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Some New Thorium (IV) Complexes of Azoester Ligands (Part-II)

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ABSTRACT

Some new complexes of thorium (IV) metal by varying anions (viz. Cl^-,I^-,NO_3^- and OAc^-) with azoester ligand have been synthesized. These complexes are characterized by conventional methods viz. melting point, conductance measurements as well as by spectral methods viz. IR including far IR, UV –visible spectral studies. Thermal studies viz. DTA analysis of some of the representatives have also been done and reported. Some of the representative complexes were also screened against some microbes to check their antimicrobial activities. Coordination number of the complexes on the basis of these studies were proposed to be 8,10 and 12. The tentative structures of these complexes were also reported.

Key words: Thorium (IV) metal/ complexes /azoester/spectral/ thermal/ antimicrobial.

INTRODUCTION

A number of complex forming compounds or ligands have been used to prepare the metal complexes of different metals including lanthanides and actinides[1-5]. Schiff bases are one of these important class of compounds used as ligands.

So far as the ligands are concerned, ligands which are capable of forming chelates are dominating in the area of higher polyhedra, in scope, in numbers and in kinetics as well as in thermodynamic stability. In fact more compact the ligands and the smaller the bite more effective is it in generating higher coordination structures.

Reactions of azo compounds have been widely studied in which nitrogen molecule is eliminated either thermally or photo chemically and two reactive sites remain react to reform a ring (Fig. 1).

The main synthetic application of azo compound decomposition is in synthesis of strained ring systems. The required azo compounds can be prepared by dipolar cycloadditions of diazocompunds and the cyclic azo-esters so formed can be photochemically or thermally decomposed to strained ring system. Such reactions have been developed for pyridazine -3, 6 – dicarboxylate esters; 1,2,4-triazines and 1,2,4,5-tetrazines etc.

A very large number of metal complexes[6-10]of Thorium (IV) and dioxo-uranium (VI) have been reported in literature but such complexes with azoester ligands are seldom found.

In this present communication studies related to thorium (IV) metal complexes with azoester ligands viz. Ethyl - α - (3 - chloro phenylazo) acetoacetate and Ethyl - α - (4 - bromo phenylazo) acetoacetate have been reported.

Ligands used for formation of complexes are reported in figure 2 below

EXPERIMENTAL

All the chemicals used for the preparation of new compounds were obtained in the sealed containers from standard companies e.g. Emerck, Aldrich, CDH and BDH. Thorium chloride, Thorium nitrate, Thorium acetate, Thorium iodide salts were obtained from the RJ (Robbert Johson Company Ltd.) and the BDH (British Drug House), Poole, England. All the chemicals were of AR, AnalR grade.

Thorium iodide was also prepared in laboratory by the reaction of Thorium nitrate with potassium iodide.

Formation of Azo-ester Ligands and their complexes

Jolly et al[11-12]have reported synthesis of many new azo-esters and have explored their activity and reactions. The complex forming capabilities of some of the azo-esters have been explored in the present investigation with thorium and dioxouranium metal salts.

The azo-ester compounds [IUPAC Name: 2-Aceto-2-N (substituted phenyl) azoethylethanoates] were prepared by the methods reported in literature[13-14]. All the substituted azo-ester compounds obtained are deeply coloured reddish brown solids with low melting points and most of them became viscous in the hot summer season of this north central region of Madhya Pradesh where the temperature in this season reaches almost 44-45^{0}C.

The new coordination compounds of Thorium were obtained by the reaction of the azoester ligand with suitable moiety at the pH ranging from 8 to 10 at the room temperature in water medium containing small amount of alcohol/ butanol/mixture of two alchohols.

All the analysis or studies done on the newly synthesized compounds were carried out as reported earlier in related literature[6-10].

RESULTS AND DISCUSSIONS

Physical Data viz. yield, color, mol. weight etc. of Azoester Ligands are reported in table 1

Mass spectral data of the ligands are also reported in the tables 2,3. The prominent peaks are listed in these tables for these compounds. Base ion peak are marked and shown in the tables itself for these compounds. Though spectra of azosters show the peaks related to fragments that may be formed after fragmentation but investigator was not able to record parent ion peak.

