



Synthesis and Characterization of O-Alkyl ,O-Aryl and O-Cycloalkyl Trithiophosphato Derivatives of Lanthanum (III) chloride and their Adduct with Nitrogen Donar Bases

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Abstract:- Chloro lanthanu (III) trithiophosphates (RO)(S)(P)(S)₂LaCl where R = Me,Et, ⁿPr, ⁱPr, ⁿBu, ^sBu, ⁱBu, ⁱAm, cyclohexyl, Phenyl, were prepared in the methanolic solution of LaCl₃ and dipotassium salt of trithiophosphates. Addition complexes of the type (RO)(S)(P)(S)₂LaCl .nL (where n=1, L=(C₆H₄N)₂ 1-10-phenanthroline and (C₅H₄N)₂ 2,2 -bipyridyl were prepared by reaction of chloro Lanthanum (III) trithiophosphate and nitrogen donar bases in dry methanol. These newly synthesized derivatives have been characterized by elemental analysis, molecular weight measurement, IR, ¹³C, ³¹P spectral studies. Coordination no of three and five are suggested for La (III) in these derivatives.

Key Words : La(III) ; 1-10-phenanthroline ; 2,2 -bipyridyl

I. Introduction

In the recent years considerable interest have been evinced in the chemistry of metallic moieties bonded with sulfur ligands such as thiolates dithiolates (1) thio β diketones (2), dithiocarbamates and O-O- alkylene dithiophosphates (3-5) .Dithiophosphinates of lanthanide elements along with the crystal structure for a few have been reported (6-7) .O,O dialkyl and alkylene dithiophosphates of Lanthanum (III) and their adducts with nitrogen and phosphorus donar bases have been prepared.(8) Lanthanum(III) complex with dithio carbamates have been synthesized.(9) Spectral and structural studies of S-methyl and S-benzyl dithiocarbamate azomathine complexes of lanthanum have also been studied (10). Potassium salt of trithiophosphates exist in two isomeric forms ;



Organic trithiophosphates esters have been used as defoliant (11) insecticides (11-12) nematocides (12) and inhibitors(13) of steel corrosion. The perusal of literature revealed only two publications on the metallic esters of tri thiophosphoric acids (14-15) . The trithiophosphate derivatives of Lanthanum are still unknown. In continuation of our research interest in ligands containing phosphorus and sulfur both, it was thought worthwhile to synthesise a number of compound of the type (RO)(S)(P)(S)₂LaCl. In the present communication , we report the synthesis and characterization of a number of chloro Lanthanum (III) trithiophosphates and their reaction with nitrogen donar bases.

Experimental-

Dipotassium salt of O-alkyl, O-aryl and O-cycloalkyl trithiophosphates were prepared by the reaction of phosphorus pentasulfide with corresponding alcohols and triethyl amine in 1:3:3 molar ratio in anhydrous benzene. The reaction mixture was stirred for 30 minute on a water bath. After stirring a methanolic solution potassium hydroxide was added and dipotassium salt was precipitated out. All chemicals were of A.R grade and were used after drying process. The complexes described in the present paper were synthesized by the following route. Synthesis of Chloro Lanthanum (III) Trithiophosphates (RO)(S)(P)(S)₂LaCl Reaction of ligand and lanthanum trichloride is carried out in dry methanol with Continuous Refluxion of 8 hours which results in the formation of the complex in 1:1 molar ratio. After refluxing the solid KCl was precipitated out. Insoluble were filtered off and the product was obtained from the filtrate by removal of volatiles under reduced pressure. The complexes numbered 1-10 were all prepared by this same procedure.

Synthesis of (RO)(S)(P)(S)₂LaCl Adducts with Nitrogen Donor Bases-A dry methanolic solution (white colored) of the chloro Lanthanum (III) trithiophosphate, dry methanolic solution of 1,10-phenanthroline was added. The mixture was refluxed for four to six hours to ensure complete reaction. Methanol was removed under vacuum. White adduct were formed. Reaction occur in 1:1 manner. The white coloured adduct of 2-2 bipyridyl (C₅H₄N)₂ were prepared by the same procedure.

Measurement-

IR spectra were recorded in KBr pellets with a Perkin Elmer Model 577 spectrophotometer in the Region 4000-200 cm⁻¹. ¹H NMR were recorded in water and DMSO-d₆ using DSS (dimethyl silyl pentyl sulphonate) and TMS (tetra methyl silane) as internal standard. These spectra were recorded on Bruker DRX-300 spectrometer at 75.47 MHz. ¹³C NMR spectra were recorded in water and DMSO using DSS (dimethyl silyl pentyl sulphonate) and TMS (tetra methyl silane) as internal standard. Proton decoupled ³¹P NMR spectra were recorded in water and DMSO using H₃PO₃ (ortho phosphoric acid) and as an internal standard. These spectra were recorded on Bruker DRX-300 spectrometer at 121.50 MHz. The melting point of the synthesized compound was recorded on B.I. Bornsted electro thermal instrument in a sealed capillary tube. Elemental analysis were carried out by standard procedure (16) Carbon, hydrogen and nitrogen were estimated by Coleman C,H,N analyzer.

