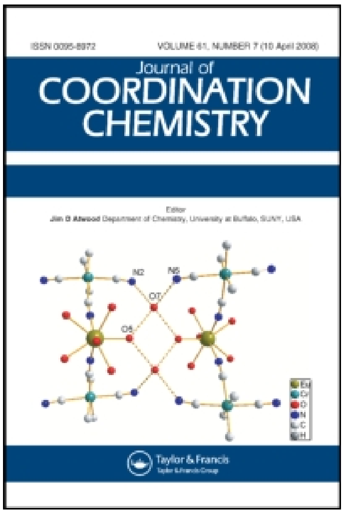

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Synthesis and characterization of O,O'-dialkyl and alkylene dithiophosphates of thorium(IV) and their adducts with nitrogen and phosphorus donors

U. N. Tripathi[a]; M. S. Ahmad[a]
[a] School of Studies in Chemistry, Vikram University, Ujjain, India

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Synthesis and characterization of O,O′-dialkyl and alkylene dithiophosphates of thorium(IV) and their adducts with nitrogen and phosphorus donors

U. N. TRIPATHI* and M. S. AHMAD

School of Studies in Chemistry, Vikram University, Ujjain, 456010, India

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Thorium(IV) tetrakis(dithiophosphates), $[Th\{S_2P(OR)_2\}_4]$ (where $R = –CH_2CH_2CH_3$ or $–C_6H_5$) and $[Th\{S_2PO_2G\}_4]$ [where $G = –C(CH_3)_2CH_2CH(CH_3)–$, $–CH_2C(CH_3)_2CH_2–$, $–C(CH_3)_2C(CH_3)_2–$ and $–CH_2CH_2CH(CH_3)–$] were prepared in methanolic solution of $Th(NO_3)_4 \cong 6H_2O$ and ammonium dithiophosphates. Adducts of the type $[Th\{S_2P(OR)_2\}_4 \cong nL]$ and $[Th\{S_2PO_2G\}_4 \cong nL]$ [where $n = 1$, $L = N_2C_{10}H_8$ or $N_2C_{12}H_8$ and $n = 2$, $L = P(C_6H_5)_3$] were prepared by the reaction of thorium(IV) tetrakis(dithiophosphates) and nitrogen or phosphorus donors in benzene. These newly synthesised derivatives have been characterized by elemental analyses, molecular weights, IR, ^1H and ^{31}P NMR spectral measurements. Coordination numbers of eight and ten are suggested for thorium(IV) in these derivatives.

Keywords: Thorium; Dithiophosphate; Triphenylphosphine

1. Introduction

Compared to well developed chemistry of sulfur-bonded derivatives of transition metals, with their fascinating modes of bonding [1–3] and increasing applications in industry [4] and agriculture [5], much less attention has been paid to lanthanides with such ligands. Initially it was thought that soft base (sulfur) and hard acid [thorium(IV)] character of the coordinating atoms [6] would make preparation of such complexes difficult. However, dithiocarbamato derivatives of actinide elements were prepared [7, 8]. Dithiophosphinates of actinide elements along with crystal structures for a few of them have been reported [9]. However O,O′-dialkyl dithiophosphates of lanthanide and actinide elements and their adducts have received little attention [10–12]. O,O′-alkylene dithiophosphates are expected to be less labile and have been explored in our laboratory [13–15]. We have reported O,O′-alkylene dithiophosphates of lanthanum(III) and their adducts with nitrogen and phosphorus donors [16]. Continuing our interest in ligands containing phosphorus and sulfur we report here

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*Corresponding author. Email: un_tripathi@yahoo.com

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the O,O′-alkylene dithiophosphates of thorium(IV) and their complexation with nitrogen and phosphorus donor.

2. Experimental

Ammonium salts of O,O′-dialkyl and alkylene dithiophosphoric acids were prepared by reaction of dry alcohol or glycol with phosphorus pentasulfide in 4 : 1 or 2 : 1 molar ratio, respectively, in dry benzene followed by passing dry ammonia gas into the reaction solution [17]. All other chemicals were of A.R. grade and used without further purification. The complexes described in the present article were synthesized by the following general routes.

