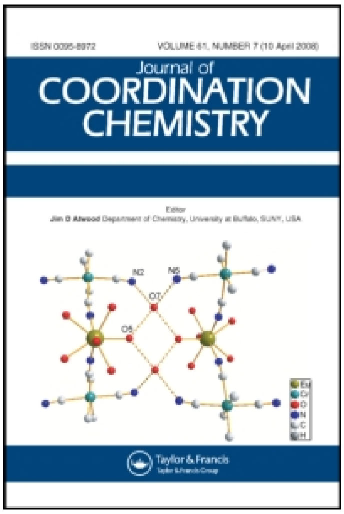

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Synthesis and Characterization of O,O' Dialkyl and Alkylene Dithiophosphates of Lanthanum(III) and their Adducts with Nitrogen and Phosphorus Donor Bases

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SYNTHESIS AND CHARACTERIZATION OF O,O′ DIALKYL AND ALKYLENE DITHIOPHOSPHATES OF LANTHANUM(III) AND THEIR ADDUCTS WITH NITROGEN AND PHOSPHORUS DONOR BASES

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Lanthanum(III) tris(dithiophosphates), $[La\{S_2P(OR)_2\}_3]$ (where $R = \text{-}CH_2CH_2CH_3$ or $\text{-}C_6H_5$) and $[La\{S_2PO_2G\}_3]$ [where $G = \text{-}C(CH_3)_2CH_2CH(CH_3)\text{-}$, $\text{-}CH_2C(CH_3)_2CH_2\text{-}$, $\text{-}C(CH_3)_2C(CH_3)_2\text{-}$ and $\text{-}CH_2CH_2CH(CH_3)\text{-}$] were prepared in methanolic solutions of anhydrous $LaCl_3$ and ammonium dithiophosphates. Addition complexes of the type $[La\{S_2P(OR)_2\}_3 \cdot nL]$ and $[La\{S_2PO_2G\}_3 \cdot nL]$ [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 reaction of lanthanum(III) tris(dithiophosphates) and nitrogen or phosphorus donor bases in benzene. These newly synthesized derivatives have been characterized by elemental analyses, molecular weights, IR, ^1H and ^{31}P NMR spectral measurements. Coordination numbers of six and eight are suggested for lanthanum(III) in these derivatives.

Keywords: Lanthanum; Dithiophosphate; Triphenylphosphine

INTRODUCTION

Compared to the well–developed chemistry of sulfur–bonded derivatives of transition metals, due to their fascinating modes of bonding [1–3] along with increasing applications in industry [4] and agriculture [5], much less attention has been paid to lanthanides with such ligands. Initially it was thought that, (a) soft base (sulfur) and hard acid [lanthanum(III)] character of the coordinating atoms [6] and (b) instability to moisture would make preparation of such complexes difficult [7–9]. However, dithiocarbamato derivatives of lanthanide elements were prepared [9–12]. Later it was suggested that

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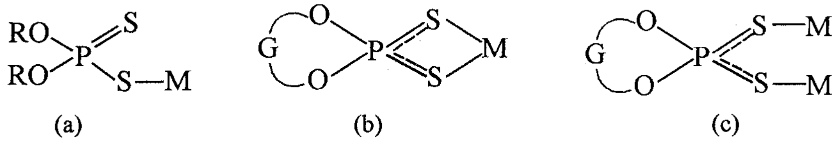

FIGURE 1 (a) Monodentate bonding of O,O′ dialkyl dithiophosphate. (b) Bidentate bonding of O,O′ alkylene dithiophosphate, (c) Bridging mode of bonding for O,O′ alkylene dithiophosphate.

use of additional neutral bases would allow preparation of air-stable complexes [13–15]. Dithiophosphinates of lanthanide elements along with crystal structures for a few of them have been reported [16–17]. However O,O′ dialkyl dithiophosphates of these elements and their adducts have received little attention [18–20]. Perusal of the literature reveals that O,O′ alkylene dithiophosphates of lanthanum(III) have not been reported. O,O′ alkylene dithiophosphates are expected to be less labile and have been explored in our laboratory [21–23]. The main bonding patterns shown by dithiophosphate ligands are shown in Fig. 1. Hence, based on the above information and due to the bridging nature of lanthanum between transition and inner transition elements, it was thought worthwhile to study the O,O′ alkylene dithiophosphates of lanthanum(III) and their complexation reaction with nitrogen and phosphorus donor bases.

