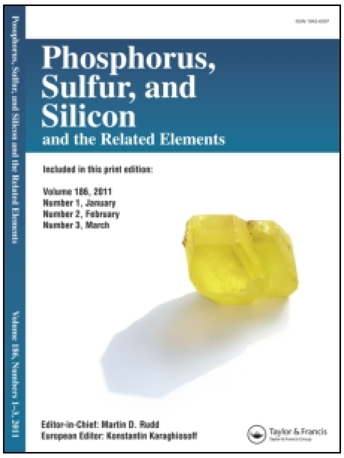

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

METAL AND ORGANOMETAL COMPLEXES OF OXY AND THIOPHOSPHORUS ACIDS PART IX: O,O'-ALKYLENE DITHIOPHOSPHATES OF ZINC AND CADMIUM

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To cite this Article Singh, O. P. , Chaturvedi, A. , Mehrotra, R. K. and Srivastava, G.(1993) 'METAL AND ORGANOMETAL COMPLEXES OF OXY AND THIOPHOSPHORUS ACIDS PART IX: O,O'-ALKYLENE DITHIOPHOSPHATES OF ZINC AND CADMIUM', Phosphorus, Sulfur, and Silicon and the Related Elements, 82: 1, 31 — 37

To link to this Article: DOI: 10.1080/10426509308047404

URL: http://dx.doi.org/10.1080/10426509308047404

Phosphorus, Sulfur, and Silicon, 1993, Vol. 82, pp. 31–37
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METAL AND ORGANOMETAL COMPLEXES OF OXY AND THIOPHOSPHORUS ACIDS
PART IX: O,O′-ALKYLENE DITHIOPHOSPHATES OF ZINC AND CADMIUM

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(Received January 11, 1993; in final form June 30, 1993)

Bis(alkylene dithiophosphates) of the type $M[S_2\overline{POGO}]_2$ (where M = Zn, Cd; G = $-CH_2CMe_2CH_2-$, $-CMe_2CMe_2-$, $-CHMeCHMe-$, $-CMe_2CH_2CHMe-$, $-CH_2CEt_2CH_2-$) obtained by the reaction of MX_2 [where X = Cl, CH_3COO, $S_2P(OR)_2$ (R = Et, Pr^i)] with alkylene dithiophosphoric acids or their ammonium salts, are white or yellow colored solids, insoluble in common organic solvents but are soluble in DMSO, DMF and pyridine. These have been characterized on the basis of elemental analyses, molar conductivity, IR and NMR (^1H and ^{31}P) spectral studies which reveal the bidentate behaviour of the dithiophosphate moiety.

Key words: O,O′-alkylene dithiophosphates, zinc chloride, zinc acetate, cadmium acetate.

INTRODUCTION

O,O′-dialkyl (or alkylene) dithiophosphoric acids constitute an important series of ligands which show an interesting versatility in their bonding modes [monodentate, bidentate (chelating/bridging), or ionic] towards different metals.[1–4] Their metal and organometal complexes have been extensively studied.[5–8] The dialkyl dithiophosphate derivatives of zinc and cadmium have received considerable attention[9] due to their crystallographic studies,[10,11] structural features and industrial applications as oil additives.[12] Although a few alkylene dithiophosphate derivatives of zinc have been studied,[13] yet the detailed study on these derivatives have not been carried out as yet.

In view of this it was considered worthwhile to synthesize alkylene dithiophosphato derivatives of zinc and cadmium in order to have a comparative study of these with corresponding open chain dialkyl dithiophosphate derivatives.

RESULTS AND DISCUSSION

Bis(alkylene dithiophosphates) of zinc and cadmium were prepared by the reaction of metal chloride (or acetate) with alkylene dithiophosphoric acids or their ammonium salts in 1:2 molar ratio in alcoholic medium (Table I):

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†Author to whom correspondence should be made.

‡This article is dedicated to (late) Dr. G. Srivastava, Associate Professor, University of Rajasthan, Jaipur, India.