2.1. *Preparation of [$Th\{S_2PO_2C_5H_{10}\}_4$]*

A methanolic (30 mL) solution of $Th(NO_3)_4 \cong 6H_2O$ (0.8299 g, 1.41 mmol) and [$NH_4\{S_2PO_2C_5H_{10}\}$] (1.2206 g, 5.67 mmol) were mixed and refluxed for 8 h. The turbidity created by the by-product (ammonium nitrate) was filtered off and volatiles were removed from the filtrate under reduced pressure. The solid thus obtained was extracted with benzene (20 mL) by stirring overnight. Again the insolubles were filtered off and the desired product was obtained from the filtrate by removal of benzene under vacuum (1.2524 g, 87.0%). The analytical details are listed in table 1. Compounds **1–6** were prepared by this procedure.

2.2. *Preparation of [$Th\{S_2PO_2C_5H_{10}\}_4 \cong N_2C_{10}H_8$]*

[$Th\{S_2PO_2C_5H_{10}\}_4$] (1.0311 g, 1.01 mmol) dissolved in 15 mL benzene was mixed and refluxed with (0.1578 g, 1.01 mmol) $N_2C_{10}H_8$ in 10 mL benzene for 2 h to ensure complete reaction. The solvent was reduced to 10 mL under reduced pressure and left overnight. White crystals thus deposited were removed and washed with *n*-hexane (1.0938 g, 92.0%). The analytical results are listed in table 2. Compounds numbered **7–12** were isolated by this route.

2.3. *Preparation of [$Th\{S_2PO_2C_5H_{10}\}_4 \cong N_2C_{12}H_8$]*

[$Th\{S_2PO_2C_5H_{10}\}_4$] (1.0413 g, 1.02 mmol) dissolved in 10 mL benzene was mixed and refluxed with (0.1838 g, 1.02 mmol) $N_2C_{12}H_8$ in 20 mL benzene for 3 h. Slow evaporation of solvent at room temperature does not yield the product, hence 10 mL *n*-hexane was mixed with it and the mixture was kept at 5°C for 2 h. White crystals thus obtained were removed and washed with *n*-hexane (1.1394 g, 93.0%). The analytical results are presented in table 1. Compounds **13–18** were prepared by this method.

Table 1. Synthetic and analytical data for the complexes.

Compound number	Compound	Yield (%)	m.p. (°C)	Analysis Found (Calcd) (in %)					Mol. Wt. Found (Calcd)
				Th	S	C	H	N	
1	$[Th\{S_2P(OCH_2CH_2CH_3)_2\}_4]$	90	225	21.29 (21.38)	23.70 (23.64)	26.51 (26.56)	5.18 (5.21)	–	1087.00 (1085.12)
2	$[Th\{S_2P(OC_6H_5)_2\}_4]$	92	240	17.11 (17.09)	18.75 (18.89)	42.36 (42.48)	2.93 (2.98)	–	1355.00 (1357.20)
3	$[Th\{S_2PO_2C_6H_{12}\}_4]$	83	235	21.72 (21.54)	23.63 (23.81)	26.58 (26.76)	4.51 (4.50)	–	1062.00 (1077.04)
4	$[Th\{S_2PO_2C_5H_{10}\}_4]$	87	215	22.91 (22.73)	25.07 (25.12)	23.57 (23.53)	3.97 (3.97)	–	1013.00 (1020.92)
5	$[Th\{S_2PO_2C_6H_{12}\}_4]$	85	232	21.50 (21.54)	23.67 (23.81)	27.05 (26.76)	4.67 (4.50)	–	1085.00 (1077.04)
6	$[Th\{S_2PO_2C_4H_8\}_4]$	88	221	24.00 (24.05)	26.81 (26.58)	19.95 (19.92)	3.36 (3.35)	–	978.00 (964.80)
7	$[Th\{S_2P(OCH_2CH_2CH_3)_2\}_4 \cong N_2C_{10}H_8]$	90	242	18.71 (18.69)	20.64 (20.66)	32.87 (32.89)	5.23 (5.21)	2.23 (2.26)	1238.00 (1241.32)
8	$[Th\{S_2P(OC_6H_5)_2\}_4 \cong N_2C_{10}H_8]$	94	238	15.30 (15.33)	16.96 (16.95)	46.06 (46.03)	3.17 (3.20)	1.86 (1.85)	1504.00 (1513.40)
9	$[Th\{S_2PO_2C_6H_{12}\}_4 \cong N_2C_{10}H_8]$	88	248	18.80 (18.81)	20.81 (20.79)	33.09 (33.11)	4.57 (4.59)	2.28 (2.27)	1236.00 (1233.24)
10	$[Th\{S_2PO_2C_5H_{10}\}_4 \cong N_2C_{10}H_8]$	92	231	19.72 (19.71)	21.77 (21.79)	30.57 (30.61)	4.08 (4.12)	2.39 (2.38)	1170.00 (1177.12)
11	$[Th\{S_2PO_2C_6H_{12}\}_4 \cong N_2C_{10}H_8]$	90	228	18.82 (18.81)	20.78 (20.79)	33.15 (33.11)	4.54 (4.59)	2.29 (2.27)	1235.00 (1233.24)
12	$[Th\{S_2PO_2C_4H_8\}_4 \cong N_2C_{10}H_8]$	95	239	20.74 (20.69)	22.83 (22.88)	27.87 (27.86)	3.63 (3.60)	2.46 (2.49)	1132.00 (1121.00)
13	$[Th\{S_2P(OCH_2CH_2CH_3)_2\}_4 \cong N_2C_{12}H_8]$	86	245	18.31 (18.34)	20.21 (20.27)	34.12 (34.17)	5.09 (5.11)	2.23 (2.21)	1268.00 (1265.34)
14	$[Th\{S_2P(OC_6H_5)_2\}_4 \cong N_2C_{12}H_8]$	88	240	15.02 (15.09)	16.64 (16.68)	46.90 (46.87)	3.18 (3.15)	1.80 (1.83)	1543.00 (1537.42)
15	$[Th\{S_2PO_2C_6H_{12}\}_4 \cong N_2C_{12}H_8]$	86	247	18.47 (18.46)	20.36 (20.39)	34.28 (34.39)	4.52 (4.49)	2.24 (2.23)	1254.00 (1257.26)
16	$[Th\{S_2PO_2C_5H_{10}\}_4 \cong N_2C_{12}H_8]$	93	239	19.30 (19.32)	21.38 (21.35)	31.95 (31.99)	4.00 (4.04)	2.29 (2.34)	1198.00 (1201.14)

