Coordination Chemistry Reviews, 55 (1984) 207–259
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

DIALKYLDITHIOPHOSPHATE DERIVATIVES OF NON-TRANSITION ELEMENTS

R.C. MEHROTRA, G. SRIVASTAVA and B.P.S. CHAUHAN
Department of Chemistry, University of Rajasthan, Jaipur 302004 (India)

(Received 7 September 1983)

CONTENTS

A. INTRODUCTION

Dialkyldithiophosphoric acids and their organic esters have been extensively employed as pesticides for a number of decades. More recently, the interesting bonding possibilities of these ligands have attracted chemists. A review article published by Wasson et al. [1] in 1973 deals with the chemistry of dialkyldithiophosphate derivatives of transition metals in detail. A considerable amount of work, also carried out on dialkyldithiophosphates of non-transition elements in recent years, has revealed many novel and interesting features for the coordination chemist, e.g. compared to the almost universal bidentate nature of these ligands in transition metal chemistry, they have been shown in recent years to behave as monodentate species in cases of organosilicon, organogermanium (in general) and triorganotin moieties, whereas these bind diorganotin moieties in a bidentate chelate manner. As in the case of transition metals, the dialkyldithiophosphates of main group elements have also been used selectively in extraction processes [2–6] and for analytical purposes [7–18]. In view of their interesting structural

0010-8545/84/$15.90

TABLE 1

Infrared spectral data (cm^{-1}) for metal dialkyldithiophosphates [a]

Series No.	Compound	ν(P)–O–C	νP–O–(C)	νasym(PS_2)	νsym(PS_2)	ν(M–S)	Ref.
1	$(CH_3O)_2PS_2Na$			760s	711s		48
2	$(C_2H_5O)_2PS_2Na$			696s			48
3	$(c\text{-}C_6H_{11}O)_2PS_2Na$			673s			48
4	$(CH_3O)_2PS_2K$			720s	690sh		45
5	$(C_nH_{2n+1})_2PS_2K$			706–670s	573–541		39,40
6	$[(CH_3O)_2PS_2]_2Zn$			600sh	501m	343vs	44
7	$[(C_2H_5O)_2PS_2]_2Hg$			658sh	567m	280vs	44
8	$[(C_2H_5O)_2PS_2]_3In$			652s	532sh	286s	44
9	$[(CH_3O)_2PS_2]_2Tl$	1010vs		652s	520m		45
10	$(CH_3O)_2PS_2Tl(CH_3)_2$	1020vs		669s	523m	287w, 251m	45
11	$(CH_3O)_2PS_2Tl(C_2H_5)_2$	1019s		680m, 633s	550w, 505m	271w	45
12	$(C_2H_5O)_2PS_2Tl(CH_3)_2$	1023s		638s	587m, 526m	253m	45
13	$(o\text{-}Cl\cdot C_6H_4O)_2PS_2Tl$	1014s		673m, 638s	539s, 519m	286w, 250w	45
14	$(p\text{-}ClC_6H_4O)_2PS_2Tl(CH_3)_2$	1028m		655s, 644s	533s	226w	45
15	$[(RO)_2PS_2]_nMR'_{4-n}$ $R = C_2H_5$, n-C_3H_7, i-C_3H_7, C_6H_5 $R' = CH_3$, C_2H_5, n-C_4H_9, C_6H_5 M = Si, Ge $n = 1,2$	1050–980vs	845–780s	660–650s	585–535m	550–475m(Si–S) 405–385m(Ge–S)	26
16	$(RO)_2PS_2SnR'_3$ $R = C_2H_5$, n-C_3H_7, i-C_3H_7, C_6H_5 $R' = CH_3$, C_2H_5, n-C_4H_9, C_6H_5	1190–1015vs	1025–775m	685–650s	550–515m	380–375w	51
	$R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, i-C_4H_9, C_6H_5 $R' = CH_3$, C_6H_{11}, C_6H_5	1175–1125s	1048–985s	645–633s	540–505m	390–380s	53

17	$[(RO)_2PS_2]_2SnR'_2$ R = C_2H_5, n-C_3H_7, i-C_3H_7 R′ = CH_3, n-C_4H_9, C_6H_5	1040–995	850–790	690–622s	555–520s	375–365w	52
	R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, i-C_4H_9, C_6H_5 R′ = CH_3, C_6H_5	1170–1145	1025–985	660–610			54
18	$[(RO)_2PS_2]_nSn(R')Cl_{3-n}$ R = C_2H_5, n-C_3H_7, i-C_3H_7, C_6H_5 R′ = CH_3, C_2H_5, C_4H_9, C_6H_5 n = 1–3	1180–1010 950vs, s	1050–975, 850–765	695–630	575–505	390–360m	55
19	$[(C_2H_5O)_2PS_2]_2Pb$			662s	571m	291sh	44
20	$[(RO)_2PS_2]_nMX_{3-n}$ R = C_2H_5, n-C_3H_7, i-C_3H_7, i-C_4H_9, C_6H_5 M = As, Sb n = 1–3	1025–975vs	890–745m	680–620vs	580–500m, w	400–250 (M–S)+(M–Cl)	56
21	$(RO)_2PS_2As\langle O \rangle_O G$ R = C_2H_5, n-C_3H_7, i-C_3H_7, i-C_4H_9, C_6H_5 G = $-CH_2CH_2-$, $-(CH_3)CHCH_2-$, $-(CH_3)_2CC(CH_3)_2-$, $-(CH_3)_2CCH_2CH(CH_3)-$, $-CH_2CH{=}CHCH_2-$	1025–975vs	890–750m	680–640vs	575–500	395–315	57
22	$[(C_2H_5O)_2PS_2]_3Bi$			620sh		271vs	44
23	$[(CH_3O)_2PS_2]_2Se$		838s	637s	477m		41
24	$[(C_2H_5O)_2PS_2]_2Se$		822s	650s	499m		41
25	$[(CH_3O)_2PS_2]_2Te$		830s	622s	481m		41
26	$[(C_2H_5O)_2PS_2]_2Te$		830s	644s	500m		41

[a] Although P–O–C and PS_2 linkages have been named in different ways, we have used (P)–O–C, P–O–(C) asym(PS_2) and sym(PS_2) band assignments which are used by most authors. w = weak, vw = very weak; s = strong; vs = very strong; b = broad.

features and applications, a brief review is being presented on dialkyldithiophosphate derivatives of non-transition elements emphasising particularly the work carried out during the last decade.

B. GENERAL

The dialkyldithiophosphoric acids can be prepared by the reactions of alcohols (or phenols) with phosphorus pentasulphide [1,19–21]

$$P_2S_5 + 4\ ROH \rightarrow 2(RO)_2PS_2H + H_2S\uparrow$$

These are unpleasant smelling strong monobasic acids having pKa values [1] in the range of -1.10 to $+0.22$. These tend to be oxidized [1] readily to the corresponding disulphides. Although these acids have been known for over a century [22], it was only in 1925 that serious efforts [23] were made to throw light on the structural features of the products, which were more accurately defined [24] in 1945.

Main group dialkyldithiophosphate derivatives have generally been prepared by the cleavage of the metal and organometal–halogen (chloride, bromide, iodide), –oxygen (oxides, hydroxides, alkoxides, acetates, nitrates, sulphates), or –carbon (alkyl or aryl) linkage by dialkyldithiophosphoric acids or their alkali metal and ammonium salts.

Dialkyldithiophosphate moieties could bind a metal in a variety of ways [25] as shown in Fig. 1. From an analysis of proton decoupled ^{31}P NMR data for a large number of derivatives, Glidewell [25] concluded that ^{31}P chemical shift could be expected in the regions 101–107, < 82 and 88–101 p.p.m. for bonding modes A, B and C(i, ii) respectively (Fig. 1). Doubts have been raised [26] about the universality of the above generalization. However, besides actual crystal structure determinations and some valuable information derived from spectral techniques like Mössbauer spectra, applicable for a few metals (e.g., tin) only, the ^{31}P spectra must be considered as the most satisfactory indicators for the bonding mode.

Infrared spectra of a number of compounds, relevant to this review have been reported [26–59]. These show some apparent variations, but efforts to correlate these with structural features have not been particularly successful [51–56]. The IR data have, therefore, been summarized in Table 1 to avoid

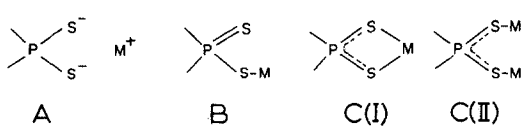


Fig. 1. Structural possibilities of metal dialkyldithiophosphate derivatives.

TABLE 2

Proton magnetic resonance spectral data for metal dialkyldithiophosphates [a]

Series No.	Compound	Chemical shift (δ p.p.m.) with shape and coupling constants (c.p.s.)	Ref.
1	$(CH_3O)_2PS_2Na$	3.6, d, J(POCH) = 14	48,60
2	$(C_2H_5O)_2PS_2Na$	4.0, o, (CH_2); 1.3, t, (CH_3)	48
3	$[(CH_2)_5CHO]_2PS_2Na$	4.4, broad, (CH); 2.7, m, (CH_2)	48
4	$[(CH_3O)_2PS_2]_2Zn$	3.81, d, J(POCH) = 16	45, 47
5	$[(CH_3O)_2PS_2]_2Cd$	3.85, d, J(POCH) = 15.7	47
6	$[(CH_3O)_2PS_2]_2In$	3.97, d, J(POCH) = 15.6	47
7	$(CH_3O)_2PS_2Tl$	3.67, d, J(POCH) = 14	45,47
8	$(C_2H_5O)_2PS_2Tl$	4.1, c, (CH_2); 1.3, t, (CH_3)	45
9	$(CH_3O)_2PS_2Tl(CH_3)_2$	3.7, d, (CH_3O), J(POCH) = 15; 1.52, d, (Tl–CH_3) J(Tl–C–H) = 347	45
10	$(C_2H_5O)_2PS_2Tl(CH_3)_2$	4.12, c, (CH_2); 1.35, t, (CH_3); 1.5, d, (Tl–CH_3) J(Tl–C–H) = 364	45
11	$(CH_3O)_2PS_2Tl(C_2H_5)_2$	3.71, d, (CH_3O), J(POCH) = 14, 1.8, c, (TlCH_2CH_3) J(Tl–C–C–H) = 632, 2.2, q, (Tl–CH_2) J(Tl–C–H) = 275	45
12	$(C_2H_5O)_2PS_2Tl(C_2H_5)_2$	1.35, t, (CH_3); 4.1, c, (CH_2O); 1.75, t, (TlCH_2CH_3) J(Tl–C–C–H) = 635; 2.1, q, (Tl–CH_2) J(Tl–C–H) = 274	45
13	$(C_2H_5O)_2PS_2Si(CH_3)_3$	3.9, m, (CH_2); 1.35, t, (CH_3) J(POCH) = 6; 1.4, s, (Si–CH_3)	26
14	$(n\text{-}C_3H_7O)_2PS_2Si(CH_3)_3$	4.35, m, (CH_2O); 2.25, m, (CH_2); 1.35, t, (CH_3); 0.55, s, (Si–CH_3)	26
15	$(C_6H_5O)_2PS_2Si(CH_3)_3$	7.4, s, (C_6H_5); 0.5, s, (Si–CH_3)	26
16	$[(C_2H_5O)_2PS_2]_2Si(C_6H_5)(CH_3)$	7.55, m, (Si–C_6H_5); 4.3, m, (CH_2); 1.55, t, (CH_3); 0.8, s, (Si–CH_3)	26
17	$[(i\text{-}C_3H_7O)_2PS_2]_2Si(C_6H_5)_2$	7.7, m, (Si–C_6H_5); 5.1, sept., (CH); 1.6, d, (CH_3)	26
18	$[(C_2H_5O)_2PS_2Ge(C_2H_5)_3$	4.25, m, (CH_2O); 1.55, m, (CH_3 + Ge–C_2H_5)	26
19	$(n\text{-}C_3H_7O)_2PS_2Ge(C_2H_5)_3$	4.0, m, (CH_2O); 1.8, q, (CH_2); 1.2, m, (CH_3 + Ge–C_2H_5)	26
20	$(i\text{-}C_3H_7O)_2PS_2Ge(C_2H_5)_3$	4.7, sept., (CH); 1.2, m, (CH_3 + Ge–C_2H_5)	26
21	$(C_2H_5O)_2PS_2Ge(C_4H_9)_3$	4.35, m, (CH_2); 1.55, m, (CH_3 + Ge–C_4H_9)	26
22	$(i\text{-}C_3H_7O)_2PS_2Ge(C_4H_9)_3$	5.15, sept., (CH); 1.45, m, (CH_3 + Ge–C_4H_9)	26
23	$(n\text{-}C_3H_7O)_2PS_2Ge(C_4H_9)_3$	4.35, m, (CH_2O); 2.2, m, (CH_3 + CH_2 + Ge–C_4H_9)	26
24	$[(i\text{-}C_3H_7O)_2PS_2]_2Ge(C_4H_9)_2$	4.6, sept., (CH); 1.45, m, (CH_3 + Ge–C_4H_9)	26
25	$(C_2H_5O)_2PS_2Sn(CH_3)_3$	4.15, m, (CH_2) J(POCH) = 10; 1.35, t, (CH_3); 0.7, s, (Sn–CH_3) J(SnCH) = 57.5	46

TABLE 2 (continued)

Series No.	Compound	Chemical shift (δ p.p.m.) with shape and coupling constants (c.p.s.)	Ref.
26	$(i\text{-}C_3H_7O)_2PS_2Sn(CH_3)_3$	4.85, m, (CH) J(POCH) = 13; 1.35, d, (CH_3); 0.7, s, (Sn–CH_3) J(SnCH) = 57.5	51,53
27	$(n\text{-}C_3H_7O)_2PS_2Sn(CH_3)_3$	4.1, m, (CH_2O); 1.9, q, (CH_2); 1.2, t, (CH_3); 0.8, s, (Sn–CH_3) $J(^{117}SnCH) = 55.5$, $J(^{119}SnCH) = 60$	51
28	$(C_6H_5O)_2PS_2Sn(CH_3)_3$	7.3, d, (C_6H_5O); 0.65, s, (Sn–CH_3) $J(^{117}SnCH) = 55$, $J(^{119}SnCH) = 59$	51
29	$(i\text{-}C_3H_7O)_2PS_2Sn(C_2H_5)_3$	4.8, m, (CH); 1.45, m, (CH_3 + Sn–C_2H_5)	51
30	$(C_2H_5O)_2PS_2Sn(C_4H_9)_3$	4.2, m, (CH_2O); 1.30, m, (CH_3 + Sn–C_4H_9)	51
31	$(i\text{-}C_3H_7O)_2PS_2Sn(C_4H_9)_3$	4.8, m, (CHO); 1.2, m, (CH_3 + Sn–C_4H_9)	51
32	$(C_2H_5O)_2PS_2Sn(C_6H_5)_3$	3.9, dq, (CH_2); J(POCH) = 10; 1.1, t, (CH_3); 7.5, m, (Sn–C_6H_5)	51,53
33	$(i\text{-}C_3H_7O)_2PS_2Sn(C_6H_5)_3$	4.7, m, (CH) J(POCH) = 12; 1.15, d, (CH_3); 7.5, m, (Sn–C_6H_5)	51,53
34	$(CH_3O)_2PS_2Sn(C_6H_5)_3$	3.45, d, (CH_3) J(POCH) = 15.5; 7.45, m, (Sn–C_6H_5)	53
35	$(n\text{-}C_3H_7O)_2PS_2Sn(C_6H_5)_3$	3.8, t, (CH_2O) J(POCH) = 9.5; 1.05, m, (CH_2 + CH_3); 7.5, m, (Sn–C_6H_5)	53
36	$(i\text{-}C_4H_9O)_2PS_2Sn(C_6H_5)_3$	3.65, m, (CH_2O) J(POCH) = 9; 1.7, m, (CH); 0.8, d, (CH_3) 7.6, m, (Sn–C_6H_5)	53
37	$(C_6H_5O)_2PS_2Sn(C_6H_5)_3$	7.6, m, (C_6H_5O + Sn–C_6H_5)	53
38	$(CH_3O)_2PS_2Sn(CH_3)_3$	3.65, d, (CH_3O) J(POCH) = 15; 0.65, s, (Sn–CH_3) $J(^{119}SnCH) = 57$	53
39	$(i\text{-}C_3H_7O)_2PS_2Sn(CH_3)_3$ (in pyridine)	5.0, m, (CH) J(POCH) = 13; 1.4, d, (CH_3); 1.0, s, (Sn–CH_3) $J(^{119}SnCH) = 70.0$	53
40	$(i\text{-}C_3H_7O)_2PS_2Sn(C_6H_{11})_3$	4.95, m, (CH) J(POCH) = 12; 1.3, d, (CH_3); 1.75, m, (Sn–C_6H_{11}).	53