EXPERIMENTAL

Ammonium salts of O,O′ dialkyl and alkylene dithiophosphoric acids were prepared by reaction of the desired 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 in the reaction solution [24]. Anhydrous lanthanum chloride was obtained by heating hydrated lanthanum chloride in a glass tube in an environment of HCl gas. All other chemicals were of A.R. grade and were used without further purification. The complexes described in the present paper were synthesized by the following general routes.

Preparation of [La{$S_2PO_2C_5H_{10}$}$_3$]

A methanolic (30 mL) solution of anhydrous lanthanum(III) chloride (0.4638 g; 1.89 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 chloride) 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 (1.1191 g; 81.0%). The analytical details are listed in Table I. Compounds numbered **1–6** were prepared by this same procedure.

Preparation of [La{$S_2PO_2C_5H_{10}$}$_3$·$N_2C_{10}H_8$]

[La{$S_2PO_2C_5H_{10}$}$_3$] (0.6885 g; 0.94 mmol) dissolved in 15 mL benzene was mixed and refluxed with (0.1472 g; 0.94 mmol). $N_2C_{10}H_8$ in 10 mL benzene for 2 h to ensure

TABLE I Synthetic and physical data for the complexes

Compd. No.	*Compound*	*Yield (%)*	*M.P. (°C)*	*Analysis Found (Calcd.) (in %)*					*Mol. wt. Found (Calcd.)*
				La	*S*	*C*	*H*	*N*	
1	$[La\{S_2P(OCH_2CH_2CH_3)_2\}_3]$	92	180	17.81	24.72	27.75	5.44	–	780.00
				(17.84)	(24.71)	(27.76)	(5.44)		(778.72)
2	$[La\{S_2P(OC_6H_5)_2\}_3]$	91	200	14.14	19.55	43.90	3.09	–	980.00
				(14.13)	(19.58)	(43.99)	(3.08)		(982.80)
3	$[La\{S_2PO_2C_6H_{12}\}_3]$	82	190	17.97	24.89	27.95	4.71	–	790.00
				(17.98)	(24.90)	(27.98)	(4.70)		(772.67)
4	$[La\{S_2PO_2C_5H_{10}\}_3]$	81	210	19.00	26.31	24.68	4.15	–	720.00
				(19.01)	(26.33)	(24.66)	(4.14)		(730.59)
5	$[La\{S_2PO_2C_6H_{12}\}_3]$	85	245	17.99	24.93	27.96	4.72	–	780.00
				(17.98)	(24.90)	(27.98)	(4.70)		(772.67)
6	$[La\{S_2PO_2C_4H_8\}_3]$	77	180	20.18	27.95	20.96	3.50	–	690.00
				(20.18)	(27.94)	(20.93)	(3.51)		(688.52)
7	$[La\{S_2P(OCH_2CH_2CH_3)_2\}_3 \cdot N_2C_{10}H_8]$	91	200	14.87	20.56	35.99	5.37	3.00	930.00
				(14.86)	(20.58)	(35.97)	(5.39)	(3.02)	(934.87)
8	$[La\{S_2P(OC_6H_5)_2\}_3 \cdot N_2C_{10}H_8]$	89	210	12.18	16.90	48.54	3.33	2.47	1130.00
				(12.20)	(16.89)	(48.51)	(3.36)	(2.46)	(1138.95)
9	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot N_2C_{10}H_8]$	96	196	14.96	20.73	36.20	4.78	3.01	930.00
