

SYNTHESIS AND CHARACTERIZATION OF THORIUM (IV) COMPLEXES USING BIDENTATE LIGAND (DONOR NS)

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New thiocyanate containing complexes of thorium (IV) with certain ligands have been synthesized and characterized by elemental analysis, molar conductance and infra red spectra. On the basis of elemental & spectral studies 8 coordinated geometry was assigned to these complexes in the presence of these result it is suggested that this ligand act as bidentate ligand.

KEYWORDS – Elemental analysis, molar conductance, ligand, spectral studies.

INTRODUCTION

Element 90 of the periodic table, thorium appears as the first element of the actinide series. The coordination chemistry of thorium (IV) ion has been less extensively investigated in spite of the fact that it presents an excellent area of research because of its possibility of formation of compounds with coordination number greater than six, a feature rarely observed in transition metal chemistry which has attracted wide attention in recent years^{1,13,14}. Thorium (IV) is an example of less 'a' electron acceptor. Coordinating strongly to smaller and more electro negative coordinating atoms, N, O & F. Thorium (IV) is also known to display a variable stoichiometry from ligand to ligand. It was considered worthwhile to study systematically the formation of complexes of thorium (IV) with various bidentate ligands. The coordination no. 7 & 8 are common among the thorium.

The thorium (IV) metal complexes with neutral oxygen donor ligands of the type X (X = C, N, P, S or As). Among the complexes the coordination number of thorium varies from 6 to 12. The thorium (IV) metal ion forms a broad range of complexes mainly the Schiff bases [2, 3].

The aim of doing this work is to make the thorium (IV) complexes using NS as a ligand.

EXPERIMENTAL

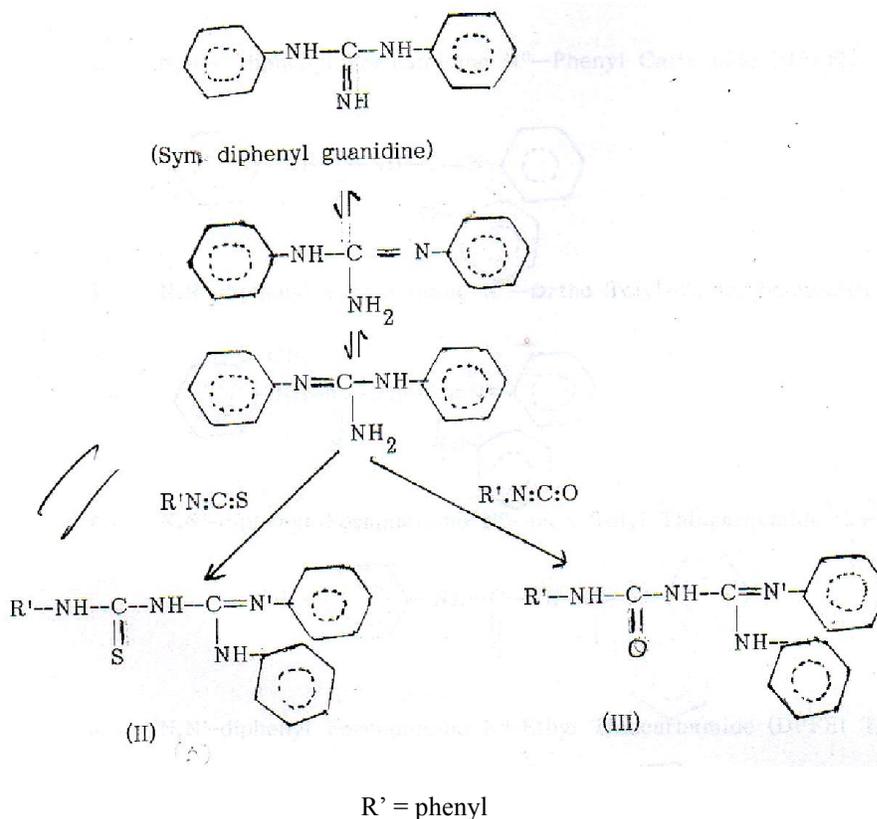
MATERIALS

All the solvent namely ethanol, methanol used are of E.merck, other organic and inorganic compound namely phenyl isothiocyanate, phenyl isocyanate is of Koch light laboratories (England). The Metal Salt namely thorium thiocyanate prepared in the laboratory.