II. Result and Discussion-

(RO)(S)(P)(S)₂LaCl

Chloro lanthanum(III) trithiophosphates are white colour solids. These complexes are soluble in coordinating solvents as DMSO. Complexes decompose very slowly at room temperature and hygroscopic but remain intact when stored in dry and cooled conditions.

IR SPECTRA-

IR spectra (table 1) of chloro lanthanum (III) trithiophosphate have been measured in the range of 4000-200 cm⁻¹ and assignments have been made by comparison with IR spectra of respective potassium trithiophosphates, 17-18. The bands present in the region 1011-1022 and 811-821 cm⁻¹ have been assigned to ν [(P)-O-C] and ν [P-O-(C)] stretching vibrations respectively. Strong bands in the region 639-645 cm⁻¹ is observed due to ν [P=S] stretching. Bands due to ν [P-S] stretch of medium intensity is observed in the region 421-430 cm⁻¹, these frequencies are lower in comparison to ligand spectra. This is the direct evidence that coordination occurs with the sulfur. 19 Two new bands also appear in the complex spectra in the region 329-339 and 340-349 cm⁻¹, they are assigned to ν [La-S] and ν [La-Cl] respectively. This indicates lowering in symmetry of the ligand because of coordination. 20

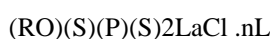
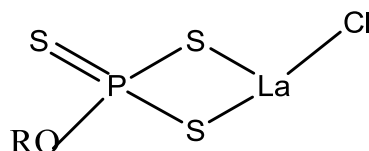
NMR SPECTRA-

In ³¹P NMR spectral data (table 2) only one signal of phosphorus has been observed which indicates that although two isomers were there in ligand but only one type of ligand isomer is present in compound form. Signals are downfield about +16 δ , ppm and it shows complexation and bidentate nature of the ligand. 21 ¹H NMR spectral data are summarized in (table 3). They are in good agreement with the corresponding alkyl group 22 but more deshielded compared to the ligand spectra. Percentage of deshielding decreases with the α , β ,

and γ carbons. Some signal obtained in ligand spectra due to $-\text{SCH}_3$ at about 2.4 δ , ppm is disappeared thus it conclude that only one type of isomer is present in the chloro lanthanum trithiophosphate complex.

Number of hydrogens by integration ratio suggests that there is only one trithiophosphate ligand associated with the lanthanum. The ^{13}C NMR spectral data (table 3) shows characteristic resonance due to the alkoxy and phenoxy group.²¹ The ^{13}C resonance for the carbon atom of [P-O-C] group appears as doublet due to coupling with ^{31}P nuclei.

Molecular weight and elemental analysis (table 4) confirm the monomeric nature of the complexes. Putting all the facts together coordination number three is proposed for lanthanum with discrete trigonal planar geometry.



(where $n=1$, $\text{L} = (\text{C}_6\text{H}_4\text{N})_2$ 1-10-phenanthroline and $(\text{C}_5\text{H}_4\text{N})_2$ 2,2'-bipyridyl). The addition complexes numbered 11-20 are white coloured solids and those numbered 21-30 are also white coloured solids. These adducts are soluble in polar solvents as alcohol acetone, chloroform etc and coordinating solvent as DMSO. They are stable at room temperature but tend to decompose near their melting point



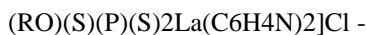
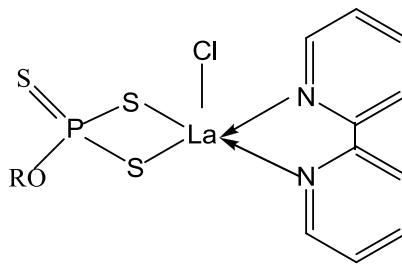
IR Spectra-

IR spectra (table 5) of chloro lanthanum (III) trithiophosphate 2,2'-bipyridyl complexes have been measured in the range of 4000-200 cm^{-1} and assignments have been made by comparison with IR spectra of the ligand, trithiophosphates, 17-18 and 2,2'-bipyridyl¹⁹. The bands present in the region 1023-1010 and 822-810 cm^{-1} have been assigned to $\nu[(\text{P})-\text{O}-\text{C}]$ and $\nu[\text{P}-\text{O}-(\text{C})]$ stretching vibrations respectively. The $\nu[\text{P}=\text{S}]$ stretching vibration occurs in the region 644-636 cm^{-1} . Bands in the region 430-422 cm^{-1} is assigned for $\nu[\text{P}-\text{S}]$ stretching it is lower in frequency with respect to the ligands is due to sulfur coordination with the lanthanum. The bands due $\nu[\text{La}-\text{S}]$ and $\nu[\text{La}-\text{Cl}]$ was observed in the region 330-341 and 340-349 cm^{-1} respectively. Bands in the region 296-284 cm^{-1} were assigned for $\nu[\text{La}-\text{N}]$ stretching mode. The bands due to $\nu[\text{C}=\text{N}]$ of the pyridyl ring is observed in region 1585-1572 cm^{-1} . Increased number of bands in the spectra shows the lowering in symmetry

NMR Spectra-

In ^{31}P NMR spectral data (table 6) only one signal of phosphorous have been observed which is down compared to ligand spectra giving the inference of bidentate nature of the ligands more deshielding indicates complexation of lanthanum.²¹ ^1H NMR spectral data are summarized in (table 7). They are in good agreement with the corresponding alkyl group.²² They are slight upfield, deshielded due to complexation. Percentage of deshielding decreases with length of carbon chain i.e. α , β , and γ carbons. Signals in nearly same region appeared as multiplet at room temperature. Signals due to pyridyl group also appeared as multiplet although they are having different environment but mixing of peaks results out as multiplet. Integration ratio is in accordance with the attachment of one 2,2'-bipyridyl ligand to trithiophosphate complex.

