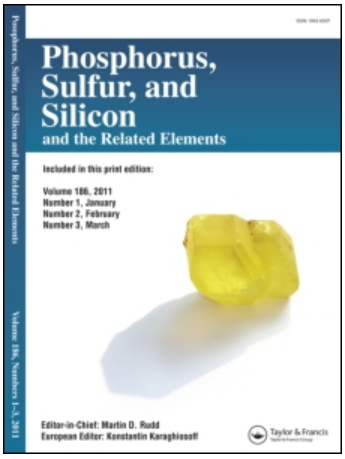

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O,O′-ALKYLENE DITHIOPHOSPHATO DERIVATIVES OF ALKALINE EARTH METALS Mg, Ca, Sr and Ba†

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Complexes of the type $M[S_2\overbrace{POGO}]_2$ (where M = Mg, Ca, Sr and Ba; G = —CMe_2CMe_2—, CMe_2CH_2CHMe—, —$CH_2CMe_2CH_2$—, CH_2CH_2CHMe—) have been synthesized by reacting MCl_2 (anhy.) with ammonium salts of alkylene dithiophosphoric acids in 1:2 molar ratio in aqueous medium and then extracted using THF. These complexes have been characterized by elemental analysis, molecular weight measurements, IR and multinuclear NMR (^1H and ^{31}P) studies. A downfield shift in ^{31}P nmr (δ = ~20 ppm) have been observed in these complexes. On the basis of these studies a four coordinated nature of the metal atom has been suggested.

Key words: Alkylene dithiophosphate; magnesium chloride; calcium chloride; strontium chloride; barium chloride.

INTRODUCTION

Work on the metal and organometal derivatives of transition[1–3] and non-transition[4–6] elements with alkylene dithiophosphate ligands has been previously reported. Several of these derivatives are mixed ligand[7–9] complexes (open chain and cyclic).

A survey of the literature reveals only a few references[10–14] to patents on the derivatives of dithiophosphoric acid with magnesium, calcium and barium. The scarcity of work on the derivatives of dithiophosphoric acids led us to investigate the synthesis of derivatives of these ligands with some alkaline earth metals viz; Mg, Ca, Sr and Ba.

RESULTS AND DISCUSSION

O,O′-Alkylene dithiophosphato derivatives of the alkaline earth metals have been synthesized by reaction of metal chlorides (anhy.) with the corresponding ammonium salts of alkylene dithiophosphoric acids in 1:2 molar ratio, in aqueous medium. The products were extracted using THF.

$$MCl_2 + 2\,NH_4[S_2\overbrace{POGO}] \xrightarrow[\Delta,10\ hrs.]{water} M[S_2\overbrace{POGO}]_2 + 2\,NH_4Cl\downarrow$$

where (M = Mg, Ca, Sr and Ba; G = —CMe_2CMe_2—, —$CH_2CMe_2CH_2$—, —CMe_2CH_2CHMe—, —CH_2CH_2CHMe—).

†This article is dedicated to the late Dr. G. Srivastava on the second anniversary of his death.
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These complexes were found to be sticky solids and/or viscous liquids, which are soluble in THF, benzene and water. Molecular weight measurements show these complexes to be monomeric in nature.

IR SPECTRA

The IR spectra show the following characteristic absorption bands:

(i) The appearance of sharp absorption bands at 670–640 cm^{-1} and 590–500 cm^{-1} is assigned to the $\nu P{=}S$[15] and $\nu P{-}S$ groups.

(ii) The appearance of a new medium intensity absorption band at 430 cm^{-1} indicates the formation of a metal-sulfur bond. The appearance of broad absorption

TABLE I

Syntheses and characterization of alkylene dithiophosphates of alkaline earth metals, $M[S_2\overbrace{POGO}]_2$

