Synthesis, Spectral, Thermal, X-ray Diffraction and Antibacterial Studies of Zinc(II) and Cadmium(II) Complexes of Piperidinobenzyl Urea

M. VISWANATHAN

*Department of Chemistry, S.N. College for Women, Kollam-691 001, India*
E-mail: jaiviswam@yahoo.co.in

Some mixed ligand complexes of zinc(II) and cadmium(II) with a Mannich base derived from urea, piperidine and benzaldehyde and various anions such as chloride, nitrate, acetate and sulphate have been synthesized and characterized. The analytical data include elemental analysis, determination of molar mass, conductivity, spectral, thermal, X-ray powder diffraction studies. The complexes exhibit the following general formulae: (i) $[M(PBU)X_2(H_2O)_2]$ and (ii) $[M(PBU)SO_4(H_2O)]$ where M = Zn or Cd, X = Cl, NO_3, or CH_3OO^- and PBU = piperidinobenzyl urea. The antibacterial activity of the metal complexes has also been studied.

Key Words: Synthesis, Spectral, Thermal, X-ray Diffraction, Zn(II), Cd(II), Complex, Piperidinobenzyl urea.

INTRODUCTION

Studies of metal complexes with formaldehyde based Mannich bases have been reported in literature[1]. However, there are only few reports on the complexes of benzaldehyde based Mannich bases. One such work is the synthesis and characterization of the complexes of N,N'-bis(morpholinobenzyl)urea[2]. Another work reported is the synthesis and characterization of piperidinobenzyl urea (PBU) **(I)** and some complexes of it[3]. The present communication reports the synthesis, spectral, thermal and X-ray diffraction studies of some mixed ligand complexes of zinc(II) and cadmium(II) with PBU as primary ligand and various anions as secondary ligands.
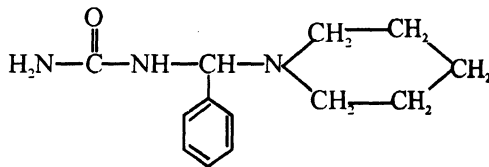
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Fig. 1. Piperidinobenzylurea (PBU)

EXPERIMENTAL

All chemicals used were of AnalaR or GR (E. Merck). Organic solvents were purified by standard methods.

The ligand was prepared by reported method[3]. To urea dissolved in minimum amount of water was added piperidine followed by benzaldehyde (1 : 1 : 1 mol ratio) maintaining a temperature of 10°C and stirred. The white crystals formed were washed with water, filtered and crystallized from methanol. The purity of

the ligand was checked by recording the IR spectrum and determining the melting point (159–161°C).

Synthesis of Metal Complexes

As the ligand is insoluble in water, the complexes were prepared in non-aqueous media. The chloro, nitrato, acetato and sulphato complexes of zinc(II) and cadmium(II) were prepared by mixing the alcoholic solutions of the ligand and the metal salt in 1 : 1 mole ratio and then refluxing for 1 h. The solid complex was washed with ethanol and dried at 100°C.

The metal ions and anions were estimated[4]. The carbon, hydrogen and nitrogen contents were determined by microanalytical method. Molar masses of the complexes were determined by the Rast method[5] using biphenyl as the solvent. The molar conductances of the complexes in methanol, acetonitrile, DMF and nitrobenzene (10^{-3} M solutions) were measured at room temperature (28 ± 2)°C. The infrared spectra of the ligand and the complexes were recorded in the range 4000–400 cm^{-1} employing the KBr disc technique. In the case of chloro complexes, the infrared spectra were recorded in the far infrared region also. The TG and DTG curves of the complexes were recorded on the thermal analyzer from ambient temperature to 800°C. The mass percentage *vs.* temperature curves were redrawn to appropriate scales. Independent pyrolysis experiment in air was carried out for these complexes and loss of mass determined. The X-ray powder patterns were recorded using Philips diffractometer (Model PW 1710) for [Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$] and [Cd(PBU)Cl$_2$(H$_2$O)$_2$]. The complexes were screened for their antibacterial activity against *S. aureus, P. aeruginosa* and *E. coli* by disc diffusion method[6] at different concentrations.