Despite of the semi solid physical state of the azo ester ligands during summer season the new coordination compounds obtained were all crystalline solid with generally high melting points and were packed in polythene tubes after filtration and re-crystallization. The purity of the new compounds was checked by the chromatographic methods. The new complexes prepared are listed below along with their physical data in table 4.

1. [Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)
2. [Bis (ethyl – α–(3 – chloro phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)
3. [Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis acetato] Thorium (IV)
4. [Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)
5. [Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)
6. [Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)
7. [Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)
8. [Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis acetato] Thorium (IV)

All the complexes are insoluble in common organic solvents. They are sparingly soluble in DMF and DMSO. Conductance measurement in DMF are too low account for disassociation of these complexes in DMF at the concentration of the 10^{-5} M. Hence the complexes may be regarded as non electrolytes.

IR spectral studies

IR spectral analysis of azoester ligands along with that of representative complexes are reported in the tables 5-10. The N=N stretching vibration[15] of a symmetrical trans-azo compound is forbidden in the infra red spectrum but absorbs in

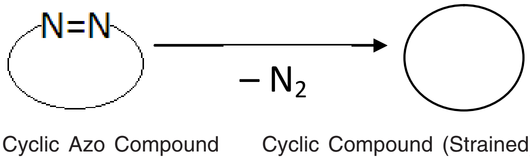
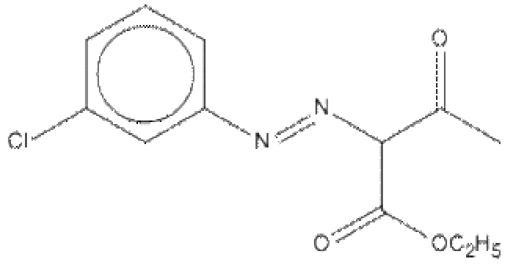


Fig. 1:



Chemical Formula: $C_{12}H_{13}ClN_2O_3$
Exact Mass: 268.06
Molecular Weight: 268.70
m/z: 268.06 (100.0%), 270.06 (32.1%), 269.06 (13.7%), 271.06 (4.5%), 270.07 (1.4%)
Elemental Analysis: C, 53.64; H, 4.88; Cl, 13.19; N, 10.43; O, 17.86

Fig. 2: Ethyl-α-(3-bromo phenylazo) acetoacetate

Table 1: Physical Data of Azoester Ligands

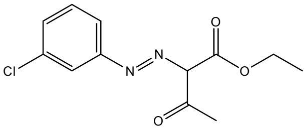
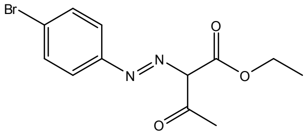
Azoester Ligands : Structure & Name	R	Yield	Color	Molecular Formula	Molecular Weight
 Ethyl - α - (3 - chloro phenylazo) acetoacetate	3 – Cl	80%	Dark Brown	$C_{12}H_{13}ClN_2O_3$	268.70
 Ethyl - α - (4 - bromo phenylazo) acetoacetate	4 – Br	80%	Light Brown	$C_{12}H_{13}BrN_2O_3$	286

Table 2 : Mass Spectral Details of Ethyl -α- (3-chloro phenylazo) acetoacetate

m/z	Relative Abundance (%)
206	5
127	99
112	10
102	15
92	20
75	2
65	35
52	10

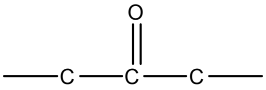
Table 3 : Mass Spectral Details of Ethyl - α - (4 - bromo phenylazo) acetoacetate)

m/z	Relative Abundance (%)
207	2
156	45
143	2
129	2
117	2
104	2
77	95
62	2
51	32

Table 4 : Physical Data of The New Metal Complexes of Th(IV) Metal Salts with Substituted Azoester Ligands

