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O-Alkyl(Aryl) Trithiophosphato Derivatives Of Alkaline Earth Metals: Mg,Ca,Sr and Ba

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Abstract: Complexes of the general formula $M[S_3P(OR)]$;Where M= Mg,Ca,Sr and Ba And R= Me, Et, Pr^i, Bu^n and Ph have been synthesized conveniently by the reaction of anhy.MCL_2 and dipotassium salts of trithiophosphoric acids in aqueous medium in 1:1 molar ratio.
The derivatives have been isolated by filtering the reaction mixture. These complexes have been characterised by elemental analysis, electronic transition studies and IR studies.

Introduction

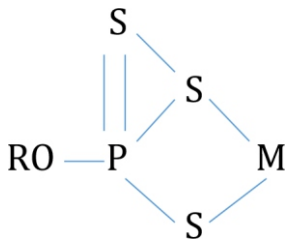
The information about the derivatives of O-alkyl (aryl) trithiophosphates is quite spare. The brief historical survey presented clearly indicates that out of all main group elements no work appear to be carried out on the chemistry of O-alkyl(aryl)trithiophosphates of Mg, Ca, Sr, Ba as yet.
so it was considered of interest to synthesied the derivatives of Mg, Ca, Sr and Ba with O-alkyl(aryl)trithiophosphates ligand and get a comperative view of these with the coresponding open chain alkyl (aryl) trithiophosphates derivatives. The continuing interest in this area is mainly due to the industrial utility of the compounds as well as their noval structural features.

Result and Discussion

O-Alkyl(aryl)trithiophosphato derivatives of the alkaline earth metals have been synthesized by reaction of metal chlorides(anhy.) with the corresponding dipotassium slats of trithiophosphoric acids in 1:1 molar ratio in aqueos medium. The product were extracted using filter.

$$MCl_2 + K_2[S_3P(OR)] \xrightarrow{\text{Water}} M[S_3P(OR)] + 2KCl$$

where (M= Mg, Ca, Sr and Ba ; R= Me, Et, Pr^i, Bu^n and Ph)
These reactions are quite facile but to ensure completion of the reaction, mixture has been refluxed for about 6-8 hours.
These complexes were found to be white solids which are sparingly soluble in DMSO and insoluble in most of the organic solvents as well as in aqueous medium. There is no effect of heating on these complexes up to 320-340^C indicating that these thermally quite stable in nature.
On the basis of IR UV spectral data a tentative geometry for the M (II) O-alkyl(aryl) trithiophosphates have been proposed.



IR Spectral Studies

IR spectra of O-alkyl(aryl)trithiophosphates derivatives of alkaline earth elements have been recorded in the region 4000-200 cm^{-1}.
The important characteristics IR absorption bands of these complexes are as follow :

(i) The absorption bands in the region 4000-200 cm^{-1} exhibites the characteristic C-H stretching vibrations associated with the methyl ,methylene and methyne moiety.
(ii) The appearance of storng absorption band at 700-640 cm^{-1} have been attributed to the v[P=S] stretching vibretions.
A band of medium intensity at 545-525 cm^{-1} is assigned to v[P=S] stretching vibrations.
(iii) A new medium intensity absorption band appeared at 420-390 cm^{-1} assigned to v[M-S] stretching vibrations indicating the formation pf metal sulfur bond.
(iv) The appearance of two characteristic strong absorption bands at 1090-980 cm^{-1} and 900-840 cm^{-1} are assigned to v[(P)-O-C] and v[P-O-(C)] stretching vibrations, respectively.
(v) [(P)-O-C] stretching modes are probably coupled with the vibrations of atoms in their vicinity.

Electronic Spectral Studies

The electronic spectra of O-alkyl (aryl) trithiophosphates derivatives of alkaline earth elements in DMSO show a broad electronic transition band in the range

225.0-193.5 nm which may due to charge transfer transition.

