Asian Journal of Chemistry Vol. 19, No. 4 (2007), 2806-2812

Synthesis and Characterization of Complexes of Thorium(IV) with Pyrrolidinobenzyl Benzamide and Various Anions

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A series of complexes of Th(IV) with pyrrolidinobenzyl benzamide (PBB), a Mannich base derived from pyrrolidine, benzamide and benzaldehyde and various anions such as chloride, nitrate, acetate, thiocyanate and perchlorate have been synthesized and characterized. Their probable structures have been determined by elemental analysis, molar mass, conductivity, spectral, thermal and X-ray diffraction studies. The complexes exhibit the formulae : $[Th(PBB)_3X]$ where X = Cl^-, NO_3^-, NCS^-, CH_3COO^- or ClO_4^-. In these complexes the PBB acts as a bidentate ligand, whereas the monovalent anions act as unidentate ligands. The biological activities of the ligand and their metal chelates against *E. coli*, *S. aureus*, *K. pneumoniae* and *P. aeruginosa* were also studied. The complexes have higher activity than that of the free Mannich base.

Key Words: Th(IV), Complexes, N-Pyrrolidinobenzyl benzamide.

INTRODUCTION

It is evident from the literature survey that the compounds containing amide moiety have a strong ability to form metal complexes and they exhibit a wide range of biological activities[1-3]. The coordination chemistry of amide group has received much attention due to its diverse coordinating behaviour and its role in biological process[4]. An amide group has two potential binding sites, *i.e.*, through oxygen and nitrogen for complexation with metal ions. For neutral amide group, both protonation and metal ion binding will be at the amide nitrogen[5]. On deprotonation the binding shifts to the amide nitrogen[6]. But due to factors such as steric hindrance, the coordination may also occur at amide nitrogen. In continuation of our earlier studies[7,8], the present communication reports the synthesis of a Mannich base, N-(pyrrolidinobenzyl)benzamide [PBB] and its complexes with Thorium(IV) salts.

EXPERIMENTAL

All the chemicals used were of Merck products. Organic solvents were purified by standard methods.

Synthesis of pyrrolidinobenzylbenzamide (PBB): Benzamide (1.21 g, 10 m mol) in 20 mL of ethanol was mixed with pyrrolidine (0.7 mL, 10 m mol) with stirring to get a clear solution at 10ºC. To this, benzaldehyde (1 mL, 10 mmol) was added in drops with stirring for about 15-20 min. The reaction mixture is kept at room temperature for 2 d. The colourless crystals were filtered and recrystallized from ethanol (yield 69.5 %; m.p. 89ºC). The structure of PBB may be represented as in Fig. 1.

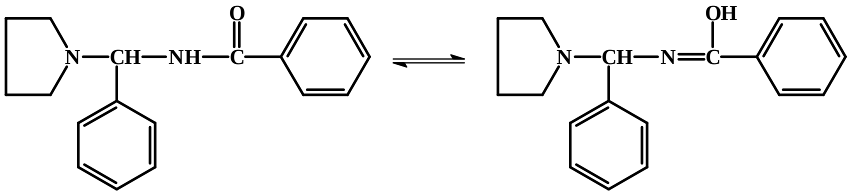


Fig.1 Proposed structure of pyrrolidinobenzyl benzamide

Synthesis of thorium(IV) complexes with PBB: The nitrato and perchlorato complexes were prepared by digesting an alcoholic solution containing PBB and metal salt (3:1 mol ratio) for about 2-3 h. The resulting solution was concentrated and cooled. The solid complex formed was filtered, washed with methanol and dried over calcium chloride in a desiccator. The preparation of thiocyanato and acetato complexes involved two stages. In the first stage, the nitrato complex was prepared. In the second stage, the nitrato complex was dissolved in methanol and was mixed with stoichiometric amount of aqueous methanolic solution of ammonium thiocyanate (or sodium acetate). The reaction mixture obtained in each case was refluxed for about 2-3 h to replace the nitrate ions with the respective anions. The resulting solution was concentrated and cooled, the solid complexes were collected and dried *in vacuo*.

