Synthesis and characterization of alkyl (aryl) trithiophosphato derivatives of thorium and their addition reaction with nitrogen donor bases

Upendra Singh
Chemistry Department, Raj Rishi College, Alwar (Raj.) India
Madhu Sharma
Chemistry Department , Govt. G.D. College, Alwar (Raj.) India
Email-dr.usingh09@gmail.com

Abstract: Complexes of the general formula $M[S3P(OR)]2$ where M= Th and R= Me, Et, Pr^i, Bu^n and Ph have been synthesized by reacting $M(NO_3)_4 6H2o$ and dipotassium salts of corresponding trithyophosphates in 1:2 molar ratio in refluxing methanol than isolates using benzene. These complexes have been characterized by elemental analysis, molecular weight measurement, IR and NMR (^{1}H and ^{31}P) studies downfield shift of about [^{31}P = 25-33 PPM] have observed.

Keywords – Alkyl trithiophosphate, Th $(No3)_{4\ Nitrogen}$ donor bases, bipridyl, 1,10- phenanthroline.

Introduction:-

The information about the metal derivatives of O- alkyl (aryl) trithiophosphates [1] is rather scanty, a very few reports are available in the literature.

The brief historical survey clearly indicates that out of all main group elements and transition metals the chemistry of trithiophosphato the derivatives of Mg, Ca, Sr, Ba, P, As, La and Th elements which have not been studies as yet. In view of this the continuing interest in this area is mainly due to the industrial utility of these compounds as their novel structural feature. The literature survey however revealed that except few patents no work appear to be carried out on alkyl (aryl) trithiophosphates of these elements. So, it was considered of interest to synthesize the derivatives of Th with alkyl trithiophosphates ligand and get a comparative view of these with the corresponding open chain derivatives.

Result & Discussion –

The complexes of the general formula $Th[S_3P(OR)]_2$ have been prepared by the reaction of the $Th(NO_3)_4 4H_2O$ with dipotassium salts of corresponding trithiophosphates in 1:2 molar ratio in refluxing methanol The products were separated out using benzene.
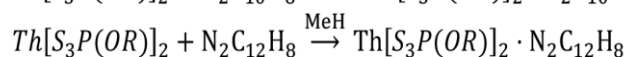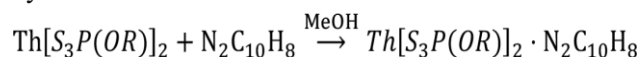
$$M(NO_3)_4 \cdot 4H_2O + 2k_2[S_3P(OR)]_2 \xrightarrow{MeOH} M[S_3P(OR)]_2 + 4KNO_3$$
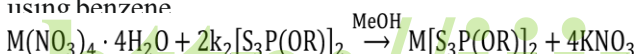
Where
$$M = Th$$
$$R = Me, Et, Pr^i, Bu^n, Ph,$$

Those complexes are dirty- white solids soluble in methanol, benzene and are the insoluble in hhexane, light petroleum etc. obtained complexes are non-volatile and tend to decompose on heating above 180° c .

Addicts of Thorium trithiophosphates with nitrogen donor bases such as 2, 2 bipyridyl and 1,10-phenanthroline in 1:1 molar ratio have been obtained by the reaction of both reactants in methanol:

$$Th[S_3P(OR)]_2 + N_2C_{10}H_8 \xrightarrow{MeOH} Th[S_3P(OR)]_2 \cdot N_2C_{10}H_8$$
$$Th[S_3P(OR)]_2 + N_2C_{12}H_8 \xrightarrow{MeH} Th[S_3P(OR)]_2 \cdot N_2C_{12}H_8$$

The reactions are quite facitile and completed even at room temperature, to ensure the completion of reaction the contents were stirred for about 4 to 6 hours The adducts of Thorium trithiophosphates with nitrogen donor bases are pink coloured solids, soluble in methanol and are found to be of monomeric in nature.

IR spectral studies [Table-3,4] The IR spectra show the following characteristics absorption bands:

(i) A sharp absorption band at 690-640 cm^{-1} is due to $\upsilon[P = S]$ and 550-525 cm^{-1} assigned to $\upsilon[P - S]$ group

(ii) The due appearance of a new medium intensity absorption band at 405- 370 is due to cm^{-1} $\upsilon[Th - S]$

(iii) The appearance of broad absorption bands in the region 1110- 990 cm^{-1} and 970- 860 cm^{-1} in assigned to $\upsilon[(P) - O - C]$ and $\upsilon[P - O - (C)]$ stretching vibration respectively.

