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Thorium(IV) Complexes of Triazene-1-Oxides

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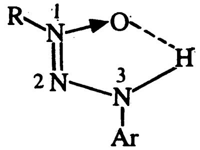
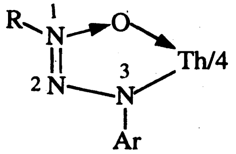
Thorium(IV) complexes of monobasic bidentate triazene-1-oxides are reported. The complexes invariably show coordination number eight. The stereochemistry assigned is dimorphic distorted square antiprism on the basis of similar IR band positions of tetrakis (triazene-1-oxidato) thorium(IV) with [Th(acac)$_4$]. The complexes reported have been found remarkably volatile and sublime near 100°C (10^{-3} torr) without decomposition.

INTRODUCTION

Thorium(IV) ion is larger and the high charge makes thorium(IV) very susceptible to forming complexes.[1] Many anionic and neutral crystalline complex compounds with high coordinaton numbers ranging from 8 to 12 have been isolated[2–5]. Numerous neutral complexes formed by 8-quinolinol, β-diketonates, dithiocarbamates, carbamates etc. have also been studied. In the present communication, the results of thorium(IV) complexes obtained by reacting variedly substituted monobasic bidentate triazene-1-oxides with $Th(NO_3)_4 \cdot 5H_2O$ and $ThCl_4 \cdot 8H_2O$ in aqueous alcoholic medium are reported. Monobasic triazene-1-oxide (TH) is represented by structure (I) and the substituents in the benzene ring are counted from the N—C(Ar) bond. The stoichiometry of the complex is indicated by structure (II).



(I)



(II)

R = alkyl, aryl or substituted aryl
Ar = aryl or substituted aryl.

EXPERIMENTAL

All chemicals used were of AnalaR grade unless otherwise specified.

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$Th(NO_3)_4 \cdot 5H_2O$ and $ThCl_4 \cdot 8H_2O$ were recrystallised from acetone. Variedly substituted triazene-1-oxides were prepared by following published procedures[6], *i.e.*, by coupling substituted phenyl hydroxylamines with benzene diazonium chloride or substituted benzenediazonium chloride at 0–5°C using sodium acetate to control pH.

Synthesis of Complexes[7]

(a) A solution (2 mmol) of $ThCl_4 \cdot 8H_2O$ in 10 mL of 0.01 M HCl was added slowly to a stirred solution of 10 mmol of variedly substituted triazene-1-oxides in 10 mL of 1 M NaOH. The precipitated complex was filtered and washed with water. The crude product was dissolved in 10 mL of methanol. The solvent was removed, and the residue was dissolved in ether. On removal of ether, a colourless residue was obtained.

(b) Tetrakis (triazene-1-oxidato) thorium(IV) complexes were also obtained by reacting 2 mmol of $Th(NO_3)_4 \cdot 5H_2O$ and 10 mmol of variedly substituted triazene-1-oxides in alcoholic medium. The pH was raised by adding alkali solution till the precipitation of the complex was complete. The complex was filtered and washed with water. The crude product was dissolved in acetone. After removal of the solvent the complex was dissolved in ether. After removal of ether, a colourless residue of the complex was obtained.

Thorium was estimated as ThO_2 by igniting the complex in a silica crucible by covering the complex with oxalic acid.[8] Analytical data as well as IR spectra in KBr pellets in the range of 4000–200 cm^{-1} were recorded at CDRI, Lucknow. Nitrogen was estimated by the method of Dumas. The conductance values in nitromethane were obtained using Phillip's conductance bridge. The molecular complexities were determined in freezing benzene.

RESULTS AND DISCUSSION

The characterization data are tabulated in Table-1 and IR spectral data in Table-2. From the characterization data it is evident that the stoichiometry of complexes conform to the formula (ThT_4). The complexes are non-electrolyte (Λ_M values range between 0–4.0 ohm^{-1} cm^2 mol^{-1}) and monomer. The complexes are soluble in organic solvents (particularly in liquid hydrocarbons), remarkably volatile, subliming near 100°C (10^{-3} torr). Repeated recrystallization gives consistent characterization data indicating that the complexes are of definite composition and not loose adducts. Attempts were made to raise the coordination number of thorium(IV) complexes beyond eight, using neutral monodentate and bidentate ligands such as amines, DMSO, pyridine, pyridine-N-oxides, 2,2′-dipyridyl and *o*-phenanthroline ligands but were unsuccessful.