The ^{13}C NMR spectral data (table 7) shows characteristic resonance due to the alkoxy and phenoxy group.²² The ^{13}C resonance for the carbon atom of [P-O-C] group appears as doublet due to coupling with ^{31}P nuclei. ^{13}C resonance due to bipyridyl carbon are in good agreement with the previous reported data of the pyridyl but they are more deshielded. This is due to complexation of 2,2'-bipyridyl with lanthanum.²¹ Molecular weight and elemental analysis (table 8) confirm the monomeric nature of the complexes. Considering all the spectral and elemental analysis data and facts, it is proposed that both the nitrogen donates their lone pair to lanthanum. Chlorine atom is intact with lanthanum. Thus coordination number of lanthanum is increased to five and trigonal bipyramidal or square pyramidal structure is tentatively proposed for the complexes.



IR Spectra

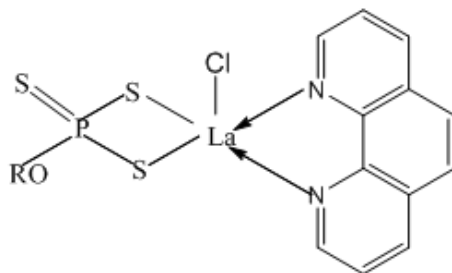
IR spectra (table 9) of chloro lanthanum (III) trithiophosphate 1,10-phenanthroline complexes have been measured in the range of 4000-200 cm^{-1} and assignments have been made by comparison with IR spectra of the ligand, trithiophosphates¹⁷⁻¹⁸ and 1,10 phenanthroline¹⁹. The bands present in the region 1020-1013 cm^{-1} and 809-821 cm^{-1} have been assigned to ν [(P)-O-C] and ν [P-O-(C)] stretching vibrations respectively. The ν [P=S] stretching vibration occurs in the region 648-635 cm^{-1} . Bands in the region 431-423 cm^{-1} is assigned for ν [P-S] stretching it is lower in frequency with respect to the ligands is due to sulfur coordination with the lanthanum. The bands due ν [La-S] and ν [La-Cl] was observed in the region 343-333 and 348-340 cm^{-1} respectively. Bands in the region 296-284 cm^{-1} were assigned for ν [La-N] stretching mode. The bands due to ν [C=N] of the pyridyl ring is observed in region 1585-1572 cm^{-1} . Increased number of bands in the spectra shows the lowering in symmetry.

NMR Spectra-

In ³¹P NMR spectral data (table 10) only one signal of phosphorus have been observed which is down compared to ligand spectra giving the inference of bidentate nature of the ligands more deshielding indicates complexation of lanthanum²¹

H NMR spectral data are summarized in (table 11). They are in good agreement with the corresponding alkyl group. They are slight upfield, deshielded due to complexation. Percentage of deshielding decreases with length of carbon chain i.e. α , β , and γ carbons. Signals in nearly same region appeared as multiplet at room temperature. Signals due to pyridyl group appeared also appeared as multiplet although they are having different environment but mixing of peaks result out as multiplet. Integration ratio is in accordance with the attachment of one 1,10-phenanthroline ligand to trithiophosphate complex.

The ¹³C NMR spectral data (table 11) shows characteristic resonance due to the alkoxy and phenoxy group.²² The ¹³C resonance for the carbon atom of [P-O-C] group appears as doublet due to coupling with ³¹P nuclei. ¹³C resonance due to pyridyl carbon are in good agreement with the previous reported data of the pyridyl but they are more deshielded. Molecular weight and elemental analysis (table 12) confirm the monomeric nature of the complexes. Considering all the spectral and elemental analysis data and facts, it is proposed that both the nitrogen donates their lone pair to lanthanum. Chlorine atom is intact with lanthanum. Thus coordination number of lanthanum is increased to five and trigonal bipyramidal or square pyramidal structure tentatively proposed for the complexes.