				(14.96)	(20.71)	(36.21)	(4.78)	(3.02)	(928.82)
10	$[La\{S_2PO_2C_5H_{10}\}_3 \cdot N_2C_{10}H_8]$	88	220	15.68	21.72	33.84	4.51	3.17	880.00
				(15.67)	(21.70)	(33.86)	(4.55)	(3.16)	(886.74)
11	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot N_2C_{10}H_8]$	80	260	14.98	20.70	36.23	4.77	3.04	930.00
				(14.98)	(20.71)	(36.21)	(4.78)	(3.02)	(928.82)
12	$[La\{S_2PO_2C_4H_8\}_3 \cdot N_2C_{10}H_8]$	84	190	16.49	22.73	31.29	3.83	3.30	890.00
				(16.45)	(22.76)	(31.28)	(3.82)	(3.32)	(884.67)
13	$[La\{S_2P(OCH_2CH_2CH_3)_2\}_3 \cdot N_2C_{12}H_8]$	93	210	14.48	20.03	37.51	5.25	2.93	960.00
				(14.49)	(20.06)	(37.57)	(5.26)	(2.92)	(958.92)
14	$[La\{S_2P(OC_6H_5)_2\}_3 \cdot N_2C_{12}H_8]$	90	220	11.92	16.52	49.59	3.27	2.40	1170.00
	S			(11.94)	(16.54)	(49.57)	(3.29)	(2.41)	(1163.00)
15	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot N_2C_{12}H_8]$	92	208	14.59	20.17	37.72	4.66	2.93	950.00
				(14.58)	(20.19)	(37.81)	(4.65)	(2.94)	(952.87)
16	$[La\{S_2PO_2C_5H_{10}\}_3 \cdot N_2C_{12}H_8]$	90	230	15.24	21.14	35.54	4.20	3.07	900.00
				(15.25)	(21.12)	(35.60)	(4.21)	(3.08)	(910.79)
17	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot N_2C_{12}H_8]$	92	268	14.57	20.20	37.76	4.66	2.95	960.00
				(14.58)	(20.19)	(37.81)	(4.65)	(2.94)	(952.87)
18	$[La\{S_2PO_2C_4H_8\}_3 \cdot N_2C_{12}H_8]$	86	200	15.97	22.16	33.20	3.72	3.21	870.00
				(15.99)	(22.15)	(33.18)	(3.71)	(3.23)	(868.71)
19	$[La\{S_2P(OCH_2CH_2CH_3)_2\}_3 \cdot 2P(C_6H_5)_3]$	82	200	10.68	14.75	49.77	5.58	–	1310.00
				(10.66)	(14.76)	(49.76)	(5.57)		(1303.26)
20	$[La\{S_2P(OC_6H_5)_2\}_3 \cdot 2P(C_6H_5)_3]$	86	210	9.22	12.77	57.40	4.00	–	1500.00
				(9.22)	(12.76)	(57.37)	(4.01)		(1507.35)
21	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot 2P(C_6H_5)_3]$	90	204	10.72	14.81	49.95	5.13	–	1300.00
				(10.71)	(14.83)	(49.99)	(5.13)		(1297.22)
22	$[La\{S_2PO_2C_5H_{10}\}_3 \cdot 2P(C_6H_5)_3]$	94	214	11.09	15.31	48.84	4.83	–	1260.00
				(11.07)	(15.33)	(48.80)	(4.82)		(1255.14)
23	$[La\{S_2PO_2C_6H_{12}\}_3 \cdot 2P(C_6H_5)_3]$	88	250	10.73	14.81	49.97	5.15	–	1290.00
				(10.71)	(14.83)	(49.99)	(5.13)		(1297.22)
24	$[La\{S_2PO_2C_4H_8\}_3 \cdot 2P(C_6H_5)_3]$	93	194	11.43	15.87	47.53	4.47	–	1210.00
				(11.45)	(15.86)	(47.52)	(4.49)		(1213.06)

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 (0.7354 g; 88.0%). The analytical results are listed in Table II. Compounds numbered **7**–**12** were isolated by this route.