PREPARATION OF LIGAND

It is considered that when an acyl group is introduced on one of the nitrogen atoms of the thiourea and guanidine molecules, better reagents are formed for analytical purpose. Nitrogen and sulphur are donors in these molecules. The addition of oxygen serves as additional donor. This increases the power of ligand for the formation of complexes. Further if a hydrogen atom of second nitrogen atom in thiourea molecule is substituted by alkyl, aryl, acyl or pyridyl group, the basic character of the ligand is increased this increases the solubility of the ligand in polar solvents. In view of these consideration, the following ligands have been prepared in the present study. The ligands N,N'-Diphenyl formamidine N''-Aryl (substituted) carbamides and thiocarbamides were prepared by the method similar to one suggested by Dixit⁴.

The interaction of N,N''-diphenyl guanidine with aryl/alkyl isothiocyanate or isocyanate (1:1 molar ratio) in alcohol yield the formation of N''-alkyl/aryl carbamide (III) by the following mechanism which is self explanatory.



Preparation of Thorium Salts :

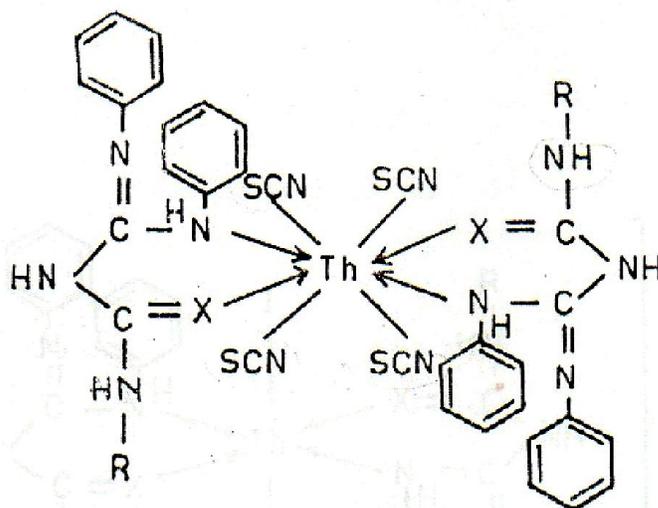


Thorium (IV) thiocyanate was prepared as follows 10% ethanolic solution of $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and potassium thiocyanate (KSCN), were mixed so as to give a Th:SCN ratio of 1:4. The precipitated KNO_3 was filtered off. Thorium tetrathiocyanate was obtained from the filtrate after concentrating by passing dry air through the solution.

Preparation of thorium thiocyanate complex :

$\text{ThX}_4 \cdot 2\text{L}$ (X = NCS)

The complexes of N, N' diphenyl formamido N'' (substituted) carbamides, thiocarbamides & N-2 (pyridyl), N' (substituted). Carbamides thiocarbamides were prepared by the following general methods.



$\text{Th}(\text{DPFSTC})_2(\text{SCN})_4$ and $\text{Th}(\text{DPFSC})_2(\text{SCN})_4$

Complexes, where x = S, O (C.N.-8)

The ethanolic solution of the metal salt and ligand with ethyl acetate in required molar ratio *i.e.* 1:2.5 were mixed. The reaction mixture was refluxed for three hours on a water bath and excess of solvent was removed by distillation. The residual mass on treatment with diethyl ether yielded crystalline solid which was filtered and washed several times with small amounts of methanol and finally with solvent ether & dried in vacuum, over fused CaCl_2 . The yield of Thorium (IV) complexes is 60% of the calculated value.