(iv) IR spectra of the adducts of the types $Th[S_3P(OR)]_2 . N_2C_{10}H_8$ and $Th[S_3P(OR)]_2 . N_2C_{12}H_8$ are similarity in the position of absorption bands patterns with the parents Thorium trithiophosphate as 1140- 1030 cm^{-1}, 1005- 870 cm^{-1} and 705-650 cm^{-1} assigned to $\upsilon(P) - O - C]$, $\upsilon[P - O - (C)]$ and $\upsilon[P = S]$ respectively.

NMR Spectra [^{1}H and P]

The ^{1}H NMR Spectra of these derivatives and their

adducts with nitrogen donor bases (Table- 7) and(Table 8) respectively.

the number of resonance signals and their integration ratios are in accordance with the stoichiometry of these complexes. In adducts the spectra shows slight up field shift with usual resonance peak patterns compared to their position in the parent. The 4,4 protons (of 2,2'- bipyridyl) depict signals at &7.85-8.80 ppm and aromatic protons of 1,10- phenonthroline adducts appeared as a broad resonance signal in the region & 8.20 - 9.20 ppm

Electronic Spectral studies (Table –5, 6)

The Electronic spectra of the complexes show a Single Electronic transition band in the region 227-219 mm which are lower wave length in comparison to corresponding dipotassium salt of trithiophosphate while in the adducts showing shifting towards higher wavelength

Experimental

Weighted amount of sample (0.2-0.4g) was taken in a beaker and boiled with minimum volume of concentrated nitric acid to decompose the compounds till dryness. This process was repeated again and dilute with 100 ml of distilled water 10% boiled oxalic acid solution added to it with stirring.

The Precipitate was filterd (WhatmanY2), wash with 3.5 cm3. Hcl acid solution and 2.5 g oralic acid in 100 cm3 distilled water and finally by water. The precipitate was ignite and weighted as ThO_2.

Dipotassium salts of alkyl trithioposphate have prepared by reacting respective alcohols on phosphorus penta sulphide in presence of base in 3:1:3 molar ratio.

A methanolic solution of thorium (iv) nitrate tetrahydrate (2.2563g, 4.08 mmole) and K2 [S3P(OR)] 2 (1.079), g, 8.10mmole) were mixed and refluxed for about 10 hours. The solid obtained was extracted using benzene.

For adducts, a methonlic solution of nitrogen donor bases was added dropwise with constant stirring to a methanolic solution of thorium trithiophosphate derivatives, a pink colur precipitate was obtained in both cases.

Elemental analyses were carried out by standard procedure. Molecular weights were measured on a Knauer- vapour pressure osmometer in benzene solution. IR spectra were recorded as KBr pettets or NuJol mulls on a perkin- Elmer spectrophotometer model 577 in the range 4000-200 cm-1.

And DMSO do and 31p NMR IN THF were recorded on a JEOL FX900 spectrometer using TMS(for 1H) and H_3PO_4(for 31p) as internal and external reference, respectively.

Reference:-

1. Wasson J.R., Wolteman G.M. and Stocklosa H.J. Fortachar Chem. Forssch,35,65(1973)
2. Chauchan H.P.S.,Srivastava G.and Mehrotra R.C. J. Indian Chem. Soc 66,558(1989)
3. Kotavich B.P. Zemlyan N.I. , Muraver I.V. and volosin M.P. Zh. Obshch Khim,8317a(1959)
4. Cotton F.A. and Willkinson G"Advanced Inogranuic Chemistry" Vth edition ,Elesvier (1988)
5. Kristin K.,Vta B. ,Evalad G.,Laus G.K.,Ubich K. Henery S.,Bernt K and Geralad H.,Z. Naturfersch,Chem. Sci B 45,@45(1990)
6. U.S. Pat No.2,820,049,Ref. Zh. Khim 83179(1959)
7. Chupp I.P. and Newallis P.E. , J.Org.Chem.,27,3832(1962)
8. Grishina O.N. and Bezzubora L.M. , Irv.Akad,Nauk,USSr.Ser. Khim 2140(1965)
9. Negoin D. and Negoin M. But.Inst. Politch , Bunuresh.Ser.Khim,46-47,145(1985)
10. Chatumedi Alok , Ph.D. Thesis , UOR,Jaipur(1992)