TABLE I

Synthetic and analytical data of bis(alkylene dithiophosphato) derivatives of zinc and cadmium

S.N.	Reactants g/(mmoles)		Product/yield, g (%)	Analyses % found (calcd.)			
	MX$_2$	Ligand		Metal	Sulfur	Carbon	Hydrogen
1	$\mathrm{Zn[S_2P(OC_3H^i_7)_2]_2}$ 0.98 (1.99)	$\mathrm{HS_2\overline{POCHMeCHMeO}}$ 0.73 (3.96)	$\mathrm{Zn[S_2\overline{POCHMeCHMeO}]_2}$ 0.80 (93)	15.30 (15.14)	29.84 (29.70)	22.04 (22.25)	3.86 (3.73)
2	$\mathrm{Zn[OOCCH_3]}$ 1.10 (5.99)	$\mathrm{NH_4S_2\overline{POCME_2CH_2CHMeO}}$ 2.49 (11.74)	$\mathrm{Zn[S_2\overline{POCMe_2CH_2CHMeO}]_2}$ 1.50 (61)	13.20 (13.40)	26.80 (26.28)	29.27 (29.54)	5.12 (4.96)
3	$\mathrm{ZnCl_2}$ 0.56 (4.10)	$\mathrm{NH_4S_2\overline{POCH_2CEt_2CH_2O}}$ 2.00 (8.23)	$\mathrm{Zn[S_2\overline{POCH_2CEt_2CH_2O}]_2}$ 1.41 (66)	13.21 (12.67)	24.80 (24.85)	32.41 (32.59)	5.56 (5.47)
4	$\mathrm{Cd[S_2P(OC_2H_5)_2]_2}$ 1.44 (2.98)	$\mathrm{HS_2\overline{POCHMeCHMeO}}$ 1.10 (5.97)	$\mathrm{Cd[S_2\overline{POCHMeCHMeO}]_2}$ 1.30 (91)	23.34 (23.47)	26.87 (26.78)	19.90 (20.07)	3.45 (3.37)
5	$\mathrm{Cd[OOCCH_3]_2}$ 1.00 (4.34)	$\mathrm{HS_2\overline{POCMe_2CMe_2O}}$ 1.89 (8.91)	$\mathrm{Cd[S_2\overline{POCMe_2CMe_2O}]_2}$ 1.38 (69)	21.08 (21.01)	23.90 (23.97)	26.88 (26.94)	4.69 (4.52)
6	$\mathrm{Cd[OOCCH_3]_2}$ 1.00 (4.34)	$\mathrm{NH_4S_2\overline{POCMe_2CH_2CHMeO}}$ 1.82 (8.58)	$\mathrm{Cd[S_2\overline{POCMe_2CH_2CHMeO}]_2}$ 1.40 (70)	21.08 (21.01)	24.20 (23.97)	26.89 (26.94)	4.61 (4.52)
7	$\mathrm{Cd[OOCCH_3]_2}$ 0.62 (2.69)	$\mathrm{NH_4S_2\overline{POCH_2CMe_2CH_2O}}$ 1.15 (5.34)	$\mathrm{Cd[S_2\overline{POCH_2CMe_2CH_2O}]_2}$ 0.83 (70)	22.21 (22.18)	25.71 (25.30)	23.51 (23.70)	4.09 (3.98)
8	$\mathrm{Cd[OOCCH_3]_2}$ 1.64 (7.11)	$\mathrm{NH_4S_2\overline{POCH_2CEt_2CH_2O}}$ 3.49 (14.36)	$\mathrm{Cd[S_2\overline{POCH_2CEt_2CH_2O}]_2}$ 3.40 (98)	20.38 (19.97)	22.54 (22.78)	30.14 (29.87)	5.03 (5.01)

$$\text{(i) } MX_2 + 2HS(S)\overline{POGO} \rightarrow M[S(S)\overline{POGO}]_2 + 2HX$$
$$\text{(ii) } MX_2 + 2NH_4S(S)\overline{POGO} \rightarrow M[S(S)\overline{POGO}]_2 + 2NH_4X$$