TECHNIQUES

Estimation :

The techniques enumerated become were employed for the characterization of the various compounds synthesized in the present investigation :-

1. Elemental analysis of complexes :-

Sulphur in all the complexes was determined by oxidizing it with alkaline KMnO_4 to sulphate and subsequent precipitation as BaSO_4 . [5] Thorium (IV) was estimated by

decomposing the compounds with boiling concentrated nitric acid and precipitating the metal hydroxide with aqueous ammonia. The hydroxide was filtered through what man filter paper and washed several times with distilled water. After ignition ThO_2 was weighed [6].

Estimation of anions : Thiocyanate was determined by oxidizing it with boromine water to sulphate and subsequent precipitation as BaSO_4 . In sulphur containing complexes the thiocyanate is determined by nitrating a slightly acidic solution of the complexes against standard silver nitrate solution⁷.

RESULT AND DISCUSSION

In the given table-1 and table-2 we record the data pertaining to the composition melting points and percentage of various elements of the complexes obtained by interaction of thorium thiocyanate with the ligands, N,N' Diphenyl Formamidino N''-phenyl thiocarbamide (DPFPTC), N, N'-diphenyl formamidino N''-phenyl carbamide (DPFPC).

Table-1: Characterization of Complexes Of Thorium Thiocyanate

Complexes	Empirical formula	Formula weight	Colour	Melting point in °C	Analysis of complexes percentage			
					Found		Calculated	
					Th	SCN	Th	SCN
$\text{Th}(\text{DPFPTC})_2(\text{SCH})_4$	$\text{Th C}_{44}\text{H}_{36}\text{N}_{12}\text{S}_6$	1156	Yellowish white	300d	20.57	20.72	20.06	20.06
$\text{Th}(\text{DPFPC})_2(\text{SCH})_4$	$\text{Th C}_{44}\text{H}_{36}\text{N}_{12}\text{S}_4\text{O}_2$	1124	White	280d	21.21	20.98	20.64	20.64

Table-2: Molar Conductance data of thorium thiocyanate complexes.

Molarity of solution = 1×10^{-3}

Complexes	Formula weight	Wt. dissolved in 25 mL ($w \times 10^{-2}$)	Molar conductance $\Lambda \text{ m ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$
$\text{Th}(\text{DPFPTC})_2(\text{SCH})_4$	1156	2.88	38
$\text{Th}(\text{DPFPC})_2(\text{SCH})_4$	1124	2.82	36

All the complexes of thorium thiocyanate are light coloured, insoluble in common organic solvent, but soluble in DMF [8].

The molar conductance :

The M.C. of these complexes were made in dimethyl formamide. The M.C. of thorium thiocyanate have the values in between 24 to 38 mhos.

The pseudohalide ion, SCN^- is known as to form complexes through the hard N end or the soft S – end or behave as a bridging ligand [9] depending on

- The nature of the central metal
- The nature of other ligands in the coordination sphere.

In thiocyanate complexes, $[\text{ThL}_2(\text{SCN})_4]$, $\nu(\text{C}\equiv\text{N})$ was observed in the 2070-2028 cm^{-1} region, strongly suggested N-bonded isothiocyanate coordination expected for a 'hard' acid like the Th (IV) ion.

I.R. Spectra :-

The I.R. spectra of the ligands & their metal complexes were recorded in KBr (Pellet techniques) using Perkin Elmer Grating. Infrared spectrophotometer, model 577, in the range

of 4000-300 cm^{-1} . The spectra of ligands and their metal complexes are quite complicated and different to interpret. All the complexes exhibit a broad bands.

No. I.R. bands for ionic thiocyanate in these complexes were obtained thus providing example of 8-coordinated Thorium (IV) complexes [10].

The analytical results correspond to the general empirical formula. $\text{Th}(\text{L}_2)(\text{SCN})_4$, where L stands for bidentate ligand [11].

CONCLUSION

All the complexes of thorium thiocyanate with N,N'-diphenyl formamidino-N''-aryl/alkyl substituted carbamide are crystalline powder coloured in soluble in common organic solvent but soluble in DMF [12]. The complexes $[\text{Th}(\text{SCN})_4(\text{L})_2]$ with 8 coordination number may have square antiprism structure (d^5p^3 -hybridization).

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