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Synthesis and Spectral Characterization of Copper(II) and Zinc(II) Complexes of An Acylhydrazone

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Abstract

Copper(II) and zinc(II) complexes have been synthesized by the reaction of copper(II) acetate and zinc(II) acetate with an acylhydrazone and sodium cyanate and characterized by analytical and spectral studies.

Keywords: Cu(II) complexes, Zn(II complexes, Acylhydrazones.

1. Introduction

Coordination compounds have been known for well over a century and the scientific interest in these compounds has increased dramatically. The importance of coordination complexes in our day-to-day life is increasing due to their complex structures and interesting magnetic, electronic and optical properties. Interest in coordination chemistry of acylhydrazones is associated with their wide use as drugs, photo-thermochromic compounds and precursors for organic synthesis [1-4]. In the case of acylhydrazones, the presence of the carbonyl oxygen atom promotes the formation of a chelate binding centre [5]. Acylhydrazones and their metal complexes possess pronounced biological and pharmaceutical activities as antitumor [6-8], antimicrobial [9], antituberculosis [10] and antimalarial agents [11].

Copper complexes of thiosemicarbazones show antitumoral, anti-inflammatory and antibacterial activity. Some acylhydrazone

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derivatives are found to be potential oral iron chelating drugs for the treatment of thalassemia. The emerging importance of Zn^{2+} in neurological signalling and some proposed functions in biological systems have generated an urgent demand for the development of Zn^{2+}-specific molecular probes, and many Zn^{2+} fluorescent sensors have been reported, exhibiting high selectivity and sensitivity over other biologically essential metal ions in specific ranges of concentration [12-14].

In this work we report the syntheses and spectral characterization of copper and zinc complexes of 2-benzoylpyridine benzoylhydrazone (HBPB). Structure of the hydrazone is shown in Figure 1.

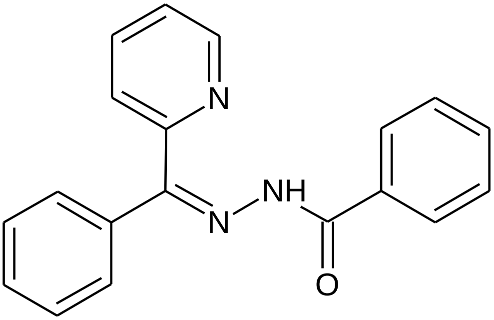


Fig 1:. 2-Benzoylpyridine benzoylhydrazone (HBPB)

2. Results and Discussion

2.1 Syntheses of copper(II) and zinc(II) complexes

The results of elemental analyses and conductivity measurements have been presented in Table 1. The results of elemental analyses show that the complexes have the molecular formulae $[Cu_2(BPB)_2(OAc)_2]$ (**1**), [Cu(BPB)NCO] (**2**) and $[Zn(BPB)_2]$ (**3**). The complexes are insoluble in most of the solvents. They are soluble in DMF. The molar conductivity values of the compounds in DMF show that they are non-conductors [15]. The molar conductivity values are given in Table 1.

Compound	Color	Elemental Anal. Found (Calcd) %			λ_m#
		C	N	H	
HBPB	Colorless	75.46 (75.73)	13.98 (13.94)	5.23 (5.02)	_
[$Cu_2(BPB)_2(OAc)_2$] (**1**)	Black	60.04 (59.64)	10.54 (9.94)	3.35 (4.05)	2.1
[Cu(BPB)NCO] (**2**)	Green	59.41 (59.18)	13.64 (13.80)	3.14 (3.48)	0.9
[$Zn(BPB)_2$] (**3**)	Yellow	69.02 (68.52)	13.08 (12.62)	4.05 (4.24)	1

#molar conductivity (in mho cm^2 mol^{-1}) taken in 10^{-3} M DMF solution.

