*Asian Journal of Chemistry* Vol. 19, No. 5 (2007), 3307-3324

***REVIEW***

# Thorium(IV) Metal Complexes with Neutral Nitrogen Donor Ligands-A Review

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The present review presents a discussion of thorium(IV) metal complexes with neutral nitrogen donor ligands including Schiff base ligands. This review contains 117 references upto year 2004.

**Key Words: Thorium(IV), Complexes, Nitrogen donor ligands.**

## INTRODUCTION

Thorium, though is a rare metal but it constitute 8.1 ppm of earth's crust and is found to be 39th most abundunt element of earth crust. It's main source is monazite sand in which it occurs as phosphate in 10% amount. Naturally occurring thorium is almost entirely $^{232}_{90}\mathrm{Th}$ and this isotope is not fissionable[1].

Starting with this general intruduction to thorium a brief review on this complex forming character is hereby presented.

The coordination chemistry of thorium has always been a keen subject of interest amongst chemical community, but this review article is afreshly different from others published on thorium.

Starting from work of Comyns and Bagnall[2,3] which is still the torch bearer in area of coordination chemistry on thorium and then the review article of Agrawal *et al*[4], on the complexing tendency of thorium with some oxygen donor ligands; to this review article where we restrict ourselves only on the neutral nitrogen donor ligands.

In this review, we take a step further as we generalise some points on the tendency and situations in which Thorium complexes. Thorium show complexation tendency in its +4 oxidation state easily[5].

$_{90}\mathrm{Th} = [\mathrm{Rn}]6d^2 7s^2$

Th(IV) is very prominent in its complexation tendency especially when it forms compounds exhibiting high coordination number. A metal acquires high coordination number only when (a) It is a small, highly charged ion, with suitable vacant orbitals of right energy, (b) It can attain a noble gas structure (effective atomic number rule), (c) It can attain a symmetrical shape and high CFSE in complex. Th(IV) ion has a high positive charge which is essential condition for high coordination because this will not allow the negative charge, donated by electrons from the ligands, to accumulate on the central metal atom. Thus, Th(IV) successfully reveals high corordination number, as shown in Table-2, alongwith the general properties of thorium in Table-1.

TABLE-1
GENERAL PROPERTIES OF THORIUM

| Properties | |
|---|---|
| Atomic number | 90 |
| Atomic weight | 232.05 |
| Electronic configuration | [Rn] $5f^{o}\ 6d^{2}\ 7s^{2}$ |
| Covalent radius | 1.82 Å |
| Ionic radius | 0.99 Å ($M^{4+}$) |
| Electronegativity | – |
| Common oxidation states | +3, +4 |
| Density | 11.7 |
| Boiling point | 3850ºC |
| Melting point | 1750°C |
| Atomic volume | 19.9 |
| Heat of fusion | 4.6 kcal/mol |
| Crystal structure | Cubic, face centered |
| Half life | $1.4 \times 10^{10}$ years |
| Decay product | Uranium, [β emitter] |
| Source | Naturally occurring ores |
| Availability | in Tonnes (8.1 ppm of earth crust) |
| State | Gold coloured solid |
| Conduction | Good conductor |
| Standard oxidation potential | $Th^{o} \xrightarrow{1.90v} Th^{4+}$ |

The reason for this high coordination number. of thorium may be attributed to the fact that thorium, also all actinides, have deeply seated incomplete 5*f*-orbitals compared to 4*f*-orbitals of lanthanides. The radial distribution of 4*f*-orbitals shows a small shell of electron density below the main 5*f*-orbital. Therefore, 5*f*-orbital are more penetrating than 4*f*-orbital. and are more diffused at the periphery of atom. Hence these can be disturbed by ligands. It is well known that the energy differences in orbitals of thorium 5*f*, 6*d*, 7*s* and 7*p* is very small. Hence while bonding, some or all of these orbitals can take part[6,7]. This fact is revealed when thorium and other actinides form ionic compounds and various complexes with not only anions such as $X^-$, $SO_4^{2-}$ but also π-bonding ligands such as alkyl phosphines, thioethers and cyclopentadiene by the use of 5*f*-orbitals.

TABLE-2
HYBRID ORBITALS AND GEOMATRY

| C. N. | Hybridi-zation | Geometry | Example |
|---|---|---|---|
| 4 | $sp^3$ | Tetrahedral | $ThCl_4$ |
| 6 | $d^2sp^3$ | Octahedral | $[Th(QO)_6][ClO_4]_4$<br>$[Th (DPSO)_6][ClO_4]_4$<br>$[Th(TMSO)_6][NCS]_4$ |
| 8 | $d^5sp^3$ | Square antiprism | $[Th (Apy)_7(ClO_4)][ClO_4]_3$<br>$[Th(acac)_4]$<br>$[Th(OMPA)_4][ClO_4]_4$<br>$K_4[Th(oxalate)_4{\cdot}4H_2O$ |
| 9 | - | Trigonal antiprism $ThF_8^-$<br>Tricapped trigonal prism | $[Th(trop)_4DMF]$<br>$(NH_4)_4[ThF_8]$ |
| 10 | - | Symmetrical bicapped square antiprism | $[Th(NO_3)_4(TPPO)_2]$<br>$[Th(trop)_5]$<br>$[Th(NO_3)_4BipyO]$ |
| 11 | - | - | $Th(NO_3)_4(DPSO)_3$ |
| 12 | - | Distorted icosahedron | $[Mg(H_2O)_6][Th(NO_3)_6].2H_2O$<br>$Th(NO_3)_4(AAPy)_2$<br>$[Th(H Saphen)_2(NO_3)_2]$ |
| - | - | Icosahedral $NO_3^-$ groups are bidentate | $[Mg(Th(NO_3)_6)]$ |

In other words the energy required for the conversion of $5f \rightarrow 6d$ is less for thorium, it can exhibit coordination number as high as 12 and rightly does so, in many of its complexes[8]. With this explanation, one can conclude that degree of complex formation for thorium has the following order-

$$Th^{4+} > Th^{3+}$$

Both singly and doubly charged anions, complex with $Th^{4+}$ along with many organic substances[8].