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Table 1- RELEVANT SYNTHETIC AND ANALYTICAL DATA FOR $Mg[S_3P(OR)]$

S.No.	Reactants, g (mmole)		Molar Ratio	Product		Analysis, % Yield	
	$MgCl_2$	$K_2[S_3P(OR)]$		g	%Yield	Mg, Found (Calcd.)	S, Found Calcd.)
1	0.4552(4.77)	$K_2[S_3P(OMe)]$	1:1	$Mg[S_3P(OMe)]$		13.27	51.28
		1.0194 (4.71)		0.5495	63.11	(13.32)	(52.66)
2	0.3422(3.59)	$K_2[S_3P(OEt)]$	1:1	$Mg[S_3P(OEt)]$		12.28	47.29
		0.8256 (3.56)		0.4966	70.00	(12.37)	(48.90)
3	0.4118(4.32)	$K_2[S_3P(OPr^i)]$	1:1	$Mg[S_3P(OPr^i)]$		11.47	45.23
		1.1206 (4.30)		0.5493	60.53	(11.57)	(45.71)
4	0.3403(3.57)	$K_2[S_3P(OBu^n)]$	1:1	$Mg[S_3P(OBu^n)]$		10.78	42.38
		0.9878 (3.55)		0.6478	80.88	(10.83)	(42.79)
5	0.4006(4.20)	$K_2[S_3P(OPh)]$	1:1	$Mg[S_3P(OPh)]$		9.88	38.93
		1.2374 (4.18)		0.8220	80.04	(9.94)	(39.29)

Table 2 - SOME PHYSICAL PROPERTIES OF THE COMPLEXES OF THE TYPE $Mg[S_3P(OR)]$

S.No.	Compound	Physical State	Melting Point (^{0}C)	
1	$Mg[S_3P(OMe)]$	White solid (powder)	No change upto 320	179.21
2	$Mg[S_3P(OEt)]$	White solid (powder)	No change upto 320	192.40
3	$Mg[S_3P(OPr^i)]$	White solid (powder)	No change upto 320	208.92
4	$Mg[S_3P(OBu^n)]$	White solid (powder)	No change upto 320	222.46
5	$Mg[S_3P(OPh)]$	White solid (powder)	No change upto 320	243.02

Table 3- SOME RELEVANT IR SPECTRAL DATA (CM^{-1}) OF THE COMPLEXES OF THE TYPE $Mg[S_3P(OR)]$

S.No.	Compound	[(P)-0-C]	[P-0-(C)]	[P=S]	[P-S]	[Mg-S]
1	$Mg[S_3P(OMe)]$	1015 s	870 s	705 s	550 s	510 m
2	$Mg[S_3P(OEt)]$	1010 s	870 s	670 s	545 m	395 m
3	$Mg[S_3P(OPr^i)]$	990 s	840 s	680 s	535 b	365 w
4	$Mg[S_3P(OBu^n)]$	1005 s	825 s	650 s	530 b	380 m
5	$Mg[S_3P(OPh)]$	1080 s	1080 s	690 s	545 m	400 w

s= sharp m= medium b= broad w= week

Table 4 - DATA FOR ELECTREONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE $Mg[S_3P(OR)]$

S.No.	Compound	Wave Length (in nm)
1	$Mg[S_3P(OMe)]$	223.5
2	$Mg[S_3P(OEt)]$	225.0
3	$Mg[S_3P(OPr^i)]$	219.5
4	$Mg[S_3P(OBu^n)]$	221.0
5	$Mg[S_3P(OPh)]$	225.0

Table 5- RELEVANT SYNTHETIC AND ANALYTICAL DATA FOR $Ca[S_3P(OR)]$

S.No.	Reactants, g (mmole)		Molar Ratio	Product		Analysis, % Yield	
	$CaCl_2$	$K_2[S_3P(OR)]$		g	%Yield	Mg, Found (Calcd.)	S, Found Calcd.)
1	0.4208(3.79)	$K_2[S_3P(OMe)]$	1:1	$Ca[S_3P(OMe)]$		20.16	48.28
		0.8153 (3.45)		0.5099	68.23	(20.19)	(48.48)
2	0.4663(4.20)	$K_2[S_3P(OEt)]$	1:1	$Ca[S_3P(OEt)]$		18.74	44.86
		0.9660 (3.86)		0.6309	70.86	(18.86)	(45.28)
3	0.3512(3.16)	$K_2[S_3P(OPr^i)]$	1:1	$Ca[S_3P(OPr^i)]$		17.52	41.59
		0.8236 (3.11)		0.5890	82.37	(17.69)	(42.47)
4	0.4066(3.66)	$K_2[S_3P(OBu^n)]$	1:1	$Ca[S_3P(OBu^n)]$		16.58	39.27
		0.9905 (3.56)		0.6908	78.58	(16.66)	(40.00)
5	0.3828(3.44)	$K_2[S_3P(OPh)]$	1:1	$Ca[S_3P(OPh)]$		15.31	35.88
		1.0232 (3.43)		0.6837	76.25	(15.38)	(36.92)