$[M = Zn;\ X = Cl,\ CH_3COO;\ G = —CMe_2CH_2CHMe—,\ —CH_2CEt_2CH_2—]$

$[M = Cd;\ X = Cl,\ CH_3COO;\ G = —CMe_2CMe_2—,\ —CMe_2CH_2CHMe—,$
$—CH_2CMe_2CH_2—,\ —CH_2CEt_2CH_2—]$

The complexes get precipitated immediately on mixing the alcoholic solution of the reactants. All these compounds are white solids except $Cd[S_2\overline{POCMe_2CMe_2O}]_2$ and $Cd[S_2\overline{POCH_2CEt_2CH_2O}]_2$, which are light yellow in color. These compounds melt around 200°C (mostly with decomposition). In contrast to dialkyl dithiophosphate derivatives, which are soluble in benzene, these are insoluble in common organic solvents but are soluble in DMF, DMSO and pyridine. In methanol these are sparingly soluble.

The above complexes have also been synthesized by an alternative route comprising of ligand exchange reaction:

$$M[S_2P(OR)_2]_2 + 2HS_2\overline{POGO} \rightarrow M[S_2\overline{POGO}]_2 + 2HS_2P(OR)_2$$
$[M = Zn,\ R = Pr^i;\ G = —CHMeCHMe—]$
$[M = Cd;\ R = Et;\ G = —CHMeCHMe—]$

The reactions were carried out in refluxing benzene and the separated products were isolated and dried under reduced pressure. The free acid liberated in the reaction was also isolated by evaporation of the solvent and identified by ^{31}P NMR spectral data.

TABLE II

Some relevant IR spectral data (cm^{-1}) and molar conductivities for bis alkylene dithiophosphates of zinc and cadmium

Compound	IR spectral data in (cm^{-1}) $\nu(P)—O—C$	 $\nu P—O—(C)$	 $\nu P{=}S$	 $\nu P—S$	 $\nu M—S$	Molar conductivity $ohm^{-1}\ cm^{-2}\ mol^{-1}$ (solvent)
$Zn[S_2\overline{POCHMeCHMeO}]_2$	1160	911	661	610	335	—
$Zn[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1131	860	662	641 619	360	—
$Zn[S_2\overline{POCH_2CEt_2CH_2O}]_2$	1126	880	668	609 531	370	50.00 (DMSO)
$Cd[S_2\overline{POCHMeCHMeO}]_2$	1223	913	666	589 547	395	54.87 (DMF)
$Cd[S_2\overline{POCMe_2CMe_2O}]_2$	1140	872	662	633 580	382	10.38 (DMSO)
$Cd[S_2\overline{POCH_2CMe_2CH_2O}]_2$	1189	862	641	591 509	350	—
$Cd[S_2\overline{POCH_2CEt_2CH_2O}]_2$	1152	885	609	530 499	380	—
$Cd[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1157	800	650	595 546	385	43.83 (DMF)

IR SPECTRA

The IR spectra of these complexes have been recorded in the range of 4000–200 cm^{-1} (Table II).

(i) The bands present in the region 1223–1126 cm^{-1} and 913–800 cm^{-1} have been assigned to ν(P)—O—C and νP—O—(C) stretching modes respectively.[14]

(ii) A strong intensity band present in the region 668–609 cm^{-1} has been attributed to νP=S frequencies.[14] It has been observed that in most of the cases there is a shift to lower wave number (12–40 cm^{-1}) in νP=S vibration in comparison to its position in the corresponding free acids. This shifting indicates the attachment of P=S group through sulfur atom to zinc and cadmium in these derivatives.