A review article by Agrawal *et al*[4]; discusses 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 6-12. The complexes have been studied by various by physical techniques like IR, X-ray diffraction, electronic absorption, *etc*. Though this review covers a lot but Th(IV) metal ion forms a wide range of complexes even with neutral nitrogen donor ligands especially Schiff bases. Therefore we restrict this review article, to deal with Th(IV) metal complexes with neutral nitrogen donor ligands such as neutral Schiff base ligands, azo group, contaning ligands and other neutral nitrogen donor ligands.

## Complexes with Schiff base ligands

Nitrogen donor ligands particularly Schiff bases have been of great interest for various coordination chemists who used them as ligands against thorium(IV) metal to form complexes. Schiff bases form a class of compounds with azomethine (>C=N-) group which can be obtained by condensation of primary amine and with carbonyl compounds by elimination of water molecule.

Schiff bases because of their physiological and pharmacological activities are more important compounds for the past many years Anticancer activities of Schiff bases mustards have also been reported[9,10]. Some of the Schiff bases displayed significant activity against L 1210, Lymphoid Luekemia Walker 256 and Dunning Lukemia[9,10]. Since mid nineteenth century[11], metal Schiff base complexes have been reported and their general preparation even before that[12]. A detailed chemistry of Schiff base complexes till the end of 1964 was reviewed by Yamada[13] but still there is a need of exhaustive review including thorium(IV) metal salts.

A research article published in 1976 by Casellato *et al.*[14] cited single example of Th(IV) chelate with N,N'-ethylene-*bis*(salicylaldimine) with the composition $Th(salen)_2$ and $Th(salen)Cl_2$ (THF). Both the compound were stable in air and found to be of yellow colour.

Using salicyldehyde another bidentate Schiff base was reported to be formed as a result of condensation reaction between salicyldehyde and *p*- toludine, *p*-anisidine and *p*-phenitidine. The formula was cited as $ThL_2X_4$ ($X = Cl^-$, $I^-$, $NO_3^-$ ) or $ThL_3(NCS)$ by Mohanta and Dash[15]. In this, the donor set is NO. These authors[16] further confirmed the Th(IV) complexes with tetradentate schiff bases ($N_2O_4$ donor this time) and again used a condensation reaction between salicyldehyde (or acetone) ethylene diamine to prepare Schiff base. The complexes possessed the formula $ThL_2X_4$ (L = $H_2$, salen, X = $Cl^-$, $Br^-$, $I^-$ or $NCS^-$ and $H_2$ acacen, X= $Cl^-$, $I^-$, $NCS^-$ or $ClO_4^-$ ) or Th $LX_4$(L = $H_2$ salen, X= $NO_3^-$ or $ClO_4^-$ and L = $H_2$ acacen X= $Br^-$, $NO_3^-$).

Salicyldehyde is key compound for preparation of various Schiff bases which are bidentate and tetradentate in nature. Various thorium(IV) complexes[17-19] have been prepared by using Schiff base of type [5-$NO_2$-salen] [5-$NO_2$-salophen], [5-Cl salen], [5-Cl-salophen], [3-meso-salen], [3-meso-salophen], [3-etosalen] All the complexes were found to have general formula $ThL_2$ X-ray crystallographic studies were carried out for *bis*[N,N-ethylene-*bis*(3- methoxysalicylaldiminato)Th(IV) monopyridine complex. The crystal was found to be triclinic a = 13.468, b = 9.932, c = 16.532 Å, $\alpha = 91.74°$, $\beta = 94.69°$ and $\gamma = 93.03°$ and space group $P_1$.

Salicyldehyde along with 2,6-diaminopyridine also forms a Schiff base which complexes with Th(IV)[20,21]. For this salicyldehyde (DAP-sal

$C_{12}H_{11}N_3O$) or vanillin (PAP van $C_{13}H_{13}N_3O_2$) were taken. The complexes were studied further by TGA and XRD studies.

It has been confirmed by various workers[22-24] that Th(IV) nitrate complexes of Schiff bases and also the complexes, with heterocyclic Schiff bases are formed in 1:1 and 1:2 molar ratios. The complexes were characterized by elemental analysis, UV-visible spectroscopy and IR spectra along with conductance measurement. The heterocyclic Schiff base was prepared by a condensation reaction between 2-amino pyridine and salicyldehyde (L) and vanillin.

Apart from salicyldehyde other aldehyde used to prepare Schiff base include benzaldehyde[25-30]. Studies reveal that Schiff base obtained from benzocain and 4-hydroxy-3- methoxy benzaldehyde and TMBAAP, FAAP, 2-$NO_2$ - BAAP, 3-$NO_2$BAAP CAAP, SAAP have been reported to form complexes with Th (IV). The complexes were confirmed by elemental analysis conductance measurement, IR and electronic spectra, TGA or DTA studies along with their decomposition kinetics[31].