(Continued)

Table 1. Continued.

Compound number	Compound	Yield (%)	m.p. (°C)	Analysis Found (Calcd) (in %)					Mol. Wt. Found (Calcd)
				Th	S	C	H	N	
17	$Th\{S_2PO_2C_6H_{12}\}_4 \cong N_2C_{12}H_8]$	90	230	18.42 (18.46)	20.43 (20.39)	34.32 (34.39)	4.51 (4.49)	2.25 (2.23)	1265.00 (1257.26)
18	$[Th\{S_2PO_2C_4H_8\}_4 \cong N_2C_{12}H_8]$	96	223	20.24 (20.26)	22.41 (22.39)	29.38 (29.37)	3.54 (3.53)	2.41 (2.45)	1148.00 (1145.02)
19	$[Th\{S_2P(OCH_2CH_2CH_3)_2\}_4 \cong 2P(C_6H_5)_3]$	94	218	14.45 (14.41)	15.90 (15.93)	44.79 (44.76)	5.36 (5.39)	–	1612.00 (1609.72)
20	$[Th\{S_2P(OC_6H_5)_2\}_4 \cong 2P(C_6H_5)_3]$	94	235	12.34 (12.33)	13.64 (13.61)	53.60 (53.61)	3.72 (3.76)	–	– (1881.80)
21	$[Th\{S_2PO_2C_6H_{12}\}_4 \cong 2P(C_6H_5)_3]$	96	241	14.52 (14.49)	16.00 (16.01)	44.95 (44.99)	4.91 (4.92)	–	1610.00 (1601.64)
22	$[Th\{S_2PO_2C_5H_{10}\}_4 \cong 2P(C_6H_5)_3]$	97	229	14.97 (15.01)	16.60 (16.59)	43.56 (43.52)	4.59 (4.57)	–	1550.00 (1545.52)
23	$[Th\{S_2PO_2C_6H_{12}\}_4 \cong 2P(C_6H_5)_3]$	89	218	14.53 (14.49)	16.24 (16.01)	44.95 (44.99)	4.94 (4.92)	–	1606.00 (1601.64)
24	$[Th\{S_2PO_2C_4H_8\}_4 \cong 2P(C_6H_5)_3]$	96	244	15.55 (15.58)	17.23 (17.22)	41.94 (41.93)	4.23 (4.20)	–	1480.00 (1489.40)

Table 2. IR spectral data (cm^{-1}) for complexes.