TABLE II IR spectral data (cm^{-1}) for complexes

Compd. No.	*ν[(P)–O–C]*	*ν[P–O–(C)]*	*Ring Vib.*	*ν[P=S]*	*ν[P–S]*	*ν[La–S]*
1	1060 (s, br)	800 (br)	–	640 (br)	510 (s)	350 (w)
2	1140 (s)	1000 (s)	–	650 (s)	530 (s)	370 (s)
3	940 (s)	830 (m)	890 (s, br)	620 (m)	550 (m)	330 (w)
4	930 (s)	820 (w)	870 (m)	680 (m)	520 (w)	340 (m)
5	1050 (s)	840 (m)	900 (m, br)	660 (w)	530 (m)	320 (w)
6	970 (s)	830 (w)	880 (s)	630 (w)	560 (s)	350 (s)
7	1090 (s, br)	810 (s)	–	650 (s)	540 (s)	360 (s)
8	1180 (s)	1020 (s)	–	650 (s)	520 (s)	360 (s)
9	1070 (s)	820 (m)	900 (s)	630 (s)	560 (m)	320 (w)
10	990 (s)	810 (m)	910 (s)	680 (m)	550 (m)	320 (s)
11	1120 (s)	840 (m)	920 (m, br)	650 (s)	530 (s)	330 (w)
12	990 (s)	820 (m)	890 (m)	640 (m)	540 (s)	350 (s)
13	1040 (s)	810 (m)	–	630 (m)	520 (s)	360 (m)
14	1160 (s)	1000 (s)	–	640 (s)	530 (m)	370 (s)
15	1050 (m)	820 (m)	900 (s)	620 (s)	540 (w)	340 (s)
16	940 (s)	800 (m)	890 (s)	670 (m)	550 (m)	330 (w)
17	1090 (s)	830 (s)	910 (s)	650 (m)	540 (s)	320 (m)
18	960 (s)	830 (s)	900 (m)	640 (s)	560 (s)	340 (s)
19	1080 (s)	800 (m)	–	650 (s)	530 (s)	350 (s)
20	1150 (s)	1010 (s)	–	660 (m)	520 (m)	360 (s)
21	1020 (m)	840 (s)	880 (m)	640 (s)	560 (s)	350 (s)
22	980 (s)	810 (s)	900 (m)	660 (s)	540 (s)	330 (w)
23	1100 (m)	820 (s)	930 (s)	630 (m)	550 (s)	360 (w)
24	980 (s)	840 (s)	880 (m)	640 (s)	560 (s)	350 (s)

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

Preparation of $[La\{S_2PO_2C_5H_{10}\}_3{\cdot}N_2C_{12}H_8]$

$[La\{S_2PO_2C_5H_{10}\}_3]$ (0.6705 g; 0.92 mmol) dissolved in 10 mL benzene was mixed and refluxed with (0.1654 g; 0.92 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 (0.7523 g; 90.0%). The analytical results are presented in Table I. Compounds numbered **13–18** were prepared by this method.

Preparation of $[La\{S_2PO_2C_5H_{10}\}_3{\cdot}2P(C_6H_5)_3]$

Benzene (10 mL) solution of $[La\{S_2PO_2C_5H_{10}\}_3]$ (0.6006 g, 0.82 mmol) was mixed with benzene (12 mL) solution of $P(C_6H_5)_3$ (0.4362 g; 0.82 mmol) and refluxed for 2(1/2) 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 (0.9699 g; 94.0%). The analytical results are presented in Table I. Compounds numbered **19–24** were crystallized by this same method.