Further, complexes of Th(IV) with neutral nitrogen donor ligands containing the azomethine (>C=N-) group includes the class of complex containing antipyrine and napthalidene moiety. These complexes formed between Th(IV) and Schiff bases obtained from 4-amino antipyrine[32-34] and HNAAP, DABAAP, MBAAP, HMBAAP, BAAP showed general formula $ThX_4{\cdot}nL$ (X = Cl, $Br^-$, $NCS^-$ or $NO_3^-$ ; n = 2X = $I^-$ or $ClO_4^-$; n = 3; L= BAAP, MBAAP, DABAAP, HMBAAP or HNAAP). The complexes were confirmed by elemental analysis, molecular weight data, conductance and magnetic measurement along with IR and TGA studies.

Use of heterocyclic aldimines (PyA/A) and ketimines (AcPyA) have also been done[35] to study Th(IV) complexes for their spectra and TG studies. The complexes are bidentate in nature and are prepared from 2-pyridine carboxyldehyde and aryl amines such as aniline, *o*- *m*-, *p*-toludines and *o*-, *p*-anisidines or *o*-, *m*-chloro anilines. The complexes have the general formula $[Th(SB)X_4]$ SB = PyA/A or ACPyA, x = $NO_3^-$ or $NCS^-$.

Exceptionally high coordination number of thorium, *i.e.*, 10 along with 6, 8 coordination number[36-56] is depicted in the complexes of Th(IV) with Schiff bases of the type BAPy, 1p-BAPy, MHA MBAPy, SAPY, 3-NBAPy, CABAB, BCABAB, FCABAB. These complexes were studied for their thermal kinetics as well.

The complexes of Th(IV) show various biological activities as well. Various tertiary amino benzaldehydes having *bis*-2'-(cyanoethyl)amino group were synthesized[57] and found to biologically potent[58]. The Schiff bases derived from these namely 2-MCABAB, 3-MCABAB, 2-MMCABAB, 3-MMCABAB, ECABAB, EMCABAB[59-64] were prepared and confirmed by their melting points and elemetal analysis. Their IR and mass-spectra were obtained. The IR spectra along with other data revealed that when azomethine nitrogen acts as ligand site to which the Th(IV) binds, then there is a shift ν(-C=N-) towards the lower frequency. This confirms the involvement of lone pair of electrons on N participating in the bond formation *i.e.*, nitrogen is neutral donor. These complexes are suggestive of coordination number of Th(IV) ranging from 6-10. The quantum chemical investigations showed that the complexes formed,were found to be quite stable.

Polychelates of Th(IV) are known to possess antimicrobial activity and exhibit semiconducting behaviour[65] such polychelates are formed with 4,4'-*bis*[(N-phenyl(salicyldimine-5))azo]biphenyl. The ligand is bis-bidentate and coordinate through azomethine N-atom.

Certain tetradentate ligands comprising of coordinating azomethine nitrogen along with other ligands like phenolic oxygen also show antimicrobial and semiconducting behaviour. The ligand is called polymeric Schiff base (PSB) and is derived from 4,4'-dihydroxy-3,3'dibenzoyl biphenyl and 1,3-diaminopropane, *o*-phenylene diamine or 2,3-butanedione dihydrozone. The chelate is studied for its IR spectra thermal activation energies by Broido method[66] and is found to be effective against various microbes. Th(IV) is known to form complexes in solution in wide range. These complexes have been studied for their stability, by potentiometric studies. One such complex is Th(IV) with (2-hydroxy acetophenone)ethylene diamine forming a Schiff base[67]. The complex was studied in 50 % (v/v) ethanol.

In solutions, Th(IV) formed complexes with a Schiff base obtained[68] from FHMB and $ML_2 \cdot H_2O$ (M = FHMB Anil) (2,2'-dipyridyl amine)-$H_2O$ [M = $UO_2$ (VI) or Th(IV)]. The complexes were studied for their IR spectra and their antimicrobial tests were conducted.

Similarly stability constant for chelate formation of Th(IV) with Schiff base derived from 5,7-dihydroxy-6-formyl-2-methylbenzopyran-2-one were studied[69] potentiometrically and conductometrically. Irving Rosotti technique for these resulted in the prediction of 1:1 and 1:2 (M:L) ratio for them. It was found that stability constant increase as ionic strength, temperature and precentage of phenol are lowered. The reaction for the formation was found to be exothermic. Magnetic moment values have been studied for these complexes. Such as for the complex of Th(IV) with a Schiff base[70] derived from 6-methyl-3-formyl-4-hydroxy-(1H)-quinolone and ethanalamine. The ligand show mono basic tetradentate or dibasic behaviour and bridging through chloro, acetate or sulfate group in dimer have been reported.

Among multidentate ligands, Schiff bases as high as tetradentate nature have been prepared and reported to show complexation with Th(IV). The Schiff base was derived from 2,6-diamino pyridine and salicyldehyde or vanillin react with $Th(NO_3)_4$ to give Th $L(NO_3)_4$ where L is Schiff base. IR, electronic spectra, conduction show the 1:1 complex with tridentate L, coordinating through azomethine and amine N atoms also phenol O atoms and were found to be potentially tetradentate. Ultrasonic absorption measurements are done on Th(IV) solution in water as function of ligands in the complexes. In the frequency range 10-170 MHz, ultrasonic predicts formation of inner sphere complexes[71] of Th(IV) with $NO_3^-$.

Apart from preparation and characterization of Schiff base complexation of Th(IV) attempts have been made[72] to study electrical and thermal properties of chelate of polymeric Schiff base and Th(IV) (PSB). PSB were characterized by various physical methods and electrical counductance of these is found to be temperature dependent. The chelates are reported to have semiconducting behaviour and their mode of decomposition and apparent activation energy and order of each of their reaction have been reported.