Table 1: Elemental analyses and molar conductances

2.2 Infrared spectral analyses

Infra red spectral analyses confirm the presence of characteristic groups present in the compounds. Strong bands due to the ν(N–H) and ν(C=O) modes at 3063 and 1678 cm^{-1} respectively are observed in the spectrum of the acylhydrazone which suggest that the hydrazone exists in the amido form in the solid state [16-18]. A prominent band at 1571 cm^{-1} due to azomethine ν(C=N) linkage is observed in the spectrum indicating that condensation between ketone moiety of carbonyl compound and that of the hydrazide has taken place resulting in the formation of the desired ligand HBPB [19]. 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 ν(N–H) and ν(C=O) stretches of the hydrazone appearing at 3063 cm^{-1} and 1678 cm^{-1} respectively disappear on complexation, which supports the coordination via iminolate form instead of amido form, formed during tautomerization process [20,21]. In complex [$Cu_2(BPB)_2(OAc)_2$] (**1**), the assignments of the IR spectrum (Figure 2) in the range 1300-1600 cm^{-1} are difficult due to the appearance of several absorption bands from both acylhydrazone and acetate. The strong band at 1640 cm^{-1} may be attributed to the ν_{as}(CO) of CH_3COO^- group. The symmetric stretching mode for the acetate is observed at 1404 cm^{-1} [22]. The separation between the two peaks (Δ) is 236 cm^{-1}. For classical carboxylate bridges (Cu–O–C–O–Cu), the value of Δ is usually ~ 180 cm^{-1}. The Δ value of complex is higher than the classical bridges but lower than the monodentate. It substantiates the non-symmetric bridging mode of the carboxylate in the complex [23]. The presence of unsymmetrical mono-atomic acetate oxygen bridge in complex **1** is also confirmed from single crystal XRD [24]. A new band appears at 1370 cm^{-1} due to ν(C–O) mode indicating the coordination in the enolic form [25]. The strong absorption band at 1571 cm^{-1} ascribed to the imine stretching frequency of the uncoordinated ligand, shifts towards lower frequency on complexation with the metal, suggesting coordination to the metal through imine nitrogen [26,27]. On complexation a new band appeared at 1584 cm^{-1} due to ν(C=N) [28, 29].

In the complex [Cu(BPB)NCO] (**2**), the azomethine band appears at 1505 cm^{-1}. A new band due to ν(C=N) at 1596 cm^{-1} indicates tautomerization and coordination of the hydrazone in the enolate form. A band at 1357 cm^{-1} indicates the coordination of C–O group. The ν(N–N) stretching band appears at 1143 cm^{-1}. The IR spectrum exhibits a strong peak at 2188 cm^{-1}, which indicates the presence of –NCO group [16]. The spectrum of [Cu(BPB)NCO] (**2**) is shown in Figure 3. In the complex [Zn(BPB)$_2$] (**3**) a band at 1585 cm^{-1} corresponds to the newly formed C=N bond. A peak at 1345 cm^{-1} corresponding to ν(C–O) indicate the oxygen coordination. The ν(N–N) band appears at 1142 cm^{-1}.

Compound	ν(C=O)	ν(N–H)	ν(C=N)	ν(C=N)^a	ν(C–O)	ν(N–N)
HBPB	1678	3063	1571	----	----	----
[$Cu_2(BPB)_2(OAc)_2$] (**1**)	----	----	1500	1584	1370	1131
[Cu(BPB)NCO] (**2**)	----	----	1505	1596	1357	1143
[$Zn(BPB)_2$] (**3**)	----	----	1508	1585	1345	1142

^{a} Newly formed C=N bond

Table 2: Infrared spectral data (cm^{-1}) of the hydrazones and their copper(II) and zinc(II) complexes

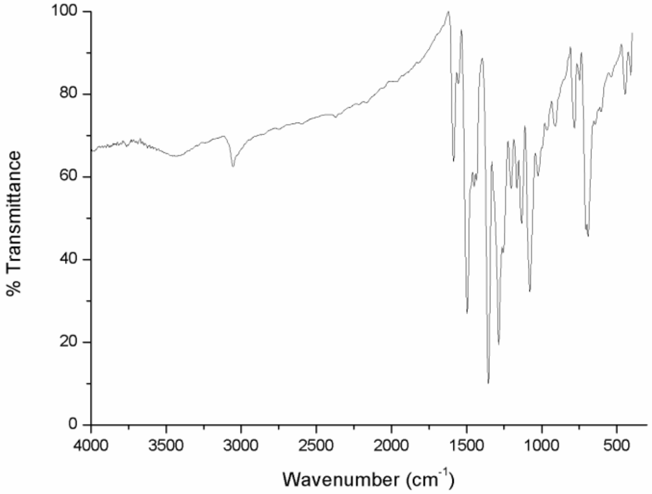


Figure 2: IR spectrum of complex [$Cu_2(BPB)_2(OAc)_2$] (**1**).

