^{-1}. The v(N–N) stretching appears at 1148 cm^{-1}. The spectra of the complexes are shown in Figs 1–4. The selected IR bands of the hydrazone and complexes are represented in Table 2.

Table 2 Infrared spectral data (cm^{-1}) of the hydrazone and its complexes

Compound	υ(C=O)	υ(N–H)	υ(C=N)	υ(C=N)[a]	υ(C–O)	υ(N–N)
HBPB	1678	3063	1571			
[Zn(BPB)Cl]			1591	1521	1358	1149
[Zn(BPB)Br]			1596	1513	1345	1150
[Hg(BPB)Cl]			1577	1577	1353	1143
[Co(BPB)Cl]·CH_3OH			1598	1520	1378	1148

[a] Newly formed C=N bond

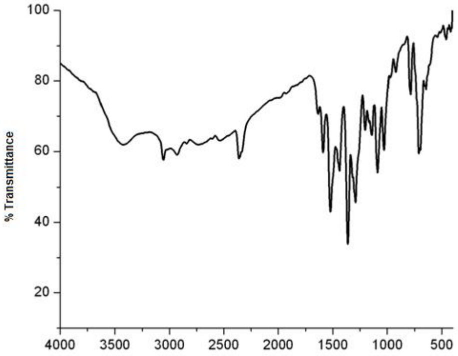


Fig. 1 IR spectrum of the complex [Zn(BPB)Cl].

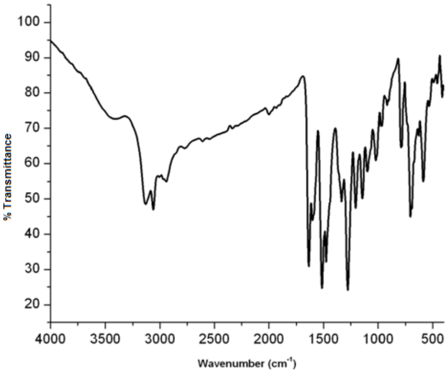


Fig. 2 IR spectrum of the complex [Zn(BPB)Br].

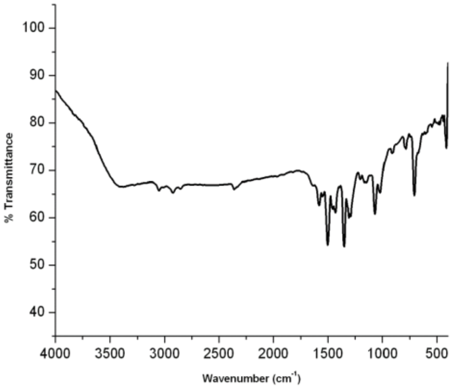


Fig. 3 IR spectrum of the complex [Hg(BPB)Cl].

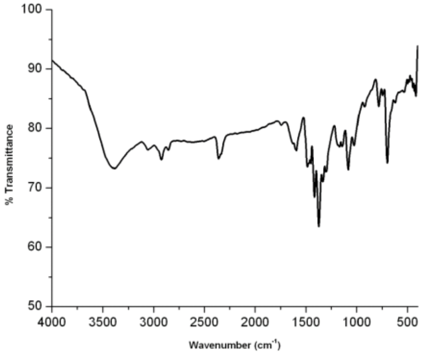


Fig. 4 IR spectrum of the complex [Co(BPB)Cl]·CH_3OH.

Electronic Spectral Analyses

The absorption of ultraviolet or visible radiation by a molecule leads to transitions among the electronic energy levels of the molecule. Molar absorption in the ultraviolet and visible region of the spectrum is dependent on the electronic structure of the molecule. The electronic transitions involved in metal complexes can be broadly classified into three types. (1) Ligand field transition or metal centered transitions which include d-d transitions and f-f transitions, (2) intraligand transitions involving σ-σ*, π-π* and n-π* transitions of the ligand [19,20] and (3) charge transfer transitions. Metal centered transitions involve transfer of an electron from one orbital to another orbital localized in the same metal ion. This may be either d-d transition or f-f transition. Charge transfer transitions are classified into three types (1) metal to ligand MLCT (2) ligand to metal LMCT and charge transfer to solvent. The bands observed in the region 24470-25450 cm^{-1} are mainly due to the charge transfer transitions [21-23]. The remaining bands correspond to the intraligand transitions. Due to filled *d* orbitals, *d-d* transitions are not expected in the case of Zn(II) and Hg(II) complexes. But these complexes are yellow colored and the colors of the complexes are attributed to metal to ligand charge transfer transitions. Here MLCT bands were observed. The intraligand transitions were found to be slightly shifted during complexation. Table 3 summarized the electronic absorptions of the complexes.

Table 3. Electronic spectral data (cm^{-1}) of complexes

Compound	Intraligand transitions	LMCT/MLCT	*d-d*
HBPB	31050, 36900, 42920	…	…
[Zn(BPB)Cl]	32600, 36700	25410	…
[Zn(BPB)Br]	30610, 36420	25360	…
Hg(BPB)Cl]	31220, 36210	25070	…
[Co(BPB)Cl] $\cdot CH_3OH$	34810	24470	…

Experimental

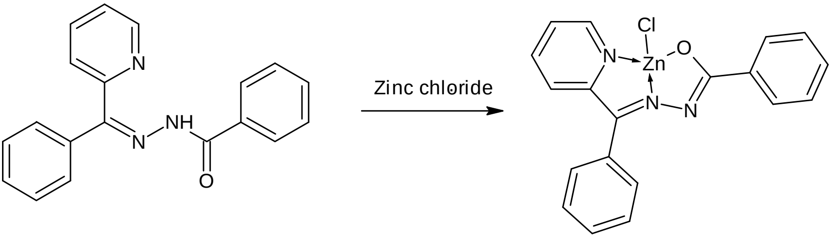
Materials

Benzoic hydrazide, 2-benzoylpyridine, zinc chloride, zinc bromide, cobalt chloride, mercuric chloride and glacial acetic acid were of Analar quality and used without further purification.