Aknowledement

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Table 1: Infra red spectral data for chloro lanthanum trithiophosphate

S.No	Compound	$\nu[(P)-O-C]$	$\nu[P-O-(C)]$	$\nu[P=S]$	$\nu[P-S]$	$\nu[La-S]$	$\nu[La-Cl]$
1	$(CH_3O)P(S)(S)_2LaCl$	1021(s)	818(s)	641(s)	427(m)	329(s)	340(m)
2	$(C_2H_5O)P(S)(S)_2LaCl$	1018(s)	817(s)	642(s)	421(m)	334(s)	349(m)
3	${}^n(C_3H_7O)P(S)(S)_2LaCl$	1022(s)	819(s)	639(s)	427(m)	332(s)	342 (m)
4	${}^i(C_3H_7O)P(S)(S)_2LaCl$	1016(s)	813(s)	643(s)	423(m)	333(s)	345(m)
5	${}^n(C_4H_9O)P(S)(S)_2LaCl$	1015(s)	819(s)	645(s)	430(m)	334(s)	349(m)
6	${}^s(C_4H_9O)P(S)(S)_2LaCl$	1013(s)	821(s)	639(s)	426(m)	335(s)	342(m)
7	${}^i(C_4H_9O)P(S)(S)_2LaCl$	1011(s)	817(s)	640(s)	423(m)	339(s)	341(m)
8	${}^i(C_5H_{11}O)P(S)(S)_2LaCl$	1011(s)	811(s)	644(s)	423(m)	335(s)	349(m)
9	$(C_6H_{11}O)P(S)(S)_2LaCl$	1017(s)	815(s)	641(s)	427(m)	332(s)	344(m)
10	$(C_6H_5O)P(S)(S)_2LaCl$	1016(s)	813(s)	643(s)	422(m)	339(s)	345(m)

S=strong,m=medium

Table2: ${}^{31}P$ NMR spectral data for chloro lanthanum trithiophosphate

S.NO	Compound	${}^{31}P$ NMR Data Chemical shift(δ ,ppm)
1.	$(CH_3O)P(S)(S)_2LaCl$	99.90
2.	$(C_2H_5O)P(S)(S)_2 LaCl$	95.29
3.	${}^n(C_3H_7O)P(S)(S)_2LaCl$	96.32
4.	${}^i(C_3H_7O)P(S)(S)_2 LaCl$	99.82
5.	${}^n(C_4H_9O)P(S)(S)_2LaCl$	101.72
6.	${}^s(C_4H_9O)P(S)(S)_2LaCl$	101.21
7.	${}^i(C_4H_9O)P(S)(S)_2 LaCl$	99.92
8.	${}^i(C_5H_{11}O)P(S)(S)_2LaCl$	98.26
9.	$(C_6H_{11}O)P(S)(S)_2LaCl$	99.28

10.	(C ₆ H ₅ O)P(S)(S) ₂ LaCl	99.92
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Table 3: ¹³C and ¹H spectral data for chloro lanthanum trithiophosphate

S.No	Compound	¹³ CNMR Data Chemicalshift(δ,ppm)	¹ H NMR Data Chemical shift(δ,ppm)
1	(CH ₃ O)P(S)(S) ₂ LaCl	57.62,d,c: ² J _{p-c} =19Hz	4.43(s, 3H,-OCH ₃)
2	(C ₂ H ₅ O)P(S)(S) ₂ LaCl	65.14,d,c: ² J _{p-c} =22Hz 22.21, C ²	4.43(q, 2H,-OCH ₂) 2.3(t,3H,-CH ₃)
3	ⁿ (C ₃ H ₇ O)P(S)(S) ₂ LaCl	71.23,d,c: ² J _{p-c} =21Hz 28.67, C ² 14.98, C ³	4.41(t, 2H,-OCH ₂) 2.21(m,2H,-CH ₂) 1.1(t,3H,-CH ₃)
4	ⁱ (C ₃ H ₇ O)P(S)(S) ₂ LaCl	67.82,d,c: ² J _{p-c} =21Hz 27.83, C ²	4.5(m, 1H,-OCH) 3.4(d,6H,-CH ₃) ₂)
5	ⁿ (C ₄ H ₉ O)P(S)(S) ₂ LaCl	70.82,d,c: ² J _{p-c} =18Hz 35.63,C ² 14.18 C ³ 25.26 C ⁴	4.8(t, 2H,-OCH ₂) 2.2(m,2H,2H,-CH ₂ ,-CH ₂) 1.2(t,3H,-CH ₃)
6	^s (C ₄ H ₉ O)P(S)(S) ₂ LaCl	73.28, d,c: ² J _{p-c} =18Hz 43.68 C ³ 24.28 C ⁴ 26.31 C ¹	4.8 (d, 2H,-OCH ₂) 2.1(m, 1H,-CH) 1.61(m,2H,-CH ₂) 1.13(m,6H,-(CH ₃) ₂)
7	ⁱ (C ₄ H ₉ O)P(S)(S) ₂ LaCl	73.16, d,c: ² J _{p-c} =19Hz 32.00 C ² 23.04 C ³	4.87(t, 2H,-OCH ₂) 2.13(q, 2H, -CH ₂) 1.13 (d,6H,-(CH ₃) ₂)
8	ⁱ (C ₅ H ₁₁ O)P(S)(S) ₂ LaCl	64.32,d,c: ² J _{p-c} =29Hz 43.42 C ² 28.73 C ³ 28.62 C ⁴	4.62(t, 2H,-OCH ₂) 2.13(q, 2H, -CH ₂) 1.62(m, 1H,-CH) 1.13(d,6H,-(CH ₃) ₂)
9	(C ₆ H ₁₁ O)P(S)(S) ₂ LaCl	77.68,d,c: ² J _{p-c} =348Hz 39.51 C ^{2,6} 29.93 C ^{3,5} 31.21 C ⁴	4.5(m, 1H,-OCH) 1.68-2.32 (m, 10H,(CH ₂) ₅)
10	(C ₆ H ₅ O)P(S)(S) ₂ LaCl	164.82,d,c: ² J _{p-c} =444Hz 121.40 C ^{2,6} 137.50 C ^{3,5}	10.6-10.3(m,5H,Arom.)