41	$[(C_2H_5O)_2PS_2]_2Sn(CH_3)_2$	4.1, dq, (CH_2) J(POCH) = 10.0; 1.4, t, (CH_3); 1.6, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 75,79	52,54
42	$[(n\text{-}C_3H_7O)_2PS_2]_2Sn(CH_3)_2$	4.2, m, (CH_2O); 2.1, q, (CH_2); 1.25, t, (CH_3); 1.8, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 75,80	52
43	$[(C_6H_5O)_2PS_2]_2Sn(CH_3)_2$	7.4, s, (C_6H_5); 1.25, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 74.80	52
44	$[(C_2H_5O)_2PS_2]_2Sn(C_4H_9)_2$	4.35, m, (CH_2); 1.75, m, (CH_3 + Sn–C_4H_9)	52
45	$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_4H_9)_2$	5.35, m, (CH); 1.55, m, (CH_3 + Sn–C_4H_9)	52
46	$[(C_6H_5O)_2PS_2]_2Sn(C_4H_9)_2$	7.3, m, (C_6H_5); 1.25, m, (Sn–C_4H_9)	52
47	$[(C_2H_5O)_2PS_2]_2Sn(C_6H_5)_2$	3.9, dq, (CH_2) J(POCH) = 10; 1.15, t, (CH_3); 7.75, m, (Sn–C_6H_5)	52
48	$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$	4.4, m, (CH); 1.15, d, (CH_3); 7.75, m, (Sn–C_6H_5)	52,54
49	$[(CH_3O)_2PS_2]_2Sn(CH_3)_2$	3.7, d, (CH_3O) J(POCH) = 15.5; 1.5, s, (Sn–CH_3) $J(^{117,118}SnCH)$ = 76,80	54
50	$[(CH_3O)_2PS_2]_2Sn(C_6H_5)_2$	3.5, d, (CH_3) J(POCH) = 15.5; 7.75, m, (Sn–C_6H_5)	54
51	$[(n\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$	3.75, dt, (CH_2O) J(POCH) = 9.5; 1.5, m, (CH_2); 0.8, t, (CH_3); 7.75, m, (Sn–C_6H_5)	54
52	$[(i\text{-}C_4H_9O)_2PS_2]_2Sn(C_6H_5)_2$	3.5, dd, (CH_2); J(POCH) = 9; 1.75, m, (CH); 0.8, d, (CH_3); 7.7, m, (Sn–C_6H_5)	54
53	$[(C_6H_5O)_2PS_2]_2Sn(C_6H_5)_2$	7.3, m, (C_6H_5O + Sn–C_6H_5)	54
54	$[(i\text{-}C_3H_7O)_2PS_2]Sn(CH_3)Cl_2$	5.35, sept., (CH); 1.85, d, (CH_3); 2.2, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 102, 106	55
55	$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(CH_3)Cl$	5.1, sept., (CH); 1.7, d, (CH_3); 2.2, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 103, 107	55
56	$[(i\text{-}C_3H_7O)_2PS_2]_3SnCH_3$	5.2, sept., (CH); 1.75, d(CH_3); 2.5, s, (Sn–CH_3) $J(^{117,119}SnCH)$ = 104,109	55
57	$[(i\text{-}C_3H_7O)_2PS_2]_3SnC_2H_5$	5.05, sept., (CH); 1.6, m, (CH_3 + Sn–C_2H_5)	55
58	$[(C_2H_5O)_2PS_2]_3SnC_4H_9$	4.45, m, (CH_2); 1.65, t, (CH_3 + Sn–C_4H_9)	55
59	$[(i\text{-}C_3H_7O)_2PS_2]_3Sn(C_4H_9)$	5.15, m, (CH); 1.5, m, (CH_3 + Sn–C_4H_9)	55
60	$[(n\text{-}C_3H_7O)_2PS_2]_3Sn(C_4H_9)$	4.35, m, (CH_2O); 2.45, m, (CH_2); 1.25, t, (CH_3 + Sn–C_4H_9)	55
61	$[(CH_3O)_2PS_2]_2Pb$	3.7, d, (CH_2O); J(POCH) = 16	47
62	$[(C_2H_5O)_2PS_2]_3As$	4.55, q, (CH_2O); 1.75, t, (CH_3)	56

TABLE 2 (continued)

Series No.	Compound	Chemical shift (δ p.p.m.) with shape and coupling constants (c.p.s.)	Ref.
63	$[(i\text{-}C_3H_7O)_2PS_2]_3As$	5.55, m, (CH); 1.6, d, (CH_3)	56
64	$[(i\text{-}C_3H_7O)_2PS_2]_2AsCl$	5.8, m, (CH); 1.85, d, (CH_3)	56
65	$[(i\text{-}C_3H_7O)_2PS_2]AsCl_2$	5.75, m, (CH); 1.8, d, (CH_3)	56
66	$[(n\text{-}C_3H_7O)_2PS_2]_3As$	4.35, m, (CH_2O); 2.6, m, (CH_2); 1.3, t, (CH_3)	56
67	$[(n\text{-}C_3H_7O)_2PS_2]_2AsCl$	4.05, m, (CH_2O); 1.7, m, (CH_2); 1.0, t, (CH_3)	56
68	$[(sec.C_4H_9O)_2PS_2]_3As$	3.75, q, (CH_2); 1.95, m, (broad), (CH); 0.95, d, (CH_3)	56
69	$[(C_6H_5O)_2PS_2]_3As$	7.45, s	56
70	$[(C_2H_5O)_2PS_2]SbCl_2$	4.25, o, (CH_2); 1.45, t, (CH_3)	56
71	$[(i\text{-}C_3H_7O)_2PS_2]_3Sb$	5.1, m, (CH); 1.7, d, (CH_3)	56
72	$[(i\text{-}C_3H_7O)_2PS_2]_2SbCl$	5.15, m, (CH); 1.7, d, (CH_3)	56
73	$[(i\text{-}C_3H_7O)_2PS_2]SbCl_2$	5.25, m, (CH); 1.8, d, (CH_3)	56
74	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb(OH_7C_3\text{-}i)$	5.15, m, (CH); 1.55, overlapping doublets, (CH_3)	56
75	$[(i\text{-}C_3H_7O)_2PS_2]Sn(OH_7C_3\text{-}i)_2$	4.95, m, (CH); 1.6, overlapping doublets, (CH_3)	56

76	$[(n\text{-}C_3H_7O)_2PS_2]_3Sb$	4.65, m, (CH_2O); 2.1, m, (CH_2); 1.4, t, (CH_3)	56
77	$[(n\text{-}C_3H_7O)_2PS_2]_2SbCl$	3.6, m, (CH_2O); 1.7, m, (CH_2); 0.9, t, (CH_3)	56
78	$[(n\text{-}C_3H_7O)_2PS_2]SbCl_2$	4.15, m, (CH_2O); 1.85, m, (CH_2); 1.6, t, (CH_3)	56
79	$[(i\text{-}C_4H_9O)_2PS_2]_3Sb$	3.85, q, (CH_2); 2.0, m, (CH); 0.95, d, (CH_3)	56
80	$[(i\text{-}C_4H_9O)_2PS_2]_2SbCl$	3.85, q, (CH_2); 2.0, m, (CH); 1.0, d, (CH_3)	56
81	$(C_2H_5O)_2PS_2AsOCH_2CH_2O$	4.55, m, (CH_2); 1.75, t, (CH_3)	57
82	$(C_2H_5O)_2PS_2AsOCH(CH_3)CH_2O$	4.35, m, ($CH+CH_2$); 1.7, m, (CH_3)	57
83	$(C_2H_5O)_2PS_2AsOC(CH_3)_2CH_2CH(CH_3)O$	3.65, m, ($CH+CH_2O+CH_2$); 0.55, t, (CH_3)	57
84	$(n\text{-}C_3H_7O)_2PS_2AsOCH_2CH_2O$	4.3, m, (CH_2O); 2.1, m, (CH_2); 1.3, t, (CH_3)	57
85	$(n\text{-}C_3H_7O)_2PS_2AsOCH(CH_3)CH_2O$	3.6, m, ($CH+CH_2O$) 1.45, m, (CH_2); 0.85, m, (CH_3)	57
86	$(n\text{-}C_3H_7O)_2PS_2AsOC(CH_3)_2CH_2CH(CH_3O)$	4.1, m, ($CH+CH_2O$); 1.7, m, (CH_2); 1.1, m, (CH_3)	57
87	$(i\text{-}C_3H_7O)_2PS_2AsOCH_2CH_2O$	5.1, m, (CH); 4.3, s, (CH_2); 1.65, d, (CH_3)	57
88	$(i\text{-}C_3H_7O)_2PS_2AsOCH(CH_3)CH_2O$	4.7, m, ($CH+CH_2$); 1.55, d, (CH_3)	57
89	$(i\text{-}C_3H_7O)_2PS_2AsOC(CH_3)_2CH_2CH(CH_3)O$	4.75, m, (CH); 1.3, t, (CH_2+CH_3)	57
90	$(i\text{-}C_3H_7O)_2PS_2AsOC(CH_3)_2C(CH_3)_2O$	5.45, m, (CH); 1.25, q, (CH_3)	57
91	$(C_6H_5O)_2PS_2AsOCH_2CH_2O$	7.3, d, (C_6H_5); 4.15, s (broad), (CH_2)	57
92	$(i\text{-}C_4H_9O)_2PS_2AsOC(CH_3)_2C(CH_3)_2O$	3.8, q, (CH_2); 2.15, m, (CH); 1.1, m, (CH_3)	57

[a] All chemical shifts and coupling constants are in δ p.p.m. and c.p.s. respectively. s = singlet, d = doublet, t = triplet, q = quartet, sept. = septate, o = octet, dq = doublet of quartet, c = complex.

TABLE 3

Dialkyldithiophosphate derivatives of metals on which work has been carried out up to 1980

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H																	He
Li [b]	Be											B	C	N	O	F	Ne
Na [b]	Mg [b]											Al [a]	Si [a]	P	S	Cl	Ar
K [b]	Ca [b]	Sc	Ti [a]	V [b]	Cr [b]	Mn [b]	Fe [b]	Co [b]	Ni [b]	Cu [b]	Zn [b]	Ga	Ge [a]	As [b]	Se [b]	Br	Kr
Rb [b]	Sr	Y	Zr [a]	Nb [a]	Mo [a]	Tc	Ru [a]	Rh [a]	Pd [a]	Ag [a]	Cd [a]	In [b]	Sn [b]	Sb [b]	Te [b]	I	Xe
Cs [a]	Ba [b]	Ln	Hf	Ta	W [b]	Re	Os	Ir [b]	Pt [b]	Au [b]	Hg [b]	Tl [b]	Pb [b]	Bi [b]	Po	At	Rn
Fr	Ra	An															
		Ln	La [b]	Ce [b]	Pr [b]	Nd [b]	Pm [b]	Sm [b]	Eu [b]	Gd [b]	Tb [b]	Dy [b]	Ho [b]	Er [b]	Tm	Yb [b]	Lu [b]
		An	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

[a] Not fully characterized or reported in the patent literature only. [b] Characterized well.

repetition in individual groupwise discussion. For similar reasons the ^1H NMR data [45,47,48,60,61] have also been summarized in Table 2.

C. DIALKYLDITHIOPHOSPHATE DERIVATIVES OF MAIN GROUP METALS

Main group metals/metalloids, the dialkyldithiophosphate chemistry of which has been investigated so far, have been indicated in Table 3. A list of individual compounds described so far is given in Table 4.

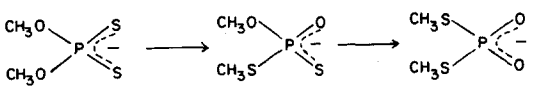
(i) Alkali metals (Li, Na and K)

Lithium, sodium and potassium salts of the dialkyldithiophosphoric acids have been prepared [62–70] by the reactions of alkali-metal carbonates, hydroxides or alkoxides with freshly prepared dialkyldithiophosphoric acids. These salts can also be prepared [24] by the reaction of dialkylthiophosphorochloridates with KSH

$$(RO)_2P(S)Cl + KSH \rightarrow (RO)_2PS_2K + HCl\uparrow$$

The alkali salts of dialkyldithiophosphoric acids are white solids, which appear to be more stable to oxidation compared to acids themselves. However, when heated to 190°C, these salts tend to decompose with oxidation to polymeric derivatives [1] of the type, $[(RO)_2PS_2]_2S_x$ ($x = 1–4$).

Sodium dimethyldithiophosphate has been shown [60] to undergo isomerization at 60°C in aqueous solution



Treating a solution of the sodium salt with ethyl iodide at 60°C, however, gives only a mixture of $(CH_3O)_2P(S)SC_2H_5$ and $(CH_3O)(CH_3S)P(O)SC_2H_5$; a higher temperature (90–95°C) is required for the formation of $(CH_3S)_2P(O)OC_2H_5$.

The UV spectra of sodium dialkyldithiophosphates are quite similar [48,71]. In methanol, these show a broad absorption beginning at 300 nm. The molar absorptivities at the shoulders have been reported as 387 at 251 nm for $NaS_2P(OCH_3)_2$, 3500 at 224 nm for $NaS_2P(OC_2H_5)_2$ and 1900 at 226 nm for $NaS_2P[OCH(CH_2)_5]_2$. The absorption has been shown to increase to the cut off point at 200–210 nm.

Proton decoupled ^{31}P NMR spectra of lithium and sodium diisopropyldithiophosphates [25,72] show chemical shifts of 95 and 111 p.p.m. indicating the chelating and ionic nature of the ligand (Fig. 1A and C(i) respectively).