MEASUREMENTS

IR spectra were recorded in KBr pellets with a Perkin-Elmer Model 577 spectrophotometer. ^1H NMR in $CDCl_3$ and ^{31}P NMR and CH_2Cl_2 solutions were recorded on a Jeol FX 90Q spectrometer. Molecular weights were measured on a Knauer Vapor Pressure Osmometer in $CHCl_3$ at 45°C. Elemental analysis for La and S were carried out by standard procedures [25,26]. Carbon, hydrogen and nitrogen were estimated by Coleman C.H.N. analyzers.

RESULTS AND DISCUSSION

Lanthanum(III) tris(dithiophosphate)

All these compounds 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 I) 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 the important bands are summarized in Table II. The bands observed in the 1140–930 and 1000–800 cm^{-1} regions have been assigned to ν[(P)–O–C] and [P–O–(C)], respectively[21–24,27–29]. The sharp/medium intensity band present in the 900–870 cm^{-1} region in the O,O′ alkylene dithiophosphates could be due to the ring vibration of dioxaphospholane or dioxaphosphorinane [27–29] rings. The ν[P=S] mode may be characterized by the presence of a band in the 680–620 cm^{-1} region indicating the bidentate nature of dithiophosphate ligands [21–24]. The band present in the 560–510 cm^{-1} region may be ascribed to ν[P–S] stretching modes [27,28]. Appearance of a new band (in comparison to free ligand) in the 370–320 cm^{-1} region indicates the formation of a metal-sulfur bond [30].

^{1}H NMR spectra of these derivatives have been recorded in $CDCl_3$ exhibiting the characteristic alkoxy and glycoxy proton signals [24] (Table III). The observed integration ratio corresponds well with the presence of three dithiophosphato groups suggesting that the ratio of metal to ligand is 1 : 3. The phosphorus atom of the dithiophosphato moiety shows one signal in the 110–90 ppm region for each compound. These signals are shifted downfield (δ 14–20 ppm) as compared to their respective positions in the free ligand spectra, indicating the bidentate nature of the dithiophosphate ligand [24,31,32].

Adducts of lanthanum(III) tris(dithiophosphate)

All these addition 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. Thse complexes are air and moisture stable at ordinary temperature, but decompose near their respective melting points, which are higher than that of the parent lanthanum(III) tris(dithiophosphate). The molecular weight measurement data indicate monomeric species for these compounds also. The IR spectral data recorded in the 4000–200 cm^{-1} region are summarized in Table II. These data are quite similar to those obtained from the original parent