The thorium content of the complexes was determined by oxalate-oxide method[9]. The carbon, hydrogen and nitrogen contents were determined by microanalytical method. The anions present in the complexes were also analyzed wherever possible[10]. The nitrate content of the complex was determined as nitron-nitrate by using nitron reagent[10]. The thiocyanate was determined as AgSCN[10] from alkali thiocynate solution using $AgNO_3$ solution in presence of nitric acid. Perchlorate was estimated by Kurz's method[11]. The molar conductance of the complexes in acetonitrile, DMF, nitrobenzene and methanol (*ca.* 10^{-3} M solutions) were measured at room temperature using an ELICO conductivity bridge type CM 82T with a dip type conductivity cell having platinum electrodes (cell constant = 0.94 cm^{-1}). Magnetic susceptibilities of the complexes were measured at room temperature. The infrared spectra of all the complexes and the ligand were recorded in the range 4000-400 cm^{-1} employing the KBr disc technique using a Bruker IFS 66V FT-IR spectrophotometer at RSIC, Madras. In the case of chloro complex, the infrared spectra was recorded in the far infrared region also. Molar masses of the complexes were determined by the Rast method using biphenyl as the solvent[12]. The X-ray powder pattern of the complexes were recorded on a Rigaku (Japan) PW 1710 X-ray powder diffractometer on a chart recorder at RRL, Pappanamcode, Trivandrum. The TG-DTG curves were recorded on a thermal analyser from ambient to 780ºC at Sree Chithra Tirunal Institute for Medical Sciences and Technology. The mass percentage *vs.* temperature curves obtained were redrawn on appropriate scales. Independent pyrolysis experiment in air was also carried out for each of the complexes studied and the loss of mass determined in each case was compared with that obtained from TG. The antimicrobial studies of the complexes at various concentrations were also done by using four different bacteria, *viz.*, *S. aureus*, *K. pneumoniae*, *P. aeruginosa* and *E. coli* by well diffusion method[12] at Sree Chithra Tirunal Institute for Medical Sciences and Technology, Trivandrum.

RESULTS AND DISCUSSION

The analytical data and molar masses of the complexes are presented in Tables 1a-b. All these complexes are moderately soluble in methanol, acetonitrile, nitrobenzene and DMF. The molar conductance values of all the complexes suggest that they behave like non-electrolytes (Table-2) in all the solvents used indicating that the anions present in all the complexes were coordinated to the thorium ion[13,14].

TABLE-1a

ANALYTICAL DATA OF Th^{4+} COMPLEXES

Complex / compound	% Analysis Found (Calcd.)				
	Th	C	H	N	m.w.
PBB	–	77.30	6.89	9.88	280
	–	(77.14)	(7.14)	(10.00)	–
$[Th(PBB)_3(OAc)]$	20.12	59.27	5.53	7.40	1117
	(20.51)	(59.42)	(5.57)	(7.43)	(1131)
$[Th(PBB)_3(ClO_4)]$	20.04	55.20	5.09	7.14	1158
	(19.80)	(55.31)	(5.12)	(7.17)	1171.5)

TABLE-1b
ANALYTICAL DATA OF Th^{4+} COMPLEXES

Complex	Th (%)	Anion (%)	m.w.
$[Th(PBB)_3NO_3]$	20.19 (20.46)	5.22 (5.47)	1119 (1134)
$[Th(PBB)_3Cl]$	20.58 (20.95)	3.41 (3.21)	1093 (1107.5)
$[Th(PBB)_3(NCS)]$	20.17 (20.53)	4.89 (5.13)	1121 (1130)
$[Th(PBB)_3ClO_4]$	20.04 (19.80)	8.28 (8.49)	1158 (1171.5)

TABLE-2
MOLAR CONDUCTANCE DATA OF THORIUM (IV)
COMPLEXES WITH PBB

Complex	Molar conductance (ohm^{-1} cm^2 mol^{-1})			
	Methanol	Acetonitrile	Nitrobenzene	DMF
$[Th(PBB)_3Cl]$	31	12	6	19
$[Th(PBB)_3(NO_3)]$	29	11	7	20
$[Th(PBB)_3(NCS)]$	28	9	5	18
$[Th(PBB)_3(OAc)]$	30	10	4	16
$[Th(PBB)_3(ClO_4)]$	26	8	8	17

All the thorium (IV) complexes with PBB are diamagnetic as expected in view of the noble gas electronic configuration of Th(IV).