TABLE 4

Dialkyldithiophosphate derivatives of main group metals/metalloids

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
1	$(RO)_2PS_2Li$	C_2H_5		b	
		i-C_3H_7		b	
2	$(RO)_2PS_2Na$	CH_3			
		C_2H_5			
		i-C_3H_7		b	
		$(CH_2)_5CH$			
3	(p-$ClC_6H_4O)_2PS_2Na3H_2O$			b	97–99 Anhydrous above 250
4	$(CH_3)_2CHCH_2O_2P(S)^{35}SNa$			d	
5	$(CH_3)_2CHCH_2O_2P(S)^{35}SNa$			d	
6	$(RO)_2PS_2K$	CH_3			
		$C_6H_5CH_2$			
		2,4-$X_2C_6H_3$			120
		X = $C(CH_3)_2(C_2H_5)$			
		o-ClC_6H_4		b	168(d)
		p-ClC_6H_4		b	210–212(d)
		C_6H_5			187–188
7	$[(RO)_2PS_2]_2Mg$	C_2H_5			
		i-C_3H_7			
8	$[(RO)_2PS_2]_2Ca$	C_2H_5			
		i-C_3H_7		b	
9	$[(RO)_2PS_2]_2Ba$	C_2H_5			
		i-C_3H_7		b	
		n-C_4H_9			
10	$[(RO)_2PS_2]_2Zn$	CH_3		b	79
		C_2H_5			
					180–181
		i-C_3H_7			
		i-C_3H_7			144
		i-C_3H_7			
		i-C_3H_7			
		n-C_3H_7			
		n-C_3H_7		b	Liquid
		i-C_4H_9			
		i-C_4H_9			
		i-C_4H_9		b	223.5–224.5
		n-C_4H_9			

Physico-chemical and other reported data	Ref.
Photometric analysis	7
^{31}P NMR, solvent effects	25
Isomorphism, PMR, UV, IR,	48, 60
Photometric analysis, UV, IR, PMR	7, 48
^{31}P NMR, solvent effects	25
Electronic, IR, PMR	48
	66
	101
	101
X-ray crystal structure	67
IR	45
X-ray crystal structure	68
	63
	66
	66
	66
Photometric analysis	7
^{31}P NMR, solvent effects	25
Photometric analysis	7
^{31}P NMR, solvent effects	25
Photometric analysis	7
^{31}P NMR solvent effects	25
X-ray electron spectroscopy	81
	45
PMR	47
Crystal and molecular structure	106
Polarography	131, 170
Thermal stability	142
Photometric analysis	7
Crystal and molecular structure	108
Thermal stability	142
X-ray analysis	106
Thin-layer chromatography	126, 128, 129
Polarography	131
Thermal stability	142
Thin-layer chromatography	126, 128, 129
Polarography	131
Thermal stability	142
X-ray electron spectra	81
X-ray analysis	106

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		t-C_4H_9		b	Unstable at room temperature
		$H_2C-CH-(CH_2)_3CH_3$			
		C_2H_5			
		$H_2C-CH-(CH_2)_3CH_3$			
		C_2H_5			
		$C_{12}H_{25}$			
		C-C_6H_{11}			
		$(CD_3)_2CH$		b	140–145
		$CH_3-CH-CH_2-CH-$		b	Liquid
		CH_3	CH_3		
11	$[(RO)_2PS_2]_3Zn_2OH$	i-C_3H_7		b	214–215
		n-C_3H_7		b	178–179
		i-C_4H_9		b	138–140
		n-C_4H_9		b	149–151
					154–155
12	$[(RO)_2PS_2]_6Zn_4O$	i-C_3H_7		b	
		n-C_4H_9		b	
13	$[(RO)_2PS_2]_2Cd$	CH_3		b	174–176
		C_2H_5			
		C_2H_5			
		C_2H_5			
		C_2H_5			
		i-C_3H_7		b	
		i-C_3H_7		b	138–139
		C_4H_9			
		$H_2C-CH(CH_2)_3CH_3$			
		C_2H_5			
14	$[(RO)_2PS_2]Hg$	CH_3			112–113
		CH_3			
		C_2H_5			124
		C_2H_5			
		C_2H_5		b	
		C_2H_5			
		C_2H_5			
		i-C_3H_7		a,b	92–93
		i-C_3H_7			
		i-C_4H_9		a,b	104
		i-C_4H_9			

Physico-chemical and other reported data	Ref.
Thermal stability	142
Metal exchange study, extraction constants	116
IR, Raman spectra	159
Thin-layer chromatography	126, 128, 129
Thin-layer chromatography	126, 128, 129
Thermal stability	142
Thermal stability	142
IR, PMR	106
	94
	94
	94
IR, PMR	106
X-ray analysis	106
X-ray analysis	106
PMR	47
Electronic spectral data	166
Polarography	170
Photometric analysis	7
Thermal stability	148, 152
Crystal and molecular structure	108
Thermal decomposition	142
X-ray electron spectra	81
IR, Raman spectra	159
	86
Influence of substituents on stability	110
	86
IR	44
Crystal and molecular structure	162
Photometric analysis	7
Influence of substituents on stability	110
	86
Crystal and molecular structure	162, 163
Thermal stability	142
	86
Stability	110

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		n-C_4H_9		a,b	61–62
		n-C_4H_9			
		i-C_5H_{11}			90
		c-C_6H_{11}			40–41
		C_6H_5			102
15	$[(RO)_2PS_2]_4HgCl_2$	CH_3		a,b	116
		C_2H_5			116
		i-C_3H_7			106–108
		i-C_4H_9			106
		n-C_4H_9			82
		i-C_5H_{11}			120–121
		n-C_5H_{11}			126–128
		C_6H_5			128
16	$(RO)_2PS_2HgR'$	CH_3	C_2H_5	a,b	
		C_2H_5	C_2H_5		
		i-C_3H_7	C_2H_5		
		i-C_4H_9	C_2H_5		
		n-C_4H_9	C_2H_5		
		i-C_5H_{11}	C_2H_5		
		n-C_5H_{11}	C_2H_5		
		C_6H_5	C_2H_5		103–105
17	$[(C_2H_5O)_2PS_2]_3Al$				
18	$(RO)_2PS_2Tl$	CH_3			122
		C_2H_5			86
		i-C_3H_7			
		p-ClC_6H_4			180
		C_6H_5			
		$-CH_2-CH(C_2H_5)-(CH_2)_3CH_3$			
19	$(RO)_2PS_2TlR'_2$	CH_3	CH_3	a	181
		CH_3	C_2H_5	a	153
		C_2H_5	CH_3	a	135–136
		C_2H_5	C_2H_5	a	132
		p-ClC_6H_4	CH_3	a	134
20	$[(RO)_2PS_2]_2TlR'$	CH_3	CH_3	a,b	
		C_6H_5	CH_3	a,b	
		C_6H_5	CH_3	a,b	
		CH_3	C_6H_5	a,b	
		C_2H_5	C_6H_5	a,b	
		C_6H_5	C_6H_5	a,b	

Physico-chemical and other reported data	Ref.
	86
Stability	110
	86
	86
	86
	86
	86
	86
	86
	86
	86
	86
	87
	87
	87
	87
	87
	87
	87
	87
Photometric analysis	7
Association, PMR, IR, conductivity	45
Association, PMR, IR, conductivity	45
Polarography	151
Photometric analysis	7
Molecular structure	167
^{31}P NMR, solvent effects	25
Association study, PMR, IR, conductivity	45
Molecular structure	167
Raman, IR	159
Conductivity, association, IR, PMR	45
Conductivity, association, IR, PMR	45
Conductivity, association, IR, PMR	45
Conductivity, association, IR, PMR	45
Conductivity, association, IR, PMR	45
	168
	168
	168
	168
	168
	168

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
21	$[(RO)_2PS_2]_3In$	C_2H_5			
		$-H_2C-CH(CH_2)_3CH_3$ (with C_2H_5)		a,b	
		$-H_2C-CH(CH_2)_3CH_3$ (with C_2H_5)			
22	$(RO)_2PS_2Si(CH_3)_3$	CH_3		d	44–46
		C_2H_5		a,d	55–56
		n-C_3H_7		a,d	100–102/8
		i-C_3H_7		a,d	98–99/8
		C_6H_5		a,d	
23	$[(RO)_2PS_2]_2SiR'_2$	i-C_3H_7	C_6H_5	a	125–128/4
		C_2H_5	C_6H_5 CH_3	a	110–113/2
		i-C_3H_7	C_6H_5 CH_3	a	115–119/2
24	$[(i\text{-}C_3H_7O)_2PS_2]_4Si$			a	
25	$(RO)_2PS_2GeR'_3$	C_2H_5	C_2H_5	a	110–113/0.5
		n-C_3H_7	C_2H_5	a	117–119/0.2
		i-C_3H_7	C_2H_5	a	115–117/0.5
		C_2H_5	C_4H_9	a	118–121/0.2
		n-C_3H_7	C_4H_9	a	128–129/0.1
		i-C_3H_7	C_4H_9	a	129–131/0.1
26	$[(RO)_2PS_2]_2Ge(C_4H_9)_2$	C_2H_5			194–197/0.1
		n-C_3H_7		a	130–132/0.1
		i-C_3H_7		a	128–132/0.2
27	$[(i\text{-}C_3H_7O)_2PS_2]_4Ge$			a	
28	$(RO)_2PS_2SnR'_3$	CH_3	CH_3	a,b,c	
		C_2H_5	CH_3	a,b	90–91/0.3
		C_2H_5	CH_3	a,b	112–115/0.2

Physico-chemical and other reported data	Ref.
IR, extraction	44
Crystal structure (X-ray)	171
Photometric determination	7
IR, Raman spectra study	159
Metal exchange reaction study	116
Refractive index	172
Refractive index	173
Refractive index, dipolemoment, mol.wt., conductivity, IR, NMR (^{1}H, ^{31}P), electronic spectra	26
Refractive index, dipole moment, mol. wt., conductivity, IR, NMR (^{1}H, ^{31}P), electronic spectra	26
Refractive index, dipole moment, mol. wt., conductivity, IR, NMR (^{1}H, ^{31}P), electronic spectra	26
Refractive index, dipole moment, mol. wt., conductivity, IR, NMR (^{1}H, ^{31}P) electronic spectra	26
Refractive index, dipole moment, mol. wt. conductivity, IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
Refractive index, dipole moment, mol. wt., conductivity, IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
^{31}P NMR, solvent effects	25
Refractive index, dipole moment, mol. wt., conductivity measurement	26
IR, NMR (^{1}H, ^{31}P), and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H, ^{31}P) and electronic spectra	26
IR, NMR (^{1}H,^{31}P) and electronic spectra	26
^{31}P NMR, solvent effects	25
IR, PMR, Mössbauer and mass spectral studies	53
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	51
Mol. wt., refractive index, dipole moment, conductivity,	53

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		n-C_3H_7	CH_3	a,b	98–99/0.1
		n-C_3H_7	CH_3	a,b	Oil
		i-C_3H_7	CH_3	a,b	80–83/0.1
		i-C_3H_7	CH_3	a,b	105–109/0.4
		C_6H_5	CH_3	a,b	–
		C_2H_5	C_2H_5	a,b	118–120/0.5
		n-C_3H_7	C_2H_5	a,b	122–124/0.2
		i-C_3H_7	C_2H_5	a,b	104–106/0.5
		C_6H_5	C_2H_5	a,b	104–106/0.5
		C_2H_5	n-C_4H_9		135–138/0.01
		n-C_3H_7	n-C_4H_9		140–143/0.01
		i-C_3H_7	n-C_4H_9		125–130/0.05
		C_6H_5	n-C_4H_9		
		CH_3	C_6H_5	a,b	83
		C_2H_5	C_6H_5	a,b	104–106
		C_2H_5	C_6H_5	a,b	105
		C_2H_5	C_6H_5		
		n-C_3H_7	C_6H_5	a,b	71–73
		n-C_3H_7	C_6H_5	a,b	63
		i-C_3H_7	C_6H_5	a,b	62–63
		i-C_3H_7	C_6H_5	a,b	73.5–74.5
		i-C_4H_9	C_6H_5	a,b	52–54
		C_6H_5	C_6H_5	a,b	121–122
		n-C_5H_{11}	C_6H_5	a,b	68–69
		i-C_3H_7	C_6H_{11}	a,b	43–44
29	$[(RO)_2PS_2]_2SnR'_2$	CH_3	CH_3	a,b	82
		C_2H_5	CH_3	a,b	32–33
		C_2H_5	CH_3	a,b	121–123/0.2
		n-C_3H_7	CH_3	a,b	126–129/0.5

Physico-chemical and other reported data	Ref.
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	53
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	53
IR, PMR and electronic spectra	
–	51
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	51
IR, PMR and electronic spectra	
	51
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	51
IR, PMR, Mössbauer and mass spectra	53
X-ray crystal analysis	201
IR, PMR, Mössbauer and mass spectra	51
	53
IR, PMR, Mössbauer and mass spectra	51
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	53
IR, PMR, Mössbauer and mass spectra	54
IR, PMR, Mössbauer and mass spectra	54
Mol. wt., refractive index, dipole moment, conductivity,	54
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	52

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		n-C_3H_7	CH_3	a,b	Oil
		i-C_3H_7	CH_3	a,b	32–33
		i-C_3H_7	CH_3	a,b	98–99/0.5
		C_6H_5	CH_3	a,b	83–85
		C_2H_5	C_4H_9	a,b	142–145/0.01
		n-C_3H_7	C_4H_9	a,b	142–145/0.01
		i-C_3H_7	C_4H_9	a,b	140–142/0.01
		C_6H_5	C_4H_9	a,b	
		CH_3	C_6H_5	a,b	118
		C_2H_5	C_6H_5	a,b	53
		C_2H_5	C_6H_5		
		n-C_3H_7	C_6H_5	a,b	41
		i-C_3H_7	C_6H_5	a,b	108
30	$(RO)_2PS_2SnR'_2Cl$	i-C_3H_7	CH_3		108–110/0.4
		i-C_3H_7	C_4H_9		131–133/0.02
		i-C_3H_7	C_6H_5		
31	$[(RO)_2PS_2]_3SnR'$	i-C_3H_7	CH_3	b	
		i-C_3H_7	C_2H_5	b	
		C_6H_5	C_2H_5	b	
		C_2H_5	C_4H_9	b	
		n-C_3H_7	C_4H_9	b	
		i-C_3H_7	C_4H_9	b	
		C_6H_5	C_4H_9	b	
		C_2H_5	C_6H_5	b	
32	$(RO)_2PS_2SnR'Cl_2$	i-C_3H_7	C_6H_5	a	
		i-C_3H_7	C_4H_9	a	

Physico-chemical and other reported data	Ref.
IR, PMR and electronic spectra	
IR, PMR, Mössbauer and mass spectra	54
IR, PMR, Mössbauer and mass spectra	54
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
IR, PMR, Mössbauer and mass spectra	54
IR, PMR, Mössbauer and mass spectra	54
X-ray crystal structure	202
IR, PMR, Mössbauer and mass spectra	54
IR, PMR, Mössbauer and mass spectra	54
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	52
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity, IR, PMR and electronic spectra	55
Mol. wt., refractive index, dipole moment, conductivity,	55

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
33	$[(RO)_2PS_2]_2SnR'Cl$	i-C_3H_7	CH_3	b	
		i-C_3H_7	C_4H_9	b	
34	$[(RO)_2PS_2]_2Sn$	C_2H_5			
		H_2C-$CH(CH_2)_3CH_3$			
		C_2H_5			
		C_6H_5		a,b	
35	$[(i\text{-}C_3H_7O)_2PS_2]_4Sn$			a	
36	$[(i\text{-}C_3H_7O)_2PS_2]SnX_2$ X = Cl, Br			a	
37	$[(RO)_2PS_2]_2Pb$	CH_3		a,b	145–147
		C_2H_5		a,b	74
		C_2H_5			
		C_2H_5			
		C_2H_5		a	
		C_2H_5			
		C_2H_5			
		C_2H_5			
		i-C_3H_7		a	
		i-C_3H_7		a	
		i-C_3H_7			131.5–132
		n-C_4H_9			
		CH_2-$CH(CH_2)_3CH_3$			
		C_2H_5			
		CH_2-$CH(CH_2)_3CH_3$			
		C_2H_5			
		o-ClC_6H_4		a	75.7
		p-ClC_6H_4		a	134–135
38	$[(RO)_2PS_2Pb(C_6H_5)_3$	CH_3, CH_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9		a,b,c	
39	$[(RO)_2PS_2]_2Pb(C_6H_5)_2$	CH_3, C_2H_5, C_6H_5		a,b	
40	$[(RO)_2PS_2]_3As$	C_2H_5			
		C_2H_5			
		C_2H_5			52
		i-C_3H_7		a	
		i-C_3H_7		a,b	100
		s-C_4H_9			114

Physico-chemical and other reported data	Ref.
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	55
IR, PMR and electronic spectra	
Mol. wt., refractive index, dipole moment, conductivity,	55
IR, PMR and electronic spectra	
Photometric analysis	7
IR, Raman	159
X-ray analysis	193
^{31}P NMR, solvent effects	25
IR	196
PMR	47
^{31}P NMR, solvent effects	24, 25
Electronic spectra	166
Polarography	170
X-ray crystal structure	199
Electronic absorption spectra reflectance	10
Photometric analysis	7
IR	44
X-ray crystal structure	175
	66
Thermal decomposition	142
X-ray electron spectroscopy	81
Raman spectra	159
Extraction constants, metal exchange reaction	116
	66
	66
	200
	200
Polarography	170
Photometric analysis	7
Conductivity, mol. wt. IR, NMR (^{1}H, ^{31}P)	56
^{31}P NMR, solvent effects	25
Conductivity, mol. wt., IR, NMR (^{1}H, ^{31}P)	56
IR, NMR (^{1}H, ^{31}P)	56