TABLE III ^{1}H NMR and ^{31}P NMR data (in δ ppm) for complexes

Compd. No.	*^{1}H NMR chemical shift in $CDCl_3$ (in δ ppm)*	*^{31}P NMR chemical shift in CH_2Cl_2 (in δ ppm)*
1	0.85, t, 18H (-CH_3), 1.86, m, 12H (-CH_2) 4.05, m, 12 H (-OCH_2)	100.72 (s)
2	6.62, s, 30H (-C_6H_5)	89.36 (s)
3	2.46–0.67, m, 33H (-CH_3 and -CH_2) 4.47–3.58, m, 3H (-OCH)	91.80 (s)
4	1.12–0.95, S, 18H (-CH_3), 4.32, d ($^3J = 17$ Hz), 12H (-OCH_2).	99.00 (s)
5	1.43, s, 36H (-CH_3)	108.10 (s)
6	2.55–1.12, m, 15H (-CH_3 and -CH_2); 5.14–4.47, m, 9H (-OCH_2 and -OCH)	98.30 (s)
7	0.89, t, 18H (-CH_3); 1.90–1.20, m, 12H (-CH_2) 5.20–4.60, m, 12H (-OCH_2); 8.60–7.90, m, 8H (-$N_2C_{10}H_8$)	100.12 (s)
8	6.48, s, 30H (-OC_6H_5); 8.96–7.88, m, 8H (-$N_2C_{10}H_8$)	88.86 (s)
9	2.10–1.13, m, 33H (-CH_3 and -CH_2) 5.00–4.56, m, 3H (-OCH); 8.60–8.10, m, 8H (-$N_2C_{10}H_8$)	92.00 (s)
10	1.00, s, 18H (-CH_3); 4.01, d ($^3J = 15$ Hz), 12H (-OCH_2); 8.65–8.16, m, 8H (-$N_2C_{10}H_8$)	100.00 (s)
11	1.49, s, 36H (-CH_3); 8.03, br, 8H (-$N_2C_{10}H_8$)	108.16 (s)
12	2.45–1.08, br, 15H (-CH_3 and -CH_2); 4.68, m, 9H (-OCH_2 and –OCH); 8.52–8.08, m, 8H (-$N_2C_{10}H_8$)	98.62 (s)
13	0.87, t, 18H (-CH_3); 1.89, m, 12H (-CH_2); 4.06, m, 12H (-OCH_2); 9.02–8.18, br, 8H (-$N_2C_{12}H_8$)	101.02 (s)
14	6.64, s, 30H (-OC_6H_5); 9.20–8.20, br, 8H (-$N_2C_{12}H_8$)	90.03 (s)
15	2.40–0.87, m, 33H (-CH_3 and -CH_2); 4.37–3.60, m, 3H (-OCH) 9.10–8.29, m, 8H (-$N_2C_{12}H_8$)	91.89 (s)
16	1.08, s, 18H (-CH_3); 4.08 d ($^3J = 16$ Hz), 12H (-OCH_2), 9.02–8.36, m, 8H (-$N_2C_{12}H_8$)	99.82 (s)
17	1.48, s, 36H (-CH_3); 9.18–8.21, m, 8H (-$N_2C_{12}H_8$)	107.92 (s)
18	2.50–1.10, m, 15H (-CH_3 and -CH_2) 4.98–4.67, m, 9H (-OCH_2 and -OCH) 9.08–8.46, m, 8H (-$N_2C_{12}H_8$)	98.92 (s)
19	0.86, t, 18H (-CH_3); 1.88, m, 12H (-CH_2) 4.85, m, 4H (-OCH_2); 7.38, m, 30H (-C_6H_5)	100.68 (s)
20	6.60, s, 30H (-OC_6H_5); 7.41, m, 30H (-C_6H_5)	89.02 (s) -2.66 (s)
21	2.37–0.92, m, 33H (-CH_3 and -CH_2) 4.98–4.43, m, 3H (-OCH); 7.90–7.29, m, 30H (-C_6H_5)	91.79 (s) -2.35 (s)
22	1.10, s, 18H (-CH_3); 4.21, d ($^3J = 17$ Hz), 12H (-OCH_2); 7.33, m, 30H (-C_6H_5)	99.77 (s) -2.15 (s)
23	1.50, s, 36H (-CH_3); 8.20–7.60, m, 30H (-C_6H_5)	108.-2 (s) -2.27 (s)
24	2.49–1.18, br, 15H (-CH_3 and -CH_2) 4.87–4.67, m, 9H (-OCH_2 and -OCH) 8.12–7.91, m, 30H (-C_6H_5)	98.88 (s) -3.49 (s)

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

lanthanum(III) tris(dithiophosphate) with only slight shifting of the bands, suggesting again the bidentate nature of the dithiophosphate ligand [21–24].

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

In ^{31}P NMR spectra of these derivatives, the phosphorus atom of the dithiophosphato moiety shows one signal in the 110–88 ppm region for each compound, and an additional phosphorus signal in the -1 to -4 ppm region was recorded in the complexes with the triphenyl phosphine base. The downfield (δ 14–20 ppm) shifting of the signal due to the dithiophosphato phosphorus atom also confirms the bidentate nature of dithiophosphato moieties in these derivatives [24,31,32]. On the basis of these studies and available literature [15], hexacoordinate and octacoordinate structures for lanthanum(III) tris(dithiophosphate) and their addition complexes, respectively, may be proposed.

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