RESULTS AND DISCUSSION

The analytical results (Tables 1a and 1b) indicate a 1 : 1 : 2 (M : L : H$_2$O) stoichiometry for all the complexes. The molar conductance values (Table-2) of the complexes show them to be non-electrolytes. This indicates the coordination of anions to the respective metal ions. The comparatively high values of conductance for the complexes in methanol are probably due to the partial displacement of the coordinated anions by polar methanol molecules[7].

TABLE-1A

ANALYTICAL DATA AND MOLAR MASSES OF THE COMPLEXES OF PIPERIDINOBENZYL UREA WITH THE NITRATES, CHLORIDES AND SULPHATES OF ZINC(II) AND CADMIUM(II)

Complex	Molar mass Found (Calcd.)	% Analysis, found (calculated)	
		Metal	Anion
[Zn(PBU)Cl$_2$(H$_2$O)$_2$]	412.8 (405.29)	15.93 (16.13)	17.27 (17.51)
[Cd(PBU)Cl$_2$(H$_2$O)$_2$]	442.4 (451.12)	24.88 (24.65)	15.46 (15.72)
[Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	468.1 (458.37)	14.55 (14.26)	26.72 (27.05)
[Cd(PBU)(NO$_3$)(H$_2$O)$_2$]	492.8 (504.2)	22.29 (22.05)	24.83 (24.59)
[Zn(PBU)SO$_4$(H$_2$O)$_2$]	441.2 (430.37)	15.45 (15.18)	22.53 (22.3)
[Cd(PBU)SO$_4$(H$_2$O)$_2$]	464.7 (476.2)	23.12 (23.35)	20.40 (20.16)

TABLE-1B
ANALYTICAL DATA AND MOLAR MASSES OF THE COMPLEXES OF PIPERIDINOBENZYL UREA WITH THE ACETATES OF ZINC(II) AND CADMIUM(II)

Complex	Molar mass Found (Calcd.)	% Analysis, found (calculated)			
		M	C	H	N
[Zn(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$]	461.8 (452.37)	14.71 (14.45)	45.88 (45.09)	6.28 (6.41)	9.44 (9.28)
[Cd(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$]	487.3 (498.2)	21.94 (22.32)	41.21 (40.9)	5.79 (5.82)	8.51 (8.43)

TABLE-2
MOLAR CONDUCTANCE DATA OF THE COMPLEXES

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})			
	Methanol	Actonitrile	Nitrobenzene	DMF
[Zn(PBU)Cl$_2$(H$_2$O)$_2$]	24.2	7.5	4.1	2.7
[Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	25.1	4.8	3.8	3.1
[Zn(PBU)SO$_4$(H$_2$O)$_2$]	26.2	3.9	2.9	2.6
[Zn(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$]	23.8	5.6	4.3	4.1
[Cd(PBU)Cl$_2$(H$_2$O)$_2$]	24.6	6.1	4.6	2.8
[Cd(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	27.3	4.2	3.9	2.7
[Cd(PBU)SO$_4$(H$_2$O)$_2$]	27.9	4.7	4.1	3.1
[Cd(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	24.3	5.0	4.8	3.4

In the infrared spectrum of piperidinobenzyl urea the v(NH) modes appear at 3462 (asymmetric) and 3360 cm^{-1} (symmetric). The carbonyl and C—N—C stretching frequencies of PBU appear at 1660 and 1160 cm^{-1}, respectively.

The infrared spectra of the zinc(II) and cadmium(II) complexes exhibit characteristic absorptions of all the functional groups of the ligand but at a shifted position in the case of coordinated groups. The infrared spectra of all the complexes reported here reveal the bidentate nature of the ligand with carbonyl oxygen and the piperidine ring nitrogen acting as donor sites. The band at 1660 cm^{-1} in the ligand which is due to the carbonyl stretching frequency shows a negative shift to 1640–1630 cm^{-1} indicating the coordination through the carbonyl group. The band at 1160 cm^{-1} in the ligand which is due to the C—N—C stretching frequency shifts to 1150–1130 cm^{-1}. This shows the coordination through the tertiary nitrogen of the piperidine ring. v(NH) modes appearing in the spectrum of the ligand remain unaltered in the spectra of the complexes which point to the non-participation of nitrogen of NH$_2$ group in coordination. All the complexes show additional bands at 3500–3480, 840–830 and 635–625 cm^{-1} indicating the presence of coordinated water[8]. The additional bands in the region 440–420 and 540–515 cm^{-1} are assigned to v(M—O) and v(M—N), respectively. The chloro complexes show additional bands in the region 280–265 cm^{-1} which may be assigned to v(M—Cl)[8]. The infrared spectra of nitrato complexes exhibit three additional bands at 1460, 1340 and 1020 cm^{-1} which are not present in the spectrum of the ligand. These three bands are attributed respectively to v_4, v_1 and