Compound number	ν[(P)–O–C]	ν[P–O–(C)]	Ring Vib.	ν[P=S]	ν[P–S]	ν[Th–S]
1	1140 (s)	830 (m)	–	680 (s)	520 (s)	360 (m)
2	1180 (s)	1060 (m)	–	690 (s)	540 (s)	380 (m)
3	1020 (s)	870 (w)	930 (m, br)	650 (s)	560 (s)	410 (w)
4	1030 (s)	890 (w)	970 (s)	660 (s)	540 (w)	380 (m)
5	1010 (s)	880 (m)	980 (s, br)	660 (s)	550 (m)	370 (w)
6	1020 (s)	860 (s)	930 (m)	650 (s)	540 (s)	390 (w)
7	1120 (s)	870 (m)	–	690 (s)	570 (m)	360 (m)
8	1160 (s)	840 (m)	–	680 (m)	530 (m)	370 (w)
9	1090 (s)	890 (s)	940 (s)	660 (m)	550 (s)	370 (w)
10	1080 (s)	860 (m)	960 (s)	670 (s)	530 (m)	380 (m)
11	1130 (s)	880 (m)	950 (m, br)	690 (s)	540 (s)	390 (m)
12	1040 (s)	840 (m)	920 (m)	640 (m)	560 (m)	350 (w)
13	1130 (s)	870 (s)	–	660 (s)	570 (s)	400 (m)
14	1170 (s)	910 (m)	–	680 (s)	580 (s)	380 (m)
15	1070 (s)	840 (m)	940 (s)	650 (s)	550 (s)	350 (w)
16	1050 (s)	820 (m)	980 (s)	690 (s)	590 (m)	370 (w)
17	1120 (s)	860 (s)	940 (m)	670 (s)	560 (s)	350 (w)
18	1100 (s)	850 (s)	930 (m)	640 (s)	580 (s)	380 (w)
19	1090 (s)	880 (m)	–	690 (m)	540 (m)	360 (w)
20	1020 (s)	940 (s)	–	660 (s)	560 (m)	390 (w)
21	1040 (s)	870 (m)	960 (m)	630 (s)	530 (m)	350 (m)
22	1100 (s)	840 (m)	990 (s)	660 (s)	580 (s)	400 (m)
23	1070 (s)	890 (m)	940 (m)	680 (m)	570 (m)	410 (w)
24	1060 (s)	860 (m)	950 (m)	640 (m)	590 (s)	370 (w)

s = strong; m = medium; w = weak; br = broad.

2.4. Preparation of $[Th\{S_2PO_2C_5H_{10}\}_4 \cong 2P(C_6H_5)_3]$

A benzene (10 mL) solution of $[Th\{S_2PO_2C_5H_{10}\}_4]$ (0.9597 g, 0.94 mmol) was mixed with benzene (12 mL) solution of $P(C_6H_5)_3$ (0.4931 g, 1.88 mmol) and refluxed for 2.5 h to ensure complete reaction. The solvent was reduced to 10 mL and left for two days at room temperature. The slow evaporation of solvent yielded the white crystalline solid which was separated from the mother liquor and washed with *n*-hexane (1.4092 g, 97.0%). The analytical results are presented in table 1. Compounds **19**–**24** were prepared by this method.

3. Measurements

IR spectra were recorded in KBr pellets with a Perkin-Elmer Model 577 spectrophotometer. ^{1}H NMR in $CDCl_3$ and ^{31}P NMR spectra in CH_2Cl_2 solutions were recorded on a Jeol 90Q spectrometer, at 90 MHz using tetramethylsilane and H_3PO_4 standards, respectively. Molecular weights were measured on a Knauer Vapor Pressure Osmometer in $CHCl_3$ at 45°C. Carbon, hydrogen and nitrogen were estimated by Coleman C.H.N. analyzers.

Sulfur was estimated by the standard method [18]. Thorium was estimated by decomposing the compound by boiling with HNO_3 till dryness. This process was repeated 4–5 times then solid was treated with water followed by oxalic acid solution.

The precipitate was filtered, washed and then ignited in a platinum crucible and weighed as ThO_2 [19].

