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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE



**Interaction of Thorium Tetrachloride With
Nitrogen and Oxygen Organic Donors**

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lit by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Interaction of Thorium Tetrachloride With Nitrogen and Oxygen Organic Donors

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ABSTRACT

Thorium tetrachloride reacts with organic compounds containing nitrogen or oxygen atom, to give complex compounds of the type $\text{ThCl}_4 \cdot n\text{L}$, where $n = 1, 1.5$ or 2 and $\text{L} =$ Diphenylphosphino ethane dioxide, diphenylphosphino methane dioxide, dimethyl-o-phenanthroline, bipyridyl, dimethyl-bipyridyl, tripyridyl, pyridine N-oxide, dipyridyl amine and picolinic acid. Some of these complexes contain coordinated water molecules. The reaction with triethyl phosphate gave the complex, $\text{Th}((\text{EtO})_2\text{PO}_2)_4$.

No adducts have been obtained from the reaction of thorium tetrachloride with some organic phosphorus ligands.

Infrared spectra, thermal stability and conductivity of the formed complexes are discussed.

INTRODUCTION

Thorium tetrachloride is insoluble in hydrocarbons and non-polar solvents. It dissolves only in polar solvents which are electron-donors. Anhydrous thorium tetrachloride forms complex compounds with alcohols of the general formula, $\text{ThCl}_4 \cdot 4\text{ROH}$ ($\text{R} =$ methyl, ethyl and isopropyl alcohols).¹

The complex of thorium with acetyl acetone $\text{Th}(\text{C}_5\text{H}_7\text{O}_2)_4$, has been studied extensively.² Like other metal acetylacetonates, it has a structure in which the metal forms part of four six-membered rings. Other complexes with amines³ aldehydes⁴ and ketones⁵ are reported, in which

the coordination number of thorium is either 6 or 8.⁶ Higher coordination numbers have been observed.⁷

Comyns⁸ has pointed out the lack of information about thorium (IV) complexes.

EXPERIMENTAL

Anhydrous solid thorium tetrachloride was prepared by boiling hydrated thorium tetrachloride with thionyl chloride.⁹ Anhydrous solutions are obtained by azeotropic distillation with ethyl acetate or ethanol-benzene as previously described.^{9,10} Solvents used, ethyl acetate, dimethyl formamide, DMF, acetonitrile, MeNO₂, methyl cyanide, MeCN, were purified and dried by conventional methods.¹¹

Organic Ligands.-Bis(diphenylphosphino) methane, DiPhOS methane, m.p. 114°C and its dioxide, DiPhOS methane dioxide, m.p. 156°C, 1,2 bis (diphenylphosphino) ethane, DiPhOS ethane, m.p. 141°C and its dioxide, DiPhOS ethane dioxide, m.p. 276°C were prepared according to the methods given by Gans and Smith¹². Triethyl phosphate, Et₃PO₄, BDH grade, was used without any further purification. 2,9-Dimethyl-o-phenanthroline, DM-phen., BDH grade, m.p. 159°C, 2,2',2''-tripyriddy, terpy. Sigma, m.p. 85°C, 2,2'-bipyridyl, bipy., Riedel, m.p. 69°C and 4,4'-dimethyl-2,2'-bipyridyl, DM-dipy., m.p. 169°C. The other ligands used during this work, pyridine-N-oxide, py-N-oxide, picolinic acid and 2,2'-dipyridylamine were generally reagent grade materials, and were recrystallised from the appropriate solvent before use.

The experimental technique adopted during this work was as previously mentioned.^{13,14}

RESULTS

I. *Reactions of Thorium tetrachloride with Organic Compounds Containing Phosphorus.* 1. *Reaction with DiPhOS ethane.*- When a solution of 1,2-bisdiphenylphosphino ethane, DiPhOS ethane (2 moles) in ethyl acetate was added to a solution of thorium tetrachloride (1 mole) in the same solvent, direct precipitation occurred. The precipitate was filtered and washed several times with ethyl acetate, then dried under reduced pressure. This adduct was identified by analysis and ir spectral studies, as tetrachloro (bis-diphenylphosphino ethane dioxide) thorium (IV),

ThCl_4 , DiPhOS ethane dioxide. Concentration of the filtrate gave the excess unreacted ligand, m.p. 141°C . An authentic sample of the complex, ThCl_4 DiPhOS ethane dioxide was obtained from the reaction of thorium tetrachloride and DiPhOS ethane dioxide in ethyl alcohol. When similar experiment was carried out with DiPhOS methane, a product was obtained which was proved, by analysis and ir, to be ThCl_4 , 1.5 DiPhOS methane dioxide, $2\text{H}_2\text{O}$. This adduct was also obtained when DiPhOS methane dioxide was used as a ligand.