Apart from their semiconducting behaviour Th(IV) complexes with Schiff bases and benzmidazole derivatives[73] show antibacterial activity. The complex are found to be effective against gram positive and negative bacteria and benzmidazole ligands were found still more potent than metal complex with Schiff base.

## Complexes including the azo (-N=N-) and other neutral nitrogen donor ligands

Among azo (-N=N-) group complexes aryl azo acetyl acetones are well known. Their complex in 40 % (v/v) in EtOH have been prepared and studied for their dissociation constant[74] of ligands along with their stability constant, various thermodynamic factors for complexing conditions have been analyzed[75].

Other well known complexes of Th(IV) including azo groups includes complex of Th(IV) in arsenazo III in 6 M HCl media. Th(IV) forms ML and $ML_2$ type complexes and exhibit isobectic points in medium[76]. These complexes have been studied[77] and determined along with U(VI) complexes using the partial least square type-I (PLS-I) method.

Arsenazo HKS has also been known to complex with Th(IV) in 1.2 mol/L in $HNO_3$ medium where a blue coloured complex is obtained in ratio 1:2 with max. absorption at 675 nm[78]. $CPA_PDMA$ have been synthesized and shown to undergo a colour reaction with Th(IV) and a blue colour n[Th(N)] : n($CPA_PDMA$) = 1 : 2 is found to be formed exhibiting a molar absortivity of $9186 \times 10^4$ L $mol^{-3}$ $cm^{-1}$ at 674 nm[79].

Th(IV) also form solid state chelates in 1:1 and 1:2 ratio with arsenazo compounds like 1-phenylazo-2-arsenoic acid-2-naphthol, 4-(1-phenylazo-2-arsenoic acid)-1-naphthol, 4-(1-phenylazo-2-arsenoic acid)-3-napthoic acid. The complexes are determined by DTA, TGA and IR studies[80].

4-Azo-pyrazolone chelates of Th(IV) have been prepared and studied potentiometrically[81]. Normally for such compounds use of cetyl-pyridinium halide is made but even in absence of cetyl-pyridinium chloride, Th(IV) complexes with *m*-carboxy chlorophosphonazo (CPAmK)[82] resulting in coloured complex with $\in = 1.50 \times 10^5$. Th(IV) complexes with chloro phosphonazo-*m*-N-cetyl pyridinium bromide system and the colour reaction is studied in $HNO_3$ where 1 : 3 [Th : CPA] complex is formed[83]. The use of such complex is to trace Th(IV) among rare earths.

Poly halogenated chromotropic acid *bis* azo reagent also complexes with Th(IV) like arsenazo and chlorophosphonazo ligands but this complex is less intense in colour[84].

Indersenen *et al*[85] reported formation of Th(IV) complexes with Schiff bases obtained from substituted hydrazones like PCIH, PCAP, PCSH, PC AAP in the general formulation $ThL_2(NO_3)_4$ [L = PCIH, PCAP, PCSH and PCAAP].

Other Schiff base complex of Th(IV) in solution includes those forming in 40 % (v/v) EtOH at ionic strength of 0.1 M[86].

One such complex of Th(IV) and Schiff base like N-salicylidene-4-carboxy-3-hydroxy aniline, (4-hydroxysalicylidene)-4-carboxy-3-hydroxy aniline and N-(2-hydroxy-1-naphthyl-methylene)-4-carboxy-3-hydroxy aniline have been confirmed by potentiometric, conductometric, IR and elemental analysis data. The M:L is fond to be 1:1 or 1:2 and coordination have been reported through the imine N or hydroxyl O atom.

Substituted 1,5-diaryl-3-acetyl and 3-cyanoformazans show complex formation with Th(IV) and the complexes can be determined potentiometrically[87]. Various other complexes of Th(IV) with neutral nitrogen donor ligands includes complex with chlorophosphonazo-*p*-aminohippuric acid ((PHA-CPA) in acidic medium in 1:3 ratio[88]; complex with aryl *bis*(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl ligands in dioxane-water system[89] of the type $[ThL_2][ThL(OH)_2]$ in ratio 1:1 and 1:2. Complexes with 5-chloro-7-amino-8-hydroxyquinoline in $HNO_3$ where stability of Th(IV) complex was studied using Irving Rosotti method[90]. Complex with penicillamine system was studied by paper electrophoresis[91]; complex with guanosine (binary and ternary) complex in 1:1 ratio, where involvement of N(7) in guanosine ring nitrogen is established[92]; complex with 4-dimethylamino cinnamylidene pyruvic acid[93] in aqueous medium; complex with mixed methionine and pencillamine[94], complex with arsenic acid *bis*-azo type derivative of chromotropic acid[95], complexes with derivative of *o*-hydroxy-phenyl-azo-1-methyl-3-phenyl-thiohydantoin[96] in the ratio 1:1 and 1:2 (M:L) in presence of EDTA, where solid complex were obtained, compelex with 4-N,N-dimethyl aminopyridine of the formula $Th(NO_3)_4(H_2O)_5L$[97]; complex with 5,17- diphenyl-7-14-dimethyl-1,4,8,11-tetraazocycloteradecane, N,N''-diacetic acid of the type $Th(H_2L_3)\cdot 4\ NO_3\cdot H_2O$ in 1:1 ratio and $Th(H_2L_4)\cdot 4NO_3\cdot 7H_2O$[98]; complex with 2,4-diamino-5-(3',4',5'-trimethoxybenzyl)pyrimidine[(tri-metho prim)(TMD)][99]; complex with *tris*(2,3-dihydroxybenzenylamino)ethyl amine (TRENCAT) in $NaClO_4$[100]; ternary complex.