S. No.	Compound Name	Molecular Formula	Color	Molecular Weight Calculated (Observed)
1.	[Bis (ethyl–α–(3–chloro phenylazo) acetoacetato] tetrakis iodo] Thorium (IV)	$C_{24}H_{26}Cl_2I_4N_4O_6Th$	Light Yellow	1277.05 (1272)
2.	[Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)	$C_{24}H_{26}Cl_6N_4O_6Th$	Light Yellow	911.24 (901)
3.	[Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis acetato] Thorium (IV)	$C_{32}H_{38}Cl_2N_4O_{14}Th$	Light Yellow	1005.61 (999)
4.	[Bis (ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)	$C_{24}H_{26}Cl_2N_8O_{18}Th$	Light Yellow	1017.45 (1011)
5.	[Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)	$C_{24}H_{26}Br_2I_4N_4O_6Th$	Brown	1365.95 (1356)
6.	[Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)	$C_{24}H_{26}Br_2Cl_4N_4O_6Th$	Brown	1000.14 (988)
7.	[Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)	$C_{24}H_{26}Br_2N_8O_{18}Th$	Light Yellow	1106.35 (1100)
8.	[Bis (ethyl–α–(4–bromo phenylazo) acetoacetato) tetrakis acetato] Thorium (IV)	$C_{32}H_{38}Br_2N_4O_{14}Th$	Light Yellow	1094.51 (1092)

Table 5 : IR Absorption Frequency in (cm^{-1}) for [Bis (Ethyl-α-(3-Chloro Phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)

Assignment	Ligand (cm^{-1})	Complexes with ThI4 in (cm^{-1})
Aromatic C - H stretching	3100	3400
Out of plane C - H vibration	900	920
C = O ester Stretching	1720	1520
 $—C—\overset{\overset{O}{\|}}{C}—C—$ Bending	1225	1350
C - Cl Stretching	1100	1120
C - N Stretching	1425	1500
Out of place C = C bending	700	750
M - N ligand vibration	-	510

the 1576 cm^{-1} region of the Raman spectrum. Unsymmetrical para-substituted azobenzenes in which the substituent is an electron donating group absorb near 1429 cm^{-1}. The bonds are weak because of the non-polar nature of the bond. The bonds at 1570 cm^{-1} and 1590 cm^{-1} due to v(N=N)

Table 6: IR Absorption Frequency in (cm^{-1}) for [Bis (Ethyl-α-(3-Chloro Phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)

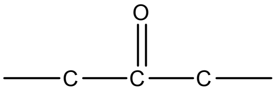
Assignment	Ligand (cm^{-1})	Complexes with ThI_4 in (cm^{-1})
Aromatic C - H stretching	3100	3400
Out of plane C - H vibration	900	900
C = O ester Stretching	1720	1600
 $—C—\overset{\overset{O}{\|}}{C}—C—$ Bending	1225	1360
C - Cl Stretching	1100	1100
C - N Stretching	1425	1600
Out of place C = C bending	700	750
M - N ligand vibration	-	500

Table 7: IR Absorption Frequency in (cm^{-1}) for [Bis (Ethyl–α–(3–Chloro Phenylazo) acetoacetato) tetrakis nitrato] Thorium(IV)

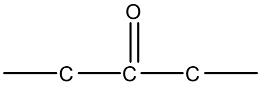
Assignment	Ligand (cm^{-1})	Complexes with ThI_4 in (cm^{-1})
Aromatic C – H stretching	3100	3400
Out of plane C – H vibration	900	800
C = O ester Stretching	1720	1690
 $—C—\overset{\overset{O}{\|}}{C}—C—$ Bending	1225	1360
C – Cl Stretching	1100	1200
C – N Stretching	1425	1690
Out of place C = C bending	700	800
M – N ligand vibration	–	500

Table 8 : IR Absorption Frequency in (cm^{-1}) for [Bis(Ethyl-α–(4 – Bromo Phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)

Assignment	Ligand (cm^{-1})	Complexes with ThI_4 (cm^{-1})
Aromatic –CH stretching	3200	3450
C = O Stretching in ester	1350	1410
C = C Stretching	1520	1520
Disubstituted benzene	1100	1100
C – H deformation for disubstituted benzene	800	890
C – Br Stretching	600	700
M – N ligand vibration	–	520

undergo bathochromic shift to 1550 cm^{-1} in metal complexes indicates that one of the azo nitrogen is bonded to the metal atom.[16-17]

Infrared (IR) spectroscopy has proved to be a tool to establish anions in the complexes. In this present report nitrate (NO_3^-); acetate (CH_3COO^-); and halo (X= Cl^- and I^-) are chiefly used as counter part to metal ions in these complexes.