		128.70 C ⁴	
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Table4:Analytical data for chloro lanthanum trithiophosphate

S.No	Compound	Mol.Wt	% La	%S	%Cl	%C	%H
1	(CH ₃ O)P(S)(S) ₂ LaCl	330.51 (332.5687)	40.51 (41.7688)	28.05 (28.9257)	9.54 (10.6603)	2.91 (3.6115)	0.91 (0.9091)
2	(C ₂ H ₅ O)P(S)(S) ₂ LaCl	341.55 (346.5955)	39.07 (40.0784)	26.95 (27.7551)	9.87 (10.2289)	5.82 (6.9304)	1.47 (1.4540)
3	ⁿ (C ₃ H ₇ O)P(S)(S) ₂ LaCl	361.23 (360.6223)	37.15 (38.5195)	25.67 (26.6755)	8.56 (9.8310)	9.75 (9.9888)	1.95 (1.9564)
4	¹ (C ₃ H ₇ O)P(S)(S) ₂ LaCl	360.23 (360.6223)	37.19 (38.5195)	25.75 (26.6755)	9.88 (9.8310)	9.89 (9.9888)	1.94 (1.9564)
5	ⁿ (C ₄ H ₉ O)P(S)(S) ₂ LaCl	370.62 (374.6491)	36.52 (37.0773)	24.52 (25.6768)	9.32 (9.4629)	11.65 (12.8237)	2.22 (2.4212)
6	^s (C ₄ H ₉ O)P(S)(S) ₂ LaCl	370.14 (374.6491)	36.82 (37.0773)	24.75 (25.6768)	9.52 (9.4629)	11.80 (12.8237)	2.31 (2.4212)
7	¹ (C ₄ H ₉ O)P(S)(S) ₂ LaCl	370.19 (374.6491)	36.59 (37.0773)	23.01 (25.6768)	8.49 (9.4629)	11.37 (12.8237)	2.33 (2.4212)
8	¹ (C ₅ H ₁₁ O)P(S)(S) ₂ LaCl	387.59 (388.6759)	34.37 (35.7392)	23.82 (24.7501)	8.14 (9.1214)	14.11 (15.4511)	2.55 (2.8584)
9	(C ₆ H ₁₁ O)P(S)(S) ₂ LaCl	400.12 (400.6869)	34.06 (34.6679)	23.68 (24.0082)	7.52 (8.8480)	16.98 (17.9856)	2.64 (2.7669)
10	(C ₆ H ₅ O)P(S)(S) ₂ LaCl	393.95 (394.6395)	36.01 (35.1992)	23.65 (24.3761)	7.01 (8.9836)	17.12 (18.2612)	1.25 (1.2769)

Observed (calculated)

Table 5 : Infra red spectral data for chloro lanthanum trithiophosphate 2,2' bipyridyl complex

S.No	Compound	$\nu[(P)-O-C]$	$\nu[P-O-(C)]$	$\nu[P=S]$	$\nu[P-S]$	$\nu[La-S]$	$\nu[(C=N)]$	$\nu[La-Cl]$	$\nu[La-N]$
11	$[(CH_3O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1012(s)	819(s)	642(s)	426(m)	330(s)	1572(s)	340(m)	290(s)
12.	$[(C_2H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1023(s)	822(s)	639(s)	429(m)	332(s)	1574(s)	345(m)	291(s)
13.	$[^n(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1010(s)	817(s)	640(s)	430(m)	333(s)	1579(s)	343 (m)	294(s)
14.	$[^i(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1019(s)	811(s)	641(s)	427(m)	335(s)	1577(s)	344(m)	292(s)
15.	$[^n(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1019(s)	815(s)	642(s)	423(m)	340(s)	1584(s)	349(m)	289(s)
16	$[^s(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1017(s)	812(s)	641(s)	422(m)	341(s)	1585(s)	340(m)	296(s)
17.	$[^i(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1015(s)	813(s)	636(s)	430(m)	339(s)	1578(s)	341(m)	295(s)
18.	$[^i(C_5H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1012(s)	819(s)	638(s)	427(m)	337 (s)	1575(s)	348(m)	291(s)
19.	$[(C_6H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1014(s)	810(s)	636(s)	424(m)	338 (s)	1581(s)	344(m)	285(s)
20.	$[(C_6H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1017(s)	813(s)	644(s)	423(m)	334(s)	1583(s)	346(m)	284(s)

S=strong,m=medium

Table6 ^{31}P NMR spectral data for chloro lanthanum trithiophosphate2,2' bipyridyl complex