Table 6 - SOME PHYSICAL PROPERTIES OF THE COMPLEXES OF THE TYPE $Ca[S_3P(OR)]$

S.No.	Compound	Physical State	Melting Point (^{0}C)	
1	Ca [$S_3P(OMe)$]	White solid (powder)	No change upto 320-340	195.96
2	Ca [$S_3P(OEt)$]	White solid (powder)	No change upto 320-340	
3	Ca [$S_3P(OPr^i)$]	White solid (powder)	No change upto 320-340	224.06
4	Ca [$S_3P(OBu^n)$]	White solid (powder)	No change upto 320-340	239.54
5	Ca [$S_3P(OPh)$]	White solid (powder)	No change upto 320-340	258.22

Table 7- SOME RELEVANT IR SPECTRAL DATA (CM^{-1}) OF THE COMPLEXES OF THE TYPE $Ca[S_3P(OR)]$

S.No.	Compound	[(P)-0-C]	[P-0-(C)]	[P=S]	[P-S]	[Mg-S]
1	$Ca[S_3P(OMe)]$	1010 s	880 s	700 s	545 s	420 w
2	$Ca[S_3P(OEt)]$	1020 s	870 s	660 s	530 b	405 m
3	$Ca[S_3P(OPr^i)]$	980 s	850 m	685 s	545 s	390 m
4	$Ca[S_3P(OBu^n)]$	1000 s	840 m	640 s	525 m	390 m
5	$Ca[S_3P(OPh)]$	1090 s	900 s	680 s	530 b	415 w

s= sharp m= medium b= broad w= week

Table 8 - DATA FOR ELECTREONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE $Ca[S_3P(OR)]$

S.No.	Compound	Wave Length (in nm)
1	$Ca[S_3P(OMe)]$	223.5
2	$Ca[S_3P(OEt)]$	201.0
3	$Ca[S_3P(OPr^i)]$	211.0
4	$Ca[S_3P(OBu^n)]$	205.0
5	$Ca[S_3P(OPh)]$	210.0

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

S.No.	Reactants, g (mmole)		Molar Ratio	Product		Analysis, % Yield	
	$SrCl_2$	$K_2[S_3P(OR)]$		g	%Yield	Mg, Found (Calcd.)	S, Found Calcd.)
1	0.4754(2.99)	$K_2[S_3P(OMe)]$	1:1	$Sr[S_3P(OMe)]$		35.61	38.57
		0.6477 (2.74)		0.4918	66.77	(35.67)	(39.08)
2	0.5348(3.37)	$K_2[S_3P(OEt)]$	1:1	$Sr[S_3P(OEt)]$		33.68	35.82
		0.7754 (3.20)		0.6286	71.79	(33.74)	(36.97)
3	0.4738(2.98)	$K_2[S_3P(OPr^i)]$	1:1	$Sr[S_3P(OPr^i)]$		31.96	34.14
		0.7873 (2.98)		0.6632	81.14	(32.02)	(35.08)
4	0.3852(2.42)	$K_2[S_3P(OBu^n)]$	1:1	$Sr[S_3P(OBu^n)]$		30.42	32.17
		0.6746 (2.42)		0.5258	75.28	(30.46)	(33.37)
5	0.3882(2.44)	$K_2[S_3P(OPh)]$	1:1	$Sr[S_3P(OPh)]$		28.41	30.58
		0.7286 (2.44)		0.6242	82.91	(31.20)	(31.20)

Table 10- SOME PHYSICAL PROPERTIES OF THE COMPLEXES OF THE TYPE $Sr[S_3P(OR)]$

S.No.	Compound	Physical State	Melting Point (^{0}C)	
1	Sr [$S_3P(OMe)$]	White solid (powder)	No change upto 320	
2	Sr [$S_3P(OEt)$]	White solid (powder)	No change upto 320	256.98
3	Sr [$S_3P(OPr^i)$]	White solid (powder)	No change upto 320	
4	Sr [$S_3P(OBu^n)$]	White solid (powder)	No change upto 320	286.14
5	Sr [$S_3P(OPh)$]	White solid (powder)	No change upto 320	356.80

