

Synthesis and Characterization of Mixed Ligand Complexes of Thorium(IV) with Piperidinobenzylurea and Various Anions

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A series of four mixed ligand complexes of Th(IV) with piperidinobenzylurea (PBU) and various anions such as acetate, nitrate, perchlorate and thiocyanate have been synthesized and characterized. The chemical composition of the complexes have been established from analytical, molar conductance, spectral and thermal studies. Antimicrobial activity of the complexes was also studied. The complexes exhibit the formulae: $[\text{Th}(\text{PBU})_2\text{X}_4]$ where $\text{X} = \text{NO}_3^-$, NCS^- or CH_3COO^- and $[\text{Th}(\text{PBU})_3\text{ClO}_4](\text{ClO}_4)_3$. In these complexes, the ligand, PBU acts as a neutral bidentate ligand whereas the monovalent anions act as unidentate ligands.

Key Words: Synthesis, Mixed ligand complexes, Thorium(IV), Piperidinobenzylurea.

INTRODUCTION

Studies of metal complexes of the benzaldehyde based Mannich base, N,N'-bis-(morpholinobenzyl) urea¹ and piperidinobenzylurea (PBU)² have been reported in literature. Another work in this field is our own studies on the complexing characteristics of PBU with some lanthanide ions³. In continuation of these studies, the present communication reports the synthesis and characterization of some mixed ligand complexes of acetate, nitrate, perchlorate and thiocyanate of Th(IV) with PBU.

EXPERIMENTAL

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

Synthesis of Th(IV) Complexes: The ligand, piperidinobenzylurea (PBU) was prepared by literature method². The nitrate and perchlorate complexes were prepared by digesting an alcoholic solution containing the ligand (PBU) and the metal salt in stoichiometric amounts for 0.5 h. It was then concentrated to half of its volume, 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 nitrate complex was prepared. In the second stage the nitrate complex was dissolved in methanol and

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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 over phosphorus(V) oxide.

The thorium content of the complexes was determined by oxalate-oxide method⁴. The anions present in the complexes were also analyzed wherever possible. The nitrate contents of the complexes were determined as nitron-nitrate⁵ by using nitron reagent. The thiocyanate was determined as AgSCN⁵ from alkali thiocyanate solution using AgNO₃ solution in presence of nitric acid. Perchlorate was estimated by Kurz's method⁶. In this method, the perchlorate complex was heated with excess sodium nitrite at about 500°C, so that perchlorate was reduced to chloride. The residue left was extracted with water and the chloride in the solution was estimated by Volhard's method⁵. The molar conductances of the complexes in acetonitrile, methanol, nitrobenzene and DMF (*ca.* 10⁻³ M) solutions were measured at room temperature using an Elico conductivity bridge type CM82I 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 ligand were in the range 4000–400 cm⁻¹. Molar mass was determined by Rast method using biphenyl as the solvent⁷. The TG-DTG curves were recorded on a thermal analyzer from ambient to 700°C. 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 using four different bacteria, *viz.*, (1) *Staphylococcus aureus* (2) *Klebsiella pneumoniae* (3) *Escherichia coli* and (4) *Pseudomonas aeruginosa* by agar diffusion method.

RESULTS AND DISCUSSION

The analytical data and molar masses of the complexes are presented in Table-1. All these complexes are moderately soluble in methanol, acetonitrile, nitrobenzene and DMF. The molar conductance values (Table-2) of the complexes in the above solvents were compared with the data available for standard substances to see

TABLE-1
ANALYTICAL AND MOLAR MASS DATA OF THE COMPLEXES OF PBU WITH THE NITRATES, ACETATES, THIOCYANATES AND PERCHLORATES OF Th(IV)

Complex	Thorium (%)	Anion (%)	Molar mass
[Th(PBU) ₂ (NO ₃) ₄]	25.12 (25.52)	25.78 (26.21)	962 (946)
[Th(PBU) ₂ (OAc) ₄]	23.98 (24.84)	24.92 (25.27)	958 (934)
[Th(PBU) ₂ (NCS) ₄]	24.61 (24.95)	24.10 (24.95)	942 (930)
[Th(PBU) ₃ ClO ₄](ClO ₄) ₃	17.58 (17.46)	29.07 (29.94)	1372 (1328.84)

Calculated value are given in parentheses.

whether the anions are coordinated or not^{8,9}. It was observed that the nitrate, acetate and thiocyanate complexes behave like non-electrolytes in all the solvents used indicating that the anions present in all the complexes are coordinated to the metal ions. The perchlorate complex with PBU behaves like 1 : 3 electrolytes in all the solvents used. These values suggest that one ClO_4^- is coordinated to the metal ion.

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

TABLE -2
MOLAR CONDUCTANCE DATA OF Th(IV) COMPLEXES WITH PBU

Complex	Molar conductance ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)			
	Methanol	Acetonitrile	Nitrobenzene	DMF
$[\text{Th}(\text{PBU})_2(\text{NO}_3)_4]$	34	11	5	2
$[\text{Th}(\text{PBU})_2(\text{NCS})_4]$	30	4	4	3
$[\text{Th}(\text{PBU})_2(\text{OAc})_4]$	29	9	3	3
$[\text{Th}(\text{PBU})_3\text{ClO}_4](\text{ClO}_4)_3$	325	410	78	228