Syntheses of the complexes

1) Preparation of [Zn(BPB)Cl]

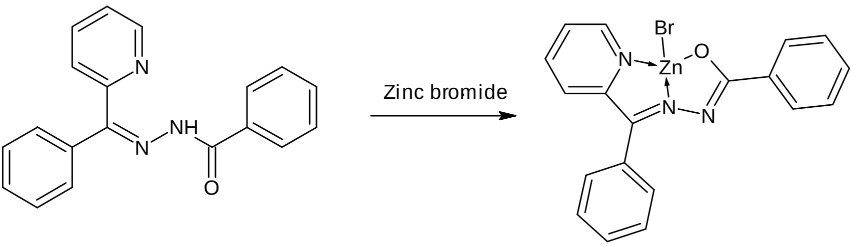
To a methanolic solution of HBPB (0.301 g, 1 mmol), zinc chloride (0.720 g, 1 mmol) in methanol was added. The reaction mixture was refluxed for 3 hours. The yellow colored solution was allowed to stand at room temperature and after slow evaporation, yellow colored crystalline product was filtered and washed with ether and dried over P_4O_{10} *in vacuo*.



HBPB [Zn(BPB)Cl]

2) Preparation of [Zn(BPB)Br]

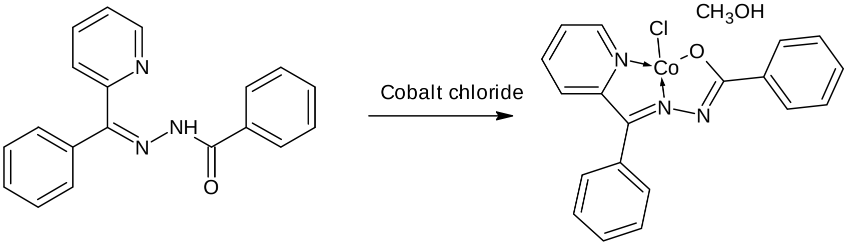
To a methanolic solution of HBPB (0.301 g, 1 mmol), zinc bromide (0.526 g, 1 mmol) in methanol was added. The reaction mixture was refluxed for 3 hours. Shining yellow colored precipitate obtained was filtered and washed with ether and dried over P_4O_{10} *in vacuo.*



HBPB [Zn(BPB)Br]

3) Preparation of $[Co(BPB)Cl]CH_3OH$

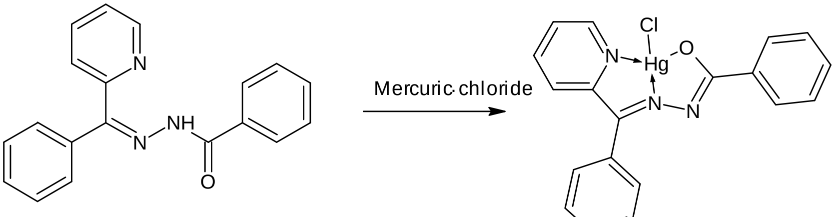
To a methanolic solution of HBPB (0.301 g, 1 mmol), cobalt chloride (0.426 g, 1 mmol) in methanol was added. The reaction mixture was refluxed for 3 hours. The solution was allowed to stand at room temperature and after slow evaporation, brown crystalline product was separated, filtered and washed with ether and dried over P_4O_{10} *in vacuo*.



HBPB [Co(BPB)Cl]·CH_3OH

4) Preparation of [Hg(BPB)Cl]

To a methanolic solution of HBPB (0.301 g, 1 mmol), mercuric chloride (0.536 g, 1 mmol) in methanol was added. The reaction mixture was refluxed for 3 hours. Yellow colored precipitate obtained was filtered and washed with ether and dried over P_4O_{10} *in vacuo*.



HBPB [Hg(BPB)Cl]

Analytical Method

Elemental analysis of HBPB and its complexes were performed on a Vario EL III CHNS analyzer at SAIF, Kochi, India. The molar conductances of the complexes in DMF (10^{-3} M) solution were measured at 298 K with a Systronic model 303 direct-reading conductivity bridge. IR spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrometer using KBr pellets in the range 4000-400 cm^{-1}. Electronic spectra were recorded in DMF on a Spectro UV-vis Double Beam UVD-3500 spectrometer in the range 200-900 nm range.

Conclusion

Cobalt, zinc and mercury complexes of 2-benzoylpyridine benzoylhydrazone were synthesised and characterized**.** The elemental analysis clearly show that the complexes have the empirical formula [Zn(BPB)Cl], [Zn(BPB)Br], [Co(BPB)Cl]·CH_3OH and [Hg(BPB)Cl], where BPB stands for deprotonated ligand. These complexes are characterized by IR and UV-visible spectral measurements.

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