4. Results and discussion

4.1. *Thorium(IV) tetrakis(dithiophosphate)*

All these are white solids, soluble in common organic (benzene, dichloromethane, chloroform, etc.) and coordinating (dimethyl sulfoxide, pyridine, tetrahydrofuran, etc.) solvents. The complexes are quite stable but decompose near their respective melting points. The stoichiometry of the compounds is fixed irrespective of the concentration of ligand used. The molecular weight measurement data (table 1) indicate monomeric species in dilute chloroform solution at 45°C.

The IR spectra of the complexes have been recorded in the 4000–200 cm^{-1} region and important bands are summarized in table 2. The bands observed in the 1180–1010 and 1060–830 cm^{-1} regions have been assigned to ν[(P)–O–C] and ν[P–O–(C)] stretching vibrations, respectively [13–17, 20–22]. The sharp/medium intensity band in the 980–930 cm^{-1} region in the O,O′-alkylene dithiophosphates could be due to ring vibration of dioxaphospholane or dioxaphosphorinane [20–22] rings. The ν[P=S] mode at 690–650 cm^{-1} indicates the bidentate nature of dithiophosphate ligands [13–17]. The band in the 560–520 cm^{-1} region may be ascribed to ν[P–S] stretching modes [20, 21]. Appearance of a new band (in comparison to free ligand) in the 410–360 cm^{-1} region indicates the formation of a metal-sulfur bond [23].

^1H NMR spectra of these derivatives have been recorded in $CDCl_3$ exhibiting the characteristic alkoxy and phenoxy proton signals [17] (table 3). The observed integration ratio corresponds well with the presence of four dithiophosphato groups suggesting that the ratio of metal to ligand is 1 : 4. The phosphorus atom of the dithiophosphato moiety shows one signal in the 107.00–91.20 ppm region for each compound. These signals are shifted downward (δ 15–19 ppm) as compared to their respective positions in the free ligand spectra, indicating the bidentate nature of the dithiophosphate ligand [17, 24, 25].

4.2. *Adducts of thorium(IV) tetrakis(dithiophosphate)*

All these complexes were crystallized from benzene solutions after refluxing at different conditions. These derivatives are white crystalline solids soluble in common organic (benzene, dichloromethane, chloroform, etc.) and coordinating (dimethyl sulfoxide, pyridine, tetrahydrofuran, etc.) solvents. These complexes are air and moisture stable at room temperature, but decompose near their respective melting points, which are higher than that of the parent thorium(IV) tetrakis(dithiophosphate). The molecular weight data indicate monomeric species. The IR spectral data recorded in the 4000–200 cm^{-1} region are summarized in table 2. These data are quite similar to those obtained from the original parent thorium(IV) tetrakis(dithiophosphate) with only slight shifting of the bands, suggesting again the bidentate nature of the dithiophosphate ligand [13–17].

Table 3. ^{1}H NMR and ^{31}P NMR data (in δ ppm) for complexes.