The infrared spectral data (Table-2) are of special importance$_1$ The $\nu(\overset{3}{N}$—H) band disappears in all complexes indicating N—Th bond and $\nu(N \rightarrow O)$ stretch lowered considerably by about 60 cm^{-1} indicating $N \rightarrow O \rightarrow Th$ bond.[9] New stretches are also found at about 410 cm^{-1} and 480 cm^{-1} which were absent in free ligands.

TABLE-1
CHARACTERIZATION DATA OF THORIUM(IV) COMPLEXES OF MONOBASIC TRIAZENE-1-OXIDES (TH)

S.No.	Complex	Substitutents		Analysis %, Found (Calcd.)		Λ_M ohm^{-1} cm^2 mol^{-1}	Mol wt. Found (Calcd.)
		R	Ar	% Th	% N		
1.	ThT_4	CH_3	C_6H_5	27.13 (27.88)	19.78 (20.19)	0.0	827.8 (832)
2.	ThT_4	C_6H_5	C_6H_5	21.30 (21.48)	15.13 (15.56)	3.0	1077 (1080)
3.	ThT_4	CH_3	$C_6H_4CH_3(p)$	25.98 (26.13)	18.74 (18.91)	2.0	886 (888)
4.	ThT_4	C_6H_5	$C_6H_4CH_3(p)$	20.14 (20.42)	14.61 (14.79)	0.0	1135 (1136)
5.	ThT_4	CH_3	$C_6H_4NO_2(p)$	22.79 22.92)	24.89 (24.11)	3.0	1009 (1012)
6.	ThT_4	C_6H_5	$C_6H_4NO_2(p)$	18.58 (18.77)	17.63 (17.78)	4.0	1258 (1260)

TABLE-2
IR BANDS (cm^{-1}) OF TETRAKIS (TRIAZENE-1-OXIDATO) THORIUM(IV)

S. No.	Ligands/ Complex	Substituents		$\nu(\overset{3}{N}—H)$	$\nu(\overset{1}{N}\rightarrow O)$	$\nu(Th—O)$	$\nu(Th—N)$
		R	Ar				
1.	TH	CH_3	C_6H_5	3200 b	1290 s	—	—
2.	TH	C_6H_5	C_6H_5	3190 b	1285 s	—	—
3.	TH	CH_3	$C_6H_4CH_3(p)$	3190 b	1290 s	—	—
4.	TH	C_6H_5	$C_6H_4CH_3(p)$	3185 b	1295 s	—	—
5.	TH	CH_3	$C_6H_4NO_2(p)$	3190 b	1290 s	—	—
6.	TH	C_6H_5	$C_6H_4NO_2(p)$	3185 b	1295 s	—	—
7.	ThT_4	CH_3	C_6H_5	—	1240 s	410 m	480 m
8.	ThT_4	C_6H_5	C_6H_5	—	1245 s	410 m	485 m
9.	ThT_4	CH_3	$C_6H_4CH_3(p)$	—	1240 s	410 m	480 m
10.	ThT_4	C_6H_5	$C_6H_4CH_3(p)$	—	1245 s	415 m	485 m
11.	ThT_4	CH_3	$C_6H_4NO_2(p)$	—	1240 s	410 m	480 m
12.	ThT_4	C_6H_5	$C_6H_4NO_2(p)$	—	1245 s	415 m	480 m

These bonds have been assigned to ν(Th—O) and ν(Th—N) stretches. Thus from characterization data and infrared spectral bands, it is established that triazene-1-oxides function as bidentate chelating ligands with both $\overset{3}{N}$— and $\overset{1}{N} \rightarrow O$ donor groups. This study also establishes that the coordination number of thorium(IV) is invariably eight in all the six reported thorium(IV) complexes. The infrared spectra to $Th(acac)_4$ were compared with that of ThT_4 complexes. The band positions were similar with slight variations. On this basis the structures of ThT_4 complexes have been assigned as dimorphic distorted square antiprism. The remarkable volatility and hydrocarbon solubility of complexes are believed due to the presence of bulky substituents in the triazene-1-oxide ligands. The dominace of steric interactions between the substituents leads to the distortion in the ideal stereochemistry. Because of their ease of formation, stability and solubility in organic solvents (particularly in liquid hydrocarbons), the present study also leads to expectation of triazene-1-oxides as potential ligands to be used in quantitative analysis and solvent extraction of actinides in general and thorium in particular[10].

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