S.N.	Reactants, g (mmole)		Molar Ratio	Product g	Product %Yield	Colour	Analyses % Yield M found (calcd)	Analyses % Yield S found (calcd)
1.	$MgCl_2$	$NH_4[S_2\overbrace{POCMe_2CMe_2O}]$	1:2	$Mg[S_2\overbrace{POCMe_2CMe_2O}]_2$		White	5.41	28.51
	0.4090 (4.29)	1.9610 (8.55)		1.1672	61.00		(5.43)	(28.64)
2.	$CaCl_2$	$NH_4[S_2\overbrace{POCMe_2CMe_2O}]$	1:2	$Ca[S_2\overbrace{POCMe_2CMe_2O}]_2$		Light green	8.62	26.56
	0.5140 (4.63)	2.0976 (9.14)		1.5152	70.80		(8.65)	(27.70)
3.	$SrCl_2$	$NH_4[S_2\overbrace{POCMe_2CMe_2O}]$	1:2	$Sr[S_2\overbrace{POCMe_2CMe_2O}]_2$		Gray	17.20	25.04
	0.8854 (5.58)	2.8432 (12.39)		1.5244	53.52		(17.18)	(25.08)
4.	$BaCl_2$	$NH_4[S_2\overbrace{POCMe_2CMe_2O}]$	1:2	$Ba[S_2\overbrace{POCMe_2CMe_2O}]_2$		Green	24.48	22.68
	0.6166 (2.95)	1.3574 (5.91)		0.8940	63.45		(24.53)	(22.86)
5.	$MgCl_2$	$NH_4[S_2\overbrace{POCH_2CH_2CHMeO}]$	1:2	$Mg[S_2\overbrace{POCH_2CH_2CHMeO}]_2$		Yellow	6.20	32.75
	0.4474 (4.69)	1.9190 (9.54)		1.0546	57.75		(6.22)	(32.79)
6.	$CaCl_2$	$NH_4[S_2\overbrace{POCH_2CH_2CHMeO}]$	1:2	$Ca[S_2\overbrace{POCH_2CH_2CHMeO}]_2$		Yellow	9.80	31.42
	0.5418 (4.88)	2.0082 (9.99)		1.1908	60.08		(9.84)	(31.52)
7.	$SrCl_2$	$NH_4[S_2\overbrace{POCH_2CH_2CHMeO}]$	1:2	$Sr[S_2\overbrace{POCH_2CH_2CHMeO}]_2$		Yellow	19.23	28.18
	0.7500 (4.72)	1.9320 (9.61)		1.4760	68.81		(19.30)	(28.20)
8.	$BaCl_2$	$NH_4[S_2\overbrace{POCH_2CH_2CHMeO}]$	1:2	$Ba[S_2\overbrace{POCH_2CH_2CHMeO}]_2$		Yellow	27.19	25.38
	1.1396 (5.47)	2.3064 (11.47)		1.7254	62.66		(27.26)	(25.43)
9.	$MgCl_2$	$NH_4[S_2\overbrace{POCH_2HMe_2CH_2O}]$	1:2	$Mg[S_2\overbrace{POCH_2CMe_2CH_2O}]_2$		White	5.84	30.44
	0.4696 (4.92)	2.0800 (9.67)		2.0660	89.48		(5.80)	(30.57)
10.	$CaCl_2$	$NH_4[S_2\overbrace{POCH_2CMe_2CH_2O}]$	1:2	$Ca[S_2\overbrace{POCH_2CMe_2CH_2O}]_2$		White	9.23	29.24
	0.5116 (4.60)	1.9800 (9.20)		1.7230	86.09		(9.20)	(29.48)
11.	$SrCl_2$	$NH_4[S_2\overbrace{POCH_2CMe_2CH_2O}]$	1:2	$Sr[S_2\overbrace{POCH_2CMe_2CH_2O}]_2$		Yellow	18.09	26.40
	0.7612 (4.80)	2.0484 (9.52)		1.6378	70.00		(18.17)	(26.55)
12.	$BaCl_2$	$NH_2[S_2\overbrace{POCH_2CMe_2CH_2O}]$	1:2	$Ba[S_2\overbrace{POCH_2CMe_2CH_2O}]_2$		White	25.77	24.04
	0.9536 (4.58)	1.9800 (9.20)		1.6076	66.08		(25.82)	(24.08)
13.	$MgCl_2$	$NH_4[S_2\overbrace{POCMe_2CH_2CHMeO}]$	1:2	$Mg[S_2\overbrace{POCMe_2CH_2CHMeO}]_2$		Light brown	5.39	28.50
	0.6528 (8.84)	3.0358 (13.24)		1.9116	62.44		(5.43)	(28.64)
14.	$CaCl_2$	$NH_4[S_2\overbrace{POCMe_2CH_2CHMeO}]$	1:2	$Ca[S_2\overbrace{POCMe_2CH_2CHMeO}]_2$		Yellow	8.67	26.66
	0.6842 (6.16)	2.8228 (12.31)		2.2660	79.48		(8.65)	(27.70)
15.	$SrCl_2$	$NH_4[S_2\overbrace{POCMe_2CH_2CHMeO}]$	1:2	$Sr[S_2\overbrace{POCMe_2CH_2CHMeO}]_2$		Light brown	17.09	24.95
	1.0150 (6.40)	2.9224 (12.74)		2.3966	73.42		(17.18)	(25.08)
16.	$BaCl_2$	$NH_4[S_2\overbrace{POCMe_2CH_2CHMeO}]$	1:2	$Ba[S_2\overbrace{POCMe_2CH_2CHMeO}]_2$		Light brown	24.44	22.43
	0.8484 (4.07)	1.8628 (8.12)		1.7780	77.99		(24.53)	(22.86)