Table 1- SOME PHYSICAL PRORERTIES OF THE COMPLEXES OF THE TYPE Th[$S_3P(OR)$]₂

S.No.	Compound	Physical State	Melting Point (°c)	Molecular Weight Found (Calcd.)
1	Th[$S_3P(OMe)$]₂	White Solid	187 (dec.)	528.42 (548.00)
2	Th[$S_3P(OEt)$]₂	White Solid	---------	554.14 (576.00)
3	Th[$S_3P(OPr^i)$]₂	White Solid	195 (dec.)	582.83 (604.00)
4	Th[$S_3P(OBu^n)$]₂	White Solid	---------	---------
5	Th[$S_3P(OPh)$]₂	White Solid	268 (dec.)	---------

Table 2- SOME PHYSICAL PRORERTIES OF THE COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2 . N_2C_{10}H_8$ and $Th[S_3P(OR)]_2 . N_2C_{12}H_8$

S.No.	Compound	Physical State	Melting Point (°c)	Molecular Weight Found (Calcd.)
1	$Th[S_3P(OMe)]_2 . N_2C_{10}H_8$	Pink Solid	223 (dec.)	684.93 (704.00)
2	$Th[S_3P(OEt)]_2 . N_2C_{10}H_8$	Pink Solid	---------	---------
3	$Th[S_3P(OPr)]_2 . N_2C_{10}H_8$	Pink Solid	---------	746.10 (760.00)
4	$Th[S_3P(OBu^n)]_2 . N_2C_{10}H_8$	Pink Solid	---------	---------
5	$Th[S_3P(OPh)]_2 . N_2C_{10}H_8$	Pink Solid	308 (dec.)	807.33 (828.00)
6	$Th[S_3P(OMe)]_2 . N_2C_{12}H_8$	Pink Solid	---------	---------
7	$Th[S_3P(OEt)]_2 . N_2C_{12}H_8$	Pink Solid	---------	731.29 (756.00)
8	$Th[S_3P(OPr)]_2 . N_2C_{12}H_8$	Pink Solid	235 (dec.)	---------
9	$Th[S_3P(OBu^n)]_2 . N_2C_{12}H_8$	Pink Solid	---------	798.36 (812.00)
10	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	Pink Solid	---------	---------

Table 3 – SOME RELEVENT IR SPECIAL DATA (IN cm^{-1}) FOR THE COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2$

S.No.	Compound	$\upsilon[(P)-O-C]$	$\upsilon[P-O-(C)]$	$\upsilon[P=S]$	$\upsilon[P-S]$	$\upsilon[Th-S]$
1.	$Th[S_3P(OMe)]_2$	990 s	860 m	670 s	540 m	380 m
2.	$Th[S_3P(OEt)]_2$	1005 s	880 m	640 s	540 m	395 m
3.	$Th[S_3P(OPr^i)]_2$	1010 s	880 m	660 s	530 w	405 m
4.	$Th[S_3P(OBu^n)]_2$	1020 s	890 m	690 s	550 m	390 m
5.	$Th[S_3P(OPh)]_2$	1110 s	970 m	660 s	525 m	370 m

S= Sharp,   m= medium,   b=broad,   w= week

Table 4 – SOME RELEVENT IN SPECIAL DATA (IN cm^{-1}) FOR THE COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2 . N_2C_{10}H_8$ and $Th[S_3P(OR)]_2 . N_2C_{12}H_8$