Concentration *ca.* 10^{-3} M

The infrared spectra of the ligand, *viz.*, piperidinobenzylurea and its complexes of Th(IV) in presence of various anions give the bonding nature of the ligand and the anions towards the metal ion. The infrared spectra of the complexes of Th(IV) with PBU reveal the bidentate nature of the ligand with carbonyl oxygen and the piperidine ring nitrogen as donor sites. The infrared spectrum of the ligand shows a band at 1660 cm^{-1} which is due to the carbonyl stretching frequency¹⁰. The spectra of the complexes show negative shift to $1640\text{--}1630 \text{ cm}^{-1}$ showing the coordination through the carbonyl group. The band at 1160 cm^{-1} in the ligand¹⁰, which is due to the C—N—C stretching frequency shifts to $1150\text{--}1135 \text{ cm}^{-1}$. This indicates the coordination through the tertiary nitrogen of piperidine ring. The $\nu(\text{NH})$ modes appearing at 3460 and 3366 cm^{-1} in the spectrum of the ligand remain unaltered in the spectra of the complexes showing the non-participation of nitrogen of NH_2 in coordination. There are no additional bands in the region around 3500 cm^{-1} indicating the absence of coordinated water. The additional bands in the region $440\text{--}420$ and $540\text{--}515 \text{ cm}^{-1}$ are assigned to $\nu(\text{M—O})$ and $\nu(\text{M—N})$ respectively.

The nitrate complex of thorium(IV) exhibits three additional bands at 1460 , 1340 and 1020 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 coordinated¹¹⁻¹³ nitrate ions. Since the difference between ν_4 and ν_1 is *ca.* 120 cm^{-1} , it is suggested that the nitrate ions are coordinated unidentately to the thorium ion¹⁴. The neutral nature of the complex indicates the presence of four nitrate ions in the coordination sphere. The molar conductance value also supports this conclusion.

The IR spectrum of the thiocyanate complex of thorium ion with PBU shows three additional bands at $2050\text{--}2040$, 860 and 460 cm^{-1} which are assigned to

$\nu(\text{CN})$, $\nu(\text{CS})$ and $\delta(\text{NCS})$ modes of the coordinated thiocyanate ion respectively. It has been well established that $\nu(\text{CN})$ occurs at lower wavenumber around 2050 cm^{-1} in N-bonded complexes compared to the position in the case of S-bonded complexes¹⁵ appearing around 2100 cm^{-1} . Moreover, $\nu(\text{CS})$ mode appears in the range $860\text{--}780\text{ cm}^{-1}$ for N-bonded complexes while it appears in the range $760\text{--}720\text{ cm}^{-1}$ for S-bonded complexes. N-bonded complexes also exhibit a single sharp band corresponding to $\delta(\text{NCS})$ 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 ions.

The IR spectrum of the acetato complex shows two additional bands at 1670 and 1320 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 occur at 1560 and 1420 cm^{-1} respectively. In the spectrum of the complex $\nu_{\text{asym}}(\text{OCO})$ mode is shifted to higher frequency, 1670 cm^{-1} whereas $\nu_{\text{sym}}(\text{OCO})$ is shifted to lower frequency, 1320 cm^{-1} . The increase in the separation between the two $\nu(\text{OCO})$ bands shows that acetate ions are coordinated unidentately to thorium ion. This conclusion is supported by the non-electrolytic nature of the complex.

In the case of perchlorato complex, the IR spectrum shows five additional bands at 1100 , 1080 , 1020 , 970 and 620 cm^{-1} . The three bands at 1100 , 1080 and 620 cm^{-1} may be assigned to ν_4 , ν_1 and ν_3 modes of coordinated perchlorate ion. This indicates the unidentate coordination of ClO_4^- into $\text{Th}(\text{IV})$ ion¹⁶. Two bands at 1020 and 970 cm^{-1} are due to $\nu(\text{ClO}_4)$ (ionic) in the complex. Thus, the infrared spectral data indicate the presence of both ionic and unidentately coordinated perchlorate ions in the complex. The conductance value supports this conclusion.

The nitrate and perchlorato complexes of $\text{Th}(\text{IV})$ with PBU were tested for their antibacterial activity. However, the test samples do not show any antibacterial activity at concentrations of 1, 5 and 10 mg per disc under the test conditions.

Thermal studies were conducted on the complexes $[\text{Th}(\text{PBU})_2(\text{NO}_3)_4]$ and $[\text{Th}(\text{PBU})_2(\text{NCS})_4]$. 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 $[\text{Th}(\text{PBU})_2(\text{NO}_3)_4]$, the TG plateau up to 208°C shows its stability and the complex starts to decompose after this temperature. This decomposition of the complex occurs in two steps as indicated by the DTG peaks at 220 and 470°C . The TG curve shows a second plateau after 530°C showing the completion of decomposition. The residual mass is about 28% which indicates that the decomposition product is ThO_2 . The independent pyrolysis confirms that the final decomposition product is ThO_2 . The thiocyanato complex, $[\text{Th}(\text{PBU})_2(\text{NCS})_4]$ undergoes two-stage decomposition at 268 and 580°C . The complex is stable up to 230°C as shown by the TG plateau. This shows the absence of water and other solvent molecules. The decomposition at 280°C is due to the dissociation of the

organic moiety, *i.e.*, the ligand PBU is removed from the parent molecule, making a mass loss of nearly 49%. The TG curve shows the second plateau at 618°C. This shows the completion of decomposition. The residual mass of about 27.5% (theoretical 28.4%) shows that the decomposition product is ThO₂.

All these studies confirm the structure of the complex as [Th(PBU)₂X₄] where X = NO₃, CH₃COO or NCS. For perchlorato complex, the structure was found to be [Th(PBU)₃ClO₄](ClO₄)₃. Thus, a coordination number 8 is assigned to thorium in the acetato, nitrate and thiocyanato complexes with PBU while coordination number 7 is assigned in the complex [Th(PBU)₃ClO₄](ClO₄)₃.

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