The mass spectrum of Mannich base, PBB was recorded. The base peak observed at M/z 122 shows the presence of benzamide moiety. The molecular ion peak for the ligand is observed at M/z = 280 ($C_{18}H_{20}N_2O$). Other important peaks at M/z 120 and 105 correspond to the presence of C_6H_5CONH and C_6H_5CO, respectively.

The infrared spectrum of the ligand, PBB shows ν(NH) modes at 3460 (asymmetric) and 3360 cm^{-1} (symmetric). The carbonyl and C–N–C stretching frequencies of PBB appear at 1650 and 1162 cm^{-1}, respectively. The ν(NH) bands appearing at 3460 and 3360 cm^{-1} remain unaltered in the spectra of the complexes showing the non participation of nitrogen of NH_2 group in coordination. The band at 1162 cm^{-1} in the ligand[15], which is due to C–N–C stretching frequency shifts to 1140-1128 cm^{-1}, in the spectra of the complexes. This shows the participation of tertiary nitrogen of pyrrolidine ring in complexation. The spectra of the complexes show negative shifts of the carbonyl band at 1650 cm^{-1} to 1638-1619 cm^{-1} indicating the coordination through the carbonyl oxygen. The additional bands in the region 435-418 and 542-518 cm^{-1} are assigned to ν(Th–O) and ν(Th–N), respectively.

The nitrato complex of thorium(IV) exhibits three additional bands at 1460, 1338 and 1021 cm^{-1}, which are not present in the spectrum of PBU. These three bands are attributed to ν_4, ν_1 and ν_2 modes of the coordinated nitrate ions[16,17]. Since the difference between ν_4 and ν_1 is *ca.* 122 cm^{-1}, it is suggested that the nitrate ions are coordinated unidentately to the thorium ion[18].

The IR spectrum of the thiocyanato complex of thorium ion with PBB shows three additional bands at 2052, 862 and 461 cm^{-1} which are assigned to ν(CN), ν(CS) and δ(NCS) modes of the coordinated thiocyanate ion, respectively. It has been well established that ν(CN) occurs at a lower wave number around 2050 cm^{-1} in N-bonded complexes compared to the position in the case of S-bonded complexes[19] appearing around 2100 cm^{-1}. Moreover, ν(CS) mode appears in the range 860-780 cm^{-1} for N-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to δ(NCS) mode around 480 cm^{-1}. S-bonded complexes show several bands with lower intensities around 420 cm^{-1}. From these it may be concluded that the thiocyanate ion is coordinated unidentately to the thorium ion through N atom. The non electrolytic conductance value of the complex agrees with the coordination of the thiocyanate ion.

The acetato complex exhibits two additional bands at 1672 and 1321 cm^{-1} which are due to asymmetric and symmetric stretching vibrations of carboxylate group. The ν_{asym} and ν_{sym} modes of the carboxylate ion in the free acid occurs at 1560 and 1418 cm^{-1}, respectively. In the spectrum of the complex, ν_{asym} (OCO) mode is shifted to higher frequency 1673 cm^{-1} whereas ν_{asym} (OCO) is shifted to lower frequency, 1318 cm^{-1}. The increase in the separation between the two ν(OCO) bands shows that acetate ions are coordinated unidentately to thorium ion. This conclusion agrees with the non electrolytic conductance value of the complex.

IR spectrum of the perchlorato complex shows three additional bands at 1100, 1080 and 620 cm^{-1} which may be assigned to ν_4, ν_1 and ν_3 modes of coordinated perchloarate ion. This shows the unidentate coordination of ClO_4^- into Th(IV) ion[20]. The conductance value supports this conclusion.

All the metal chelates were tested for their antibacterial activity against *S. aureus*, *K. pneumoniae*, *E. coli* and *P. aeruginosa* by using well diffusion method. All the complexes were found to be active towards these bacteria (Table-3). The complexes are found to be more active than the free ligand and the control (ampicillin).