Table 11- SOME RELEVANT IR SPECTRAL DATA (CM^{-1}) OF THE COMPLEXES OF THE TYPE $Sr[S_3P(OR)]$

S.No.	Compound	[(P)-0-C]	[P-0-(C)]	[P=S]	[P-S]	[Mg-S]
1	Sr [$S_3P(OMe)$]	1020 s	890 s	685 s	530 s	400 w
2	Sr [$S_3P(OEt)$]	1030 s	870 s	650 s	540 m	380 m
3	Sr [$S_3P(OPr^i)$]	1005 m	870 s	670 s	525 w	385 m
4	Sr [$S_3P(OBu^n)$]	990 m	860 m	640 s	535 m	390 m
5	Sr [$S_3P(OPh)$]	1110 s	910 s	690 s	540 s	405 w

s= sharp m= medium b= broad w= week

Table 12 - DATA FOR ELECTREONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE $Sr[S_3P(OR)]$

S.No.	Compound	Wave Length (in nm)
1	Sr [$S_3P(OMe)$]	220.0
2	Sr [$S_3P(OEt)$]	193.5
3	Sr [$S_3P(OPr^i)$]	201.0
4	Sr [$S_3P(OBu^n)$]	197.0
5	Sr [$S_3P(OPh)$]	209.0

Table 13- RELEVANT SYNTHETIC AND ANALYTICAL DATA FOR $Ba[S_3P(OR)]$

S.No.	Reactants, g (mmole)		Molar Ratio	Product		Analysis, % Yield	
	$SrCl_2$	$K_2[S_3P(OR)]$		g	%Yield	Mg, Found (Calcd.)	S, Found Calcd.)
1	0.8292(3.98)	$K_2[S_3P(OMe)]$	1:1	$Ba[S_3P(OMe)]$		46.46	31.64
		0.6477 (2.74)		0.8910	75.80	(46.50)	(32.50)
2	0.6658(3.20)	$K_2[S_3P(OEt)]$	1:1	$Ba[S_3P(OEt)]$		44.37	30.30
		0.7754 (3.20)		0.6420	65.00	(44.39)	(31.03)
3	0.7792(3.74)	$K_2[S_3P(OPr^i)]$	1:1	$Ba[S_3P(OPr^i)]$		42.49	29.96
		0.7873 (2.98)		0.9801	81.04	(42.47)	(29.69)
4	0.6712(3.21)	$K_2[S_3P(OBu^n)]$	1:1	$Ba[S_3P(OBu^n)]$		40.64	27.82
		0.6746 (2.42)		0.8624	79.35	(40.71)	(28.45)
5	0.8664(4.15)	$K_2[S_3P(OPh)]$	1:1	$Ba[S_3P(OPh)]$		38.38	26.12
		0.7286 (2.44)		1.1008	74.13	(38.43)	(26.86)

Table 14- SOME PHYSICAL PROPERTIES OF THE COMPLEXES OF THE TYPE Ba[$S_3P(OR)$]

S.No.	Compound	Physical State	Melting Point (^0C)	
1	Ba[$S_3P(OMe)$]	White solid (powder)	No change upto 330	292.14
2	Ba[$S_3P(OEt)$]	White solid (powder)	No change upto 330	-
3	Ba[$S_3P(OPr^i)$]	White solid (powder)	No change upto 330	321.98
4	Ba[$S_3P(OBu^n)$]	White solid (powder)	No change upto 330	-
5	Ba[$S_3P(OPh)$]	White solid (powder)	No change upto 330	355.96

Table 15- SOME RELEVANT IR SPECTRAL DATA (CM^{-1}) OF THE COMPLEXES OF THE TYPE Ba[$S_3P(OR)$]

S.No.	Compound	[(P)-0-C]	[P-0-(C)]	[P=S]	[P-S]	[Mg-S]
1	Ba[$S_3P(OMe)$]	1010 s	880 s	700 s	545 m	395 m
2	Ba[$S_3P(OEt)$]	1010 s	880 s	705 s	530 b	380 b
3	Ba[$S_3P(OPr^i)$]	980 m	890 s	680 s	545 w	390 m
4	Ba[$S_3P(OBu^n)$]	1000 m	860 m	670 s	520 w	370 b
5	Ba[$S_3P(OPh)$]	1120 s	920 m	695 s	530 b	400 m

s= sharp m= medium b= broad w= week

Table 16 - DATA FOR ELECTREONIC SPECTRAL STUDIES OF THE COMPLEXES OF THE TYPE Ba[$S_3P(OR)$]

S.No.	Compound	Wave Length (in nm)
1	Ba[$S_3P(OMe)$]	205.0
2	Ba[$S_3P(OEt)$]	201.0
3	Ba[$S_3P(OPr^i)$]	195.0
4	Ba[$S_3P(OBu^n)$]	203.0
5	Ba[$S_3P(OPh)$]	201.0