v_2 modes of the coordinated nitrate ions[9-11]. Since the difference between v_4 and v_1 is 120 cm^{-1}, it is suggested that the nitrate ions are coordinated unidentately to the metal ions in the present complexes. Molar conductance values also support this conclusion. The infrared spectra of the acetato complexes of the metals with PBU show two additional bands at 1670 and 1320 cm^{-1}. These bands are assigned respectively to asymmetric and symmetric stretching vibrations of coordinated carboxylate group. The large separation between these two bands confirms the unidentate coordination of carboxylate ion[12, 13].

Antibacterial Screening

The antimicrobial activities of the complexes were tested by disc diffusion method[6] by using three different bacteria: *Staphylococcus aureus, Escherichia coli* and *Pseudomonas aeruginosa*. It was found that some of the complexes show antimicrobial activities towards certain bacteria.

The complexes were dissolved in absolute methanol and impregnated in Whatmann No. 1 filter paper to get a concentration of 1, 5 and 10 mg per disc. The methanol in the discs was evaporated and the discs were sterilized by autoclaving.

Mueller-Hinton agar plates were inoculated with the test bacterial strains, *E. coli, S. aureus* and *P. aeruginosa*. The test and control samples were placed on the media surface and incubated at 37°C for 24 h. The positive control used was Gentamicin disc. The negative control used was Whatmann No. 1 filter paper discs impregnated with 150 mL of absolute methanol. The methanol in the discs was evaporated off and the discs were sterilized by autoclaving.

All the complexes were found to be active towards *S. aureus* and *E. coli*. The chloro complexes were found to be more active than the acetato, nitrato or sulphato complexes. However, all the complexes were found to be inactive towards *P. aeruginosa* (Table-3).

TABLE-3

ANTIMICROBIAL ACTIVITY OF MIXED LIGAND COMPLEXES OF ZINC(II) AND CADMIUM(II) AT DIFFERENT CONCENTRATIONS

Complex	Zone of inhibition (mm)								
	S. aureus			*E. coli*			*P. aeruginosa*		
	1 mg/ disc	5 mg/ dis	10 mg/ disc	1 mg/ disc	5 mg/ dis	10 mg/ disc	1 mg/ disc	5 mg/ disc	10 mg/ disc
[Zn(PBU)Cl$_2$(H$_2$O)$_2$]	8	9	9	9	10	10	NZ	NZ	NZ
[Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	5	6	6	5	6	6	NZ	NZ	NZ
[Zn(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$]	5	5	5	6	6	6	NZ	NZ	NZ
[Zn(PBU)(SO$_4$)(H$_2$O)$_2$]	6	6	6	7	7	7	NZ	NZ	NZ
[Cd(PBU)Cl$_2$(H$_2$O)$_2$]	9	9	9	8	9	9	NZ	NZ	NZ
[Cd(PBU)(NO$_3$)$_2$(H$_2$O)$_2$]	6	7	7	5	5	5	NZ	NZ	NZ
[Cd(PBU)SO$_4$(H$_2$O)$_2$]	7	7	7	5 .	6	6	NZ	NZ	NZ
[Cd(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$]	5	6 .	6	7	7	7	NZ	NZ	NZ

NZ: No zone of inhibition.

Thermal Studies

Thermal studies were conducted on all the complexes. Independent pyrolysis experiment in air was also carried out for each of the complexes studied. For this, a known quantity of the complex was heated in a porcelain crucible up to 800°C for 1 h. From the mass of the residue the loss of mass was calculated in each case, which was compared with the percentage loss of mass obtained from the experiment.