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		$H_2C-CH(CH_2)_3CH_3$ (C$_2$H$_5$)			
		C_8H_{17}			
		C_8H_{17}			
		i-C_8H_{17}			
41	$[(s\text{-}C_4H_9O)_2PS_2]_2AsCl$	i-C_8H_{17}		a	147(sticky)
42	$(RO)_2PS_2As\langle O \rangle R'$	C_2H_5	$-CH_2CH_2-$	a	
		C_2H_5	$CH_3-CH-CH_2-$	a	
		C_2H_5	$(CH_3)_2-C-$ (CH_2) CH_3CH-	a	
		C_2H_5	$(CH_3)_2-C-$ $(CH_3)_2-C-$	a	
		n-C_3H_7	CH_2- CH_2-	a	
		n-C_3H_7	CH_3-CH- CH_2-	a	
		n-C_3H_7	$(CH_3)_2C-$ (CH_2) CH_3-CH-	a	
		n-C_3H_7	$(CH_3)_2C-$ $(CH_3)_2C-$	a	
		i-C_3H_7	CH_2- CH_2	a	
		i-C_3H_7	CH_3CH- CH_2-	a	
		i-C_3H_7	$(CH_3)_2C-$ (CH_2) CH_3CH-	a	

Physico-chemical and other reported data	Ref.
Raman spectra	159
Distribution coefficient, thermal stability	154
Mechanism of extraction by IR, UV	2
Thermal decomposition, search for selection extractant	5
Conductivity, mol. wt., IR, NMR (^1H, ^{31}P)	56
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^1H, ^{31}P)	57

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		i-C_3H_7	$(CH_3)_2C-$ | $(CH_3)_2C-$	a	
			CH_3CH_2- | CH_2-	a	
		C_6H_5	CH_2- | CH_2-	a	
		C_6H_5	$(CH_3)_2C-$ | CH_2- | CH_3CH	a	
		s-C_4H_9	$(CH_3)_2C-$ | $(CH_3)_2C-$	a	
43	$[(RO)_2PS_2]_3Sb$	C_2H_5			
		C_2H_5		a	55
		i-C_3H_7		a	
		i-C_3H_7		a	
		i-C_3H_7			79–80
		n-C_3H_7		b	Liquid at 0°C
		i-C_4H_9		b	
		C_5H_{11}		b	
		C_6H_{11}		b	
		$H_2C-CH(CH_2)_3CH_3$ | C_2H_5		b	
44	$[(C_5H_5O)_2PS_2]_nSb$	$n = 3,5$			
45	$[(RO)_2PS_2]_2SbCl$	C_2H_5		a,b	100
		i-C_3H_7		a,b	92
46	$[(i\text{-}C_3H_7O)_2PS_2]_2$	$Sb(CH_7C_3\text{-}i)$		a,b	76
47	$[(RO)_2PS_2]_3Bi$	C_2H_5		a,b	
				a,b	
				a	
		i-C_3H_7		a	
					67.8
		C_6H_5			
		$H_2C-CH(CH_2)_3CH_3$ | C_2H_5			
48	$[(RO)_2PS_2]_2Se$	CH_3		a	61–62
		C_2H_5			

Physico-chemical and other reported data	Ref.
Conductivity, mol. wt., IR and NMR (^{1}H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^{1}H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^{1}H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^{1}H, ^{31}P)	57
Conductivity, mol. wt., IR and NMR (^{1}H, ^{31}P)	57
Raman spectra	159
Conductivity, mol. wt., IR, NMR (^{1}H, ^{31}P)	56
	56
^{31}P NMR, solvent effects	25
	204
	204
	204
	204
	204
	204
Photometric analysis	7
Conductivity, mol. wt., IR, NMR (^{1}H, ^{31}P)	56
Conductivity, mol. wt., IR, NMR (^{1}H, ^{31}P)	56
Conductivity, mol. wt., IR, NMR (^{1}H, ^{31}P)	56
IR	44
Polarography	170
Photometric analysis	7
^{31}P NMR, solvent effects	25
Crystal structure (X-ray)	205
Gravimetric extraction by spectrophotometry	3
Gravimetric extraction by spectrophotometry	3
Metal exchange reaction extraction constants	116
IR	41
	185
Photometric analysis	7

TABLE 4 (continued)

Series no.	Compound	R	R′	Method of preparation	Melting point (b.p., °C mm^{-1})
		C_2H_5		[b]	
				[b]	87–88
		i-C_3H_7		[b]	
		C_6H_5			
49	$[(RO)_2PS_2]_2Te$	CH_3			
				[b]	
				[a]	90.5–91.5
		C_2H_5		[a]	65–66

[a] By reaction of organometal or metal halides with alkali metal dialkyldithiophosphates or dialkyldithiophosphoric acid. [b] By reaction of organometal or metal oxides, hydroxides, alkoxides, acetates, nitrates and sulphates with alkali metal dialkyldithiophosphates or

The X-ray structure of $KS_2P(OCH_3)_2$ determined by Coppens et al. [67] shows bond distances of 1.95, 1.65 and 1.60 Å for the P–S, P–O and O–C bonds respectively with a tetrahedral arrangement of the PS_2O_2 species. Potassium ions are present in an irregular 8-coordination sphere of dimethyldithiophosphate ligands. The structure of $KS_2P(OCH_2C_6H_5)_2$ is similar [68].

(ii) Alkaline earth metals (Mg, Ca and Ba)

Information on the above derivatives is rather scanty. The methods of preparation [25,64,73–77] adopted for these compounds are similar to those described above for derivatives of alkali metals.

Magnesium, calcium and barium dialkyldithiophosphates appear to be more stable than their alkali analogues. They are generally white solids with sharp melting points insoluble in common organic solvents as well as in water. These are generally polymeric in the solid state and a number of barium dialkyldithiophosphates [78] have been reported to form aggregates of up-to ten unit molecules. Thermal stability of these derivatives has been shown [79,80] to depend both upon the length of the alkyl chain and the nature of the metal.

Physico-chemical and other reported data	Ref.
	207, 208
	209
^{31}P NMR, solvent effects	25
Reaction and extraction	4
	4
IR	41
X-ray analysis	210
X-ray analysis	209
Photometric analysis	7

dialkyldithiophosphoric acids. [c] By metal–carbon bond cleavage by dialkyldithiophosphate ligands. [d] Special methods.

In the ^{31}P NMR spectra [25] of $M[S_2P(OCH(CH_3)_2)_2]_2$ (M = Mg, Ca and Ba), the appearance of two signals at 105–109 and 80 p.p.m. has been interpreted by Glidewell [25] to indicate the presence of both monodentate as well as bidentate dialkyldithiophosphate moieties in these derivatives.

A comparative study of the X-ray electronic spectra of $M[S_2P(OC_4H_9)_2]_2$ (M = Zn, Cd, Ba and Pb) and those of analogous dithiocarbamates and monothiophosphates has shown [81] that the binding energy of the inner level electrons of the metals in $M[S_2P(OC_4H_9)_2]_2$ and $M[O(S)P(OC_4H_9)_2]_2$ is higher than in $M[S_2CN(C_4H_9)_2]_2$ and the ionicity of the bond in $M[S_2CN(C_4H_9)_2]_2$ is lower than in $M[S_2P(OC_4H_9)_2]_2$ and $M[O(S)P(C_4H_9)_2]_2$ complexes.

(iii) Group IIB metals (Zn, Cd and Hg)

Compared to the alkaline earth analogues, dialkyldithiophosphates of group IIB metals have received greater attention. Zinc(II), cadmium(II) and mercury(II) derivatives have been prepared [65,82–105] by the reactions of oxides or chlorides of these metals with dialkyldithiophosphoric acids or their alkali metal salts in water or organic solvents. The acidity of the

solution appears to play a significant role in these reactions. For example, in slightly basic solutions, zinc(II) complexes of the type $Zn_4[S_2P(OR)_2]_6O$ are obtained in place of the normal $Zn[S_2P(OR)_2]_2$ compounds obtained in acidic solutions [106].

Dialkyldithiophosphates of these metals have been shown to be associated. In the solid state [107], zinc and cadmium complexes are dimeric whereas the mercury complexes are polymeric. In benzene solution, the complexes of zinc and mercury (and also lead) undergo monomer–dimer equilibrium while the corresponding cadmium complex is dimeric [78,108]. The molecular association of Zn(II) dialkyldithiophosphate complexes in benzene has been shown to be broken down in the presence of pyridine [109].

Mercury(I) dialkyldithiophosphate complexes are unstable and undergo disproportionation [65] yielding the mercury(II) complexes.

Complexation studies [110] of derivatives of mercury(II) with a number of related ligands have shown that their stability constants in 40% ethanol decrease in the order $(C_2H_5)_2P(S)S^- > (C_2H_5O)_2P(S)S^- > (C_2H_5)_2P(S)O^- > (C_2H_5O)_2P(S)O^-$. It has been observed that in the above solvent, mercury(II) forms HgL_3^- and HgL_4^{2-} type complexes with $(RO)_2PS_2H$ ($R = C_2H_5$, n-C_3H_7, i-C_3H_7 and n-C_4H_9) ligands.

In view of the extensive applications of zinc(II) dialkyldithiophosphates as oil additives, their reactions with peroxides and hydroperoxides [111–121] as well as with amines [109,122,123] have been investigated in detail under varying conditions and free radical mechanisms [115,124] have been suggested.

Purification of zinc(II) dialkyldithiophosphates by chromatographic methods has been the subject of several investigations [125–130]. Complex formation studies have been carried out employing polarographic techniques [131,132].

Thermal stabilities of dialkyldithiophosphate derivatives of main group IIB metals (mainly zinc) have been investigated [133–158] in detail. Depending on the nature of the ligand, decomposition of these derivatives has been shown to occur generally at high temperature (150–250°C) yielding volatile olefins, mercaptans, hydrogen sulphide and non-volatile polymeric residue. The mechanisms [133–143,157] of the formation of these products have also been discussed.

The effect of the metals Zn(II), Cd(II) and Hg(II) and the nature of the alkyl group on the rate of thermal decomposition of metal dialkyldithiophosphate were studied by Dickert and Rowe [142] at 155°C. In an autocatalytic thermal reaction, the rate of decomposition increases with increasing number of hydrogens on the β-carbon atom in the alkyl groups and with decreasing metal cation size. The effects of added reagents and

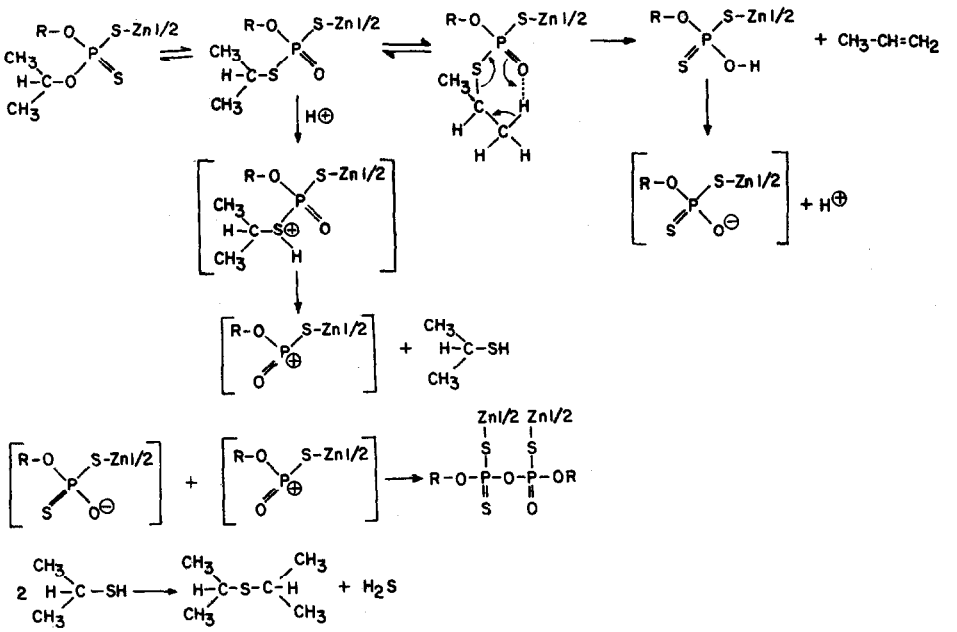


Fig. 2. The mechanism of thermal decomposition of zinc diisopropyldithiophosphate.

deuteration of the alkyl group on the thermal degradation process have also been studied. The mechanism includes isomerization followed by an intramolecular (*cis*) elimination as key steps to the formation of olefins. The mechanism of the thermal decomposition of $Zn[S_2P(O\ i\text{-}C_3H_7)_2]_2$ can be represented by the scheme shown in Fig. 2.

The Raman spectra of $(BuEtCH \cdot CH_2O)_2PS_2H$ and its salts with Zn(II), Cd(II), Tl(I), In(III), Sn(II), Pb(II), As(III), Sb(III) and Bi(III) etc. were investigated [159]. Only in the spectra of the ligand and the salts of cations with an external electronic structure of 18 + 2 (Zn(II) and Cd(II)), is a band at 500–700 cm^{-1} observed which can be assigned to the (P : S) in the ligand and asym(PSS) vibrations in the salts. The configuration of the external electronic shell of the metal plays an essential role in the appearance of the νasym(PSS) vibration.

The NMR spectral studies of the reactions of $Zn[S_2P(OR)_2]_2$ with tetraethylenepentamine show [61] a higher reactivity of dialkyldithiophosphates compared to diaryldithiophosphates. ^{31}P NMR spectral data for diisopropyldithiophosphates of zinc, cadmium and mercury in $CDCl_3$ show [25] chemical shift values in the range 94–96 p.p.m. indicating covalent bidentate behaviour of the ligand. Solvent effects on NMR spectral data have also been studied. In a recent investigation, Bond et al. [160] have shown that

dialkyldithiophosphate ligands attached to Cd and Hg are labile in solution at ambient temperature as indicated by ^{31}P, ^{113}Cd and ^{199}Hg NMR spectral data. A comparison with the corresponding dithiocarbamates showed stronger bonding with these latter ligands.

X-ray crystallographic studies of some zinc(II) [106,161], Cd(II) [108] and Hg(II) [162–164] dialkyldithiophosphates have been made. Substitution of one R group for another may lead to a change in structure. Thus, the diethyldithiophosphate complex of zinc is a polymer held by bridging dithiophosphate moieties while the corresponding diisopropyl derivative contains dimeric units.

The crystal and molecular structures of isomorphous zinc(II) and cadmium(II) diisopropyldithiophosphates depict [108] both as binuclear species in which each metal atom is coordinated with four sulphur atoms in a

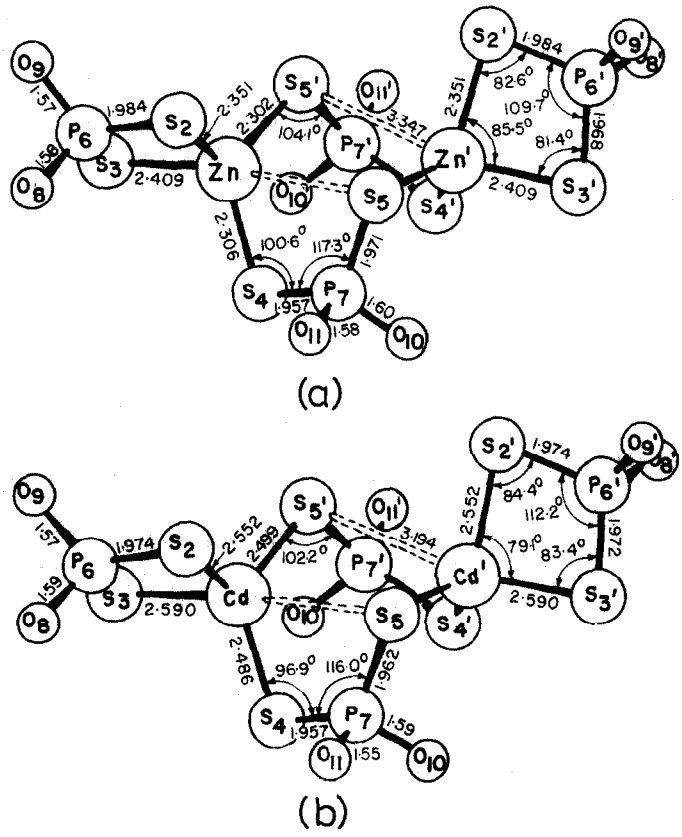


Fig. 3. Selected bond lengths and bond angles in (a) $Zn[S_2P(O\ i\text{-}C_3H_7)_2]_2$ and (b) $Cd[S_2P(O\ i\text{-}C_3H_7)_2]_2$ molecules.

distorted tetrahedral environment. Associated with each metal atom are two diisopropyldithiophosphate groups one of which functions as an intrachelating group bound wholly to one metal atom and the other functions as a bridging or interchelating group linking two monomeric molecules together to form the dimer. The "cradle" type configurations of these zinc and cadmium diisopropyldithiophosphates with selected bond lengths and bond angles can be shown by the structure given in Fig. 3.