Compound number	^{1}H NMR chemical shift in $CDCl_{l3}$ (in δ ppm)	^{31}P NMR chemical shift in CH_2Cl_{l2} (in δ ppm)
1	0.92, t, 24H ($-CH_3$); 1.75, m, 16H ($-CH_2$); 5.03, m, 16H ($-OCH_2$)	100.72 (s)
2	7.15, s, 40H ($-C_6H_5$)	93.42 (s)
3	2.46–1.12, m, 44H ($-CH_3$ and $-CH_2$); 5.50–4.56, m, 4H ($-OCH$)	96.40 (s)
4	1.04, s, 24H ($-CH_3$); 4.23, d ($^3J = 16$ Hz), 16H ($-OCH_2$)	107.00 (s)
5	1.38, s, 48H ($-CH_3$)	106.20 (s)
6	2.46–1.03, m, 20H ($-CH_3$ and $-CH_2$); 4.25–3.58, m, 12H ($-OCH_2$ and $-OCH$)	91.20 (s)
7	0.96, t, 24H ($-CH_3$); 1.78–1.31, m, 16H ($-CH_2$); 5.86–5.20, m, 16H ($-OCH_2$) 8.54–7.65, m, 8H ($-N_2C_{10}H_8$)	104.01 (s)
8	6.98, s, 40H ($-C_6H_5$) 8.71–7.65, m, 8H ($-N_2C_{10}H_8$)	93.91 (s)
9	2.54–1.57, m, 44H ($-CH_3$ and $-CH_2$); 5.96–5.15, m, 4H ($-OCH$) 8.37–7.98, m, 8H ($-N_2C_{10}H_8$)	96.76 (s)
10	0.98, s, 24H ($-CH_3$); 4.05, d ($^3J = 14$ Hz), 16 H ($-OCH_2$); 8.67–8.24, m, 8H ($-N_2C_{10}H_8$)	108.00 (s)
11	1.42, s, 48H ($-CH_3$); 7.98, br, 8H ($-N_2C_{10}H_8$)	106.33 (s)
12	2.39–1.00, m, 20H ($-CH_3$ and $-CH_2$); 4.17–3.44, m, 12H ($-OCH_2$ and $-OCH$); 8.49–8.15, m, 8H ($-N_2C_{10}H_8$)	91.52 (s)
13	0.95, t, 24H ($-CH_3$); 1.76–1.31, m, 16H ($-CH_2$); 5.23, m, 16H ($-OCH_2$); 9.11–8.34, br, 8H ($-N_2C_{12}H_8$)	105.14 (s)
14	7.24, s, 40H ($-C_6H_5$); 9.23–8.47, br, 8H ($-N_2C_{12}H_8$)	94.06 (s)
15	2.41–1.19, m, 44H ($-CH_3$ and $-CH_2$); 5.43–4.61, m, 4H ($-OCH$) 9.15–8.37, m, 8H ($-N_2C_{12}H_8$)	96.47 (s)
16	1.01, s, 24H ($-CH_3$); 4.12, d ($^3J = 15$ Hz), 16 H ($-OCH_2$); 9.12–8.63, m, 8H ($-N_2C_{12}H_8$)	107.87 (s)
17	1.41, s, 48H ($-CH_3$); 9.23–8.31, m, 8H ($-N_2C_{12}H_8$)	105.95 (s)
18	2.42–1.01, m, 20H ($-CH_3$ and $-CH_2$); 4.20–4.09, m, 12H ($-OCH_2$ and $-OCH$); 9.13–8.54, m, 8H ($-N_2C_{12}H_8$)	91.84 (s)
19	0.93, t, 24H ($-CH_3$); 1.75, m, 16H ($-CH_2$); 5.92, m, 16H ($-OCH_2$); 7.47, m, 30H ($-C_6H_5$)	104.46 (s) –2.69 (s)
20	7.12, s, 40H ($-C_6H_5$); 7.52, m, 30H ($-C_6H_5$)	93.08 (s) –2.78 (s)
21	2.38–1.24, m, 44H ($-CH_3$ and $-CH_2$); 5.94–5.03, m, 4H ($-OCH$) 7.86–7.36, m, 30H ($-C_6H_5$)	96.38 (s) –2.46 (s)
22	1.05, s, 24H ($-CH_3$); 4.13, d ($^3J = 16$ Hz), 16 H ($-OCH_2$); 7.42, m, 30H ($-C_6H_5$)	107.69 (s) –2.21 (s)
23	1.43, s, 48H ($-CH_3$); 8.16–7.65, m, 30H ($-C_6H_5$)	106.11 (s) –2.32 (s)
24	2.41–1.09, m, 20H ($-CH_3$ and $-CH_2$); 4.09–4.01, m, 12H ($-OCH_2$ and $-OCH$); 8.08–7.97, m, 30H ($-C_6H_5$)	91.58 (s) –3.92 (s)

s = singlet, d = doublet, t = triplet, m = multiplet, br = broad.

^{1}H NMR spectra of these derivatives have been recorded in $CDCl_3$ exhibiting the characteristic alkoxy and phenoxy proton signals along with aromatic proton signals from the additional ligands. The observed integration ratios correspond well with the presence of one nitrogen donor and two phosphorus donors in these compounds.

In ^{31}P NMR spectra of these derivatives, the phosphorus atom of the dithiophosphato moiety shows one signal in the 108.00–91.52 ppm region for each compound; an additional phosphorus signal in the –2.21 to –3.92 ppm region was recorded in the complexes with the triphenylphosphine. The downfield (δ 15–19 ppm) shifting of the signal due to the dithiophosphato phosphorus atom confirms the bidentate nature of dithiophosphato moieties in these derivatives [17, 24, 25]. On the basis of these studies and available literature, octacoordinated and decacoordinated structures for thorium(IV) tetrakis(dithiophosphate) and their adducts, respectively, may be proposed.

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