For the complex, [Zn(PBU)Cl$_2$(H$_2$O)$_2$] the TG plateau up to 158°C shows that the complex is stable up to 158°C. The DTG curve has three peaks at 173°C, 315.4°C and 592°C. The presence of coordinated water molecule suggested from infrared spectrum is confirmed by TG analysis. According to Nikolaev et al.[14], water eliminated below 150°C can be considered as lattice water and that eliminated above 150°C may be due to its coordination to the metal atom present in chelates. In the present case, the weight loss of the complex at 158–188°C is 8.6% (8.88%), the value in parenthesis corresponds to two coordinated water molecules. The second stage of decomposition is in the range of 290–330°C which corresponds to the breaking up of the organic moiety and shows a weight loss of 56.8% (theoretical 57.48%). The TG curve shows a second plateau after 620°C indicating the completion of decomposition. The residual mass is about 20.8% (theoretical 20.07%) which corresponds to the metal oxide.

For the complexes [Zn(PBU)SO$_4$(H$_2$O)$_2$] and [Zn(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$] the TG plateau shows that the complexes are stable up to 156° and 163°C respectively. The DTG curves of both the complexes have three peaks at 170–175°, 318–322° and 541–550°C showing the decomposition of the complexes in three stages. The weight losses in the first stage (156–180°C) are 8.2% (theoretical 8.36%) and 7.84% (theoretical 7.96%) respectively. These complexes show weight losses at 318–322°C equal to 53.6% (theoretical 54.14%) and 50.4% (theoretical 51.51%) due to the breaking of organic moiety. The TG curves show second plateau at about 620–625°C showing the completion of decomposition. The residual masses are about 18% (theoretical 18.9%) and 16.85% (theoretical 17.98%) respectively for the sulphato and acetato complexes. These correspond to the metallic oxide.

For the complexes [Cd(PBU)Cl$_2$(H$_2$O)$_2$], [Cd(PBU)(NO$_3$)$_2$(H$_2$O)$_2$], [Cd(PBU)SO$_4$(H$_2$O)$_2$] and [Cd(PBU)(CH$_3$COO)$_2$(H$_2$O)$_2$] the TG plateu shows that the complexes are stable up to 155–162°C. The DTG curves of all these complexes have three peaks indicating 3 stages of decomposition in the range 155–180°C, the weight losses are 7.72% (theoretical 7.98%), 6.92% (theoretical 7.14%), 7.38% (theoretical 7.56%) and 6.91% (theoretical 7.22%), respectively for the chloro, nitrato, sulphato and acetato complexes. These weight losses correspond to two coordinated water molecules. Corresponding to the breaking up of the organic moiety, the chloro, nitrato, sulphato and acetato complexes show weight losses at 315–325°C equal to 27.5% (theoretical 28.2%), 24.1% (theoretical 25.2%), 25.1% (theoretical 26.71%) and 24.4% (theoretical 25.53%) respectively. The TG curves show second plateau at about 610–630°C indicating the completion of decomposition. The residual masses for the chloro, nitrato, sulphato and acetato complexes are about 29.1% (theoretical 28.2%), 26.1% (theoretical

25.2%), 27.4% (theoretical 26.71%) and 24.9% (theoretical 25.53%), respectively which correspond to the metal oxide.

The X-ray powder patterns were recorded for the complexes [Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$] and [Cd(PBU)Cl$_2$(H$_2$O)$_2$]. The diffraction patterns were indexed using the method developed by Hesse[15] and Lipson[16, 17]. Both of these complexes are found to be orthorhombic.

The lattice constants for [Zn(PBU)(NO$_3$)$_2$(H$_2$O)$_2$] are A = 0.0034, B = 0.0063 and C = 0.034. Hence, A = 13.20 Å, B = 9.7 Å and C = 4.18 Å. Thus, the cell volume for the complex is 535.2072 (Å)^3. The density of the complex is 0.8372 (n = 0.9932). So the number of molecules per unit cells is one. For the complex, [Cd(PBU)Cl$_2$(H$_2$O)$_2$] the lattice constants are: A = 0.00367, B = 0.00543 and C = 0.0321. Hence a = 12.70 Å, b = 10.44 Å and c = 4.29 Å. Thus, the cell volume of the complex is 568.8 (Å)^3 and the density is 0.7912 which gave a value of 0.982 for n. So the number of molecules per unit cell is one.

On the basis of the experimental evidence gathered and the discussion therefrom it is concluded that all the complexes discussed in the present work have octahedral geometry.

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