Basic salts of formula $Zn_4[S_2P(OR)_2]_6O$ (R = n-C_4H_9, i-C_3H_7) resemble basic beryllium acetate in their structures [106].

In a recent crystal structure determination of $[Me_4N]Zn\{S_2P(OC_6H_4\text{-}Me\text{-}p)_2\}_3$, the anion was found to be distorted tetrahedral having two unidentate and one bidentate ligand moieties [161].

Structures of $Hg[S_2P(OR)_2]_2$ (R = i-C_3H_7 [162] and C_2H_5 [164]) have been elucidated by X-ray techniques. The derivative $Hg[S_2P(O\ i\text{-}C_3H_7)_2]_2$ has been shown to consist of helical chain polymers in which one dithiophosphate ligand behaves as bidentate and the other one is a bridging species linking two mercury atoms together. Each mercury atom is surrounded by five sulphur atoms: two at relatively short distances of 2.388 and

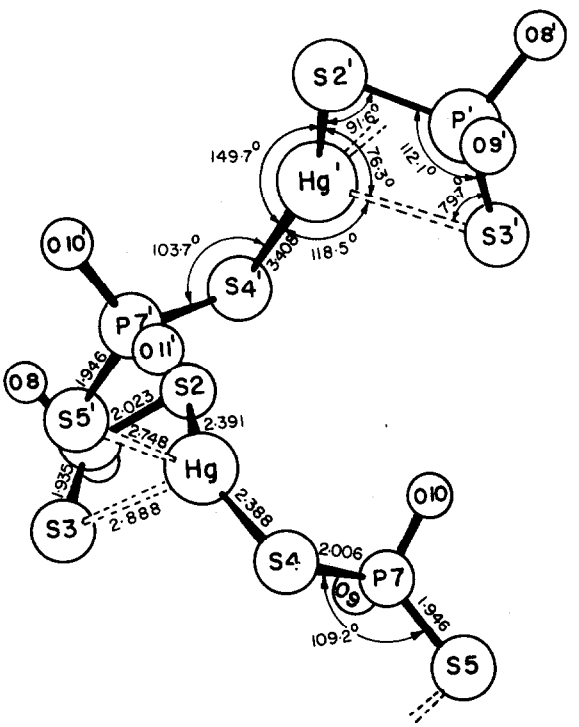


Fig. 4. Molecular structure of $Hg[S_2P(O\ i\text{-}C_3H_7)_2]_2$ with selected bond lengths and bond angles.

2.391 Å, two at intermediate distances of 2.748 Å (the polymeric bridge) and 2.888 Å and the remaining one making a van der Waals contact at 3.408 Å. The structure of this compound with selected bond distances and bond angles is shown in Fig. 4.

(iv) Group IIIA metals (Al, In and Tl)

Except for a patent by Sudek [165] claiming the synthesis and oil additive properties of mixed alkoxyaluminium(III) dialkyldithiophosphate derivatives $[(RO)_2PS_2]_nAl(OR')_{3-n}$ ($R = C_4H_9$, C_8H_{17}, $C_8H_{17}C_6H_4$, CH_3-c-C_6H_{11}; $R' = CH_3$, i-C_3H_7; $n = 1-3$), no work appears to have been published on dialkyldithiophosphate derivatives of aluminium.

Indium(III) [47,166], thallium(I) [45] and organothallium(III) [45,167–169] dialkyldithiophosphates have been prepared by the reactions of nitrates and chlorides of these metals with alkali-metal dialkyldithiophosphates or dialkyldithiophosphoric acids in benzene or alcoholic medium. For example, organothallium dialkyldithiophosphates have been obtained by the following routes [168]

$$RTlX_2 + 2(R'O)_2PS_2H \rightarrow RTl[S_2P(OR')_2]_2 + 2\,HX$$

$$R_3Tl + (R'O)_2PS_2H \rightarrow R_2TlS_2P(OR')_2 + RH$$

($R = C_2H_5$, C_6H_5; $R' = CH_3$, C_6H_5 and X = halogen, $O_2CCH(CH_3)_2$)

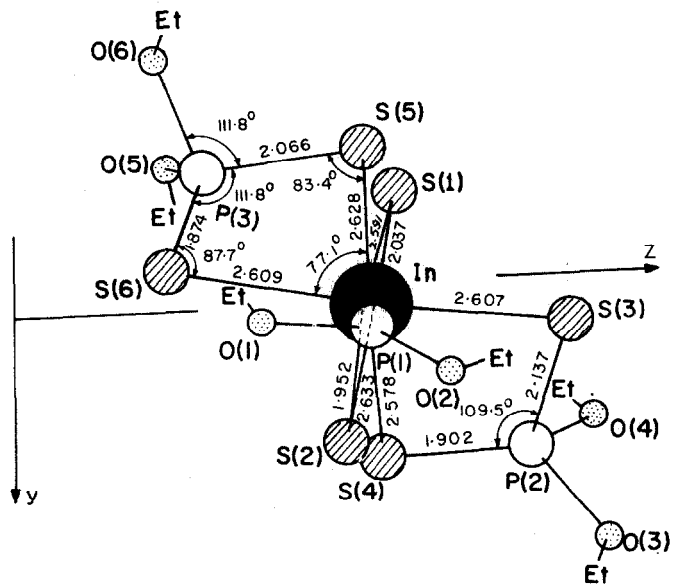


Fig. 5. Selected bond lengths and bond angles in the $In[S_2P(OEt)_2]_3$ molecule.

The $R_2TlS_2P(OR')_2$ compounds [45] are not ionic in the solid state, but evidence for species like Me_2Tl^+ has been obtained in acetonitrile and dimethylformamide solutions of $Me_2TlS_2P(OR)_2$ derivatives. Spectral studies indicate that dialkylthallium compounds are dimeric with D_{2h} symmetry.

Polarographic determination of some metals such as zinc, cadmium, thallium, lead, bismuth and arsenic by extraction with dialkyldithiophosphoric acids has also been carried out [170]. The electroreduction of these metals appeared to be inhibited by products of the corresponding complexes absorbed on the electrode.

On the basis of its ^{31}P NMR chemical shift value (93 p.p.m.), thallium(I) diisopropyldithiophosphate has been proposed to have $>P\langle\begin{matrix}S\\S\end{matrix}\rangle Tl$ type bonding [25].

The crystal structure of only one compound of this class, $In[S_2P(OEt)_2]_3$ has been investigated [171]. It has C_{3v} symmetry and unequal P–S bond lengths within each ligand. The average bond lengths of P–S (shorter), P–S (longer), P–O, C–O and In–S are 1.91, 2.08, 1.60, 1.50 and 2.61 Å respectively and the structure is shown in Fig. 5.

(v) Group IVA metals (Si, Ge, Sn and Pb)

Compounds containing the grouping $Si–S–P(S)(OR)_2$ were synthesized [26,172–175] by different methods which can be represented by

$$(CH_3)_3SiCl + (RO)_2PS_2NH_4 \rightarrow (CH_3)_3SiS_2P(OR)_2 + NH_4Cl$$

$$[(CH_3)_3Si]_2NH + 3\,(RO)_2PS_2H \rightarrow 2\,(CH_3)_3SiS_2P(OR)_2 + (RO)_2PS_2NH_4$$

$$(CH_3)_3SiNHR + 2\,(RO)_2PS_2H \rightarrow (CH_3)_3SiS_2P(OR)_2 + (RO)_2PS_2NH_3R$$

$$(CH_3)_3SiNCS + 2\,(RO)_2PS_2H \rightarrow (CH_3)_3SiS_2P(OR)_2 + (RO)_2PS_2C(S)NH_2$$

The Si–S bond in these esters is quite reactive as shown by their reactions with bromine [176] and alkylene oxides [177].

Mehrotra and co-workers have recently synthesized [26] organosilicon and organogermanium dialkyldithiophosphates $R_{4-n}M[S_2P(OR')_2]_n$ ($R = CH_3$, C_2H_5, n-C_4H_9, $C_6H_5CH_3$, C_6H_5; $R' = C_2H_5$, n-C_3H_7, i-C_3H_7, C_6H_5; M = Si(IV), Ge(IV) and $n = 1,2$) by the following route

$$R_{4-n}MCl_n + n\,(R'O)_2PS_2Na \rightarrow R_{4-n}M[S_2P(OR')_2]_n + n\,NaCl\downarrow$$

Syntheses and biocidal character of organotin(IV) and tin(IV) dialkyldithiophosphates had been reported only in patent literature [178–192] up to 1976. Recently, Mehrotra and co-workers [51,52,55] and Zuckerman and co-workers [53,54] have described the synthesis of organotin(IV) dial-

kyldithiophosphates by the following routes

$$R_{4-n}SnCl_n + n(R'O)_2PS_2H \rightarrow R_{4-n}Sn[S_2P(OR')_2]_n + nHCl\uparrow$$

$$R_{4-n}SnCl_n + n(R'O)_2PS_2M \rightarrow R_{4-n}Sn[S_2P(OR')_2]_n + n\,MCl\downarrow$$

$$R_{4-n}SnO_{\frac{n}{2}} + n\,(R'O)_2PS_2H \rightarrow R_{4-n}Sn[S_2P(OR')_2]_n + \frac{n}{2}H_2O$$

($R = CH_3$, C_2H_5, n-C_4H_9, C_6H_5; $R' = C_2H_5$, n-C_3H_7, i-C_3H_7, C_6H_5; M = Na, NH_4, $Pb_{0.5}$; $n = 1-3$) .

According to the latter workers [53], the synthesis of $(C_6H_5)_3SnS_2P(O\ i\text{-}C_3H_7)_2$ by the sodium salt method was accompanied by the cleavage of the phenyl–tin bond to produce the bis compound i.e. $(C_6H_5)_2Sn[S_2P(O\ i\text{-}C_3H_7)_2]_2$. These workers have further shown that triphenyltin(IV) diisopropyldithiophosphate can be obtained by a tin–carbon bond cleavage reaction

$$(C_6H_5)_4Sn + (i\text{-}C_3H_7O)_2PS_2H \rightarrow (C_6H_5)_3SnS_2P(O\ i\text{-}C_3H_7)_2 + C_6H_6$$

1,2-Bis(dimethyldithiophosphato)tetramethylditin was obtained from the corresponding dichlorocompound by the sodium salt method [193].

Eremeeva and Vorsina [159] and Zuckerman and co-workers [194,195] have described the synthesis of compounds of the type $Sn[S_2P(OR)_2]_2$ by the following reactions

$$SnX_2 + 2\,(RO)_2PS_2H \rightarrow Sn[S_2P(OR)_2]_2 + 2\,HX$$

($R = C_6H_5$, $CH_2CH(C_2H_5)(C_4H_9)$; X = Cl, OCH_3)

The reactions of $[(i\text{-}C_3H_7O)_2PS_2]_2$ with SnX_2 (X = Cl, Br) appear [196] to yield 1 : 1 adducts, which undergo electron distribution to yield derivatives, $[(i\text{-}C_3H_7O)_2PS_2]_2SnX_2$, in which the tin atom is in a hexacoordinated tetravalent form.

Very similar methods have been used for the synthesis of lead(II) [24,47,197–199] and organolead(IV) [200] dialkyldithiophosphates.

The properties of dialkyldithiophosphates of Group IVA elements show gradation of the expected type. Organosilicon(IV), organogermanium(IV) and organotin(IV) dialkyldithiophosphates are all monomeric in nature. Whereas the former two derivatives are generally liquids (at ambient temperatures) which can be volatilized under reduced pressure, some of the organotin(IV) derivatives are powdery solids with sharp melting points. Trialkyl- and dialkyltin(IV) derivatives can also be volatilized but the monoalkyltin analogues appear to decompose when attempts are made to volatilize these. Lead compounds are generally white powdery solids and some of these show associated nature [78] in the solid state.

Electronic spectra [26,51,52,55] of organo-silicon(IV), -germanium(IV) and -tin(IV) dialkyldithiophosphates show a broad strong band at ca. 224 nm which has been assigned to intraligand $\pi-\pi^*$ electronic transitions.

Raman spectral studies of compounds $M[S_2P(OCH_2CH(Et)Bu)_2]_n$ (M = Sn(II), As(III), Sb(III), Pb(II) and Bi(III)) have also been carried out [159]. The Raman spectra of As(III), Sb(III), Sn(II), Pb(II) and Bi(III) 2-ethylhexyldithiophosphates formed a series in which the degree of depolarization increased, integral and relative intensities of the band at 500–700 cm^{-1} decreased, and the first ionization potential decreased from As to Bi.

The signals of the methyl protons bonded to tin in methyltin(IV) dialkyldithiophosphate derivatives in ^1H NMR spectra appear [51,52,55] as a sharp singlet at 0.9–1.8 p.p.m. with double satellite resonances due to ^{117}Sn and ^{119}Sn isotopes. In the case of dimethyltin(IV) dialkyldithiophosphates [52], the methyl signals are markedly shifted to the lower field at 1.9 p.p.m. compared to the positions in the corresponding trimethyltin dialkyldithiophosphates (δ = 0.9 p.p.m.) [51]. This is due to the strong deshielding effect of dithio ligands. On the basis of tin–proton coupling constants the coordination number of the tin(IV) atom has also been established [51,52,55]. For example, in tri-, di- and monomethyltin(IV) dialkyldithiophosphates, the coupling constants ($^{119}Sn–C–^1H$) fall in the range of 58 Hz in the first case (four coordination) and 80 and 107 Hz in the latter two cases (coordination number higher than four). In pyridine solution, the coordination number of the central tin atom in trimethyltin(IV) diisopropyldithiophosphate has been shown [53] to increase.

As mentioned earlier, Glidewell [25] and other workers [26,52,55] have correlated the chemical shift values with the type of bonding. Accordingly, the diisopropyldithiophosphate moiety in $M[S_2P(O\ i\text{-}C_3H_7)_2]_4$ (M = Si(IV), Ge(IV) or Sn(IV)) and $Pb[S_2P(O\ i\text{-}C_3H_7)_2]_2$ have been given monodentate–covalent and bidentate-covalent binding modes respectively [25]. In the latter case, solvent effects on chemical shifts in deuterochloroform, benzonitrile, acetone, tetrahydrofuran and pyridine have also been studied.

With the help of dipole moments, the geometries of organotin(IV) dialkyldithiophosphates have also been discussed [51,52,55]. The values fall in the range 3.50–4.00 D except in the case of $MeSnCl_2S_2P(OR)_2$ for which it was found to be ca. 7.90 D indicating *cis* positions of chlorine atoms [55].

Mössbauer spectral studies have been carried out for some organotin(IV) dialkyldithiophosphates by Zuckerman and co-workers [53,54]. The values of isomeric shifts (IS), quadrupole splittings (QS) and ρ(QS/IS) were used to define the coordination number of the central tin atom. The Mössbauer data and structural assignments of a few selected compounds are summarized in Table 5.