S.NO	Compound	^{31}P NMR Data Chemicalshift(δ ,ppm)
11	$[(CH_3O)P(S)(S)_2La(C_5H_4N)_2]Cl$	102.98
12.	$[(C_2H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	103.73
13.	$[^n(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	104.13
14.	$[^i(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	98.86
15.	$[^n(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	99.49
16	$[^s(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	96.88
17.	$[^i(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	97.10
18.	$[^i(C_5H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	96.35
19.	$[(C_6H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	103.68
20.	$[(C_6H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	104.21

S.No	Compound	$\nu[(P)-O-C]$	$\nu[P-O-(C)]$	$\nu[P=S]$	$\nu[P-S]$	$\nu[La-S]$	$\nu[(C=N)]$	$\nu[La-Cl]$	$\nu[La-N]$
21.	$[(CH_3O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1012(s)	819(s)	642(s)	426(m)	330(s)	1572(s)	340(m)	290(s)
22.	$[(C_2H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1023(s)	822(s)	639(s)	429(m)	332(s)	1574(s)	345(m)	291(s)
23.	$[^n(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1010(s)	817(s)	640(s)	430(m)	333(s)	1579(s)	343 (m)	294(s)
24.	$[^i(C_3H_7O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1019(s)	811(s)	641(s)	427(m)	335(s)	1577(s)	344(m)	292(s)
25.	$[^n(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1019(s)	815(s)	642(s)	423(m)	340(s)	1584(s)	349(m)	289(s)
26.	$[^s(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1017(s)	812(s)	641(s)	422(m)	341(s)	1585(s)	340(m)	296(s)
27.	$[^i(C_4H_9O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1015(s)	813(s)	636(s)	430(m)	339(s)	1578(s)	341(m)	295(s)
28.	$[^i(C_5H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1012(s)	819(s)	638(s)	427(m)	337 (s)	1575(s)	348(m)	291(s)
29.	$[(C_6H_{11}O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1014(s)	810(s)	636(s)	424(m)	338 (s)	1581(s)	344(m)	285(s)
30.	$[(C_6H_5O)P(S)(S)_2La(C_5H_4N)_2]Cl$	1017(s)	813(s)	644(s)	423(m)	334(s)	1583(s)	346(m)	284(s)

Table 10:³¹P NMR spectral data for chloro lanthanum trithiophosphate 1,10-phenanthroline complex

S.NO	Compound	³¹ P NMR Data Chemicalshift(δ ppm)
21.	$[(CH_3O)P(S)(S)_2La(C_6H_4N)_2]Cl$	103.42
22.	$[(C_2H_5O)P(S)(S)_2La(C_6H_4N)_2]Cl$	102.23
23.	$[^n(C_3H_7O)P(S)(S)_2La(C_6H_4N)_2]Cl$	111.89
24.	$[^i(C_3H_7O)P(S)(S)_2La(C_6H_4N)_2]Cl$	97.63
25.	$[^n(C_4H_9O)P(S)(S)_2La(C_6H_4N)_2]Cl$	98.69

26.	$[\text{}^8(\text{C}_4\text{H}_9\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	94.72
27.	$[\text{}^1(\text{C}_4\text{H}_9\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	99.36
28.	$[\text{}^1(\text{C}_5\text{H}_{11}\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	98.21
29.	$[(\text{C}_6\text{H}_{11}\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	97.72
30.	$[(\text{C}_6\text{H}_5\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	99.63

Table 11 ^{13}C and ^1H spectral data for chloro lanthanum trithiophosphate1,10-phenanthroline complex

S.No	Compound	^{13}C NMR Data	^{13}C NMR Data	^1H NMR Data
		Chemical shift δ ppm TrithiophosphateCarbons	Chemicalshift δ ppm Pyridyl Carbons	Chemicalshift δ ,ppm
21.	$[(\text{CH}_3\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	52.83,d,c: $^2j_{p-c}=28\text{Hz}$.146.40 , C^2 122.42 , C^3 119.88, C^4 136.15, C^5 151.82, C^6	4.74(s, 3H,-OCH ₃) 7.8-8.8 (m,8H,PyridylH)
22.	$[(\text{C}_2\text{H}_5\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	61.38,d,c: $^2j_{p-c}=26\text{Hz}$ 18.45, C^2	146.86 , C^2 122.72 , C^3 120.18, C^4 126.18, C^5 153.20, C^6	4.4(s, 2H,-OCH ₂) 2.6(t,3H,-CH ₃) 7.6-8.7 (m,8H,PyridylH)
23.	$[\text{}^n(\text{C}_3\text{H}_7\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	72.61,d,c: $^2j_{p-c}=32\text{Hz}$ 26.65, C^2 14.85, C^3	147.92 , C^2 123.45 , C^3 120.60, C^4 134.88, C^5 153.18, C^6	5.5(t, 2H,-OCH ₂) 2.6(m,2H,-CH ₂) 1.3(t,3H,-CH ₃) 7.8-8.8 (m,8H,PyridylH)
24.	$[\text{}^1(\text{C}_3\text{H}_7\text{O})\text{P}(\text{S})(\text{S})_2\text{La}(\text{C}_6\text{H}_4\text{N})_2]\text{Cl}$	71.98,d,c: $^2j_{p-c}=32\text{Hz}$	148.24 , C^2	5.9 (m,1H,-OCH)