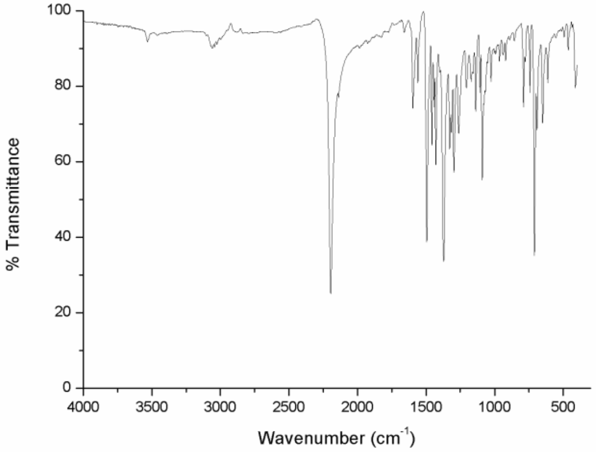


Figure 3: IR spectrum of complex [Cu(BPB)NCO] (**2**).

2.3 Electronic Spectral Analyses

The electronic spectra of the complexes were recorded in DMF solution. The Cu(II) complexes with d^9 configuration is expected to experience Jahn-Teller distortion which leads to the further splitting of the ^2E_g and ^2T_g levels and give rise to three spin allowed transitions *viz.* ${}^2A_{1g} \leftarrow {}^2B_{1g}$, ${}^2B_{2g} \leftarrow {}^2B_{1g}$ and ${}^2E_g \leftarrow {}^2B_{1g}$ which occur in the ranges 12000 - 17000, 15500 - 18000 and 17000 - 20000 cm^{-1} respectively. But in practice it is difficult to resolve them into separate bands due to the low energy difference between these energy levels.

The presence of broad band in all complexes in the range 14630-14380 cm^{-1} can be assigned to *d-d* transition. The bands observed in the region 24980-25450 cm^{-1} are mainly due to the phenoxy O→Cu(II) charge transfer transitions [30-32]. 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) 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 summarises the electronic absorption data of the complexes.

Compound	Intraligand Transitions	LMCT/MLCT	*d-d*
HBPB	31050, 36900, 42920	----	----
$[Cu_2(BPB)_2(OAc)_2]$ (1)	35380	25090	14630
[Cu(BPB)NCO] (2)	30050	24980	14380
$[Zn(BPB)_2]$ (3)	34540, 42110	25450	----

Table 3: Electronic spectral assignments (cm^{-1}) of Cu(II) and Zn(II) complexes

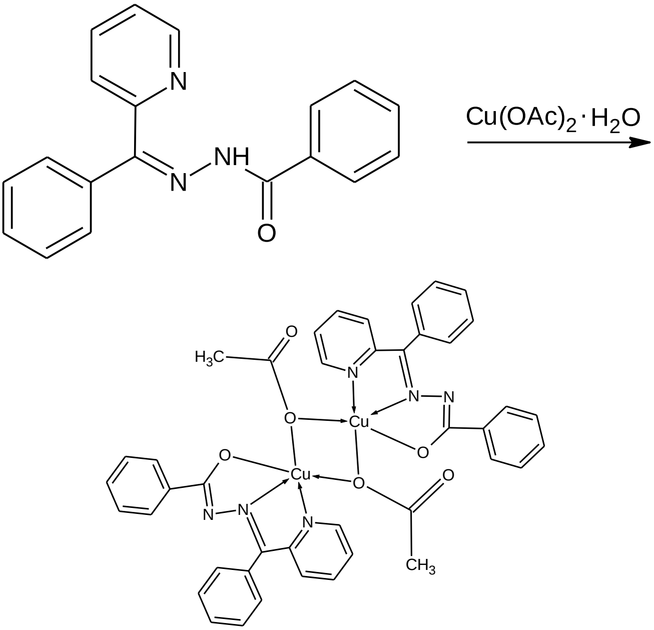
3. Experimental

Copper(II) acetate, benzoic hydrazide, 2-benzoylpyridine, sodium cyanate, zinc acetate were of Analar quality and were used without further purification.