The X-ray powder patterns were recorded for the complexes $[Th(PBB)_3Cl]$ and $[Th(PBB)_3NO_3]$. The diffraction patterns were indexed by using the method developed by Hesse[21] and Lipson[22]. Both the complexes were found to be orthorhombic. The unit cell dimensions of the complex, $[Th(PBB)_3Cl]$ are : a = 15.448 Å, b = 10.816 Å and c = 7.2312 Å. Thus, the cell volume of the complex is, 1208.732 $Å^3$. These gave

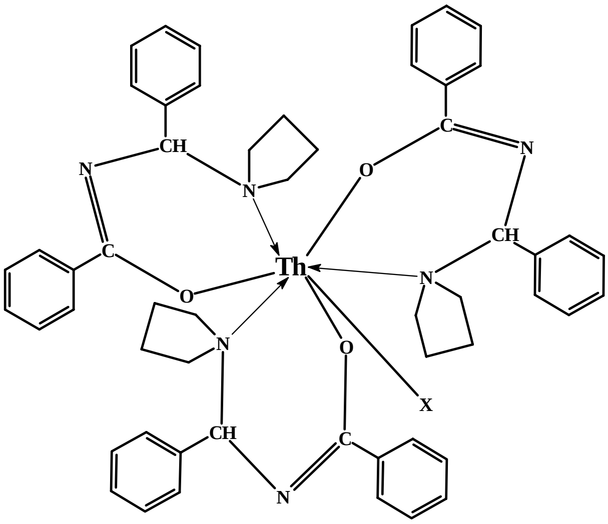
TABLE-3
ANTIBACTERIAL ACTIVITY OF THE LIGAND AND THE METAL CHELATES, ZONE OF INHIBITION (mm)

Compound	*S. aureus*	*E. coli*	*P. aeruginosa*	*K. pneumoniae*
Ampicillin	10	12	15	12
PBB	8	9	7	6
$[Th(PBB)_3(OAc)]$	14	15	16	14
$[Th(PBB)_3(ClO_4)]$	15	17	14	15
$[Th(PBB)_3Cl]$	18	21	20	19
$[Th(PBB)_3NO_3]$	16	15	14	15
$[Th(PBB)_3NCS]$	15	17	18	16

n = 1.0235. Thus, the number of molecules per unit cell is one. For the complex $[Th(PBB)_3NO_3]$ the unit cell dimensions are a = 15.6298 Å, b = 9.9812 Å and c = 7.65 Å. The cell volume is 1193.299 Å and density is 0.9198. This gave n = 0.9679. Thus, the number of molecules per unit cell is one.

Thermal studies were conducted on $[Th(PBB)_3Cl]$ and $[Th(PBB)_3(NO_3)]$. Independent pyrolysis experiment in air was also carried out for both the complexes studied. For this a known amount of the complex was heated in a porcelain crucible upto 780ºC for about 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, $[Th(PBB)_3Cl]$ the TG plateau upto 194ºC shows its stability and the complex decomposes after this temperature. The DTG curve has two peaks at 212.1 and 708.2ºC. The TG curve shows a second plateau after 729ºC. This shows the completion of decomposition. At 212.1ºC, the complex shows a weight loss of 56.61 % which is ude to the release of $C_6H_5CO–NCH–C_6H_5$ parts of the organic moeity. The residual weight is about 22.85% which is due to ThO_2. For $[Th(PBB)_3(NO_3)]$, the plateau upto 190ºC shows its stability upto this temperature. The DTG curve shows two peaks at 218.1 and 698ºC. TG curve shows a second plateau after 720ºC indicating the completion of decomposition. At 218.1ºC the weight loss is 55.2 %. This is due to release of the $C_6H_5–CO–NCH–C_6H_5$ parts of the organic moiety. The residual mass is about 22.8 %, which is due to the oxide, ThO_2. Independent pyrolysis experiment also confirms that ThO_2 is the decomposition product.

From the above studies, it is concluded that the complexes have the general structure $[Th(PBB)_3X]$, where $X=NO_3^-$, Cl^-, SCN^- or ClO_4^-. Thus the structure may be represented as follows in which the coordination no. of thorium is 7.



X = Cl$^-$, NO$_3^-$, SCN$^-$ or ClO$_4^-$

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(*Received*: 7 April 2006; *Accepted*: 12 January 2007) AJC-5325