Mass spectral studies showing the fragmentation pattern of organotin(IV) dialkyldithiophosphates have also been discussed [53,54]. The major pathway for decomposition of trimethyltin(IV) diisopropyldithiophosphate appears to

TABLE 5

Mössbauer spectral parameters of a few organotin(IV) dialkyldithiophosphates

Serial no.	Compound	IS (mms^{-1})	QS (mms^{-1})	(QS/IS) ρ	Structural assignments
1	$(C_6H_5)_3SnS_2P(OR)_2$ R = CH_3, C_2H_5, i-C_3H_7, n-C_3H_7, i-C_4H_9, C_6H_5)	1.27–1.31	2.07–2.32	1.63–1.77	Tetrahedral with four-coordinated tin
2	(c-$C_6H_{11})_3SnS_2P$(O i-$C_3H_7)_2$	1.52	2.56	1.68	Tetrahedral with four coordinated tin
3	$(CH_3)_3SnS_2P(OR)_2$ (R = C_2H_5, i-C_3H_7)	1.35–1.38	2.92–3.09	2.16–2.24	Trigonal bipyramidal with five coordinated tin
4	$(C_6H_5)_2Sn[S_2P(OR)_2]_2$ (R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, i-C_4H_9, C_6H_5)	1.35–1.47	3.34–3.67	2.18–2.62	*trans*-Diphenyltin configuration in an octahedral geometry with six coordinated tin
4	$(CH_3)_2Sn[S_2P(OR)_2]_2$ (R = CH_3, C_2H_5)	1.43–1.44	3.34–3.35	2.32–2.34	*trans*-Dimethyltin in an octahedral geometry with six coordinated tin

be by sequential loss of the alkene from the dithiophosphate group after initial loss of CH_3 from tin. This pathway is also applicable to methyltin(IV) diethyldithiophosphates. On the other hand, the methyltin(IV) dimethyldithiophosphates cannot eliminate the alkene since it has no available β-hydrogen for abstraction. Therefore, the fragmentation of these particular compounds appears to occur by loss of methyl radicals from tin and by loss of the entire dithiophosphate group. Most of the high abundance fragments are even-electron ions [53]. Odd-electron ions fragment to give high-abundance even-electron ions by loss of radicals such as $CH_3^{\cdot}$ or $(RO)_2PS_2^{\cdot}$. The cracking pattern of $Me_3SnS_2P(OR)_2$ (R = CH_3, C_2H_5, i-C_3H_7) can be shown by the scheme in Fig. 6.

The fragmentation of dimethyltin dialkyldithiophosphates [54] was also observed to be of a similar type to that shown in Fig. 6.

The crystal structures of $(C_6H_5)_3SnS_2P(OC_2H_5)_2$ [201], $(C_6H_5)_2Sn[S_2P(OC_2H_5)_2]_2$ [202], $(C_6H_5)_2Sn[S_2P$(O i-$C_3H_7)_2]_2$ [203], $Sn[S_2P(OC_6H_5)_2]_2$ [193], $Pb[S_2P(OC_2H_5)_2]_2$ [199] and $Pb[S_2P$(O i-$C_3H_7)_2]_2$ [197,198] have been determined by X-ray analysis.

In triphenyltin(IV) diethyldithiophosphate, the molecule contains [201] a four-coordinated tin atom with a monodentate dithiophosphate ligand; an

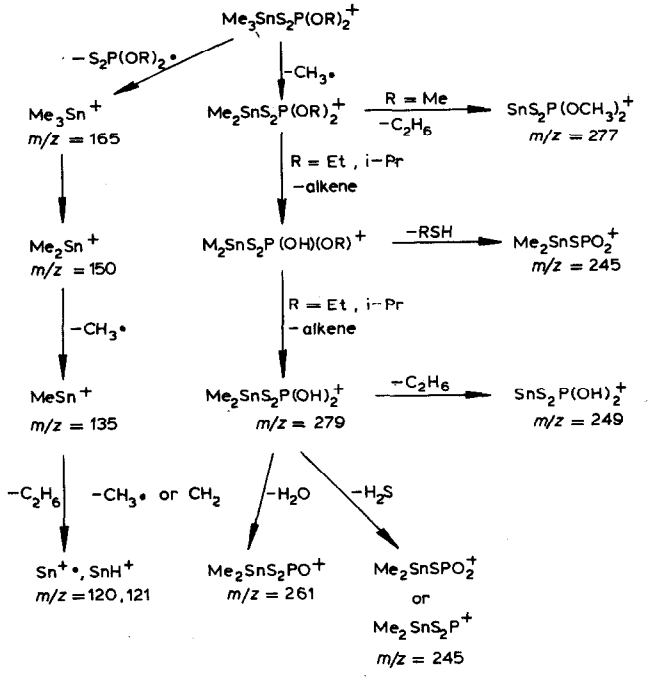


Fig. 6. Fragmentation pattern of $(CH_3)_3SnS_2P(OR)_2$ (R = CH_3, C_2H_5 or i-C_3H_7).

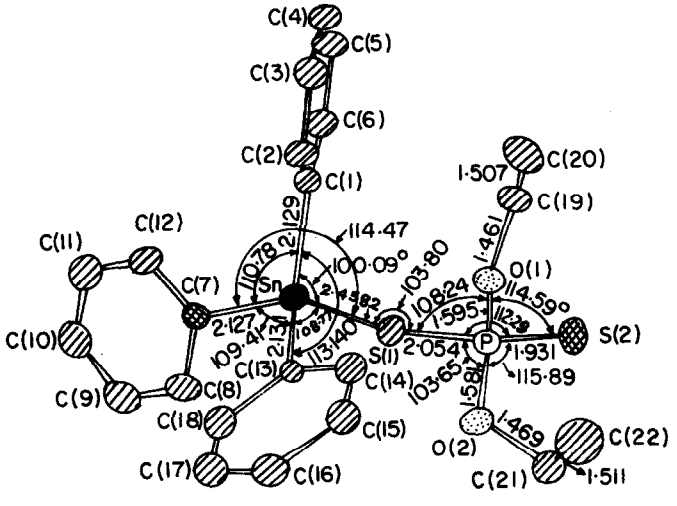


Fig. 7. Molecular structure of triphenyltin(IV) diethyldithiophosphate.

unusual example of a dithiophosphate moiety which is neither chelating nor bridging in spite of the larger size of tin atom (cf. the monodentate behaviour of these ligands in the case of silicon and germanium is ascribed mainly to steric factors). The structure of the molecule with selected bond distances and bond angles is given in Fig. 7.

Zuckerman and co-workers [53] have suggested a similar structure for the corresponding isopropyl derivatives on the basis of the identity of their Mössbauer spectra with those of the ethyl analogue.

The structure of diphenyltin(IV) diethyldithiophosphate [202] is octahedral with chelating, anisobidentate dithiophosphate ester ligands in which two of the tin–sulphur distances are 2.48, 2.49 Å and the other two are 3.20, 3.23 Å. The diphenyl system exhibits a C–Sn–C angle of 135° about the six-coordinated tin atom, with the four sulphur atoms in equatorial plane. On the other hand, the crystal structure of diphenyltin(IV) diisopropyldithiophosphate adopts [203] a *trans* octahedral polymeric configuration which is extremely symmetrical with tin–sulphur distances of 2.7 Å and an angle of 180° in the diphenyl system. The structure is given in Fig. 8.

Tin(II) diphenyldithiophosphate [194] is a bicyclic dimer held together in part by η^6-C_6H_5 to tin(II) lone-pair interactions. This dimer is unusual, however, for two reasons. Firstly, this is the only example of an η^6-C_6H_5 main group metal π-bond, and secondly, the only known example of such an interaction contributing to the formation of dimer from the constituent

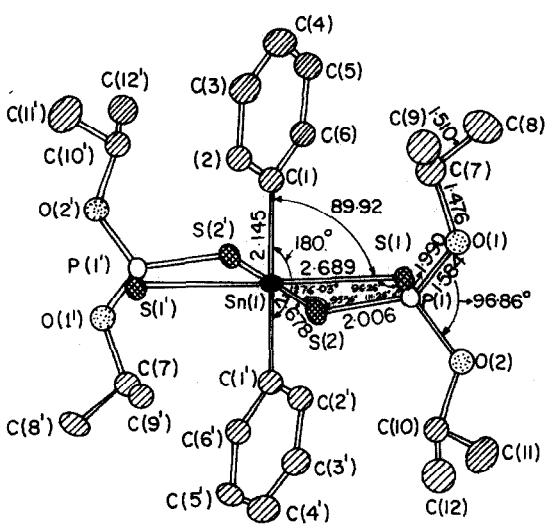


Fig. 8. Molecular structure of diphenyltin(IV) diisopropyldithiophosphate.

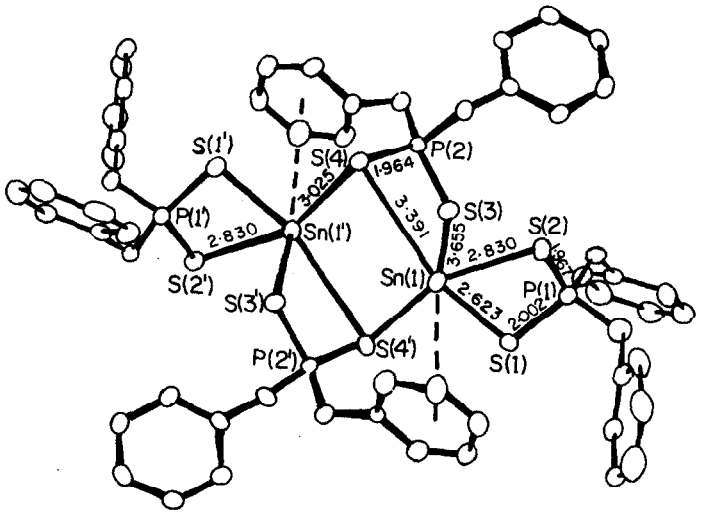


Fig. 9. Molecular structure of tin(II) diphenyldithiophosphate with selected bond lengths and bond angles.

monomers. The structure with selected bond lengths and bond angles can be represented by Fig. 9.

The above structure (Fig. 9) is in contrast with that adopted by lead(II) diethyldithiophosphate in which [199] lead atoms are chelated in a monomeric derivative while in its diisopropyl analogue the metal atom is coordi-

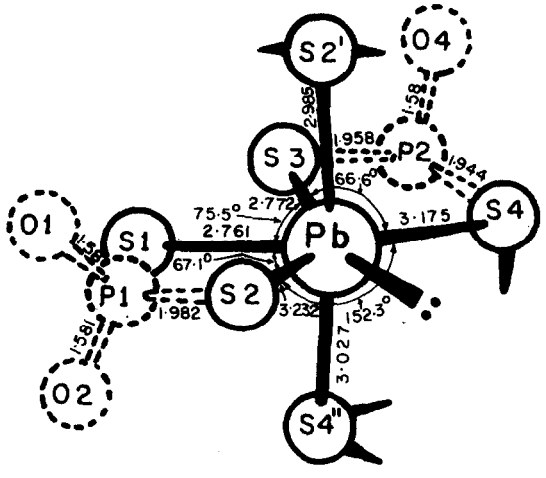


Fig. 10. Molecular structure of lead(II) diisopropyldithiophosphate.

nated by six sulphur atoms, two of which are bonded intermolecularly to give a polymeric lattice.

The polymeric structure of lead(II) diisopropyldithiophosphate [198] is shown in Fig. 10. In this structure each lead atom is surrounded by six sulphur atoms, two at relatively short distances of 2.766 Å, two at intermediate distances of 3.011 Å and two at 3.20 Å. There are fourteen electrons (seven pairs) in the valence shell of lead, of which six pairs are bonding and the last one is a stereochemically active lone pair. The resulting configuration closely approximates an irregular pentagonal bipyramid in which the lone pair occupies an equatorial position.

(vi) Group VA metals (As, Sb and Bi)

The dialkyldithiophosphate derivatives of arsenic, antimony and bismuth have been synthesized [56,57,204,205] by the reactions of ammonium or alkali metal dialkyldithiophosphates or acids themselves with chlorides, oxides or alkoxides of these metals. Recently, Mehrotra and co-workers [56,57] have synthesized compounds of arsenic and antimony(III) by the following routes and characterized them by conductance measurements, molecular weight determinations, IR, NMR (^{1}H and ^{31}P) and electronic spectral studies.

$$M_2O_3 + 6\ (i\text{-}C_3H_7O)_2PS_2H \rightarrow 2[(i\text{-}C_3H_7O)_2PS_2]_3M + 3\ H_2O$$

$$MX_3 + 3\ (i\text{-}C_3H_7O)_2PS_2H \rightarrow [(i\text{-}C_3H_7O)_2PS_2]_3M + 3\ HX$$

(M = As, Sb; X = O i-C_3H_7, Cl)

$$MCl_3 + 3(RO)_2PS_2M' \rightarrow [(RO)_2PS_2]_3M + 3\ M'Cl\downarrow$$

(M = As, Sb; M′ = Na, NH_4; R = C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9, C_6H_5)

$$3 - n(i\text{-}C_3H_7O)_3Sb + n[(i\text{-}C_3H_7O)_2PS_2]_3Sb \rightarrow 3[(i\text{-}C_3H_7O)_2PS_2]_nSb(O\ i\text{-}C_3H_7)_{3-n}$$

(n = 1,2)

$$G\langle{}^{O}_{O}\rangle AsCl + (RO)_2PS_2M \rightarrow G\langle{}^{O}_{O}\rangle AsS_2P(OR)_2 + MCl\downarrow$$

(G = $-CH_2CH_2-$, $-(CH_3)CHCH_2-$, $-(CH_3)_2CC(CH_3)_2-$, $-(CH_3)_2CCH_2CH(CH_3)-$, $-CH_2CH{=}CHCH_2-$; R=C_2H_5, n-C_3H_7, i-C_3H_7, s-C_4H_9; M = Na, NH_4, $Pb_{0.5}$)

Day et al. [206] have determined the X-ray crystal structure of $Sb[S_2P(OEt)_2]_3$ which may be described as a distorted capped octahedron with a stereochemically active lone pair in the capping position.

The crystal structure of Bi(III) diisopropyldithiophosphate $Bi[S_2P$-

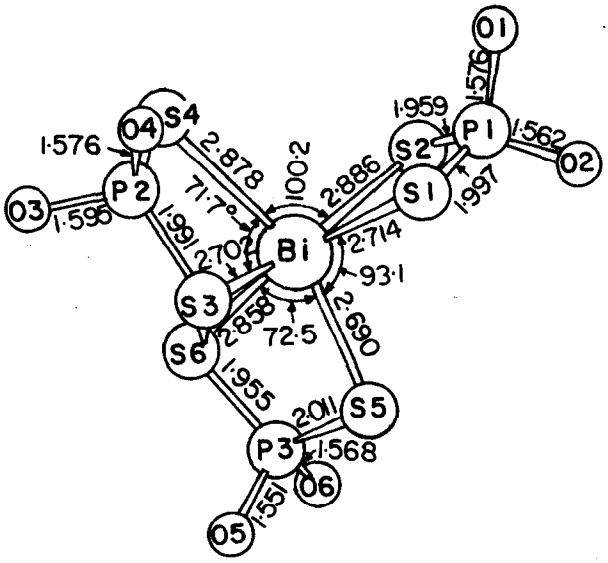


Fig. 11. Molecular structure of bismuth(III) diisopropyldithiophosphate.

$(O\ i\text{-}Pr)_2]_3$ has been investigated by Lawton et al. [205] in which the bismuth ion is coordinated to three ligands in a pseudotrigonally distorted octahedral environment displaying C_{3v} symmetry. Stretching and bending deformations within the BiS_6 group are consistent with the apportioning of fourteen electrons (seven pairs in the valence shell of bismuth, of which six pairs are bonding and one is a stereochemically active lone pair. The three Bi–S bonds adjacent to the lone pair are longer (averaging 2.874 Å) than the three (averaging 2.702 Å) most remote from the lone pair. Interligand angles between the longer bonds are greater (at 99.9°) than those between the shorter bonds (91.2°), whereas intraligand S–Bi–S angles average only 72.0° as dictated by the ligand bite. The relatively small size of this bite (3.28 Å), which is markedly shorter than the 3.70 Å van der Waals radius sum, leaves enough interligand room to allow the stereochemical activity of the lone pair of electrons. The structure is given in Fig. 11.

(vii) Group VIA metals (Se and Te)

The compounds, $M[S_2P(OR)_2]_2$ ($M = Se$ or Te, $R = CH_3$, C_2H_5) have been synthesized by the reduction of M(IV) oxides by Ni(II) dialkyldithiophosphates [207,208] or by adding [209] aqueous solutions of the alkali dialkyldithiophosphates to hydrochloric acid solution of Te(IV) and

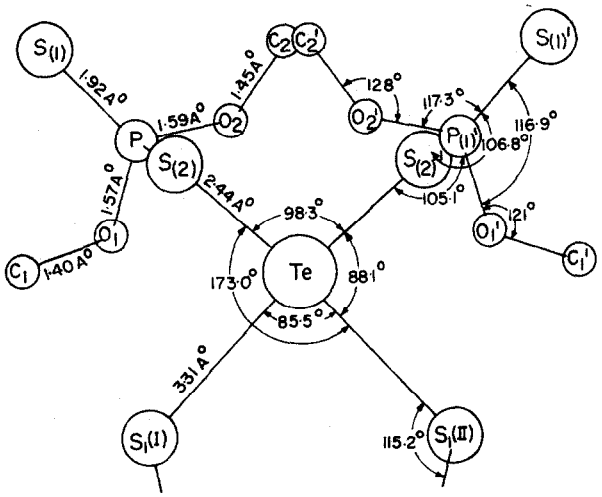


Fig. 12. Molecular structure of tellurium(II) dimethyldithiophosphate.