S.No.	Compound	$\upsilon[(P)-O-C]$	$\upsilon[P-O-(C)]$	$\upsilon[P=S]$	$\upsilon[P-S]$	$\upsilon[Th-S]$
1.	$Th[S_3P(OMe)]_2 . N_2C_{10}H_8$	1040 m	880 m	680 s	570 m	345 m
2.	$Th[S_3P(OEt)]_2 . N_2C_{10}H_8$	1070 m	890 m	660 s	580 m	350 m
3.	$Th[S_3P(OPr^i)]_2 . N_2C_{10}H_8$	1085 s	885 m	680 s	560 w	370 b
4.	$Th[S_3P(OBu^n)]_2 . N_2C_{10}H_8$	1080 m	910 m	710 m	590 m	355 m
5.	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	1140 s	1000 m	690 s	560 w	340 m
6.	$Th[S_3P(OMe)]_2 . N_2C_{12}H_8$	1030 m	870 m	680 s	560 b	340 m
7.	$Th[S_3P(OEt)]_2 . N_2C_{12}H_8$	1050 m	890 m	650 s	580 m	350 m
8.	$Th[S_3P(OPr^i)]_2 . N_2C_{12}H_8$	1070 s	880 m	670 s	580 m	380 b
9.	$Th[S_3P(OBu^n)]_2 . N_2C_{12}H_8$	1070 m	900 m	705 s	570 m	340 m
10.	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	1120 m	1005 m	680 s	550 w	335 m

S= Sharp,   m= medium,   b=broad,   w= week

Table 5 – DATA FOR ELECTRONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2$

S.No.	Compound	Wave length (in nm)
1.	$Th[S_3P(OMe)]_2$	221.0
2.	$Th[S_3P(OEt)]_2$	219.0
3.	$Th[S_3P(OPr^i)]_2$	223.0
4.	$Th[S_3P(OBu^n)]_2$	227.5
5.	$Th[S_3P(OPh)]_2$	220.0

Table 6 – DATA FOR ELECTRONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2 . N_2C_{10}H_8$ and $Th[S_3P(OR)]_2 . N_2C_{10}H_8$

S.No.	Compound	Wave length (in nm)
1.	$Th[S_3P(OMe)]_2 . N_2C_{10}H_8$	252.0
2.	$Th[S_3P(OEt)]_2 . N_2C_{10}H_8$	238.0
3.	$Th[S_3P(OPr^i)]_2 . N_2C_{10}H_8$	261.0
4.	$Th[S_3P(OBu^n)]_2 . N_2C_{10}H_8$	258.5
5.	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	244.0
6	$Th[S_3P(OMe)]_2 . N_2C_{12}H_8$	242.0
7	$Th[S_3P(OEt)]_2 . N_2C_{12}H_8$	234.0
8	$Th[S_3P(OPr^i)]_2 . N_2C_{12}H_8$	246.0
9	$Th[S_3P(OBu^n)]_2 . N_2C_{12}H_8$	240.0
10	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	234.0

Table 7 – NMR SPECTRAL DATA FOR COMPLEXES OF THE TYPE $Th[S_3P(OR)]_2$

S.No.	Compound	1_H NMR Chemical Shifts in $CDCL_3/DMSO-d_6$ (in 5 ppm)	31_P NMR Chemical Shifts in THF (in 5 ppm)
1.	$Th[S_3P(OMe)]_2$	$3.58 - 3.71$, m (OMe)	103.40
2.	$Th[S_3P(OEt)]_2$	$1.36 - 1.48$, t, 6H (Me) $3.66 - 4.37$, m, 4H($-OCH_2$)	99.10
3.	$Th[S_3P(OPr^i)]_2$	$1.30 - 1.36$, d, 12H (Me) $4.54 - 5.20$, m, 4H($-OCH$)	95.73
4.	$Th[S_3P(OBu^n)]_2$	0.95, t, 6 H(Me) $1.22 - 2.22$, m, 8H (CH_2) $3.54 - 4.20$, m, 4H (OCH_2)	96.10
5.	$Th[S_3P(OPh)]_2$	7.18, s, 10H (oph)	99.52

S= Singlet,   d= dublet , t= triplet ,   m = multiplet

Table 8 – NMR SPECTRAL DATA FOR THE COMPLEXES OF THE TYPE $TH[S_3P(OR)]_2 . N_2C_{10}H_8$ and $TH[S_3P(OR)]_2 . N_2C_{12}H_8$

