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E: ISSN NO.: 2349-980X **Shrinkhla Ek Shodhparak Vaicharik Patrika**

Synthesis and Characterization of Thorium (IV) Iodide Complexes Using Bidentate Ligand (Donor NS)

Abstract

New iodide 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 6 coordinated geometry was assigned to these complexes in the presence of these result it is suggested that this ligand act as bidentate ligand.

Keywords: Thorium (IV), Elemental Analysis, Molar Conductance, Ligand, Spectral Studies.

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Introduction

Thorium is a rare metal but it covers 8.1ppm of earth's crust. Element 90 of the periodic table, thorium appears as the first element of the actinide series. Starting with this general introduction to thorium.

Review of Literature

A brief review on this complex forming character is presented as follows.

The coordination chemistry of thorium (IV) ion has been less extensively investigated inspite 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[4]. 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. Most of the workers gave emphasis on the area of coordination of thorium with some oxygen donor ligands to this review article where we laid emphasis on the nitrogen sulphur donor ligands and characterized the newly synthesized complex by chemical analysis, conductance molecular weight measurement. 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 prepare the thorium (IV) iodide complexes using NS as a ligand. The investigation it is hoped will extend the present day knowledge of the coordination chemistry of thorium (IV).

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Experimental

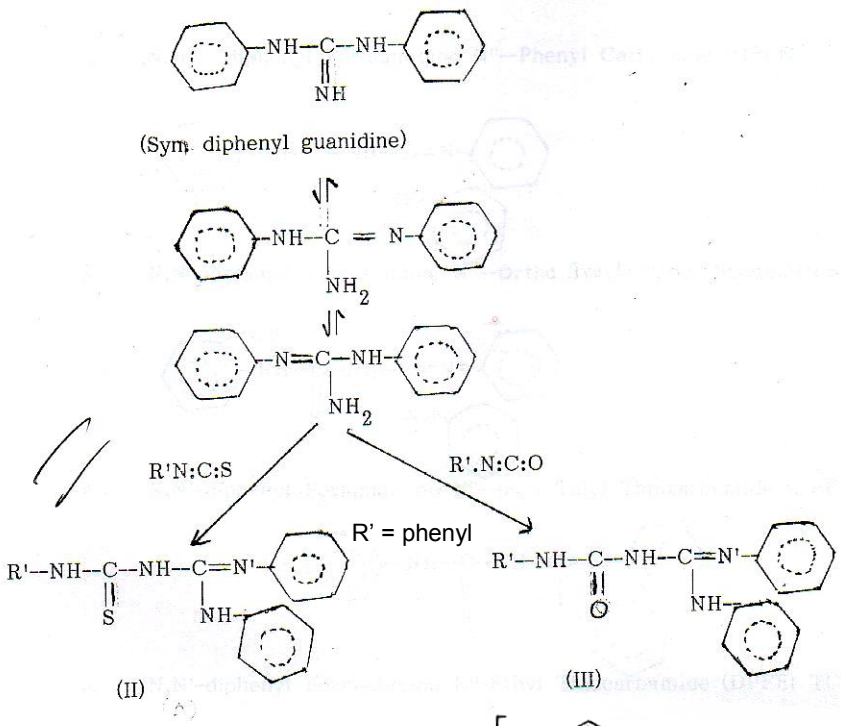
Materials

All the solvent namely ethanol, methanol used are of E.merck, other organic and inorganic compound namely potassium iodide SD – Fine Chem. Pvt. Ltd. The Metal Salt namely thorium iodide 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 guauidine 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 submitted by alkyl, aryl, acyl or pyridyl group, the basic character of the ligand is increased this increases thesolubility of the ligand in polar solvents. In view of these considerations, 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 Dixit[4].

The interaction of N'N"-diphenyl guanidine with aryl/alkyl isothiocynate or isocynate (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

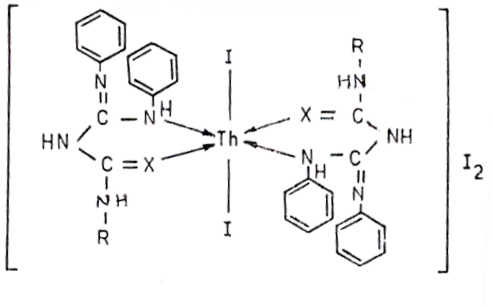
ThI_4

Thorium tetraiodide was prepared by treating 10% methanolic solution of $Th(NO_3)_4.5H_2O$ and KI (Th: I ratio 1:4) and separating the KNO_3 precipitate by filtration. The filtrate containing ThI_4 was used for the preparation of complexes. All the Th(IV) salts being hygroscopic were stored in a desicator over conc. H_2SO_4

Preparation of Thorium Iodide Complex

$ThX_4.2L$ (X = I)

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



$[Th\ I_2\ (DPFSTC)_2\ ]\ I_2$ and $[ThI_2\ (DPFSC)_2]\ I_2$
Complexes
Where x = S,O
(C.N. – 6)

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

by 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,

Elemental Analysis of Complexes

Thorium (IV) was estimated by decomposing the compounds with boiling concentrated nitric acid and precipitating the metal hydroxide with aqueous ammonia[5]. 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

Iodide was determined by Volhard's Method[7].

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 iodide with the ligands, N,N' Diphenyl Formamidino N"-phenyl thiocarbamide (DPFPTC), N, N'-diphenyl formamidino N"-phenyl carbamide (DPFPC).

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

The Molar Conductance

The molar conductance of these complexes were made in dimethyl formamide.The M.C. of thorium iodide have the values in between 180 to 206 mhos.

It shows that the complex of thorium iodide shows the property of 1:2 electrolyte.[9]

I.R. Spectra

The I.R. spectra of the ligands & their metal complexes were recorded in KBr (Pellet techniques) using Perkin Elmer Grating. Infrared spectro photometer 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[10].

The analytical results correspond to the general empirical formula. Th (L_2) $(I)_4$, where L stands for bidenlate ligand[11].

Table-1: Characterization of Complexes of Thorium Iodide

Complexes	Empirical Formula	Formula Weight	Colour	Melting ^{0} point in ^0C	Analysis of Complexes Percentage			
					Found		Calculated	
					Th	SCN	Th	SCN
$Th(DPFPTC)_2(I)_4$	$Th\ C_{40}H_{36}N_8S_2I_4$	1432	Yello wish white	240d	16.42	36.24	16.20	35.47
$Th(DPFPC)_2(I)_4$	$ThC_{40}H_{36}N_8O_2I_4$	1400	Light Yellow Color	260d	16.88	37.11	16.57	36.28

d = decomposed

Table-2: Molar Conductance Data of Thorium Iodide Complexes

Molarity of Solution = 1×10^{-3}

Complexes	Formula Weight	Wt. Dissolved in 25 mL (w x 10^{-2})	Molar Conductance Λ m ohm^{-1}. cm^{2-} mole^{-1}
$Th(DPFPTC)_2(I)_4$	1432	3.58	180
$Th(DPFPC)_2(I)_4$	1400	3.5	189

Conclusion

All the complexes of thorium iodide 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 $[Th(I)_4(L)_2]$ with 6 coordination number may have octahedral structure (d^2sp^3-hybridization).

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