TABLE II

Infrared spectral data for alkylene dithiophosphates of alkaline earth metals, $M[S_2\overset{\cdot}{P}OG\overset{\cdot}{O}]_2$ (in cm^{-1})

S.N.	Compounds	ν(P)—O—C	νP—O—(C)	Ring vibration	ν(P=S)	ν(P—S)	ν(M—S)
1.	$Mg[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1120 m	880 b	940 m	650 s	530 m	430 m
2.	$Ca[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1120 m	910 m	945 m	660 s	540 b	430 m
3.	$Sr[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1120 m	890 b	945 m	660 s	520 b	430 m
4.	$Ba[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1120 m	890 m	945 m	660 s	520 b	430 m
5.	$Mg[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1040 b	845 m	940 m	660 s	590 m	430 m
6.	$Ca[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1040 b	870 m	950 b	660 s	590 m	430 m
7.	$Sr[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1050 b	850 m	940 m	650 s	590 m	430 m
8.	$Ba[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1050 m	855 m	935 m	670 s	590 m	430 m
9.	$Mg[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	1030 b	890 m	970 m	650 s	560 b	420 m
10.	$Ca[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	1020 b	885 m	970 b	650 s	545 b	430 m
11.	$Sr[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	1020 b	840 m	970 b	650 s	590 m	430 m
12.	$Ba[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	1020 b	890 m	970 b	660 s	590 b	430 m
13.	$Mg[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1030 b	865 m	920 b	640 s	500 b	430 m
14.	$Ca[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1030 b	870 m	940 b	650 s	510 b	430 m
15.	$Sr[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1020 b	860 m	935 b	640 s	510 b	430 b
16.	$Ba[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1040 b	860 m	940 b	640 s	515 b	430 b

s = sharp, m = medium and b = broad.

TABLE III

^1H and ^{31}P NMR spectral data (in δ ppm) of $M[S_2\overset{\cdot}{P}OG\overset{\cdot}{O}]_2$