S.No.	Compound	^1H HNR Chemical Shifts in $CDCL_3/DMSO-d_6$ (in $ ppm)	^{31}P NMR Chemical Shift in THF (in $ ppm)
1.	$Th[S_3P(OMe)]_2 . N_2C_{10}H_8$	$3.54 -3.80$, m, (OMe) $8.00 - 8.80$, m, 8H($N_2C_{10}H_8$)	102.64
2.	$Th[S_3P(OEt)]_2 . N_2C_1H_8$	$1.38 - 1.48$, t, 6H(Me) $3.70 - 4.38$, m, 4H (- OCH_2) $7.85 - 8.50$, m, 8H($N_2C_{10}H_8$)	98.86
3.	$Th[S_3P(OPr^i)]_2 . N_2C_{10}H_8$	$1.30 - 1.38$, d, 12H(Me) $4.50 - 5.22$, m, 12H (- OCH_2) $8.00 - 8.70$, m, 8H($N_2C_{10}H_8$)	94.78
4.	$Th[S_3P(OBu^n)]_2 . N_2C_{10}H_8$	0.98, t, 6H (Me) $1.20 - 2.18$, m, 8H(CH_2) $3.56 - 4.22$, m, 4H 8H(OCH_2) 8.00 - , m, 8H($N_2C_{10}H_8$)	95.77
5.	$Th[S_3P(OPh)]_2 . N_2C_{10}H_8$	7.28, s, 10H(OPh) $8.00 - 8.70$, m, 8H($N_2C_{12}H_8$)	99.13
6.	$Th[S_3P(OMe)]_2 . N_2C_{12}H_8$	$3.58 - 3.78$, m, (OMe) $8.30-9.20$, b, 8H($N_2C_{12}H_8$)	102.50
7.	$Th[S_3P(OEt)]_2 . N_2C_{12}H_8$	$1.40 - 1.48$, t, 6H (Me) $3.72 - 4.40$, m, 4H (- OCH_2) $8.20 - 9.20$, b, 8H($N_2C_{12}H_8$)	98.80
8.	$Th[S_3P(OPr^i)]_2 . N_2C_{12}H_8$	$1.32 - 1.40$, d, 12H (Me) $4.48 - 5.18$, m, 2H (- OCH) $8.20 - 9.10$, b, 8H($N_2C_{12}H_8$)	94.50
9.	$Th[S_3P(OBu^n)]_2 . N_2C_{12}H_8$	1.02, t, 6H (Me) $1.22 - 2.20$, b, 8H(CH_2) $3.56 - 9.20$, m, 4H(OCH_2) $8.30 - 9.20$, b, 8H($N_2C_{12}H_8$)	95.00
10.	$Th[S_3P(OPh)]_2 . N_2C_{12}H_8$	7.30, s, 10H(OPh) $8.20 - 9.20$, b, 8H($N_2C_{12}H_8$)	98.82

Table 9- RELEVANT SYNTHETIC AND ANALYTICAL DATA FOR $Th[S_3P(OR)]_2$

S.No	Reactants g(mmole)		Molar Retio	Product			Analysis, % Yield	
	$Th(NO_3)_4 . 4H_2O$	$K_2[S_3P(OR)]_2$			g	%Yield	Th, Found (Calcd.)	S, Found (Calcd.)
1	2.1914(4.10)	$K_2[S_3P(OMe)]_2$	1:2	$Th[S_3P(OMe)]_2$			42.31 (42.33)	34.70 (35.03)
		0.9682 (8.12)			1.8051	82.97		
2	2.0889 (3.97)	$K_2[S_3P(OEt)]_2$	1:2	$Th[S_3P(OEt)]_2$			40.23 (40.27)	32.83 (33.33)
		0.9925 (7.90)			1.7712	81.25		
3	2.2563 (4.08)	$K_2[S_3P(OPr^i)]_2$	1:2	$Th[S_3P(OPr^i)]_2$			38.37 (38.41)	30.07 (31.78)
		1.0791 (8.10)			2.1058	85.29		
4	2.2302(4.04)	$K_2[S_3P(OPr^n)]_2$	1:2	$Th[S_3P(OBu^n)]_2$			36.66 (36.70)	29.00 (30.37)
		1.1232 (8.02)			2.2471	88.00		
5	1.8990 (3.44)	$K_2[S_3P(OPh)]_2$	1:2	$Th[S_3P(OPh)]_2$			34.47 (34.52)	27.41 (28.57)
		1.0252 (6.80)			1.9162	82.88		