Lever separation rule may be applied to distinguish between monodentate or bidentate nitrato ions. Lever et. Al[18] showed that this to be true that the separation for monodentate nitrate in (u_1 -

Table 9: IR Absorption Frequency in (cm^{-1}) for [Bis(Ethyl-α–(4–Bromo Phenylazo) acetoacetato) tetrakis nitrato] Thorium(IV)

Assignment	Ligand	Complexes with Th $(NO_3)_4$ in C_2H_5OH	Complexes with Th $(NO_3)_4$ in C_2H_5OH+KOH
Aromatic –CH stretching	3200	3380	3100
C = O Stretching in ester	1350	1400	1400
C = C Stretching	1520	1500	1500
Disubstituted benzene	1100	1100	1100
C – H deformation for disubstituted benzene	800	890	850
C – Br Stretching	600	680	650
M – N ligand vibration	–	500	500

Table 10: IR Absorption Frequency in (cm^{-1}) for [Bis(Ethyl-α–(4–bromo Phenylazo) acetoacetato) tetrakis chloro] Thorium (IV)

Assignment	Ligand (cm^{-1})	Complex with Thorium Chloride
Aromatic C – H stretching	3200	3290
C = O Stretching in ester	1350	1400
C = C Stretching	1520	1510
Disubstituted benzene	1100	1150
C – H deformation for disubstituted benzene	800	860
C – Br Stretching	600	680
M – N ligand vibration	-	520

Table 11: Electronic Spectral Data of Ligand [Bis (Ethyl–α–(3– Chloro Phenylazo) acetoacetato] with Thorium Complexes

S. No.	Ligand/Complex	π–π*(nm)	π–π (nm)	M – N (nm)
1.	(Ethyl – α– 3–chloro phenylazo) aceto acetate	402	487	-
2.	Complex Bis(Ethyl-α-3-chloro phenylazo aceto acetate tetrakis nitrato Th(IV)	280	340	360
3.	Complex Bis(Ethyl-α-3-chloro phenylazo aceto acetate tetrakis chloro Th(IV) (solvent butanol)	250	350	370
4.	Complex Bis(Ethyl-α-3-chloro phenylazo aceto acetate tetrakis chloro Th(IV) (solvent butanol + KOH)	230	310	340
5.	Complex Bis(Ethyl-α-3-chloro phenylazo aceto acetato tetrakis iodo Th(IV)	265	310	360

Table 12: Electronic Spectral Data of Ligand (Ethyl - α - (4 - bromo Phenylazo) acetoacetate) with Thorium Complexes

S. No.	Ligand/Complex	π–π*	π–π	M – N
1.	(Ethyl - α - 4 - bromo phenylazo) aceto acetate	437	374	-
2.	Complex Bis (Ethyl α-(4-bromo phenylazo aceto acetate tetrakis nitrato Th(IV)	270	230	330
3.	Complex Bis (Ethyl α-(4-bromo phenylazo aceto acetate tetrakis iodo Th(IV)	300	230	330
4.	Complex Bis (Ethyl α-(4-bromo phenylazo aceto acetate tetrakis chloro Th(IV)	390	340	430
5.	Complex Bis (Ethyl α-(4-bromo phenylazo aceto acetate tetrakis nitrato Th(IV) (solvent C_2H_5OH + KOH)	280	240	385

Table 13: DTA Study of [Bis (Ethyl-α-(3-chloro phenylazo) acetoacetato) tetrakis iodo] Thorium (IV)

S. No.	Temperature Range (°C)	Peaks	Final Product
1.	37° - 50°	Endo	-
2.	125° - 135°	Exo	-
3.	325° - 345°	Exo	ThO_2

Table 14 : DTA Study of [Bis (Ethyl-α-(4-bromo phenylazo) acetoacetato) tetrakis nitrato] Thorium (IV)