It seems that oxidation, by air or slight traces of water in the solvent occurred during the reactions of ThCl_4 with DiPhOS ethane and DiPhOS methane.

No evidence could be found for the formation of a simple adduct of the type, ThCl_4 , DiPhOS ethane or methane. This is probably because of the lower donor strength of the phosphorus atom than that of the oxygen atom with respect to thorium (IV). It is generally accepted that thorium (IV) is a Class A^{15,16} electron-acceptor, in which the coordinating ability of nitrogen and oxygen donors is very much greater than that of phosphorus donors.

Reaction with Triethyl phosphate.- Anhydrous thorium tetrachloride dissolves in triethyl phosphate, with heat evolution. This may be attributed to the formation of the complex compound, ThCl_4 , $n\text{-Et}_3\text{PO}_4$, similar to that, ThCl_4 , $3\text{Bu}_3\text{PO}_4$, reported by Ferraro et al.¹⁷ On heating the solution at $140\text{--}170^\circ\text{C}$ under reduced pressure the formed complex, ThCl_4 , $n\text{-Et}_3\text{PO}_4$ decomposes to yield ethyl chloride and a solid product separated out. The excess unreacted triethyl phosphate was decanted. A hygroscopic grey powder was obtained, which was identified by analysis and ir as, tetrakis (diethyl phosphato) thorium (IV), $\text{Th}[(\text{EtO})_2\text{PO}_2]_4$. $\text{Th}[(\text{BuO})_2\text{PO}_2]_4$ was prepared¹⁷ by adding sodium hydroxide to a mixture of dibutyl hydrogen phosphate in ethanol and an aqueous solution of thorium nitrate. This substantiate the result obtained in this work. Similar adducts, with some transition metals and also uranium, were reported.¹⁸

II. *Reactions of Thorium tetrachloride with Organic-N-Donors.*-When solutions of the organic ligands (1 or 2 moles) in ethyl acetate were added to thorium tetrachloride (1 mole) in the same solvent, precipitation occurred. The adducts obtained, in high yields, were washed

several times with ethyl acetate then dried. These adducts are of the general formula, $\text{ThCl}_4 \cdot 2\text{L} \cdot n\text{H}_2\text{O}$. Similar compounds are known¹⁹ in which water appears to compete fairly evenly for places in the coordination sphere. The compounds obtained are insoluble in most organic solvents except DMF from which the compounds cannot be recovered unchanged. All these adducts are air-stable complexes except the bipyridyl one, which is very hygroscopic.

Analytical data are recorded in Table 1.