Th: BCO: CPB in ratio 1:1:1[101]; macrocylic complex of Th(IV) with tetra amide used for cleavage of RNA and phosphate diester linkage[102]; complex with 2',2-(hydroxyphenyl)benzothiazolhydrazone, 2'-(2-hydroxy -5-chloroactophenyl)benzothiazoyl hydrazone 2'(2,5-dihydroxyacetophenyl)benzothiazoyl hydrazones on silica gel[103]; complex with 3 acetyl-1,5-diaryl and 3 cyano-1,5-diaryl formazan with coordination number 6 and 8[104]; with formula $Th(HL)_{1-2}(OH)_{0-3}$. 14 Different complexes of Th(IV) with formazan derivatives with O-acidic substituent on end phenyl[105]; a hexadonor macrocyclic complex with Schiff base obtained from apropriate metal salt, dicarbonyl and diamine condensation used for radiation therapy[106]; complex with hydroxy pyridione system II on the type $ThL(OH)_3\cdot 6H_2O$ (HL = 1-hydroxy-2(1H)pyridone and 3-hydroxy-2(1H)-pyridone in the ratio HL : metal (1:1)[107]; complex with Eriochrome cyanine R and cetyl pyridinium chloride, ternary complex of ratio 1:3:3, 1:3:6, and 1:3:9[108]; complex with benzazolyl formazan in ratio 1:2[109] thorium (IV) and dioxouranium(VI) metal complexes with Schiff base ligands $L_1$ and $L_2$ *viz.*, 2-MMCABAB and 3-MMCABAB, respectively which were derived from the condensation of *o*-methyl-*p*-(N,N'-dicyanoethyl)amino benzaldehyde with *o*-methyl aniline and *m*-methyl aniline were synthesized and characterized by electrical conductance, molecular weight and spectral studies by Arora *et al*[110].

Same authors have also reported synthesis and characterization of Schiff bases derived from condensation of *m*-methyl aniline and *p*-(N,N′-dicyanoethyl)amino benzaldehyde and by the condensation of *p*-aminoethyl benzoate and *p*-(N,N′-dicyanoethyl) amino benzaldehyde[111,112].

A new series of complexes of Th(IV) with polydentate ligands N,N′-diethylene amino-*bis*(3-carboxy propenamide) derived from maleic anhydride and diethylene triamine and various anions such as nitrate, perchlorate and thio cyanate have been synthesized. The complexes were characterized by various physicochemical data such as C, H, N metal ion contents, spectral, magnetic and molar conductivities. The complexes confirm[113] the composition $[Th(DBCP)X_2]$, where x = $NO_3^-$, $NCS^-$ and $ClO_4^-$.

## Conclusion

Thus with these facts and various complexes studies, a fact is clearly established that Th(IV) is a Lewis acid of the hard type. As per its high coordination no and wide range of complexes with varying stoichiometeries;

lately its metal salts were also studied. Various complexes of thorium(IV) metallic salts like halides, nitrates, thiocyanates, perchlorates, *etc.* were prepared and studied.

In this review, attempts have been made to include wide range of complexes of thorium(IV) with Schiff base, azo groups containing ligands and various other neutral nitrogen donor ligands with stress on substituted hydrazones (Table-3).

TABLE-3
VARIOUS COMPLEXES OF NEUTRAL NITROGEN DONOR LIGANDS WITH Th(IV) METAL

| Metal Salt | Ligand (L) | M:L Ratio | Physicochemical method | Ref. |
|---|---|---|---|---|
| $ThCl_4$ | Salen | 1:2 | - | 14 |
| $ThCl_4$ | $H_2$-salen | 1:2 | - | 14 |
| $ThI_4$ | S.B. [salicyldehyde + *p*-toludiene or phenitidine or *p*-anisidine | 1:2 | - | 15 |
| $Th(NO_3)_4$ | S.B. [salicyldehyde + *p*-toludiene or phenitidine or *p*-anisidine | 1:2 | - | 15 |
| $Th(NCS)_4$ | S.B. [salicyldehyde + *p*-toludiene or phenitidine or *p*-anisidine | 1:2 | - | 15 |
| $ThCl_4$ | S.B. [salicyldehyde (acetone) + ethylene diamine ($H_2$, salen) | 1:2 | - | - |
| $Th(NO_3)_4$ | S.B. [salicyldehyde + *p*-toludiene or phenitidine or *p*-anisidine | 1:2 | - | 15 |
| $ThBr_4$ | $H_2$-salen | 1:2 | - | 16 |
| $ThI_4$ | $H_2$-salen | 1:2 | - | 16 |
| $Th(NCS)_4$ | $H_2$-salen | 1:2 | - | 16 |
| $ThCl_4$ | $H_2$-acacen | 1:2 | - | 16 |
| $ThI_4$ | $H_2$-acacen | 1:2 | - | 16 |
| $Th(NCS)_4$ | $H_2$-acacen | 1:2 | - | 16 |
| $Th(ClO_4)_4$ | $H_2$-acacen | 1:2 | - | 16 |
| $Th(NO_3)_4$ | $H_2$-salen | 1:1 | - | 16 |
| $Th(ClO_4)_4$ | $H_2$-salen | 1:1 | - | 16 |
| $ThBr_4$ | $H_2$-acacen | 1:1 | - | 16 |
| $Th(NO_3)_4$ | $H_2$-acacen | 1:1 | - | 16 |
| $Th(NO_3)_4$ | 5-$NO_2$-salen | 1:1 | - | 16 |
| $Th(NO_3)_4$ | 5-$NO_2$-salophen | 1:1 | - | 16 |
| $ThCl_4$ | 5-Cl-salen | 1:1 | - | 17 |
| $ThCl_4$ | 5-Cl-salophen | 1:1 | - | 17 |
| $Th(NO_3)_4$ | S.B. from salicyldehyde and 2,6 diamin *o*-pyridine | 1:1 | TGA, XRD | 20 |
| $Th(NO_3)_4$ | [DAP-Sal $C_{12}H_{11}N_3O$] PAP -van $C_{13}H_{13}N_3O_2$ | 1:1 | TGA, XRD | 21 |
| $Th(NO_3)_4$ | Heterocyclic S.B. (2-amino pyridine + salicyldehyde (L) and vanillin | 1:1, 1:2 | UV, IR | 22, 23, 24 |
| $Th(NO_3)_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +TMBAAP | - | E.a. IR, UV, TGA, DTA | 25 |
| $ThI_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +TMBAAP | - | E.a. IR, UV, TGA, DTA | 25 |