S. No.	Temperature Range (°C)	Peaks	Final Product
1.	80° - 90°	Endo	-
2.	150° - 170°	Exo	-
3.	320° - 340°	Exo	ThO_2

Table 15 :Biological Activity Zone of Inhibition for Fungal Growth for Various Complexes of Thorium(IV)

Complexes (20 mg/ml)	Zone of Inhibition (mm)				
	Fungal M.F.	SP M.G.	A.N.	P.S.	S.C.
Control Cyclohexamide (10mg/ml)	10	12	16	16	20
[Bis (Ethyl – α – (3 – chloro phenylazo) aceto acetate) tetrakis iodo] Thorium (VI)	-	-	-	-	-
[Bis (Ethyl – α – (3 – chloro phenylazo) aceto acetate) tetrakis chloro] Thorium (VI)	-	-	-	-	-
[Bis (Ethyl – α – (3 – chloro phenylazo) acetoacetate) tetrakis nitrato] Thorium (VI)	-	-	-	-	-
[Bis (ethyl – α – (4 – bromo phenylazo) acetoacetate) tetrakis chloro] Thorium (VI)	-	-	-	-	-

MF= Microsporum fulvum MG= Microsporum gypseum AN = Aspergillus niger PS= Penicillium species SC= Saccharomyces cerevisiae

Table 15 :Biological Activity Zone of Inhibition for Fungal Growth for Various Complexes of Thorium(IV)

Complexes (20 mg/ml)	Zone of Inhibition (mm)				
	Fungal M.F.	SP M.G.	A.N.	P.S.	S.C.
Tetracycline (10mg/ml)	20	25	10	32	30
[Bis (Ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis iodo] Thorium (VI)	-	-	-	-	-
[Bis (Ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis chloro] Thorium (VI)	-	-	-	-	-
[Bis (Ethyl–α–(3–chloro phenylazo) acetoacetato) tetrakis nitrato] Thorium (VI)	-	9	-	8	-
[Bis (Ethyl – α – (4 – bromo phenylazo) acetoacetato) tetrakis chloro] Thorium (VI)	-	-	-	-	-

EA= Enterobacter aerogens PV= Proteus vulgaris EC= Escherichia coil
SA= Staphylococcus aureus BS= Bacillus subtilis

u_4) is appeared to be 5 – 26 cm^{-1} and that for bidentate nitrato group this may lies in 20–60 cm^{-1}. This method has been tried in present case of complexes and a separation of Ca 250 – 200 cm^{-1} in the combination bands in the region 1550 – 1290 cm^{-1} suggest that nitrato ion is bidentate in nature in these complexes[19-21]. Similar to nitrato acetate ion in the present study of complexes also appears to be bidentate ligand. In case of halo complexes (M-X) vibrations could not be assigned because they are out of the range of studied region in the present investigations.

UV- Visible spectral studies

UV- Visible spectral analysis of the representatives complexes are also done and are reported in tables 11,12 below

Magnetic Behaviour of Complexes

Complexes of Thorium (IV) metal salts are diamagnetic in nature depending upon the other ions present and the corresponding ligand field. The magnetic susceptibilities are independent of field strength and temperature. In the present studies complexes are weakly diamagnetic as observed[22-24]as they contain no unpaired electrons.

DTA studies of the Complexes

The results of these studies done on representative complexes are reported in Table 13 -14. The observed DTA graphs clearly show the stability of complexes upto considerably higher temperature range. The Exo and Endo peaks are located in these DTA graphs and are mentioned in Tables. In all the cases oxides are formed as final product of analysis viz. stable ThO_2 and U_3O_8. These metal oxides are formed over a comparatively high range of temperatures. These studies confirm the high stability of these complex compounds under studies upto high temperature. In intermediate steps ligands may left the complex molecules.

Based on the studies done on newly synthesized complexes of thorium (IV) metal salts their structures were proposed along with their coordination numbers. These are given in figure 3 below.

Antimicrobial studies of Complexes

The biological activity of different representative samples were tested against different microbial species using Methods reported earlier[25-27] on NA medium and paper disc method. Results are reported in the table 15,16 given below. After 24 hrs incubation observed the plates for zone of inhibition around the well & the results are recorded in tabulated form. None of the products showed any significant antimicrobial activity

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