Se(IV) at room temperature

$$2\,[(RO)_2PS_2]_2Ni + H_2MO_3 + 4\,HCl \rightarrow M[S_2P(OR)_2]_2 + 2\,NiCl_2 + 3\,H_2O + [(RO)_2PS_2]_2$$

$$4\,(RO)_2PS_2Na + H_2MO_3 + 4HCl \rightarrow M[S_2P(OR)_2]_2 + 4\,NaCl + 3\,H_2O + [(RO)_2PS_2]_2$$

The dialkyldithiophosphate derivatives of Se(II) and Te(II) are orange to yellow solids with sharp melting points, soluble in common organic solvents. Their physicochemical properties such as volatility, molecular association, electronic, infrared and nuclear magnetic resonance spectral studies, to our knowledge, have not yet been studied.

An X-ray crystal structure study [209,210] of $Te[S_2P(OCH_3)_2]_2$ reveals a square planar TeS_4 group in a polymeric system and the molecular structure is shown in Fig. 12. The molecule contains a $(CH_3O)_2\overset{\|}{P}(S)-S-Te-S-\overset{\|}{P}(S)(OCH_3)_2$ chain in the *trans* form, with a STeS/TeSP dihedral angle of 90.7°. Other molecular dimensions are: Te–S = 2.44 Å; P–S = 1.92 and 2.09 Å; P–O = 1.57 and 1.59 Å; S_2–Te–S_2 = 98.3°. The molecules are mounted together by weak intermolecular Te · · · S bonds of length 3.31 Å. Each tellurium atom participates in two such bonds at a S–Te–S angle of 85.5°.

REFERENCES

1 J.R. Wasson, G.M. Woltermann and H.J. Stoklosa, Fortschr. Chem. Forsch., 35 (1973) 65.

2 I.S. Levin, V.V. Sergeeva and I.A. Vorshina, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1975) 107; Chem. Abstr., 83 (1979) 66255g.
3 A. Shishkov and D. Atanasova: Nauchni, Tr.- Plovdivski Univ., 13 (1975) 209; Chem. Abstr., 89 (1978) 36020h.
4 A. Shishkov, B. Atanasova and A. Georgieva, Nauchni Tr.- Plovdivski Univ., 13 (1975) 199; Chem. Abstr. 89 (1978) 49545h.
5 G.A. Marinkina, I.L. Kotlyarevskii and I.S. Levin, Zh. Prikl. Khim., 50 (1977) 427; Chem. Abstr., 86 (1977) 146568p.
6 N.A. Ulakhovich, G.K. Budnikov and N.K. Shakurova, Zh. Anal. Khim., 35 (1980) 1081; Chem. Abstr., 93 (1980) 178882x.
7 H. Bode and W. Arnswald: Z. Anal. Chem., 185 (1962) 99; Chem. Abstr., 57 (1962) 1515b.
8 M.I. Ivanyutin: Org. Reagenty Anal. Khim. Korroz. Met. Uchebn. Eksp., (1973) 42; Chem. Abstr., 83 (1975) 125659a.
9 M.I. Ivanyutin: Org. Reagently Anal. Khim. Korroz. Met. Uchebn. Eksp., (1973) 50; Chem. Abstr., 83 (1975) 125660k.
10 L.M. Kurashvili, and N.A. Zavorokhina: Zh. Prikl. Spektrosk., 24 (1976) 938; Chem. Abstr., 85 (1976) 101513e.
11 J. Madar, Ropa Uhlie, 18 (1976) 72; Chem. Abstr., 86 (1977) 6960k.
12 K.N. Bagdasarov, V.D. Chigirintsev, V.K. Chebotarev, Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol., 20 (1977) 373; Chem. Abstr., 87 (1977) 126564b.
13 N.A. Ulakhovich, G.K. Budnikov, I.V. Postnova and N.K. Shakurova, Zavod. Lab., 46 (1980) 587; Chem. Abstr., 93 (1980) 125128z.
14 P. Kozak and V. Rabl, Sb. Vys. Sk. Chem.-Technol. Praze, Technol. Paliv, D39 (1978) 141; Chem. Abstr., 93 (1980) 134697m.
15 M.M. Fialko, A.A. Fufaev and A.N. Balashova, Khim. Tekhnol. Topl. Masel, (1980) p. 37; Chem. Abstr. 93 (1980) 242248z.
16 W. Szczepaniak and K. Ren, Chem. Anal., 25 (1980) 449; Chem. Abstr., 94 (1981) 408015s.
17 K. Meyer, K. Homann and H. Berndt, Vide, Couches Minces, 201 (1980) 463; Chem. Abstr., 94 (1981) 86765d.
18 V.S. Chigirintsev and V.K. Chebotarev, U.S.S.R. Pat. No., 771535 (1980); Chem. Abstr., 94 (1981) 95377f.
19 W.M. LeSuer and H.J. Dunn, Fr. Demande, 2209769 (1974); Chem. Abstr., 82 (1975) 155758v.
20 W.M. LeSuer and H.J. Dunn, S. African Pat. No., 7308713 (1975); Chem. Abstr., 83 (1975) 205973e.
21 G.H. Sin and G.S. Ryom, Hwahak Kwa Hwahak Kongop, 17 (1974) 234; Chem. Abstr., 82 (1975) 124652b.
22 L. Carius, Ann. Chem. Pharm. 112 (1859) 119; 180 (1861) 289.
23 P.S. Pishchimuka, J. Russ. Phys. Chem. Soc., 56 (1925) 11.
24 T.W. Mastin, G.R. Norman and E.A. Weilmuenster, J. Am. Chem. Soc., 67 (1945) 1662.
25 C. Glidewell, Inorg. Chim. Acta, 25 (1977) 159.
26 B.P. Singh, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met.-Org. Chem., 12 (1982) 105.
27 L. Almasi, A. Hantz and L. Paskucz, Acad. Repub. Pop. Rom., 12 (1961) 291.
28 L.C. Thomas and R.A. Chittenden, Chem. Ind. (London), (1961) 1913.
29 L. Almasi, Acad. Repub. Pop. Rom., 13 (1962) 109.
30 L. Almasi and A. Hantz, Acad. Repub. Pop. Rom., 13 (1962) 229.

31 L. Almasi, A. Hantz and L. Paskucz, Acad. Repub. Pop. Rom., 13 (1962) 245.
32 J. Rockett, Appl. Spectrosc., 16 (1962) 39.
33 L. Almasi and L. Paskucz, J. Prakt. Chem., 19 (1963) 138.
34 A.F. Vasilev, Zh. Obshch. Khim., 33 (1963) 874.
35 R. Ripan, I. Eger and C. Mirel, Rev. Chim., Acad. Rep. Pop. Roum., 8 (1963) 163.
36 R.S. Edmundson, Tetrahedron, 20 (1964) 2781.
37 R.A. Chittenden and L.C. Thomas, Spectrochim. Acta, 20 (1964) 1679.
38 L.C. Thomas and R.A. Chittenden, Spectrochim. Acta, 20 (1964) 489; Chem. Abstr., 60 (1964) 8783.
39 G.I. Balotova, G.G. Kotova, K.I. Zimina and V.I. Isagulyants, Izv. Vyssh. Uchebn. Zaved., Neft Gaz, 8 (1965) 62; Chem. Abstr., 63 (1965) 6897b.
40 G.I. Balotova, G.G. Kotova, K.I. Zimina and V.I. Isagulyants, Zh. Prikl. Khim., 38 (1965) 1580; Chem. Abstr., 63 (1965) 13028.
41 S. Husebye, Acta Chem. Scand., 19 (1965) 774.
42 K.I. Zimina, G.G. Kotova, P.I. Sanin, V.V. Sher and G.N. Kuzmina, Neftekhimiya, 5 (1965) 629.
43 L.C. Thomas, Proc. 12th Spectrosc., Colloq. Int. Exeter, 1965, p. 672.
44 D.M. Adams and J.B. Cornell, J. Chem. Soc. A, (1968) 1299.
45 F. Bonati and G. Minghetti, Inorg. Chim. Acta, 3 (1969) 161.
46 D.E.C. Corbridge, Topics Phosphorus Chem., 6 (1969) 235.
47 G.M. Woltermann and J.R. Wasson, Inorg. Nucl. Chem. Lett., 6 (1970) 475.
48 D.C. Pantaleo and R.C. Johnson, Inorg. Chem., 10 (1971) 1298.
49 L.C. Thomas, Interpretation of the Infrared Spectra of Organophosphorus Compounds, Heyden, New York, 1974.
50 E.I. Markova, G.N. Kuzmina, L.G. Khanakova, V.V. Sher and P.I. Sanin, Neftekhimiya, 15 (1975) 311; Chem. Abstr., 83 (1975) 68386z.
51 B.P. Singh, G. Srivastava and R.C. Mehrotra, J. Organomet. Chem., 171 (1979) 35.
52 B.P. Singh, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met.-Org. Chem., 10 (1980) 359.
53 J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, G. Guta and D. Ruse, Inorg. Chem., 19 (1980) 1662.
54 J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, M. Curtui, C. Guta and D. Ruse, Inorg. Chem., 19 (1980) 2861.
55 B.P. Singh, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met-Org. Chem., (August 1983) in press.
56 H.P.S. Chauhan, G. Srivastava and R.C. Mehrotra, Polyhedron, 2 (1983) 359.
57 H.P.S. Chauhan, G. Srivastava and R.C. Mehrotra, Synth. React. Inorg. Met.-Org. Chem., 11 (1981) 565.
58 P.A. Willermet, L.R. Mahoney and C.M. Bishop, ASLE Trans., 23 (1980) 217; Chem. Abstr., 93 (1980) 242241.
59 I.A. Lapin, Yu.V. Kolodyazhnyi, N.N. Tsapkova, E.F. Bugerenko and O.A. Osipov, Zh. Obshch. Khim., 51 (1981) 2179; Chem. Abstr., 96 (1982) 52400g.
60 C.K. Tseng and J.H.H. Chan, Tetrahedron Lett., (1971) 699.
61 A.I. Kupreev, A.B. Vipper and V.N. Baumann, Khim. Tekhnol. Topl. Masel, 18 (1973) 51; Chem. Abstr., 80 (1974) 103361z.
62 J.H. Fletcher, J.C. Hamilton, I. Hechenbleikner, E.I. Hoegberg, B.J. Sertl and J.T. Cassaday, J. Am. Chem. Soc., 72 (1961) 2461.
63 M.G. Imaev, Zh. Obshch. Khim., 35 (1965) 1864; Chem. Abstr., 64 (1966) 1991h.
64 G.M. Verley, U.S. Pat. No. 2838557 (1958); Chem. Abstr., 52 (1958) 16197d.

65 R.F. Makens, H.H. Vaughn and R.C. Chelberg, Anal. Chem., 27 (1955) 1062.
66 N.I. Zemlyanskii and B.S. Drach, Zh. Obshch. Khim., 32 (1962) 1962.
67 P. Coppens, C.H. MacGillavry, S.G. Hovenkamp and H. Douwes, Acta Crystallogr., 15 (1962) 765; Chem. Abstr., 57 (1962) 13251h.
68 J.P. Hazel and R.L. Collin, Acta Crystallogr. Sect. B, 28 (1972) 2279; Chem. Abstr., 78 (1973) 102993d.
69 V.A. Parfenova, P.S. Belov and N.M. Kuznetsova, Tr. Mosk. Inst. Neftekhim. Gaz. Prom-sti, (1976) 108; Zh. Khim., (1977); Chem. Abstr., 88 (1978) 22062z.
70 K. Dittrich, F. Frotscher, B. Gebhardt, F. Grimmer, W. Kochmann, J. Mueller, D. Sass, R. Springer and S. Tiffe, Ger. (East) DD Pat. No., 151001 (1981); Chem. Abstr., 97 (1982) 6521v.
71 C.K. Jorgensen: Inorg. Chim. Acta, Rev., 2 (1968) 65.
72 M.M. Gruchfield, C.H. Dungan, J.H. Letcher, V. Mark and J.R. Van Wazer, Topics Phosphorus Chem., (1967) 373.
73 E.W. Cook and W.D. Thomas, U.S. Pat. No., 2342572 (1944).
74 E.W. Cook and W.D. Thomas, U.S. Pat. No., 2382775 (1945).
75 E.W. Cook and W.D. Thomas, U.S. Pat. No., 2365938 (1944).
76 C.H. Freuler, U.S. Pat. Nos., 2364283, 2364284 (1944).
77 P.A. Asseff, U.S. Pat. No., 2540084 (1951).
78 I.J. Heilweil, Am. Chem. Soc., Div. Pet. Chem. Prepr., 10 (1965) 19.
79 O.N. Grishina, V.A. Bylev and M.I. Potekhina, Mater. Nauchn. Konf., Inst. Org. Fiz. Khim. Akad. Nauk SSSR, (1969) 150; Chem. Abstr., 78 (1973) 42616w.
80 J. Mostecky and V. Rabl, Sb. Vys. Sk. Chem.-Technol. Praze, Technol., Paliv, D 26 (1972) 23; Chem. Abstr., 78 (1973) 100129c.
81 E.K. Zhumadilov, E.I. Markova and V.I. Nefedov, Koord. Khim., 4 (1978) 997; Chem. Abstr., 89 (1978) 138095d.
82 J.G. McNab, N.V. Hakala and J.P. McDermott: U.S. Pat. No., 2552570 (1951); Chem. Abstr., 45 (1951) 7785e.
83 E.A. Evans and J.S. Elliot, U.S. Pat. No., 2579037 (1951); Chem. Abstr., 46 (1952) 2795b.
84 P.K. Mulvany, U.S. Pat. No., 2689220 (1954); Chem. Abstr., 49 (1955) 605e.
85 P.K. Mulvany: U.S. Pat. No., 2680123 (1954); Chem. Abstr., 50 (1956) 2653g.
86 P.F. Hu and W.Y. Chen, Hua Hsueh Hsueh Pao, 22 (1956) 215; Chem. Abstr., 52 (1958) 7186c.
87 P.F. Hu and C. Wanpyi, Sci. Sin., 6 (1957) 661; Chem. Abstr., 52 (1958) 7186h.
88 R.F. Reeves and D.J. Cestoni, U.S. Pat. No., 2837549 (1958); Chem. Abstr., 52 (1958) 19112d.
89 ESSO Research and Engineering Co., Brit. Pat. No. 796181 (1958); Chem. Abstr., 54 (1960) 1298h.
90 Continental Oil Co., Brit. Pat. No., 876505 (1959); Chem. Abstr., 56 (1962) 14082b.
91 J.R. Dunn and J. Scanlan, J. Polym. Sci., 35 (1951) 267.
92 C.S. Lynch, W.E. Lifson and R.F. Finn, U.S. Pat. No., 3014940 (1961); Chem. Abstr., 56 (1962) 13164d.
93 S.A. Francis and A.H. Ellison, J. Chem. Eng. Data, 6 (1961) 83.
94 W.E. Bacon and J.F. Bork, J. Org. Chem., 27 (1962) 1484.
95 I.M. Qrudzheva and S.M. Novruzov, Azerb. Neft. Khoz., 48 (1969) 41; Chem. Abstr., 71 (1969) 126851n.
96 O.N. Grishina, I.A. Elfimova and N.A. Andreev, Mater. Nauchn. Konf., Inst. Org. Fiz. Khim. Akad. Nauk SSSR, (1969) 143; Chem. Abstr., 78 (1973) 72345z.