(iii) The bands in the region 641–499 cm^{-1} and 395–350 cm^{-1} have been assigned to νP—S and νM—S stretching frequencies respectively. Position of νM—S in these compounds is comparable to the position of νZn—S (325 cm^{-1}) and νCd—S (318 cm^{-1}) in their diisopropyl dithiophosphate derivatives.[9]

^{1}H NMR SPECTRA

The ^{1}H NMR spectra (Table III) of these compounds could be determined only in DMSO-d_6 due to their insolubility in other solvents. In tetramethylethylene dithiophosphato derivatives of cadmium the signal due to the methyl protons shift to higher field in the region 1.32 ppm as compared to free acids (1.50 ppm). Signal due to S—H proton in the region 3.30–3.70 ppm in alkylene dithiophosphoric acids was expectedly absent in the corresponding metal complexes. Signals due to protons present on α-carbon atom of the alkylene chain e.g., in 2,2-dimethyl- and 2,2-diethyltrimethylene dithiophosphate get doubled due to coupling with phosphorus [$^3J(^1H-^{31}P)$ values of 16–18 Hz)]. These coupling constant values are the same as observed in the dithiophosphoric acids.[4]

^{31}P NMR SPECTRA

Due to the insolubility in common organic solvents their proton decoupled ^{31}P NMR spectral data (Table III) could be obtained only in coordinating solvents like DMSO and pyridine. In order to observe the solvent effect on ^{31}P chemical shift, the spectra of a few derivatives were recorded in methanol also, in which these compounds show slight solubility. Zinc derivatives show upfield shift (~5 ppm) in methanol in comparison to DMSO. However almost to effect on this shift has been observed on changing the solvent in case of cadmium derivatives. All these compounds exhibit a shift 20–30 ppm towards lower field with respect to free acids suggesting bidentate nature of the ligands in these compounds.

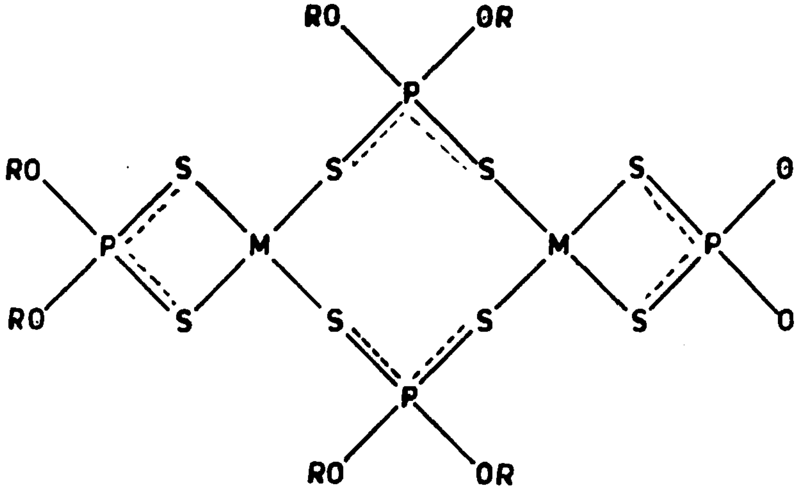
Ionic nature of the ligands in these compounds were ruled out on the basis of their low molar conductivity values (Table II). The molecular weights of these compounds could not be determined due to the lack of solubility in a suitable solvent. Thus the extent of association in these compounds could not be determined.

TABLE III

^1H and ^{31}P NMR spectral data for bis(alkylene dithiophosphato) derivatives of Zn and Cd

	^1H	^{31}P		
Compound	DMSO-d_6	DMSO	Methanol	Pyridine
$Zn[S_2\overline{POCHMeCHMeO}]_2$	1.29, s, 12H(CH_3); 4.12–4.56, m, 4H(OCH)	120.9	116.1	—
$Zn[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1.21–1.66, m, 22H(CH_3 + CH_2); 4.61–4.92, m, 2H(CH)	102.8	97.5	—
$Zn[S_2\overline{POCH_2CEt_2CH_2O}]_2$	0.77, t, 12H(CH_3), J = 7 Hz; 1.56–1.03, q, 8H(CH_2) 3.80, d, 8H(OCH_2), J = 16.0 Hz	112.2	108.2	—
$Cd[S_2\overline{POCMe_2CMe_2O}]_2$	1.32, s, 24H(CH_3)	121.2	122.2	—
$Cd[S_2\overline{POCMe_2CH_2CHMeO}]_2$	1.26–1.69, m, 22H(CH_3 + CH_2); 4.66–4.99, m, 2H(CH)	102.7	103.2	102.9
$Cd[S_2\overline{POCH_2CMe_2CH_2P}]_2$	—	108.9	109.4	—
$Cd[S_2\overline{POCH_2CEt_2CH_2O}]_2$	0.76, t, 12H(CH_3), J = 8 Hz; 1.49–1.10, q, 8H(CH_2) 3.86, d, 8H(OCH_2); J = 16.0 Hz	110.8	110.3	109.2