Table 1

	Required %			Formula	Found %		
	C	H	N/P		C	H	N/P
1. ThCl_4 , Di-PhOS ethane dioxide	38.8	3.0	7.7	$\text{C}_{26}\text{H}_{24}\text{Cl}_4\text{O}_2\text{P}_2\text{Th}$	39.15	3.7	7.1
2. ThCl_4 , DiPhOS methane dioxide, $2\text{H}_2\text{O}$	43.5	3.6	—	$\frac{1}{3}(\text{C}_{75}\text{H}_{66}\text{Cl}_8\text{O}_6\text{P}_6\text{Th}) \cdot 2\text{H}_2\text{O}$	44.00	3.6	—
3. $\text{Th}[(\text{EtO})_2\text{PO}]_4$	22.8	4.7	14.7	$\text{C}_{16}\text{H}_{40}\text{O}_6\text{P}_4\text{Th}$	22.60	4.9	14.5
4. ThCl_4 , 2DM-phen., $8\text{H}_2\text{O}$	36.0	4.3	6.0	$\text{C}_{28}\text{H}_{40}\text{Cl}_4\text{N}_4\text{O}_8\text{Th}$	36.00	3.5	5.4
5. ThCl_4 , 2bipy.	34.9	2.3	8.6	$\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{N}_4\text{Th}$	33.90	2.4	7.6
6. ThCl_4 , 1.5DM-bipy., $2\text{H}_2\text{O}$	31.5	3.2	6.1	$\text{C}_{18}\text{H}_{22}\text{Cl}_4\text{N}_3\text{O}_2\text{Th}$	31.70	4.4	5.8
7. ThCl_4 , 2tripy., $8\text{H}_2\text{O}$	36.6	4.0	8.5	$\text{C}_{30}\text{H}_{38}\text{Cl}_4\text{N}_6\text{O}_8\text{Th}$	35.90	4.6	7.9
8. ThCl_4 , 2dipy. amine, $2\text{H}_2\text{O}^+$	31.9	3.0	11.2	$\text{C}_{20}\text{H}_{22}\text{Cl}_4\text{N}_6\text{O}_2\text{Th}$	32.60	3.7	11.6
9. ThCl_4 , 2Py-N-oxide, $2\text{H}_2\text{O}$	20.0	2.3	4.7	$\text{C}_{10}\text{H}_{14}\text{Cl}_4\text{N}_2\text{O}_4\text{Th}$	19.95	3.0	4.0
10. ThCl_4 , 2picolinic acid ⁺⁺	23.2	1.6	4.5	$\text{C}_{12}\text{H}_{10}\text{Cl}_4\text{N}_2\text{O}_4\text{Th}$	23.00	1.8	4.2

* m.p. 110 °C ** m.p. 115 °C, other complexes do not melt up to 240 °C

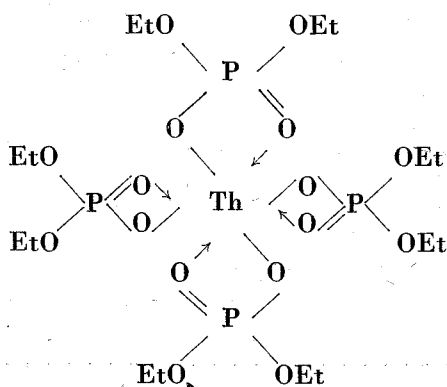
DISCUSSION

Infrared Studies.- Thorium tetrachloride hydrate exhibits bands at $3550\text{--}3300\text{ cm}^{-1}$ and 1620 cm^{-1} caused by the absorption of water molecules. No other bands are observed in the region $4000\text{--}650\text{ cm}^{-1}$. Thorium halogen stretching bands appear at low frequency²⁰, e.g. Th-Cl at 245 cm^{-1} .

The $\text{P}=\text{O}$ absorption band in DiPhOS- ethane and methane dioxides is reported²¹ to be at 1190 cm^{-1} . This band shifts to lower frequency region, and is found at 1175 and 1140 cm^{-1} respectively in the complexes. The shift observed reflect an overall decrease in $\text{p}\pi\text{-d}\pi$ bond order.

Similar shifts is reported which is attributed to coordination through oxygen.^{21,22}

The $\text{P}=\text{O}$ stretching band, which occurs at 1270 cm^{-1} in triethyl phosphate²³, shifts to 1120 cm^{-1} in the complex $\text{Th}[(\text{EtO})_2\text{PO}_2]_4$; confirming that the $\text{P}=\text{O}$ group forms a coordinate bond through the oxygen and not the phosphorus atom. This complex probably has a structure in which the coordination number of thorium is eight, as in the acetylacetonate.² The structure of this compound may be represented as:



The spectrum of the adduct with dipyriddy amine indicates a shift of the band corresponding to $\gamma\text{C}-\text{N}$ from 1572 cm^{-1} in the free ligand to 1510 cm^{-1} in the complex. The amine ring vibration present at 995 cm^{-1} in the pure ligand shifts to lower frequency at 965 cm^{-1} in the complex. These observations support the coordination of the dipy. amine through its nitrogen.²⁴

In the pyridine-N-oxide adduct spectrum, the band at 1180 cm^{-1} , which corresponds to the frequency of N-oxide in the free ligand, shifts to 1230 cm^{-1} on coordination. This indicates that the ligand is linked to thorium by the N-O oxygen. Similar results are reported.²⁵

The $\text{C}=\text{N}$ vibration band in picolinic acid occurs at 1610 cm^{-1} is not altered by complex formation, whereas the $\text{C}=\text{O}$ band at 1720 cm^{-1} in the free ligand is shifted to lower frequency 1675 cm^{-1} in its thorium complex. These observations indicate the coordination of picolinic acid through its carboxylic group.