		25.61, C ²	123.62, C ³ 120.83, C ⁴ 137.26, C ⁵ 153.49, C ⁶	2.8 (d, 6H, -CH ₃) ₂ 7.7-8.6 (m, 8H, PyridylH)
25.	[¹³ C ₄ H ₉ O)P(S)(S) ₂ La(C ₆ H ₄ N) ₂]Cl	73.82, d, c: ² J _{p-c} =30Hz 37.18, C ² 25.18 C ³ 18.68 C ⁴	147.84, C ² 123.71, C ³ 121.62, C ⁴ 137.58, C ⁵ 153.98, C ⁶	5.4(t, 2H, -OCH ₂) 2.9(m, 2H, 2H, -CH ₂ , CH ₂) 1.8(t, 3H, -CH ₃) 7.9-8.8 (m, 8H, PyridylH)
26.	[⁸ C ₄ H ₉ O)P(S)(S) ₂ La(C ₆ H ₄ N) ₂]Cl	75.86, d, c: ² J _{p-c} =22Hz 34.73 C ² 14.18 C ³ 25.31 C ⁴	147.82, C ² 123.26, C ³ 121.39, C ⁴ 137.50, C ⁵ 153.64, C ⁶	5.7 (t, 2H, -OCH ₂) 3.0(m, 1H, -CH ₂) 2.2(m, 2H, -CH ₂) 1.03 (m, 6H, -(CH ₃) ₂) 7.7-9.2 (m, 8H, PyridylH)
27.	[¹ C ₄ H ₉ O)P(S)(S) ₂ La(C ₆ H ₄ N) ₂]Cl	73.83, d, c: ² J _{p-c} =26Hz 32.67 C ² 23.59 C ³	147.73, C ² 123.88, C ³ 120.92, C ⁴ 136.79, C ⁵ 153.62, C ⁶	5.7(t, 2H, -OCH ₂) 2.43(q, 2H, -CH ₂) 1.32 (d, 6H, -(CH ₃) ₂) 7.3-9.2 (m, 8H, PyridylH)
28.	[¹ C ₅ H ₁₁ O)P(S)(S) ₂ La(C ₆ H ₄ N) ₂]Cl	66.43, d, c: ² J _{p-c} =36Hz 44.86 C ² 28.92 C ³ 25.37 C ⁴	148.27, C ² 124.33, C ³ 121.73, C ⁴ 137.39, C ⁵ 153.55, C ⁶	5.4(t, 2H, -OCH ₂) 2.8(q, 2H, -CH ₂) 2.03 (m, 1H, -CH) 1.20(d, 6H, -(CH ₃) ₂) 7.9-9.03(m, 8H, PyridylH)
29.	[(C ₆ H ₁₁ O)P(S)(S) ₂ La(C ₆ H ₄ N) ₂]Cl	76.28, d, c: ² J _{p-c} =342Hz 34.83 C ^{2,6} 28.46 C ^{3,5} 30.57 C ⁴	149.71, C ² 126.29, C ³ 123.31, C ⁴ 138.19, C ⁵ 156.02, C ⁶	6.0(m, 1H, -OCH) 1.2-2.5 (m, 10H, -(CH ₂) ₅) 7.9-9.4 (m, 8H, PyridylH)

30.	$[(C_6H_5O)P(S)(S)_2La(C_6H_4N)_2]Cl$	164.59, d, c: $^2J_{P-C}=437Hz$ 122.4, C ^{2,6} 138.9, C ^{3,5} 126.38, C ⁴	149.94, C ² 124.66, C ³ 121.73, C ⁴ 137.61, C ⁵ 154.57, C ⁶	9.3-13.7 (m, 5H, Arom.) 7.9-9.4 (m, 8H, PyridylH)
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Table12: Analytical data for chloro lanthanum trithiophosphate 1,10-phenanthroline complex