| Metal Salt | Ligand (L) | M:L Ratio | Physicochemical method | Ref. |
|---|---|---|---|---|
| $Th(NCS)_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +TMBAAP | - | E.a. IR, UV, TGA, DTA | 25 |
| $Th(ClO_4)_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +TMBAAP | - | E.a. IR, UV, TGA, DTA | 25 |
| $ThBr_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +TMBAAP | - | E.a. IR, UV, TGA, DTA | 25 |
| $ThX_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde +FAAP | - | E.a. IR, UV, TGA, DTA | 26 |
| $ThX_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde+ $2NO_2^-$ BAAP | - | E.a. IR, UV, TGA, DTA | 27 |
| $ThX_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde+ $3NO_2^-$ BAAP | - | E.a. IR, UV, TGA, DTA | 28 |
| $ThX_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde + CAAP | - | E.a. IR, UV, TGA, DTA | 29 |
| $ThX_4$ | S.B. (benzocain + 4-hydroxy-3-methoxy benzaldehyde + SAAP | - | E.a. IR, UV, TGA, DTA | 30, 31 |
| $ThCl_4$ | HNAAP | 1:2 | E.a. Mol. Wt. | 32 |
| $ThBr_4$ | HNAAP | 1:2 | Conductance | 32 |
| $Th(NCS)_4$ | HNAAP | 1:2 | M.m IR, TGA | 32 |
| $Th(NO_3)_4$ | HNAAP | 1:2 | M.m IR, TGA | 34 |
| $ThCl_4$ | DABAAP | 1:2 | M.m IR, TGA | 32 |
| $ThBr_4$ | DABAAP | 1:2 | M.m IR, TGA | 32 |
| $Th(NCS)_4$ | DABAAP | 1:2 | M.m IR, TGA | 32 |
| $Th(NO_3)_4$ | DABAAP | 1:2 | M.m IR, TGA | 32 |
| $ThCl_4$ | MBAAP | 1:2 | M.m IR, TGA | 32 |
| $ThBr_4$ | MBAAP | 1:2 | M.m IR, TGA | 32 |
| $Th(NCS)_4$ | MBAAP | 1:2 | M.m IR, TGA | 32 |
| $Th(NO_3)_4$ | MBAAP | 1:2 | M.m IR, TGA | 32 |
| $ThCl_4$ | HMBAAP | 1:2 | M.m IR, TGA | 33 |
| $ThBr_4$ | HMBAAP | 1:2 | M.m IR, TGA | 33 |
| $Th(NCS)_4$ | HMBAAP | 1:2 | M.m IR, TGA | 33 |
| $Th(NO_3)_4$ | HMBAAP | 1:2 | M.m IR, TGA | 33 |
| $ThCl_4$ | BAAP | 1:2 | M.m IR, TGA | 33 |
| $ThBr_4$ | BAAP | 1:2 | M.m IR, TGA | 33 |
| $Th(NCS)_4$ | BAAP | 1:2 | M.m IR, TGA | 33 |
| $Th(NO_3)_4$ | BAAP | 1:2 | M.m IR, TGA | 33 |
| $Th(ClO_4)_4$ | BAAP | 1:3 | M.m IR, TGA | 34 |
| $ThI_4$ | BAAP | 1:3 | M.m IR, TGA | 34 |
| $Th(ClO_4)_4$ | MBAAP | 1:3 | M.m IR, TGA | 34 |
| $ThI_4$ | MBAAP | 1:3 | M.m IR, TGA | 34 |
| $Th(ClO_4)_4$ | DABAAP | 1:3 | M.m IR, TGA | 34 |
| $ThI_4$ | DABAAP | 1:3 | M.m IR, TGA | 34 |
| $Th(ClO_4)_4$ | HMBAAP | 1:3 | M.m IR, TGA | 34 |
| $ThI_4$ | HMBAAP | 1:3 | M.m IR, TGA | 34 |
| $Th(ClO_4)_4$ | HNAAP | 1:3 | M.m IR, TGA | 34 |
| $ThI_4$ | HNAAP | 1:3 | M.m IR, TGA | 34 |
| $Th(NO_3)_4$ | PyAA | 1:1:1 | IR TG | 35 |
| $Th(NCS)_4$ | PyAA | 1:1:1 | IR TG | 35 |
| $Th(NO_3)_4$ | AcPyA | 1:1:1 | IR TG | 35 |
| $Th(NCS)_4$ | AcPyA | 1:1:1 | IR TG | 35 |