3.1 Syntheses of the complexes

1) Preparation of $[Cu_2(BPB)_2(OAc)_2]$ (**1**)

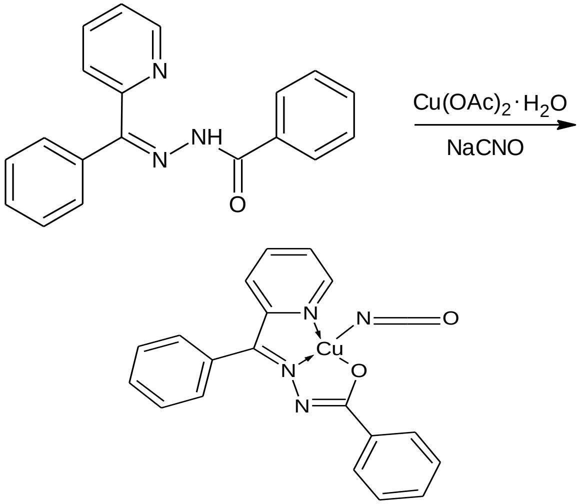
$Cu(OAc)_2{\cdot}H_2O$ (0.199 g, 1 mmol) dissolved in methanol was added to a methanolic solution of HBPB (0.301 g, 1 mmol). The reaction mixture was refluxed for 3 hours. The solution was kept for two days for evaporation. Black shining crystals were separated, filtered, washed with methanol followed by ether and dried over P_4O_{10} *in vacuo* (Scheme 1).



Scheme 1: Preparation of $[Cu_2(BPB)_2(OAc)_2]$

2) Preparation of [Cu(BPB)NCO] (**2**)

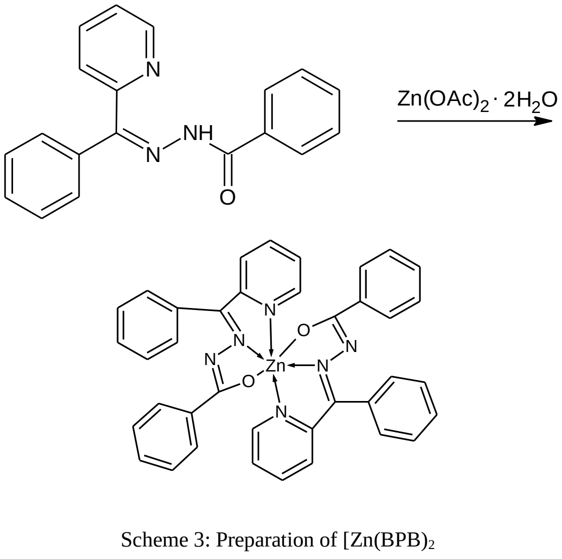
To a methanolic solution of HBPB (0.301 g, 1 mmol), sodium cyanate (0.065 g, 1 mmol) dissolved in methanol was added and refluxed for half an hour. Then a methanolic solution of $Cu(OAc)_2 \cdot H_2O$ (0.199 g, 1 mmol) was added and refluxed for 3 hours. Dark green precipitate obtained was filtered, washed with methanol, followed by ether and dried over P_4O_{10} *in vacuo* (Scheme 2).



Scheme 2: Preparation of [Cu(BPB)NCO]

3) Preparation of $[Zn(BPB)_2]$ (**3**)

To a methanolic solution of HBPB (0.602 g, 2 mmol), a methanolic solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.219 g, 1 mmol) was added and refluxed for 3 hours. Yellow precipitate that was obtained was filtered, washed with methanol, followed by ether and dried over P_4O_{10} *in vacuo* (Scheme 3).



Scheme 3: Preparation of $[Zn(BPB)_2$

3.2 Analytical Method

Elemental analyses of 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.

4. Conclusion

Copper and zinc complexes of an acylhydrazone were synthesized and characterized. The elemental analyses data clearly show that the complexes have the empirical formula [Cu(BPB)(OAc)], [Cu(BPB)CNO] and [Zn(BPB)], where BPB stands for deprotonated ligand. These complexes are characterized by IR and UV-visible measurements. Complex $[Cu_2(BPB)_2(OAc)_2]$ (**1**) is a mono-atomic acetate oxygen bridged dimer.

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