97 Standard Oil Co., Fr. Pat. No., 2102494 (1972); Chem. Abstr., 78 (1973) 58033q.
98 H. Luther, E. Baumgarten and K. Ul-Islam, Erdoel Kohle, Erdgas, Petrochem. Brennst.-Chem., 26 (1973) 509; Chem. Abstr., 79 (1973) 142466.
99 O.W. Rigdon, R.S. Edwards and W.J. Powers, Ger. Offen. 2249980 (1974); Chem. Abstr., 81 (1974) 37242d.
100 I. Haiduc and E. Veres, Synth. React. Inorg. Met.-Org. Chem., 5 (1975) 115; Chem. Abstr., 83 (1975) 114590m.
101 H. Okabe and T. Horita, Yukagaku, 25 (1976) 227; Chem. Abstr., 85 (1976) 32359v.
102 H. Okabe and Y. Takada, Yukagaku, 28 (1979) 106; Chem. Abstr., 91 (1979) 91104e.
103 V.P. Wystrach, E.O. Hook and G.L.M. Christopher, J. Org. Chem., 21 (1956) 705.
104 C.E. Legate and H.D. Burnham. Anal. Chem., 32 (1960) 1042.
105 I. Hrabovecky, Czech. C.S., 193818 (1982); Chem. Abstr., 97 (1982) 24002f.
106 A.J. Burn and G.W. Smith, Chem. Commun., (1965) 394; Chem. Abstr., 66 (1967) 69696m.
107 T. Ito and H.H. Igarashi, Acta Crystallogr. Sect. B, 25 (1969) 2303.
108 S.L. Lawton and G.T. Kokotailo, Inorg. Chem., 8 (1969) 2410.
109 D.R. Dakterniecks and D.P. Graddon, Aust. J. Chem., 23 (1970) 1989, 2521.
110 V.F. Toropova, R.A. Cherkasov, N.I. Savel'eva and A.N. Pudovik, Zh. Obshch. Khim., 40 (1970) 1043; Chem. Abstr., 73 (1970) 92187z.
111 T. Colclough and J.I. Cunneen, J. Chem. Soc., (1964) 4790.
112 D. Hoerding and H. Fischer, Schmierst. Schmierungstech., 31 (1968) 25; Chem. Abstr., 71 (1969) 93279b.
113 A.J. Burn, R. Cecil and V.O. Young, J. Inst. Petrol., 57 (1971) 319.
114 E. Rossi and L. Imparato, Chim. Ind. (Paris), 53 (1971) 838.
115 J.A. Howard Y. Ohkatsu, J.H.B. Chenier and K.U. Ingold, Can. J. Chem., 51 (1973) 1543.
116 I.S. Levin and V.V. Sergeeva, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1974) 53; Chem. Abstr., 81 (1974) 69138h.
117 V.V. Sher, E.I. Markova, L.G. Khanakova, G.N. Kuzmina and P.I. Sanin, Neftekhimiya, 13 (1976) 876; Chem. Abstr., 80 (1974) 95168z.
118 J. Mostecky, V. Rabl, P. Kozak and V. Kubelko, Ropa Uhlie, 16 (1974) 557; Chem. Abstr., 83 (1975) 52539h.
119 O.N. Grishina, V.M. Bashinova and M.I. Potekhina, Neftekhimiya, 20 (1980) 451; Chem. Abstr., 93 (1980) 188792g.
120 A.J. Bridgewater, J.R. Dever and M.D. Sexton, J. Chem. Soc. Perkin Trans. 2, (1980) 1006.
121 V.V. Sher, L.K. Bogomolova, E.I. Markova, G.N. Kuzmina and P.I. Sanin, Neftekhimiya, 21 (1981) 424; Chem. Abstr., 95 (1981) 149572g.
122 A. Goldschmidt, U.S. Pat. No., 3813336 (1974); Chem. Abstr., 82 (1975) 46239f.
123 K.A. Egorva and V.N. Bauman, Neftepererab. Neftekhim. (Kiev), 11 (1974) 10; Chem. Abstr., 83 (1975) 52539h.
124 J.H.B. Chenier, J.A. Howards and J.C. Tait. Can. J. Chem., 55 (1977) 1645.
125 S.G. Perry, J. Gas Chromatogr., 2 (1964) 93.
126 L. Geldern, Erdoel Kohle, 18 (1965) 545; Chem. Abstr., 63 (1965) 9713h.
127 N. Murata and M. Okutsu, Junkatsu, 12 (1967) 286; Chem. Abstr., 69 (1968) 113150s.
128 J. Auvray and A. Lamotte, Bull. Soc. Chim. Fr., (1974) 407; Chem. Abstr., 82 (1975) 105983u.
129 T.J. Cardwell and P.S. McDonough, Inorg. Nucl. Chem. Lett., 10 (1974) 283.
130 G.E. Fodor and F.M. Newman, ASLE Trans., 22 (1979) 389; Chem. Abstr., 92 (1980) 8628f.

131 N.K. Shakirova, N.A. Ulakhovich, G.K. Budnikov, G.A. Kutyrev and R.A. Cherkasov, Zh. Obshch. Khim., 49 (1979) 302; Chem. Abstr., 91 (1979) 65214w.
132 V. Giancotti and A. Ripamonti, J. Chem. Soc. A, (1969) 706.
133 I.-M. Feng, Wear, 3 (1960) 309.
134 R.F. Kendall and A. Rimmer, Chem. Ind. (London), (1962) 1864.
135 I.-M. Feng, W.L. Peristein and M.R. Adams, ASLE Trans., 6 (1963) 60.
136 M.C. Goodwin and C.R. Begeman, SAE (Soc. Automot. Eng.) Prepr., 7 (1962) 4581g; Chem. Abstr., 59 (1963) 11159d.
137 N.E. Gallopoulos, ASLE Trans., 7 (1964) 55.
138 W.W. Hanneman and R.S. Porter, J. Org. Chem., 29 (1964) 2996.
139 H. Luther and S.K. Sinha, Erdoel Kohle, 17 (1964) 91.
140 J.S. Ashford, L. Brethirick and P. Gould, J. Appl. Chem., 15 (1965) 170.
141 B.E. Jackson, N.Z. J. Sci., 8 (1965) 368; Chem. Abstr., 63 (1965) 17754c.
142 J.J. Dickert and C.N. Rowe, J. Org. Chem., 32 (1967) 647.
143 A.J. Burn, Adv. Chem. Ser., 75 (1968) 323.
144 B.E.M. Hassan, Chem. Tech. (Leipzig), 23 (1971) 540; Chem. Abstr., 75 (1971) 117829s.
145 O.N. Grishina, M.I. Potekhina, I.A. Elfimova and S.M. Klyuchanskalya, Sb. Nekot. Probl. Org. Khim. Mater. Nauch. Sess. Inst. Org. Fiz. Khim. Akad. Nauk SSSR, (1972) 63; Chem. Abstr., 78 (1973) 42790y.
146 O.N. Grishina, M.I. Potekhina, I.A. Elfimova and S.M. Klyuchanskaya, Neftekhimiya, 14 (1974) 484; Chem. Abstr., 83 (1975) 64831t.
147 O.N. Grishina, I.P. Lipatova, I.A. Elfimova and M.I. Potekhina, Neftekhimiya, 14 (1974) 147; Chem. Abstr., 81 (1974) 4015d.
148 S.V. Larionov, L.A. Kosareva and A.F. Malikova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1974) 120; Chem. Abstr., 81 (1974) 144946h.
149 O.N. Grishina, N.P. Anoshina and V.M. Bashinova, Neftekhimiya, 14 (1974) 307; Chem. Abstr., 81 (1974) 13041m.
150 F.G. Rounds, ASLE Trans., 18 (1975) 79; Chem. Abstr., 83 (1975) 118259h.
151 M. Bajus and V. Vesely, Zb. Pr. Chemekotechnol. Fak. SVST (1975–76) 123; Chem. Abstr., 90 (1979) 214488x.
152 S.V. Larionov and L.A. Kosareva, Proc. Int. Conf. Therm. Anal., 1 (1975) 877; Chem. Abstr., 87 (1977) 47527p.
153 V. Trdlicka, J. Kada and J. Mostecky, Erdoel Kohle, Erdgas, Petrochem., 29 (1976) 310; Chem. Abstr., 86 (1977) 54764w.
154 G.A. Marinkina, I.L. Kotlyarevskii and I.S. Levin, Zh. Prikl. Khim., 50 (1977) 427; Chem. Abstr., 86 (1977) 146568p.
155 C. Jentsch, C. Coers and W. Klostermann, Erdoel Kohle, Erdgas, Petrochem., 33 (1978) 176; Chem. Abstr., 93 (1980) 98084y.
156 O.N. Grishina, V.M. Bashinova, and M.I. Potekhina, Neftekhimiya, 19 (1979) 92; Chem. Abstr., 90 (1979) 167769c.
157 R.B. Jones and R.C. Coy; ASLE Trans., 24 (1981) 91; Chem. Abstr., 94 (1981) 142296h.
158 H. Berndt and U. Thorl: Schmierungstechnik, 11 (1980) 337; Chem. Abstr., 95 (1981) 45621f.
159 T.P. Eremeeva and I.A. Vorsina: Izv. Sub. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, (1976) 24; Chem. Abstr., 85 (1976) 101538s.
160 A.M. Bond, R. Colton, D. Dakternieks, M.L. Dillon, J. Hauenstein and J.E. Moir, Aust. J. Chem., 34 (1981) 1393.
161 R.Z. Kowalski, N.A. Bailey, R. Mulvany, H. Adams, D.A. O'Cleirigh and J.A. Mc-Cleverty, Transition Met. Chem., 6 (1981) 64; Chem. Abstr., 94 (1981) 18377s.

162 S.L. Lawton, Inorg. Chem., 10 (1971) 328.
163 Y. Watanabe and H. Hagibara, Acta Crystallogr. Sect B, 28 (1972) 4.
164 Y. Watanabe, Sci. Pap. Inst. Phys. Chem. Res. (Jpn.), 74 (1980) 150; Chem. Abstr., 94 (1981) 130700e.
165 V. Sudek, Czech., Pat. No., 156937 (1975); Chem. Abstr., 83 (1975) 78839r.
166 C.K. Jorgensen, J. Inorg. Nucl. Chem., 24 (1962) 1571.
167 W. Kuchen and H. Mayatepak, Chem. Ber., 101 (1968) 3454; Chem. Abstr., 69 (1968) 102630x.
168 B. Walther, Z. Anorg. Allg. Chem., 395 (1972) 112; Chem. Abstr., 78 (1973) 58503t.
169 W. Szczepaniak, B. Juskowiak and K. Ren, Poe. J. Chem., 53 (1979) 755; Chem. Abstr., 91 (1979) 133290v.
170 G.K. Budnikov, N.K. Shakurova, N.A. Ulakhovich, R.A. Cherkasov, V.V. Ovchinnikov, G.A. Kutyrev and U.F. Toropova, Zh. Anal. Khim., 32 (1977) 1326; Chem. Abstr., 88 (1978) 145516z.
171 P.L. Coggon, J.D. Lebedda, A.T. McPhail and R.A. Palmer, Chem. Commun., 78 (1970).
172 F. Feher and A. Bliimeke, Chem. Ber., 90 (1957) 1934.
173 M. Becke-Goehring and G. Wunsch, Chem. Ber., 93 (1960) 326.
174 G. Oertel, H. Holtschmidt and H. Malz, German Pat. No. 1157226 (1963); Chem. Abstr., 60 (1964) 6858.
175 G.A. Kutyrev, R.T. Nigametzyanov, R.A. Cherkasov and A.N. Pudovik, Zh. Obshch. Khim., 49 (1979) 724; Chem. Abstr., 91 (1979) 39568v.
176 G.A. Kutyrev, A.A. Kutyrev and R.A. Cherkasov, U.S.S.R. Pat. No., SU 891683 (1981); Chem. Abstr., 97 (1982) 6523x.
177 J. Michalski, M. Potrzebowski and A. Lopusinski, Angew. Chem., 94 (1982) 134; Chem. Abstr., 97 (1982) 23883g.
178 ESSO Research and Engineering Co., Brit. Pat. No., 737392 (1955); Chem. Abstr., 50 (1955) 9010g.
179 J.P. McDermott, U.S. Pat. No. 2786812 (1957); Chem. Abstr., 51 (1957) 10892f.
180 O.A. Homberg and I. Hechenbleikner: Fr. Pat. No., 1365375 (1964); Chem. Abstr., 61 (1964) 14711d.
181 H. Kubo: Agr. Biol. Chem., 29 (1965) 43.
182 Y. Nagae, and K. Vakemori, Japan Pat. No., 4576 (1966); Chem. Abstr., 65 (1966) 22981n.
183 M. Nakanishi and A. Tsuda, Japan Pat. No., 15290 (1966); Chem. Abstr., 65 (1966) 20164f.
184 N.K. Bliznyuk, P.S. Khokhlov and Y.A. Andrianov, U.S.S.R. Pat. No., 181103 (1966); Chem. Abstr., 65 (1966) 8962e.
185 E.N. Walsh and A.F. Kopacki, U.S. Pat. No., 3296193 (1967); Chem. Abstr., 66 (1967) 55981p.
186 R.W. Walker and H.E. Ramsden, U.S. Pat. No., 3410797 (1968); Chem. Abstr., 70 (1969) 21592e.
187 C. Pfizer and Co., Inc., British Pat. No., 1163738 (1969); Chem. Abstr., 72 (1970) 2550q.
188 T. Toda, K. Ida and K. Kimoto, Japan Pat. No., 7019512 (1970); Chem. Abstr., 73 (1970) 77830k.
189 D.R. Baker, U.S. Pat. No., 3947481 (1976); Chem. Abstr., 85 (1976) 46858u.
190 D.R. Baker, U.S. Pat. No., 3992425 (1976); Chem. Abstr., 86 (1976) 90031p.
191 D.R. Baker, U.S. Pat. No., 4012421 (1977); Chem. Abstr., 87 (1977) 6201j.
192 A. Mihailovski, U.S. Pat. No., 4071545 (1978); Chem. Abstr., 88 (1978) 170295j.
193 B. Mathiasch and T.N. Mitchell, J. Organomet. Chem., 185 (1980) 351.

194 J.L. Lefferts, M.B. Hossain, K.C. Molloy, D. Van der Helm and J.J. Zuckerman, Angew. Chem., 19 (1980) 309.
195 J.L. Lefferts, K.C. Molloy, M.B. Hossain, D. Van der Helm and J.J. Zuckerman, Inorg. Chem., 21 (1982) 1410.
196 A.A. Muratova, O.B. Sobanova, E.G. Yarkova, A.S. Khramov and A.N. Pudovik, Zh. Obshch. Khim., 49 (1979) 1903; Chem. Abstr., 91 (1979) 185826u.
197 S.L. Lawton and G.T. Kokotailo, Nature (London), 221 (1969) 550.
198 S.L. Lawton and G.T. Kokotailo, Inorg. Chem., 11 (1971) 363.
199 T. Ito, Acta Crystallogr. Sect. B, 28 (1972) 1034.
200 I. Haiduc, F. Martinas, D. Ruse and M. Curtui, Synth. React. Inorg. Met.-Org. Chem., 5 (1975) 103; Chem. Abstr., 83 (1975) 114581j.
201 K.C. Molloy, M.B. Hossain, D. Van der Hel, J.J. Zuckerman and I. Haiduc, Inorg. Chem., 18 (1979) 3507.
202 B.W. Lieblich and M. Tomassini, Acta Crystallogr. Sect. B, 34 (1978) 944.
203 K.C. Molloy, M.B. Hossain, D. Van der Helm, J.J. Zuckerman and I. Haiduc, Inorg. Chem., 19 (1980) 2041.
204 H.H. Farmer, B.W. Malone and H.F. Tompkins, Lubr. Eng., 23 (1967) 57; Chem. Abstr., 66 (1967) 97175j.
205 S.L. Lawton, C.J. Fuhrmeister, R.G. Haas, C.S. Jarman and F.G. Lohmeyer, Inorg. Chem., 13 (1974) 135.
206 R.O. Day, M.M. Chauvin and E. McEwen, Phosphorus Sulphur, 8 (1980) 121.
207 A.I. Busev, Min-Teao Huang, Zh. Neorg. Khim., 7 (1962) 88.
208 A.I. Busev, Talanta, 11 (1964) 485.
209 S. Husebye, Acta Chem. Scand., 19 (1965) 1045.
210 S. Husebye, Acta Chem. Scand., 20 (1966) 24.