| Metal Salt | Ligand (L) | M:L Ratio | Physicochemical method | Ref. |
|---|---|---|---|---|
| $ThCl_4$ | 1-Phenyl-azo-2-arsenoic-acid-2-naphthol | 1:1or 1:2 | DTA, TGA, IR | 80 |
| $ThCl_4$ | 4-(1-Phenylazo-2-arsenoic-acid)-1-naphthol | 1:1or 1:2 | DTA, TGA, IR | 80 |
| $ThCl_4$ | 4-(1-Phenylazo-2-arsenoic-acid)-1-3-naphthol acid | 1:1or 1:2 | DTA, TGA, IR | 80 |
| $ThCl_4$ | 4-azo-pyrazolone | - | Potentiometric | 81 |
| $ThCl_4$ | CPAmk | - | - | 82 |
| $Th(NO_3)_4$ | Chlorophosphanazo-*m*-*N*-cetyl pyridinium bromide | 1:3 | - | 83 |
| $Th(NO_3)_4$ | PCIH | 1:2 | - | 85 |
| $Th(NO_3)_4$ | PCAP | 1:2 | - | 85 |
| $Th(NO_3)_4$ | PCSH | 1:2 | - | 85 |
| $Th(NO_3)_4$ | PCAAP | 1:2 | - | 85 |
| $ThCl_4$ | PHA-CPA | 1:3 | Conductrometric | 88 |
| $Th(OH)_4$ | Aryl bis-(5-hydroxy-methyl-1-phenyl-4-pyrazolyl) | 1:1 | Conductrometric | 89 |
| $Th(OH)_4$ | Aryl bis-(5-hydroxy-methyl-1-phenyl-4-pyrazolyl) | 1:2 | Conductrometric | 89 |
| $Th(NO_3)_4$ | 5-Chloro-7-amino-8-hydroxy quinoline | - | Irving Rosotti | 90 |
| Th(IV) | Pencillamine | - | Paper electrophoresis | 91 |
| $ThCl_4$ | Guanosine | 1:1 | pH studies | 92 |
| Th(IV) | 4-Dimethyl amino annanylidene pyruvic acid H-DMCP | - | Stability constant | 93 |
| Th(IV) | Methonine and pencillamine | - | paper electrophoresis | 94 |
| $Th(ClO_4)_4$ | Bis-azo type derivative of chromotropic acid (4-CAsA-DBSN) | - | Molar absorption | 95 |
| Th(IV) | Derivative of 6-hydroxy phenyl azo-1-methyl-3-phenyl-2-thiohydantion | 1:1, 1:2 | Spectrophotometric Conductometric DTA, TGA, IR | 96 |
| $Th(NO_3)_4$ | 4-N,N-dimethyl aminopyridine | 1:1 | - | 97 |
| $Th(NO_3)_4$ | $H_2L^3$ | 1:1 | E.a. IR, potentiometric | 98 |
| $Th(NO_3)_4$ | $H_2L^4$ | 1:1 | E.a. IR, potentiometric | 98 |
| $Th(OH)_4$ | 2,4-Diamino 5(3',4',5'-trimethoxy benzyl pyrimidine) | - | Formation constant | 99 |
| $Th(ClO_4)_4$ | TRENCAT | - | Potentiometric | 100 |
| $ThCl_4$ | BCO : CPB | - | Spectophotometric | 101 |
| Th(IV) | Tetra amide | - | - | 102 |
| Th(IV) | 2', 2-(Hydroxyphenyl)-benzothiazol hydrozone | - | TLC | 103 |
| $Th(HL)_{1-2}(OH)_3$ or $(NO_3)$or$Cl_3$ | HL = 3-acetyl-1,5-diaryl and 3-cyano-1,5-diaryl formazans | - | E.a. IR, NMR, TGA, DTA | 104 |
| $ThX_4$ | 14 Formazans with *o*-acidic substituent on end-phenyl | - | IR , UV | 105 |
| $ThX_4$ | S B (dicarbonyl and diamine) | - | Fluoroscent | 106 |
| $Th(OH)_4$ | 1-Hydroxy-2(IH)-pyridone | - | - | 107 |

| Metal Salt | Ligand (L) | M:L Ratio | Physicochemical method | Ref. |
|---|---|---|---|---|
| $Th(OH)_4$ | 3-Hydroxy-2(IH)-pyridone | - | IR , UV | 107 |
| $ThX_4$ | Eriochrome cyanine R and cetyl pyridinium chloride | 1:3:3,<br>1:3:6,<br>1:3:9, | Photometric | 108 |
| $ThX_4$ | 1-(2-Hydroxy-R-phenyl)-ethyl-5-benzazolyl formazan | 1:2 | Conductometric | 109 |
| $Th(OH)_4$ | SB($\beta$-ketoesters of $PyHBr_Z$ ) | - | - | 110 |
| $ThX_4$ | 4-Azo-pyrazolone | - | Potentiometric | 111 |
| $Th(NO_3)_4$ | 5-Chloro-7-amino-8-hydroxy quinoline | - | Irving Rosotti | 112 |

Remark- *S.B. = Schiff Base, E.a. = Elemental Analysis, M.m. = Magnetic measurement.