The spectra of the other complexes formed between thorium tetrachloride and N-donors show slight change from the pure ligands, on complex formation. The ring vibration frequencies; which occur in the region 1650–1400 cm^{-1} in the free ligand, shift to higher frequencies on complexing with thorium (IV). Multiple splitting occurs in the region 850–700 cm^{-1} . Similar behaviour is observed for other complexes with organic ligands.²⁶

Thermal Decomposition of Thorium tetrachloride Complexes.- Thorium tetrachloride compounds decompose on heating. The molecular weights of the intermediate compounds are calculated from the graphs. The final products: after heating up to 800 °C are usually ThOCl_2 or Th and some of these complexes volatilized.

Table (2) shows the effect of heat of some thorium tetrachloride complexes, the letters indicate intermediate stages.

Table (2)
Thermal Decomposition of Some Thorium tetrachloride Complexes

Temp. (°C)	M _{Obs.}	Formula	M _{cal.}
<i>ThCl₄, Diphos ethane dioxide</i>			
20 - 210	804.2	ThCl ₄ , Diphos ethane dioxide	804.2
500 - 550	498.6	ThOCl ₂ , Ph ₂ P (A)	504
580 - 800	466.4	ThO ₂ , Ph ₂ P (B)	449
<i>ThCl₄, 1.5Diphos methane dioxide, 2H₂O</i>			
20 - 80	1034.4	ThCl ₄ , 1.5Diphos methane dioxide 2H ₂ O	1034.4
120 - 150	993.02	ThCl ₄ , 1.5Diphos methane dioxide (C)	998.4
240 - 320	951.6	ThCl ₄ , 1.5Diphos methane (D)	950.6
560 - 800	320.6	ThOCl ₂ (E)	319
<i>ThCl₄, 2DM-o-phen., 8H₂O</i>			
20 - 70	934.5	ThCl ₄ , 2DM-o-phen., 8H ₂ O	934.5
140 - 160	817.7	ThCl ₄ , 2DM-o-phen., 2H ₂ O (G)	826.5
260 - 320	584.1	ThCl ₄ , 0-phen., 2H ₂ O (H)	590.2
460 - 800	233.6	Th (I)	232.03
<i>ThCl₄, 2tripy., 8H₂O</i>			
20 - 400		decomposition	
400 - 800	230	Th (J)	232.04
<i>ThCl₄, 2dipyridyl amine, 2H₂O</i>			
20 - 180	752.28	ThCl ₄ , 2dipy., amine, 2H ₂ O (K)	752.28
300 - 800		volatile	
<i>ThCl₄, 2picolinic acid</i>			
20 - 40	620.1	ThCl ₄ , 2picolinic acid	620.1
160 - 180	486.5	ThCl ₄ , picolinic acid (L)	496.96
500 - 800	238.5	Th (M)	232.04

Conductivity Measurements.- Conductivity measurements in non-aqueous solutions have frequently been used in structural studies of thorium (IV) chloride complexes. Within the limits of the solubilities of the complexes prepared, the authors have measured the molar conductivities of millimolar solutions in acetonitrile, MeCN, nitromethane: MeNO₂ and dimethylformamide: DMF. The molar conductivities reported for millimolar solutions of 1:1 electrolytes in these solvents are 150, 70-120 and 70-100 ohm⁻¹ cm². The results are recorded in Table (3).

Table (3)

Conductivities of Some Thorium Chloride Complexes In Different Solvents

Compound	ohm ⁻¹ cm ²		DMF
	MeCN	MeNO ₂	
ThCl ₄ , Diphos ethane dioxide	—	—	W
ThCl ₄ , 1.5Diphos methane dioxide, 2H ₂ O	W	W	—
ThCl ₄ , 2 (0-phen.)	—	—	W
ThCl ₄ , 2 (DM-0-phen.), 8H ₂ O	—	—	W
ThCl ₄ , 2(2,2',2''-tripy.), 8H ₂ O	—	—	W
ThCl ₄ , 1.5 (DM-bipy.), 2H ₂ O	—	—	W
ThCl ₄ , 2(Dipy. amine), 2H ₂ O	—	—	W
ThCl ₄ , 2-picolinic acid	—	—	W

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