S.N.	Compounds	^1H chemical shift (δ ppm)	^{31}P chemical shift (δ ppm)
1.	$Mg[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1.39, s (24H)—CH_3	113.00
2.	$Ca[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1.46, s, (24H)—CH_3	114.60
3.	$Sr[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1.47, s, (24H)—CH_3	113.20
4.	$Ba[S_2\overset{\cdot}{P}OCMe_2CMe_2\overset{\cdot}{O}]_2$	1.49, s, (24H)—CH_3	114.60
5.	$Mg[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1.17–2.22, m, (6H)—CH_3, —CH_2 4.45–4.53, m, (—OCH_2, —OCH)	90.30
6.	$Ca[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1.27–2.19, m, (6H)—CH_3, —CH_2 4.39–4.61, m, —OCH_2, —OCH	101.00
7.	$Sr[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1.14–2.19, m, (6H), —CH_3, —CH_2 4.37–4.60, m, —OCH_2, —OCH	97.20
8.	$Ba[S_2\overset{\cdot}{P}OCH_2CH_2CHMe\overset{\cdot}{O}]_2$	1.24–2.2, m, (6H) —CH_3, —CH_2 4.29–4.61, m, —OCH_2, —OCH	99.60
9.	$Mg[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	0.89, s (12H)—CH_3; 4.33, d, 3J = 17 Hz, (8H)—OCH_2	112.00
10.	$Ca[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	0.94, s (12H)—CH_3; 3.93 (8H), —OCH_2	111.50
11.	$Sr[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	0.98, s (12H)—CH_3; 4.06, 3J = 16 Hz, (8H)—OCH_2	112.00
12.	$Ba[S_2\overset{\cdot}{P}OCH_2CMe_2CH_2\overset{\cdot}{O}]_2$	0.93, s (12H)—CH_3; 3.97 (8H)—OCH_2	115.70
13.	$Mg[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1.20–2.23, m (22H)—CH_3, CH_2 3.04, m, —OCH	95.40
14.	$Ca[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1.23–2.22, m, (22H), —CH_3—CH_2 3.09, m, —OCH	91.40
15.	$Sr[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1.27–2.19, m, (22H), —CH_3—CH_2 3.07, m, —OCH	93.30
16.	$Ba[S_2\overset{\cdot}{P}OCMe_2CH_2CHMe\overset{\cdot}{O}]_2$	1.22–2.24, m, (22H), —CH_3—CH_2 3.02, m, —OCH	93.30

bands in the region 1120–1020 cm^{-1} and 910–845 cm^{-1} is assigned to ν(P)—O—C and νP—O—(C) stretching vibrations, respectively.

The absorption band in the region 970–920 cm^{-1} has been assigned to ring vibrations.

NMR SPECTRA [^1H and ^{31}P]

The ^1H NMR spectra of these derivatives (Table III) shows a minor upfield shift for all characteristic resonance signals compared to the free alkylene dithiophosphates.

^{31}P NMR spectra exhibit a characteristic downfield shift of ~15–20 ppm, showing the bidentate nature of the dithiophosphato moieties.[16] On storing, these compunds tend to decompose slowly as indicated by more than one resonance signal in the ^{31}P NMR spectra.

On the basis of the molecular weight measurements and IR, ^1H and ^{31}P NMR spectra of these complexes, the existence of a tetra-coordinated environment around the metal atom is suggested.

EXPERIMENTAL

Dry HCl gas was passed through solid (powder) metal chlorides ($MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$ and $BaCl_2 \cdot 2H_2O$) placed in a sublimation tube at high temperature. Water vapor was removed with the help of a flame. The process was repeated 4 to 5 times to obtain anhydrous and pure starting materials. Yields of the anhydrous metal chlorides as white solid powders were *ca.* 90%.

Ammonium salts of O,O'-alkylene dithiophosphoric acids were prepared as previously reported.[17]

Elemental analyses were carried out by standard procedures.[18] Molecular weights were measured on a Knauer-Vapour pressure osmometer in benzene solution. IR spectra were recorded as KBr pellets or Nujol mulls on a Perkin-Elmer spectrophotometer model 577 in the range 4000–200 cm^{-1}. ^1H NMR in $CDCl_3$ and DMSO-d_6, and ^{31}P NMR in THF were recorded on a JEOL FX90A spectrometer using TMS (for ^1H) and H_3PO_4 (for ^{31}P) as internal and external references, respectively.

Synthesis of Mg $[S_2\overline{POCH_2C(CH_3)_2CH_2O}]_2$. An aqueous solution of $MgCl_2$ anhydrous (0.4696 g, 4.92 mmol) in distilled water (25 ml) was added dropwise with constant stirring to the aqueous solution of $NH_4[S_2\overline{POCH_2C(CH_3)_2CH_2O}]$ (2.0300 g, 9.67 mmol) in water (50 ml). The color of the reaction mixture changed immediately from colorless to white. The reaction-mixture was refluxed for 10 h, and the precipitate isolated by filtration. The product was dried under reduced pressure.

The other derivatives have been synthesized by a similar method and the relevant analytical data for the other complexes are listed in Table I.

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