For their studies IR spectroscopy is found satisfactory along with X-ray crystal structure determination. Solid complexes have been studied by TGA and DTA methods but for complexes in solution only conductometric and potentiometric methods have been applied. In future through new devices and methods, more revelation on various attractive features of Th(IV) in forming complexes with high coordination number is possible. All these complexes were studied and their formulae were established by various physical methods and Schiff base complexes, derived from $\beta$-diketones or $\beta$-ketoesters of (Py, H, $Br_2$) in EtOH producing Th(IV) chelate of $\gamma$-bromo type stable in alkaline medium[114]. Chelates of 4-azo-pyrozolone with Th(IV) also have been studied potentiometrically[115] and in nitric acid 5-chloro-7-amino-8-hydroxy quinoline also complexes with thorium(IV) which was studied by Irving Rosotti method which confirmed formation of stable complex[116]. The combinatorialtopol structure of thorium(IV) is studied for sub-lattices in coordination compounds of cambridge crystal structure data and 14 neighbours rule is applied[117].

## Abbreviations

acacen - acetonylacetoneethylenediamine

BAAP - 4-N-[(benzalidene)]amino antipyrine

BCABAB - 2-Bromo-1-N[4-N,N-*bis*-2-(cyanoethyl)amino benzalidene]amino benzene

P'-BCO - Bromocresol orange

BAPy - 2-N-(benzalidene)amino pyridine

5-Cl-Salen - N,N-Ethylene-*bis*-(5-chlorosalicyldehyde)

5-Cl-Salophen - N,N-*o*-Phenylene-*bis*-(5-chlorosalicyldehyde)

CAAP - 4-[N-(Cinnmaldehyde)amino]antipyrine

CABAB - N -[(4-N,N-*bis*(2-Cyano ethyl)amino benzalidene) amino benzene

$CPA_pDMA$ - *p*-Dimethylamino chlorophosphonazo

CPAk - *m*-Carboxychloro phosphonazo
CPB - Cetylpyridinium bromide
DABAAP - 4-N-[(*p*-Dimethylaminobenzalidene)]amino antipyrine
3-etosalen - N,N'-Ethylene-*bis*(3-ethoxysalicyldehyde)
ECABAB - Ethyl-4-N-[4-NN-*bis*-2'-(cyanoethyl)amino benzalidene]amino benzoate
EMCABAB - Ethyl-4-N-[2-methyl,4-N,N-bis-2'-(cyanoethyl) aminobenzalidene]amino benzoate
FAAP - 4-[N-(furfural)]amino antipyrine
FCABAB - 4 fluoro-1-N[4-N,N-bis-2-cyano ethyl amino benzalidene]amino benzene
FHMB - 8-Formyl-7-hydroxy-4-methyl-2H-1-Benzopyran-2-one
$H_2L^3$ - 5,12-diphenyl-, 14-dimethyl-1,4,8,11-tetraza cyclotetradecane-N',N''-diacetic acid
H2L4 - 2,2,4,13,15-Hexamethyl-1,5,12,16-tetraza cyclodosane-N',N''-diacetic acid
LINAAP - 4-N-[(2-Hydroxy-napthalidene)]amino antipyrine
HMBAAP - 4-N-[(4-Hydroxy-3-methoxy benzalidene)]amino antipyrine
3-Meo-Salen - N,N-Ethylene-*bis*(3-methoxysalicyldehyde)
3-Meso-Salephen - N,N-*o*-Phenylene-*bis*(3-methoxysalicyldehyde)
MBAAP - 4-N-[(*m*-Methoxy benzalidene)]amino antipyrine
MHAMBAPy - 2-N-(4-Hydroxy-3-methoxy benzalidene)amino pyridine
2-MCABAB - 1-N[4-N,N-*bis*-2-(cyanoethyl)amino benzalidene] amino benzene
3-MCABAB - 3-Methyl-1-N-[4-N,N-*bis*-2-(cyanoethyl)amino benzalidene]amino benzene
2-MMCABAB - 2-Methyl-1-N-[2-methyl-4-N,N-*bis*-2'-(cyanomethyl)amino benzalidene]amino benzene
3-MMCABAB - 3-Methyl-1-N-[2-methyl-4-N,N-*bis*-2'-(cyanoethyl)amino benzalidene]amino benzene
5-$NO_2$-Salen - N,N-Ethylene-*bis*(5-nitrosalicyldehyde)
5-$NO_2$-Salophen - NN-*o*-Phenylene-*bis*(5-nitrosalicyldehyde)
2-$NO_2$-BAAP - 4-[N-(2-Nitro benzalidene)amino]antipyrine
3-$NO_2$-BAAP - 4-[N-(3-Nitro benzalidene)amino]antipyrine
PCAAP - 4-N-(Pyridine-2-carboxyaldehyde)amino antipyrine
3-NBAPY - 2-N-(3-Nitro benzalidene)aminopyridine
PCAP - N-(Pyridine-2-carboxyaldehydeaminophenol)

PCIH - N-(Pyridine-2-carboxyaldehyde)isonicotinyl hydrazone
PCSH - N-(Pyridine-2-carboxyaldehyde salcylol hydrazone)
P-BAPy - 2-N-(*p*-Dimethylaminobenzalidene)amino pyridine
PHA-CPA - Chlorophosphonazo-*p*-aminohippuric acid
PLS - Partial least square
PSB - Polymeric Schiff base
PyHBz - Pyridinium bromide perbromide
Salen - N-N'-Ethylene-*bis*(salicyldiamine)
SAAP - 4-[N-(Salicylidene)amino]antipyrine
SAPY - 2-N-(Salicylidene)aminopyridine
THF - Tetra-hydrofuran
TMBAAP - 4-N-[(3,4,5-Trimethoxybenzalidene)]amino antipyrine
TRENCAT - *Tris*-(2,3-Dihydroxy benzyl amino)ethyl amine

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(*Received*: 23 September 2005; *Accepted*: 12 February 2007) AJC-5408