It is well known that sulfur bonded compounds of Zn and Cd are generally associated in solid[15] as well as in solution.[16] Complexes of these elements with 1,1-dithio ligand (e.g., dialkyl dithiocarbamates, dialkyl dithiophosphates, etc.) are usually dimeric.[11] The isomorphous diisopropyl dithiophosphates of zinc and cadmium were reported dimeric with two bridinging and two chelating dithiophosphate moieties whereas the corresponding diethyl dithiophosphate of zinc is polymeric. Due to the nonavailability of suitable crystals, the authentic structures of the compounds synthesized by us, could not be determined by X-ray crystallography. However by analogy with the open chain dithiophosphates, the cyclic alkylene dithiophosphates of zinc and cadmium may also be envisaged to possess a dimeric structure.



The NMR data of these complexes are consistent with the bidentate behaviour of dithiophosphate moiety. However the data obtained at room temperature is unable to differentiate between chelating and bridging moieties due to their labile nature and only one ^{31}P signal is obtained for each compound. Low temperature NMR data could not be obtained due to lack of facilities.

EXPERIMENTAL

Moisture was carefully excluded during the experimental work. Alkylene dithiophosphoric acids and their ammonium salt were prepared by the method reported earlier.[17] Zinc, cadmium and sulfur were estimated by the method.[18] The IR spectra were recorded on Perkin Elmer-577 spectrophotometer as nujol mulls, using CsI cell in the range 4000–200 cm^{-1}. The NMR spectra were recorded on JEOL FX 90Q spectrophotometer in DMSO-d_6 (^1H) and DMSO and pyridine (^{31}P) using TMS (for ^1H) and H_3PO_4 (for ^{31}P) as external references.

Reaction of zinc acetate with ammonium 1,1,3-trimethyltrimethylene dithiophosphate in 1:2 molar ratio. Zinc acetate (1.10 g; 5.99 mmole) in aqueous ethanol (~30 ml) was added to ammonium 1,1,3-trimethyltrimethylene dithiophosphate (2.49 g; 11.74 mmole) in the same solvent. A white precipitate appeared which was filtered off, washed with aqueous ethanol and dried to yield a white powdery solid (1.50 g) in 66% yield. Analysis, calcd. for $C_{12}H_{24}O_4P_2S_4Zn$: C, 29.54; H, 4.96; Zn, 13.40; S, 26.28%. Found: C, 29.27, H; 5.12; Zn: 13.20; S, 26.80%. Other zinc and cadmium bis(alkylene dithiophosphate) derivatives were synthesized similarly and are listed in Table I.

Reaction of zinc bis(diisopropyl dithiophosphate) with 1,2-dimethylethylene dithiophosphoric acid in 1:2 molar ratio. A mixture of zinc bis(diisopropyl dithiophosphate) (0.98 g, 1.99 mmole) and 1,2-dimethylethylene dithiophosphoric acid (0.73 g; 3.96 mmole) in benzene (~30 ml) was refluxed for ~3 hrs.

The solid product was filtered, washed with ether and dried. The product analyzed for zinc bis(1,2-dimethylethylene dithiophosphate), 0.80 g, 93%. Analysis calcd. for $C_8H_{16}O_4P_2S_4Zn$: C, 22.25; H, 3.73; Zn, 15.14; S, 29.70%. Found: C, 22.04; H, 3.86; Zn, 15.30; S, 29.84%.

A similar procedure was utilized for the synthesis of zinc bis(2,2-dimethyltrimethylene dithiophosphate) and cadmium bis(1,2-dimethylethylene dithiophosphate). The relevant data are given in Table I.

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