S.NO	COMPOUND	Mol.Wt	%La	%S	%Cl	%H	%C	%N
21.	$[(CH_3O)P(S)(S)_2La(C_6H_4N)_2]Cl$	511.06 (512.7773)	26.11 (27.0897)	17.82 (18.7601)	5.87 (6.9143)	1.45 (2.1621)	29.78 (30.4504)	4.31 (5.4630)
22.	$[(C_2H_5O)P(S)(S)_2La(C_6H_4N)_2]Cl$	525.21 (526.8041)	25.82 (26.3684)	17.11 (18.2606)	5.32 (6.7298)	1.54 (2.4872)	30.89 (31.9196)	4.23 (5.3176)
23.	$[^n(C_3H_7O)P(S)(S)_2La(C_6H_4N)_2]Cl$	539.85 (540.8309)	24.78 (25.6845)	16.38 (17.7870)	5.87 (6.5552)	2.01 (2.7954)	32.01 (33.3126)	4.87 (5.1796)
24.	$[^l(C_3H_7O)P(S)(S)_2La(C_6H_4N)_2]Cl$	539.04 (540.8309)	24.24 (25.6845)	16.13 (17.7870)	5.22 (6.5552)	2.23 (2.7954)	32.65 (33.3126)	3.99 (5.1796)
25.	$[^p(C_4H_9O)P(S)(S)_2La(C_6H_4N)_2]Cl$	553.57 (554.8577)	24.15 (25.0352)	16.79 (17.3374)	5.09 (6.3895)	2.58 (3.0880)	33.54 (34.6351)	4.98 (5.0487)
26.	$[^s(C_4H_9O)P(S)(S)_2La(C_6H_4N)_2]Cl$	553.27 (554.8577)	24.49 (25.0352)	16.34 (17.3374)	5.34 (6.3895)	2.89 (3.0880)	33.45 (34.6351)	4.81 (5.0487)
27.	$[^l(C_4H_9O)P(S)(S)_2La(C_6H_4N)_2]Cl$	553.32 (554.8577)	24.78 (25.0352)	16.42 (17.3374)	5.23 (6.3895)	2.89 (3.0880)	33.22 (34.6351)	4.71 (5.0487)
28.	$[^l(C_5H_{11}O)P(S)(S)_2La(C_6H_4N)_2]Cl$	555.25 (556.8845)	23.42 (24.4179)	15.55 (16.9099)	5.76 (6.2323)	2.98 (3.3662)	34.45 (35.8925)	3.13 (4.9242)
29.	$[(C_6H_{11}O)P(S)(S)_2La(C_6H_4N)_2]Cl$	579.35 (580.8955)	22.92 (23.9130)	15.27 (16.5602)	4.45 (6.1031)	2.45 (3.2966)	36.76 (37.2180)	3.04 (4.8224)
30.	$[(C_6H_5O)P(S)(S)_2La(C_6H_4N)_2]Cl$	573.61	23.18	15.64	4.99	2.44	36.78	3.92

		(574.8481)	(24.1646)	(16.7345)	(6.1677)	(2.2793)	(37.6095)	(4.8731)
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Observed (calculated)

References-

1. R.Verma, V.D.Gupta and R.C.Mehrotra. *Nat . Acad Sci .Lett.*, 2,130 (1979)
2. S.K.Saini V.D.Gupta and R.C.Mehrotra, *Inorg.Nucl.Chem.Lett*, 1 4.109(1978)
3. S.K.Pandey,G..Srivastav and R.C.Mehrotra *Ind, J.Chem.,29A*, 339 (1990)
4. R.Ratnani G..Srivastav and R.C.Mehrotra *Inorg. Chem.Acta* 161. 253(1989)
5. G..Srivastav R.C.Mehrotra and H.P.S.Chauhan.*Coordination.Chem.Rev.*,55,207 (1984)
6. A.A.Pinkaeton and D.Schwarzenbach (1979)*J.Chem.Soc.Dalton Trans.*,1300
7. P.N.M.Das,W.Kuchen,H.Keck andG.Hagele (1977). *Jinorg.Nucl.Chem.*39.833
8. TripathiU.N,Bipin P.P.,Mirza R and Shukla *J.Coord Chem*,55(10) (2002) 1111-1118
9. [Volume Anita Rai Soumitra K. Sengupta and Om P. Pandey Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 64, Issue 3, June \(2006\), Pages 789-794](#)
10. Ritu singh,S.P.Mittal et al *Indian Journal of Chwmistry Vol 46 –A sept (2007) pages 1406-1413.*
11. V.I.Derybin, *Tr.Vses. Nauch Iss. Inst. Khlo.*, 28, 86 (1974)
12. S.Kishino, A.Shitamatsu and K.Shiokawa, *Japan* 7600, 179 (CL.A01N:COF) (1976)
13. N.M.Kozhevnikova and V.S.Mikhailov,*Khim, Serd. Zashch. Rast.*,5, 43 (1975)
14. F.Goto and N.Koichi, *Mokuzai Kenkyu*, 32, 15 (1964); *Chem. Abstr.*, 65,6221h(1966)
15. K.Kirschbaum ,U.Boenninghausem, E.Gesing, B.Krebs and G.Henkil, *Z.Naturforsch. B.Chem. Sci.*, 45, 245 (1990)
16. Vogel,A,I.,*Test book of quantitative inorganic analysis.Else and Longman. London (1985)*
17. Kotovich,B,P,Zemlyanskii,N.I,Maravev,I.V,Voloshin,M,P,*Zh.ObshchKhim*, 38(6),(1968)1282-6,Gupalo,A.P,Zemlyanskii,Maravev,I.V,USSR,165,457 (Cl.CO7c) ,*Appl.*(1964) 1964
18. Gupalo,A.P,Zemlyanskii,N.I(USSR).*Vlsn.Lviv,Derzh.Univ.Ser.Khim.*11(1969)55-60.
19. Nakamoto,K.,*Infra red and Raman Spectra of Inorganic and Coordination compound 5th Edition, John Willey & Sons New York (1997).*
20. Russel S. Prago, *Physical method in Inorganic chemistry, Chapman and Hall Ltd London (1995).*
21. Alan K. Bridson,*Inorganic spectroscopic methods, Oxford Science (1995).*
22. Silverstein, R.M., Bassler, C.C., Morill, T.C. *Spectroscopic Identification Organic Compounds, 4th Edition, John Willey & Sons (1981).*